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LINEAR POLYBENZYL AND ITS DERIVATIVES

A Dissertation Presented
By
Wen-cheng Kuo

Sumitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 1973

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LINEAR POLYBENZYL AND ITS DERIVATIVES

A Dissertation Presented
By
Wen-cheng Kuo

Approved as to style and content by:

Robert H. F. Kerr
(Chairman of Committee)

(Head of Department)

J. W. Chien
(Member)

May 1973
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To
My Parents,
My Wife, Karen
and
My Daughter, Anita
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CHAPTER ONE
INTRODUCTION

Benzyl chloride (1,2,3,4) in the presence of many Lewis acid catalysts will undergo a rapid self-condensation reaction during which HCl is evolved and polybenzyl is produced. Various other catalysts, such as metal powders (5,6), metal oxides (7) and aluminum alkyls (8), are also known to polymerize benzyl chloride to this polymer, but all polymers thus obtained have been found to be highly branched and relatively low molecular weight (7,9,11,12). As a result, the products are generally amorphous resins which soften in the range 60°-80°C.

A crystalline, presumably linear, polybenzyl was first obtained by Kennedy and Isaacson (12,13) by the polymerization of benzyl chloride in ethyl chloride solvent with aluminum chloride as catalyst at about -130°C, but the yield and the molecular weight were both low. However, using the same condition, Montaudo and coworkers (14) failed to obtain, directly, crystalline polymers. Only fractionation of low conversion samples (10%), combined with selective extraction with the appropriate solvents yields crystalline polymer. This result indicates that the polymer obtained under Kennedy's conditions still contained significant amounts of branching. The objective of the present study, therefore,
has been to investigate the cause of the branching and to obtain an insight into the factors which affect both the degree of branching and the molecular weight so as to be able to prepare linear polymers with useful properties.

In the course of this work, polybenzyl, poly-2,5-dimethylbenzyl and poly-α-methylbenzyl were prepared from the polycondensation of benzyl chloride, 2,5-dimethylbenzyl chloride and α-chloroethylbenzene respectively, with either Friedel-Crafts or Zieler-Natta catalyst, in various kinds of solvents at different temperatures (i.e., room temperature to -130°C) in order to investigate the effect of reactions and monomer structure on the linearity of polymers. The past investigations on the effect of polymerization conditions on polymer structure, based upon the results of various methods of characterization of the polymers, have been inexact and sometimes uncertain. Because of this, the model compound reactions of polybenzyl (i.e., diphenylmethane with benzyl chloride) and poly-α-methylbenzyl (i.e., 1,1-diphenylethane or diphenylmethane with α-chloroethylbenzene) were conducted at different reaction conditions to attempt to obtain a single and clear picture of the effect of the reaction conditions, substitution distribution, and thereby, alternately, polymer structure. The degree of branching of the polymers was characterized by IR or NMR and was correlated with the properties of polymers and the results of the model compound
reactions.

I. LITERATURE REVIEW

A. Polybenzyl and Its Derivatives.

The formation of insoluble resin from the polycondensation of benzyl chloride in the presence of Lewis acid was observed a long time ago by Friedel and Crafts (1). The early literature was summarized by Jacobson (2), who was the first to investigate the nature of the polymer prepared from the polycondensation of benzyl chloride in the presence of aluminum chloride, ferric chloride and stannic chloride. Only the last catalyst yielded an entirely soluble polymer, and it was assumed that the polymer molecules contained predominately the p-phenylenemethylene structure in its repeating units. The insoluble and infusible nature of some of the polymers was explained by assuming the formation of a three-dimensional network structure.

In 1928, Ingold and Ingold (15) described the preparation of benzyl fluoride and reported that it polymerized violently to a glass-like solid of composition \( (C_7H_6)_n \) when it was treated with a catalyst amount of concentrated sulfuric acid or when in the presence of glass. Leicester and Hennel (38) also reported that benzyl fluoride was unstable and readily polymerized to yield the ethylenic polymer having
a pendent type of structure as follows:

\[
\begin{array}{c}
\text{CH} \\
\text{C}
\end{array}
\]

Benstein and coworkers (16) found that some substituted benzyl fluorides, e.g., p-nitrobenzyl fluoride and p-bromobenzyl fluoride, are stable and give no polymer in the presence of concentrated sulfuric acid, but will polymerize when boron trifluoride is used as catalyst. It was believed that inactivating substituents on the aromatic ring caused the difficulty in the polymerization (16).

Benzyl alcohol was also found (17) to polymerize on treatment with cold, concentrated sulfuric acid. The polymer was believed to have the same structure and amorphous properties as those prepared from benzyl halides. In the same year, 1941, Dermer and Hopper (3) investigated the effect of about 40 various inorganic chlorides on the polycondensation of benzyl chloride. All polymers obtained were thermoplastic resins varying in color from red through orange to brown and even gray blue. However, no study was conducted on the structure of the polymers.

Labeder and coworker (4) in 1949 carried out the polymerization of benzyl chloride in the presence of aluminum
chloride, ferric chloride and zinc chloride at room temperature. Only low molecular weight (1900-2100), amorphous polymers were obtained in all reactions. The results from the pyrolysis of the polymers indicated that these polymers contained dihydroanthracene units as end groups. It was believed that these units were formed by ring closure at the ortho-position through the reaction of terminal CH₂Cl groups with the penultimate benzene ring as follows:

\[ \text{CH}_2\text{Cl} \rightarrow \text{CH}_2 \]

The first systematic study on the structure of the polymer was conducted by Hass and coworkers (9). The results based on the infrared, X-ray, oxidation and pyrolysis studies, showed that the polymers were amorphous and highly branched. Catalysts other than Lewis acid, e.g., alkyl aluminum (8) or metal powder (5,6), were also used for the polycondensation of benzyl chloride. The polymers thus obtained were again amorphous.

The first attempt to synthesize a crystalline polymer from a derivative of benzyl chloride was also made by Hass and coworkers (9), who treated durymethyl chloride with a trace of iron oxide at 100°C. The solid material thus obtained melted in the range of 260-280°C, and was believed to
be a linear polymer with an average degree of polymerization of 4. Recently, by using SnCl$_4$ instead of iron oxide, Montaudo and coworkers (19) were able to obtain poly-2,3,5,6-tetramethylbenzyl with a $M_n$ of 2380 and a melting point of 370°C. 2,3,5,6-Tetramethylbenzyl methyl ether was also polymerized under the same condition, and the polymer was also crystalline with a melting point of 350°C.

Moore (20) in 1964 used a less-substituted benzyl chloride, 2,5-dimethylbenzyl chloride, as the monomer and treated it with AlCl$_3$ in nitrobenzene at room temperature. The polymer so obtained had a low molecular weight and was only soluble in hot o- or p-chlorobenzene. X-ray diffraction analysis indicated that the polymer was not a simple amorphous material, but no positive conclusions were drawn on the crystallinity of this polymer.

Relative high molecular weight ($M_n = 6400$), amorphous polybenzyl was reported by Mararigna and Montaudo (21) in 1964. The polymer was obtained by the polycondensation of benzyl chloride in the presence of SnCl$_4$ at 200°C in autoclave.

Crystalline polybenzyl and its $\alpha$-substituted derivatives were obtained for the first time by Kennedy and Isaacson in 1966 (10,13). In their work, benzyl chloride, when treated with AlCl$_3$ in ethyl chloride at about -130°C, gave a partially crystalline polymer which melted at 142°C.
The linear structure was apparently confirmed by the analyses of their IR and NMR spectra, although few details were given in their paper. Crystalline poly-α-methylbenzyl was obtained in this work from the polycondensation of α-chloroethylbenzene under the same conditions. However, the yields (10-15%) and the molecular weights (2400) of all polymers are low. Crystalline poly-2,5-dimethylbenzyl was also obtained in this study, but at relatively higher temperature (-78°C) compared to those used for polymerization of monomer which did not contain ring substituents. Nevertheless, the melting temperature of these polymers prepared at -78°C was lower than those prepared at -134°C.

Montaudo and coworkers (14) repeated Kennedy's work, the polycondensation of benzyl chloride, but failed to obtain directly the crystalline polybenzyl. In their work the crystalline polymer could only be obtained by fractionation of a low conversion sample (10%) combined with selective extraction with methyl ethyl ketone.

Crystalline polybenzyls prepared at relative higher temperature (-30° to 0°C), in the presence of Ziegler-Natta catalysts were also reported by Kennedy and Isaacson (22). The polymers had the same properties as those obtained from low temperature polymerization with aluminum chloride.

Recently, the polymerization of benzyl chloride in the presence of various group II metal oxide, e.g., CaO, MgO and BaO, at 150°C to 175°C was examined (7), but only low
molecular weight (1400-2500), amorphous polymers were obtained.

There are some reports on the synthesis of polybenzyls using other monomers than those mentioned before. Derivatives of benzyl halides with alkyl groups in the para-position (e.g., p-isopropylbenzyl chloride (9), p-methylbenzyl bromide (9), p-bromobenzyl chloride (20) when treated with Lewis acids also formed polybenzyls. However, no information about the structure and properties of the polymers was reported. Polycondensation of p-methoxybenzyl chloride (19) in the presence of p-toluenesulfonic acid or Lewis acids gave raise to amorphous polymers with molecular weight in the range 2000-4000. Further heating of the polymers in the presence of SnCl₄ or in vacuum caused an increase in molecular weight to 10000. Other alkyl-substituted benzyl halides, e.g., 2-ethyl-5-pentylbenzyl iodide, 2-cyclohexylbenzyl chloride and 2-methyl-5-isopropylbenzyl bromide (22), in the presence of Ziegler-Natta catalyst at the temperature from -25 to -30°C also formed crystalline polymers with the melting points in the range of 150-300°C. Other types of substituted benzyl chlorides, e.g., 2-chloroisopropylbenzene (23) and benzylhydryl chloride (24), were also reported to form polybenzyls in the presence of Lewis acids. However, only low degrees of polymerization (10-30, and 8-9) were achieved. The glass temperature of the former polymer (120°C)
was higher than that of polybenzyl (60-80°C).

Multiple ring compounds, such as, 9-chloromethylanthracene (25) in the presence of SnCl₄ at 67°C, were found to form crystalline polymers with melting point of 308-312°C. This particular polymer was soluble in benzene and had an Mn of 2000.

Insoluble and infusible polybenzyls were also synthesized (26) when bis-chloromethyl compounds (e.g., 1,4-bis-chloromethylbenzene, 1,4-bis-chloromethyl-2,5-dimethylbenzene or 1,3-bis-chloromethyl-4,6-dimethylbenzene), were treated with aluminum chloride at room temperature. These polymers discolored at 200°C and decomposed above 300°C.

Another type of monomer, 2-phenylethylchloride, was reported (27) to form polyphenylethyl under the normal Friedel-Crafts condition. The polymer was insoluble and infusible and was believed (20) to be a network polymer similar to the highly-branched polybenzyls.

In addition to the self-condensation of benzyl halides and their derivatives, polybenzyls can be prepared from the condensation of aromatic compounds with dichloroalkyls or formaldehyde as indicated in Table I-1. Polycondensations of bis(1,4-chloromethyl)benzene with benzene, thiophene, pyridine, indole, quinoline or pyrrole using SnCl₄ as catalyst have been conducted by Grassie and Meldrum (28). The thermal stability of the polymers, in increasing order,
<table>
<thead>
<tr>
<th>Monomer 1</th>
<th>Monomer 2</th>
<th>Catalyst</th>
<th>Solubility</th>
<th>$\overline{Mn}$</th>
<th>M.P. °C</th>
<th>Crystallinity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClCH$_2$-CH$_2$Cl</td>
<td>C</td>
<td>TiCl$_4$</td>
<td>i</td>
<td></td>
<td></td>
<td></td>
<td>74</td>
</tr>
<tr>
<td>ClCH$_2$-CH$_2$Cl</td>
<td>C</td>
<td>TiCl$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>TiCl$_4$</td>
<td>DPM</td>
<td>285</td>
<td>+</td>
<td></td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>TiCl$_4$</td>
<td>BN</td>
<td>$\overline{DP}=4$</td>
<td>285</td>
<td>+</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>TiCl$_4$</td>
<td>B</td>
<td>$\overline{DP}=2-3$</td>
<td>140-170</td>
<td>+</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>TiCl$_4$</td>
<td>B</td>
<td>$\overline{DP}=4-5$</td>
<td>350</td>
<td>-</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>TiCl$_4$</td>
<td>i</td>
<td></td>
<td></td>
<td>+</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>TiCl$_4$</td>
<td>B</td>
<td>$\overline{DP}=4-5$</td>
<td>130-140</td>
<td>+</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>TiCl$_4$</td>
<td>BN</td>
<td>$\overline{DP}=4$</td>
<td>350</td>
<td>+</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>TiCl$_4$</td>
<td>DPM</td>
<td>315</td>
<td>+</td>
<td></td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>TiCl$_4$</td>
<td>BN</td>
<td>$\overline{DP}=4$</td>
<td>300</td>
<td>+</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>TiCl$_4$</td>
<td>DPM</td>
<td>315</td>
<td>-</td>
<td></td>
<td>71</td>
</tr>
</tbody>
</table>

i : Insoluble in the common solvents.

B : Benzene.

DPM : Diphenylmethane.

BN : $\alpha$-Bromonaphthalene.
Table I-1

Properties of Polybenzy and Its Derivatives Prepared from Condensation of Two Monomers

<table>
<thead>
<tr>
<th>Monomer 1</th>
<th>Monomer 2</th>
<th>Catalyst</th>
<th>Solubility</th>
<th>$\bar{M}_n$</th>
<th>M.P. $^\circ$C</th>
<th>Crystallinity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$O</td>
<td>C-[-C-]</td>
<td>H$_2$SO$_4$ conc.</td>
<td>DPM</td>
<td>265</td>
<td>245-265</td>
<td>+</td>
<td>71</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>TiCl$_4$</td>
<td>s</td>
<td>600-700</td>
<td></td>
<td></td>
<td>+</td>
<td>73</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>TiCl$_4$</td>
<td>BN</td>
<td>340-350</td>
<td></td>
<td></td>
<td></td>
<td>73</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>TiCl$_4$</td>
<td>i</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>74</td>
</tr>
<tr>
<td>ClCH$_2$Cl</td>
<td></td>
<td>AlCl$_3$</td>
<td>s</td>
<td>2970</td>
<td></td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>ClCH$_2$-CH$_2$Cl</td>
<td></td>
<td>TiCl$_4$</td>
<td>BN</td>
<td>320</td>
<td></td>
<td>+</td>
<td>74</td>
</tr>
<tr>
<td>ClCH$_2$-CH$_2$Cl</td>
<td></td>
<td>TiCl$_4$</td>
<td>i</td>
<td></td>
<td></td>
<td></td>
<td>74</td>
</tr>
</tbody>
</table>

s: Soluble in the common solvents.

i: Insoluble in the common solvents.

DPM: Diphenylmethane

BN: α-Bromonaphthalene.
was found to be as follows: indole < pyrrole < benzene < thiophene. However, no information about their melting points and molecular weights was reported. Further studies on the polycondensation of thiophene with bis(1,4-chloromethyl)benzene by Grassie and Colford (29) concluded that this polymer contained many individual cyclic structures which did not occur in the benzene polymer. The cyclic structures were believed to be responsible for their different thermal stabilities compared to polybenzyl.

Polybenzyl prepared from polymers other than those obtained with Friedel-Crafts reaction have also been reported. Linear, m-substituted polybenzyl (30) was obtained from the dehydrogenation of polymethylenecyclohexane, which was prepared by the polymerization of 1,6-heptadiene using TiCl₄ and triisobutyl aluminum as catalyst as follows:

\[
\text{Polybenzyls have also been obtained by solid-state polymerization of crystalline benzyl tosylate and its derivatives (78,79). Most polymers thus obtained were highly branched, except for that prepared at -70°C in which a fairly strong}
\]
para-substitution peak was observed in the infrared spectrum of the polymer.

B. Friedel-Crafts Reaction.

The definition of a Friedel-Crafts reaction proposed by Olah (66) is "any substitution, isomerization, elimination, cracking, polymerization, or addition reactions which takes place under the catalytic effect of Lewis acid type acidic halides (with or without co-catalyst) or proton acids". Generally, Friedel-Crafts reactions can be divided into two types, namely, alkylation and acylation.

1. Alkylation of Aromatic Compounds.

In the alkylation of aromatic compound, a hydrogen atom (or other substituent groups) of an aromatic nucleus in replaced by an alkylating agent in the presence of a Friedel-Crafts catalyst, as indicated for the general case as follows:

\[
\text{ArH} + \text{RX} \rightarrow \text{Ar·R} + \text{HX}
\]

The aromatic compounds (ArH) are usually hydrocarbons, aryl chlorides and bromides, mono- and polyhydric phenols or their ethers. The reactivity of the aromatic compounds in Friedel-Crafts alkylation depends on the structure of the
aromatic nucleus. Electron-donating substituents, e.g., R-, RO-, generally facilitated the alkylation of the aromatic rings whereas electron-withdrawing substituents, e.g., Cl-, F-, RCO-, NO2-, usually inhibit Friedel-Crafts alkylation by deactivating the aromatic ring.

The most frequently used alkylating agents (RX) are alkyl halides, alkenes and alcohols. The ease of alkylation with alkyl halides (with AlCl3 as catalyst (31)) depends on the nature of the alkyl group and the halogen atom. For a series of alkyl halides, the order of activity is: tert-R > sec-R > R, and for a given alkyl group, the order of activity is: F > Cl > Br > I.

Lewis acids and protonic acids are the two general types of catalysts used in the Friedel-Crafts alkylation. Although few direct measurements of catalytic activities are available, the general order among some of the Lewis acids seems to be AlCl3 > SbCl5 > FeCl3 > TeCl2 > SnCl4 > TiCl4 > BiCl3 > ZnCl2 (32). The general order of activity of the acidic catalysts is HF > H2SO4 > P2O5 > H3PO4 (32). However, the relative activities of Friedel-Crafts catalyst depend somewhat upon the nature of the alkylating agent employed. Thus, sulfuric and phosphoric acid are more effective catalysts with alkenes or alcohols than with alkyl halides as alkylating agents (33).

It is generally believed that many Friedel-Crafts
reactions proceed by a free carbonium ion mechanism involving the formation of an intermediate complex and cyclohexadienyl cation as follows:

\[
\begin{align*}
RX + MX & \rightleftharpoons R^+ + MX_2^- \\
H^+ + MX_2^- & \rightarrow HX + MX \\
\text{C} + R^+ & \rightarrow \text{C}^+ \xrightarrow{H} \text{R} \rightarrow \text{C} \text{R} + H^+
\end{align*}
\]

However, for primary halide the reaction most likely proceeds by a bimolecular mechanism instead of through a free carbonium ion. Generally, the possibility of carbonium ion mechanism decreases in the following order: tert-RX > sec-RX > prim-RX.

a. Orientation.

Because all the carbon atoms of the planar benzene ring are equivalent, monosubstitution of the benzene can lead to just one product. When the ring is already substituted by a single group R, the remaining five carbon atoms are not equivalent for substitution. Depending on the identity of R, substitution of the aromatic ring generally results in the predominance of either the m-product or the o-,
^-product. Usually, electron-donating groups (e.g., hydrocarbons, NH₂, NHR, NR₂, NHCOR, OH, OR) which activate the aromatic ring for alkylation are ortho- and para-directing, and electron-withdrawing groups (e.g., NR³, NO₂, CHO, COR, COOR, CN, SO₃R) which deactivate the aromatic ring for alkylation are meta-directing. The exception to this rule is the halogens which, though ortho-, para-directing, nevertheless deactivate the aromatic ring toward alkylation.

The directing effect of the substituent can be explained by the resonance effect. For instance, nitrobenzene has four resonance hybrid structures as follows:

The effect of resonance in nitrobenzene is to set up positive centers at the ortho- and para-position, and hence render these sites particularly inaccessible to electrophilic agents. As a result, higher meta-isomer contents in the reaction products are expected. In the case of anisole, distribution of the negative charge among three centers increases the electron density at these positions and results in higher ortho-, para-substitution.
The charge on the above hybrid ion is shown to be equally shared between three carbon atoms in these resonance forms, but Norman and Radda (34) have pointed out that this is not the case. The evidence from the NMR measurements of the proton shifts in the pentamethylcyclohexadienyl cation indicate that the positive charge in the cyclohexadienyl cation is rather more heavily concentrated in the para- than in the ortho-position. The distribution of the charge has been calculated to be 0.25, 0.125, 0.16 at p-, o- and m-position, respectively. The calculated positive charge densities for this ion from a perturbation method allowing for electron interaction shows the same order of charge density (p > o > m). The higher concentration of charge in the para- than in the ortho- and meta- position can be understood from the principles of electron correlation (35) in that the formal \( \pi \)-electrons in the residual aromatic system in the hybrid ion tend to be distributed in pairs, with the pairs lying as far from each other as possible; i.e., on the opposite side of the nucleus.
It was believed that under kinetically controlled reaction, a π-complex formation between aromatic ring and electrophile was the rate-determining step of the alkylation reaction (84). Brown (103) suggested that this π-complex formation should be considered as an oriented π-complex in which the electrophilic substituent does not move around unhindered, but rather have a greater probability of being found in the vicinity of the higher electron density points of the ring. Thus, under this condition, the isomer distribution of the reaction product will be high in ortho- and para-content and low in meta-content.

However, the sometimes significant difference in isomer distributions of alkylation systems could be accounted for by the fact that isomer distribution could be easily effected by thermodynamically controlled isomerizations which have σ-complexes as intermediates (105). The relative stability of this arene complex, or relative basicity of arene depends upon orientation of the substituted groups (i.e., o-, m-, or p-) on the aromatic ring. meta-Orientation was found (104) that it contributes most to basic character; for instance, m-xylene is by far the most basic of the xylenes. Therefore, high meta-isomer content was generally observed in thermodynamically controlled isomerizations.

The isomer distribution of the reaction products is not only influenced by the substituents on the nucleus, but
also by the reactivity of alkylating species and the steric requirements of both the entering group and the substituent already present (44). The higher the reactivity of the alkylating species, the lower will be the position selectivity of the alkylation, i.e., higher meta- to para- and ortho- ratio. As the size of the entering group or the substituents on the aromatic ring increases, the ortho- to para- ratio show a steady decrease, but the para- to meta- ratio shows only a small variation.

The isomer distribution can also be affected by the reaction temperature. Morris and Rubinstein (36) reported that the methylation of toluene at lower temperature shows higher o- and p-xylene and higher temperature forms predominately m-xylene. Recently, the temperature effect on the isomer distribution of the benzylation of toluene was also reported (37). The para-isomer contents increased from 52.2% to 66.4% as the reaction temperatures decreased from -1°C to -130°C.

b. Polyalkylation.

Polysubstitution is one of the characteristics of Friedel-Crafts alkylation. It is usually believed (32) that the tendency toward polysubstitution is due to the greater reactivity of the initially-produced alkylbenzene products
toward further substitution. However, Francis (18) attributed this polyalkylation to the heterogeneous reaction system rather than to the greater reactivity of the substituted benzene nucleus. It was suggested that the reason for polyalkylation is the preferential extraction of the early reaction product by the catalyst layer in the heterogeneous system. In that case, the tendency toward polysubstitution can be minimized by the use of a solvent for the hydrocarbon and catalyst layer, by operating in the vapor phase or by operating at a temperature sufficiently high that the catalyst is soluble in the hydrocarbon layer.

2. Polymerization by Benzylation.

The benzylation reaction of aromatic compounds applied to the preparation of the polybenzyl is one of the typical Friedel-Crafts alkylation as follows:

\[
\begin{align*}
\overset{\text{Catalyst}}{n\underset{\text{CH}_2X}} & \quad \rightarrow \quad \left[ \underset{\text{CH}_2}{} \right]_n + n \text{HX}
\end{align*}
\]

As in the regular Friedel-Crafts alkylation, benzylation can occur at any of the three positions, (o-, p- or m-positions) on the aromatic nucleus of the species to be substituted.
In this manner, benzylation occur either at the end group or at the disubstituted aromatic nucleus of the polymer chain. Neglecting steric effects, the latter attack is more favorable than the benzylation of the end group (37) because of the higher reactivity of the disubstituted aromatic nucleus than the monosubstituted aromatic nucleus. As the polymer chains grow, the statistical probability of benzylation on the disubstituted aromatic nuclei of the repeating units will increase while those of monosubstituted aromatic nuclei of the end groups will decrease proportionally. As a result, the polymer products are expected to be highly substituted with many branches.

The structure of polybenzyl so prepared was first proposed by Jacobson (2) to be mainly para-disubstitution for the soluble polymer and a three-dimensional branched structure for the insoluble, infusible polymer. However, no experimental data were given to support this proposal. Henne and Leicester (38) from the polymerization of benzyl fluoride reported that the polymer had a pendent type structure as follows:
Later, Shriner and Berger (17), from the oxidation of the polymer which was obtained from benzyl alcohol and concentrated sulfuric acid, suggested that a ratio of para- to ortho-substitution in this polymer was approximately 6 to 1. The elementary analysis of their oxidized polymer had a composition fairly close to that of the following polyketone:

\[
\begin{array}{c}
\text{CH} \\
\text{O}
\end{array}
\]

Flory in his text (67) suggested that the polymers obtained from benzyl halides are randomly branched structures without network formation.

The first systematic study on the structure of polybenzyl was conducted by Hass and coworkers (9). From the study of infrared spectra (IR), X-ray diffraction pattern, oxidation products and pyrolysis products of the polymer obtained from benzyl fluoride, they showed that the ethylenic polymer with a pendant type of structure proposed by Henne and Leicester (38) was incorrect. They believed that the polymers contained a nucleus of almost completely
substituted phenyl rings with a periphery of pendant benzyl groups as illustrated in Figure 1-1. From further studies on the structure of the polybenzyl from the results of IR analysis (11) and degradation products, Lady and coworkers (39) also reached the same conclusion as that drawn by Hass and coworkers (9). However, Parker (40) did not completely agree with the structure proposed by Hass (Figure 1-1).

From the oxidation products of polybenzyl, he found a considerable portion of tricarboxylic acids, but only a very small amount of tetra-, penta- and hexa-carboxylic acids and concluded that a high degree of multiple branching is rare because of the steric effects. He proposed that a globular structure as indicated in Figure 1-2 was more probable. The insolubility of these polybenzyls was believed to be caused by the small ratio of the surface units, which are solvated by the solvent, to non-solvated internal units of the globular polymer molecules.

IR absorption in the region 600-900 cm⁻¹ is usually used for the characterization of repeating unit structures in polybenzyls. The usual assignments of the absorptions in this region are indicated in Table I-2. The linear polymer obtained by Kennedy and Isaacson using Kennedy's low temperature polymerization method, reportedly showed the 805 cm⁻¹ characteristic bands in the IR spectra for the p-disubstituted aromatics. However, Young and Fernandey (41) recently
Figure 1-1. Branched structure of polybenzyl.

Figure 1-2. Two dimensional representation of globular polybenzyl molecule.
reported that polybenzyls containing essentially completely linear para- structures prepared by the Kennedy-Isaacson method (6) may not exhibit the characteristic 805 cm\(^{-1}\) band. They found that the 805 cm\(^{-1}\) band of supposedly linear polymers diminished upon melting and recooling, and they attributed the absence of this characteristic band to the conformational factor in the solid polymer.

In addition to the branched characteristic of the structure of polybenzyl, there are some reports on anthracene unit formation in the polymer chain. Vallentine and Winter (11) suggested that the relative low chlorine content of the polybenzyl may be caused by the formation of dihydroanthracene at the chain end as follow:

\[
\text{CH}_2\text{Cl} + \text{HCl} \rightarrow \text{CH}_2\text{Cl} + \text{HCl}
\]
Other studies have shown that anthracene is formed in the attempted reaction of benzyl chloride with benzene in the presence of AlCl₃ at a temperature higher than 25°C (43), presumably by the following reaction:

\[
\text{CH}_2\text{Cl} + \text{CH}_2\text{Cl} \xrightarrow{\text{AlCl}_3, 25^\circ\text{C}} \text{benzene} \xrightarrow{\text{AlCl}_3} \text{anthracene}
\]

Mantaudo and coworkers (49), from the study of UV absorption of polybenzyl between 325 to 400 μm, confirmed the formation of anthracene group in the polymer. However, no anthracene terminal units were observed from the polybenzyl prepared at -135°C, in the presence of AlCl₃ (42).

A detailed study conducted by Ellis and coworkers (45) on the fluorescence and absorption spectra of polybenzyl, which was prepared by treating benzyl chloride with stannic chloride, concluded that a benzyl substituted 9-phenyl- or 9,10-diphenylanthracene formed in the polymer chain was the causes of the fluorescence observed in these polymers. A mechanism was proposed for the formation of this fluorescent group through the formation of a carbonium ion of the diphenylmethane type as shown in the following reaction sequence:
In an early study on the mechanism of polymerization, Valentine and Winter (11) reported an unusual behavior for the presumed step-growth polymerization reaction which was believed to be involved in the self-condensation of benzyl chloride in the presence of SnCl\textsubscript{4}. The degree of polymerization increased rapidly with the extent of reaction at first but became constant after the extents of reaction became
greater than 30%. This behavior is different from that of a normal step-growth in which the degree of polymerization increases as the reaction proceeds in accordance with the equation: degree of polymerization = 1/(1-p), where p is conversion (46).

The kinetic study of this polymerization showed that the reaction was first order in benzyl chloride. The rate of the polymerization was directly proportional to the concentration of catalyst, up to a concentration of 0.6 M, but then reverse. It was later suggested by Parker and co-workers (47) that the reduction in overall rate of reaction at higher concentration of catalyst was due to the rather low concentration of uncomplexed monomers, which was more active than the complexed monomers.

It was suggested from this study that the reaction might take place by way of either benzyl cations or complexes of monomer with stannic chloride, the latter possibly being a π-complex, as shown below:

\[
\text{PhCH}_2\text{Cl} + \text{SnCl}_4 \rightarrow \begin{array}{c}
\text{PhCH}_2\text{Cl} \\
\text{SnCl}_4
\end{array}
\]

The complex between dimer and catalyst could then be further
substituted, and so on. However, the results of this kinetic study contrast to those obtained by Brown and Grayson (48), who studied the benzylation of aromatic compounds by benzyl halides in the presence of AlCl₃. The overall reaction was found to depend on the concentration of both reactants.

Other studies on the kinetics of the polymerization of benzyl chloride using SnCl₄ and AlCl₃, which were reported by Montaudo and coworkers (52), were agreement with the mechanism suggested by Brown and Grayson for aromatic alkylation. The reaction rate was found to follow the equation: \( K [M]^2 [C] \); where \([M]\) is monomer concentration and \([C]\) is catalyst concentration.

Derivatives of benzyl chloride (e.g., α-chloroethylbenzene, p-chlorobenzylchloride and 2,6-dichlorobenzyl chloride) were also found to follow the same reaction kinetics as does benzyl chloride (50); i.e., second-order in monomer. On the other hand, the reaction of benzhydryl chloride was reported to show first order kinetics for both monomer and catalyst (50). This behavior was believed to be due to the formation of benzhydryl carbonium ion, rather than complex of monomer with catalyst as in the case of benzyl chloride (24). Thus, a more reasonable and simplified reaction scheme for the polycondensation of benzyl chloride at room temperature was proposed by Montaudo and coworkers (24).
as following:

\[
\begin{align*}
M + C & \rightarrow \text{MC} \quad \text{(A)} \\
\text{MC} + M & \rightarrow \text{D} + \text{C} + \text{HCl} \quad \text{(B)} \\
\text{MC} + \text{D} & \rightarrow \text{P} + \text{C} + \text{HCl} \quad \text{(C)}
\end{align*}
\]

The first step consists of a rapid and reversible formation of a strongly polarized complex (MC) between benzyl chloride (M) and the Lewis acid (C). The formation of dimer (D) is the rate determining step. A rate constant of \(7.88 \times 10^{-4} \text{ mol}^{-2} \text{ sec}^{-1}\) has been calculated by Grassie and Meldrum for this reaction (51).

The relationship between molecular weight and extent of reaction are essentially the same for both room and low temperature polycondensation of benzyl chloride (22, 24, 49). At room temperature, the molecular weight built up very fast at an early stage of reaction (11, 49) and remained nearly constant from that point up to about 80% conversion. At higher extents of reaction, the molecular weights increased sharply, and it was believed that this increase was due to the reaction of the endgroup of one polymer molecule with the backbone of another (49). At low temperature, the reaction had the same type of behavior except no increase in the molecular weight was observed at the high conversion. The reason was believed to be the precipitation of the polymer molecules formed during the reaction which prevented further benzylat-
While use of the Friedel-Crafts reaction for polymer synthesis was at first largely restricted to alkylation reactions, the preparations of polyketones and polysulfones by the acylation and sulfonylation, respectively, have received attention more recently.

3. Polymerization by Acylation.

In general, the mechanism of Friedel-Crafts acylation is quite similar to that of an alkylation process. However, there is one difference in the functioning of the catalyst between these two types of Friedel-Crafts reactions (53).

In acylation the catalyst not only (A) interacts with the acylating agent to produce an actual or potential carbonium ion, but also (B) is capable of forming a stable complex with the carbonyl group of acylating agent as follow:

\[
\begin{align*}
R-\text{C}l + \text{AlCl}_3 & \quad \overset{\delta+ \delta-}{\longleftrightarrow} \quad R-\text{C}\cdot\text{AlCl}_4 \quad \text{or} \quad R-\text{C}=\text{Cl}---\text{AlCl}_3 \quad (A) \\
R-\text{C}l + \text{AlCl}_3 & \quad \overset{\delta+ \delta-}{\longleftrightarrow} \quad R-\text{C}=\text{O}---\text{AlCl}_3 \quad \overset{\delta+ \delta-}{\longleftrightarrow} \quad R-\text{C}=\text{O}---\text{AlCl}_3 \quad (B)
\end{align*}
\]

Therefore, in the Friedel-Crafts acylation reaction more than catalytic amounts of catalyst are needed, which leads to experimental difficulties in isolating pure samples of polymers.
from such reactions (54).

Many of the polyketones prepared by Friedel-Crafts acylation reactions have been described in French (55), American (56,57), British (58) and Japanese (59,60) patents. In general, the polymerization reactions used can be divided into two types: (A) the self-condensation of aryl carbonyl halides and their derivatives (55,59,60), and the (B) condensation of dicarbonyl halides with aryl compounds (56,57,58) as follows:

\[
\begin{align*}
\text{n} & \text{Y} - \text{O} - \text{C} & \text{X} & \text{Catalyst} & \left[ \text{n} \text{Y} - \text{O} - \text{C} \right] + \text{n} \text{HX} & \text{(A)} \\
\text{n} & \text{X} & \text{C} & \text{Y} & \text{O} & \text{C} & \text{X} & \text{Catalyst} & \left[ \text{2n} \text{HX} \right] + \left[ \text{n} \text{Y} - \text{O} - \text{C} & \text{Z} & \text{O} \right] & \text{(B)} \\
\text{where Y} & = 0, S, \text{etc.} \\
\text{X} & = \text{halides} \\
\text{Z} & = 0, \text{SO}_2, \text{CO etc.}
\end{align*}
\]

The polymers thus prepared usually have high softing points (250°C) (58) or melting points (170-195°C) (58,59). Film and fiber-forming polyketone copolymers have been found to be useful in high temperature electrical insulation (57).
4. Polymerization by Sulfonylation.

In contrast to the acylation with carboxylic acid chlorides, sulfonylation with sulfonyl chlorides has been reported to proceed in the presence of only catalytic quantities of anhydrous ferric chloride (2). The activity of catalysts in the polycondensation of sulfonyl chlorides were found to be as follows, in decreasing order: FeCl₃, SbCl₅ >> TiCl₃, SnCl₄, AlCl₃ >> TiCl₄, ZnCl₂, BF₃, Et₂O, MgCl₂ (54). The order is somewhat different to that in alkylation (32).

Unlike alkylation, polysulfonylation on an aromatic ring usually does not occur because substitution of a hydrogen atom by a sulfonyl group on the benzene nucleus decreases its reactivity toward electrophilic reagents (68). Thus in the polycondensation of this type, the rings in the polymer chains are less reactive than the rings of the monomer or the rings at the chain ends. The formation of linear chains is, therefore, favored. However, in the early work of the synthesis of polyarylene sulfones, Jennings and coworkers (54) reported that the polymers obtained from disulfonyl chlorides (e.g., diphenylether-4,4'-bis-sulfonyl chloride) with dinucleus aromatic compounds (e.g., diphenyl ether) using Lewis acids as catalyst were amorphous with high glass transition temperatures (e.g., around 250°C). From the analysis of the IR and NMR spectra of these polymers, Cudby and coworkers (61,62) concluded that the polymers were 90% linear.
From further studies on model compound reactions, they found that disubstituted rings containing ether and sulfonyl substituents could still be sulfonylated in spite of deactivation by sulfonyl groups.

It has been found that the deactivation in the Friedel-Crafts reaction can be upset by the simultaneous presence of powerful electron-donating groups (37). Thus although sulfonyl groups deactivate the aromatic nucleus within the polymer chains, the aromatic rings in diaryl ether units can still be sulfonylated because of deactivation is offset by the electron-donating ether linkage. The molecular weight and the linearity of the polymer were found to depend not only on the structure of the reactants but also on the reaction temperature (54).

Highly linear polymers were obtained from the self-condensation of diphenyl ether-4-sulfonyl chloride (62) in the presence of FeCl₃ at 120°C in nitrobenzene. The results show that this polymer consisted essentially of 4,4'-disubstituted unit (ca. 99%) and contained less than 0.7% of the branch units. However, no information about the crystallinity of the polymers was reported. The molecular weight and the quantity of insoluble polymer both increased with the reaction temperature. Therefore, the reaction temperature which yielded high molecular weight and low amounts of insoluble polymer was the best compromise temperature.
Crosslinking and branching were caused by the aryl radical formed at high temperature and subsequently attacked rings in the polymer chain (64).

Most of the polyarylene sulfones are noncrystalline except the polymer from self-condensation of diphenyl-4-sulfonyl chloride. The amorphous polymers have high glass transition temperatures, ranging from 200°C to over 350°C, and usually have good thermal and oxidation stability (65). Thermograms from the TGA analysis show roughly the same pattern both in air (oxidizing) and in nitrogen (inert) atmosphere which demonstrates the exceptional resistance of the arylsulfone polymers against oxidative degradation. This exceptionally good thermal oxidative resistance is believed (65) to be due to deactivation of the aromatic chain units by the sulfonyle groups.

C. The Branching in Polybenzyls.

Branching is one of the most important factors affecting the properties of the polymers (69). There are various types of branched molecules as illustrated in Figure 1-3 (80). Type a and type b are the comb-type molecules with long and short branches, respectively, while type c is the dendritic type with branched branches. Type d is the star type molecules. The branched polybenzyls are more
likely to have type c structures.

1. **Measuring the Degree of Branching.**

The degree of branching can, in principle, be measured from direct determination of the number of endgroups or branching points provided that they are present in high enough amounts and can be detected by the analytical methods. For low degree of branching, the most satisfactory method is intrinsic viscosity measurement on both of branched and linear polymers (69).

The first qualitative measurement of the degree of branching of polybenzyl was reported by Finnocchiano and
Passerini (42). The relative degree of branching was determined from IR spectrum through use of the ratio of bands at 800 and 1266 cm\(^{-1}\). The 800 cm\(^{-1}\) band was believed to be due to the para-substitution on the aromatic ring (10), and the 1266 cm\(^{-1}\) band was attributed to \(-\text{CH}_2\text{Cl}\) (42). Quantitative measurement of the degree of branching was made by measuring the ratio of the band 800 and 1605 cm\(^{-1}\) and by assuming a 100\% linearity for a polybenzyl prepared from benzyl chloride with AlCl\(_3\) at -135\(^\circ\)C at very low conversion (0.5\%) (14). No assignment for band 1605 cm\(^{-1}\) was given in this work, and the assumption of 100\% linearity is probably incorrect, because \(p\)-isomer content of the corresponding model compound reaction is only 67\% as indicated in Table II-2.

2. Effect of the Branching on Some of the Polymer Properties.

In general, long-branched molecules are more compact and smaller than linear molecules of the same molecular weight. The degree of polymer-solvent contact in branched molecules are, therefore, less than in linear molecules. On this basis, the solubility of the long branched molecules should be lower than that of linear ones. However, if the branching is short and the number of branches is not very large, the effect on the solubility will probably be very small (72). Moreover, the short chain branched molecules do not pack well in the solid state and have lower crystal-
linities than linear molecules, and it is expected that they should be more soluble than linear polymers.

The polybenzyls obtained from normal Friedel-Crafts reactions usually contain both soluble and insoluble portions as described in Section I-A. It is believed (40) that both soluble and insoluble polymers are all highly branched globular-like structure as illustrated in Figure 1-2. The only difference between these two types of polymers may be that the insoluble polymer has a higher molecular weight with a resulting larger size of globular molecules than the soluble molecules. As suggested above, for linear polybenzyl, the solubility should be less than that of branched polybenzyls because of the crystallinity of the linear polymer. Nevertheless, no report on this comparison has been found in the literature.

Glass transition temperatures of polymers are also affected by branching. The increase in the branches causes an increase in the number of endgroup per unit volume, and that, in turn, will cause an increase in free volume and a decrease in the glass transition (77). However, crowding at the junction points, like crosslinks, may be expected to raise a glass transition temperature (77). Therefore, the branches can either raise or lower the glass transition temperature, or have no effect. No detailed study has been reported on polybenzyls on the relationship between the struc-
ture and the glass transition temperature.

The low crystallinity or amorphous character of branched polymers is simply caused by the poor packing of the irregular branched molecules in the solid state. Branched polybenzyls are all amorphous (9,11,47) and only polybenzyls containing linear units are crystalline (10,14,22,74).

At a given molecular weight, random branches on polymer chains are generally found to cause a decrease in elasticity and flexibility of polymer film and increase brittleness (75). This effect and low molecular weight are presumably responsible for the fact that branched polybenzyls are brittle.

Thermal stability of the polymer is also known to be affected by branching in polymers (76). The thermal stability of branched polybenzyl was found to be lower than that of linear polybenzyl from the thermal gravimetric study (10,42). In addition, branched polybenzyls volatilize over a much wider temperature range than linear polybenzyls.
CHAPTER TWO
EXPERIMENTAL
I. CHEMICALS

Monomers:

- Benzyl Chloride
- 2,5-Dimethylbenzyl Chloride
- α-Chloroethyl Benzene

Sources:

- Aldrich Chemical Company, Inc.
  Eastman Kodak Company
- Eastman Kodak Company

Catalysts:

- Stannous Chloride
- Zinc Chloride
- Diethylaluminum Chloride
- Stannic Chloride-4M in Methylene Chloride
- Aluminum Chloride-Anhydrous
- Stannous Chloride-Anhydrous
- Molybdenum Pentachloride
- Palladium-10% in Charcoal
- Antimony Pentachloride
- Titanium Tetrachloride
- Silver Tetrafluoroborate

Sources:

- J. T. Baker Chemical Company
- Fisher Scientific Company
- Pfaltz and Bauer, Inc.
- Research Organic/Inorganic Chemical Corporation
- Fisher Scientific Company
- Research Organic/Inorganic Chemical Corporation
- Fisher Scientific Company
- Research Organic/Inorganic Chemical Corporation

Solvents:

For Polymerizations:

- Ethyl Chloride
- n-Pentane
- Nitromethane-Spectra Grade
- n-Hexane
- Trichloroethylene
- Sulfur Dioxide-Anhydrous
- Methyl Chloride
- Fluorosulfonic Acid

Sources:

- The Matheson Gas Products
- Fisher Scientific Company
- Matheson, Coleman, and Bell
- J. T. Baker Chemical Company
- Eastman Kodak Company
- The Matheson Gas Products
- The Matheson Gas Products
- Research Organic/Inorganic Chemical Corporation

For Model Compound Reactions:
Ethyl Chloride  
Nitromethane—Spectra Grade  
Sulfur Dioxide—Anhydrous  
Nitrobenzene  
Ethanol—95%  
Ether—Anhydrous

For Characterization: Solubility

Tetrahydrofuran  
p-Xylene  
Benzene  
Phenyl Ether  
Mesitylene  
Diphenylmethane  
Decaline  
o-Dichlorobenzene  
Tetrachloroethylene  
Chloroform

For Characterization: NMR

Carbon Tetrachloride  
Carbon Disulfide

For Characterization: Molecular Weight

1,2,4-Trichlorobenzene  
Benzene

For Characterization: Infrared

Chloroform  
Carbon Disulfide

For Characterization: Viscosity

p-Xylene

For Grignard Reagents Syntheses:

Tetrahydrofuran—Chromato-quality

For Complexation Studies:

Carbon Tetrachloride—Spect. Grade
n-Hexane

Reagents:

For Model Compound Studies:

- 1,1-Diphenylethylene
- 1,4-Bischloroethylbenzene
- 1,3-Bischloroethylbenzene
- 1,2-Bischloroethylbenzene
- Benzene
- Diphenylmethane

For Complexation Studies:

- Sulfur Dioxide
- p-Xylene
- Toluene-Spect. Grade
- Tetranitromethane

For Grignard Reagents Syntheses:

- Dibromobenzene-Practical Grade
- Magnesium Turnings
- Iodine
- Hydrochloride Solution
- Sodium Hydroxide Solution-1 N
- Benzyl Bromide

II. MONOMER PURIFICATION

Benzyl Chloride. Benzyl chloride was distilled, under vacuum, in a compact fractionation apparatus from Ace Glass Company, and the middle cut at 62°C/20 mm. was collected. The monomer was stored under a nitrogen atmosphere in the refrigerator; analysis by gas chromatography, GC, (10% SE 30 on Aeropak 30) at its highest sensity, showed no impurity remaining.
2,5-Dimethylbenzyl Chloride. 2,5-Dimethylbenzyl chloride was vacuum distilled in the same apparatus as above, and the middle cut was taken at 91°C/20 m.m. and stored under a nitrogen atmosphere.

α-Chloroethylbenzene. α-Chloroethylbenzene was distilled under vacuum in a 16-inch long column packed with helices. The middle fraction of the distillate at 95-96°C/19 m.m. was collected and stored under nitrogen atmosphere in a refrigerator. Analysis of the monomer by GC showed that there was a small peak with the major peak which had the same retention time as styrene. The size of the peak decreased with time when the monomer solution was saturated with dry hydrogen chloride for 12 hours. It is quite clear that this impurity is styrene, which could occur from the dehydrochlorination of α-chloroethylbenzene or from the unreacted starting material during the synthesis of α-chloroethylbenzene.

The results of the GC analysis are indicated in Table II-1. The boiling points of styrene and α-chloroethylbenzene are 145°C and 195°C at 760 mm Hg, respectively. By using a 16-inch column packed with helices, it should be possible to eliminate styrene from the middle cut of α-chloroethylbenzene, but the results in Table II-1 showed that distillation did not give 100% pure monomer. It is believed that dehydrochlorination of monomer occurred during the distillation.
Table II-1

GC Analysis of α-Chloroethylbenzene Under Different Treatment*

<table>
<thead>
<tr>
<th>Monomer Treatment</th>
<th>Purity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer as received</td>
<td>97.0</td>
</tr>
<tr>
<td>Monomer distilled</td>
<td>98.1</td>
</tr>
<tr>
<td>Monomer distilled then saturated with HCl for 12 hours</td>
<td>99.4</td>
</tr>
<tr>
<td>Monomer without distillation but saturated with HCl for 12 hours</td>
<td>99.2</td>
</tr>
</tbody>
</table>

* Using 10% Cargowax 20 M on Chromosorb W
  
  Column temperature: 215°C
  Injection port temperature: 245°C

The final purification of monomer was, therefore, done by passing dry hydrogen chloride through the monomer for 12 hours, and the excess HCl dissolved in monomer was expelled by purging with dry nitrogen until no acid can be detected in the exit gas with wet litmus paper.

III. PURIFICATION OF SOLVENTS AND REAGENTS

**Ethyl Chloride.** Ethyl chloride was first passed through a column of potassium hydroxide pellets and then through a column of Linde molecular sieves (3A) before being condensed into the reaction flask.

**Nitromethane.** Spectral grade nitromethane was passed through a dry column containing Linde molecular sieves (3A) into the reaction flask. No water was detected
in the solvent by GC analysis.

**n-Hexane and n-Pentane.** These solvents were purified by washing consecutively with fuming sulfuric acid, water, dilute sodium carbonate solution, and water. They were then refluxed over metallic sodium and were distilled through a 12-inch column packed with glass helices. In the complexation studies, spectral grade n-hexane was used without further purification. The solvent was dried over Linde molecular sieves (3A).

**Trichloroethylene.** Trichloroethylene was washed consecutively with 2M HCl, water and 2M K₂CO₃, then dried and stored over CaCl₂. The stored solvent was distilled before the polymerization.

**Nitrobenzene.** Reagent grade nitrobenzene was dried over CaCl₂ and distilled through a 12-inch column packed with glass helices.

**Benzene.** Analytical grade benzene was refluxed with metallic sodium for about 12 hours and distilled in a stream of dry nitrogen. The purified solvent was stored temporarily in a desiccator prior to use for the model compound synthesis.

**Toluene.** Spectral grade toluene was dried over Linde molecular sieves (2A) before use for the complexation studies.

**Carbon Tetrachloride.** Reagent grade carbon
tetrachloride was fractionated and the middle cut was collected for complexation studies.

**Dibromobenzene.** Dibromobenzene was recrystallized twice from isopropyl alcohol and dried in vaccum oven at room temperature for 48 hours prior to use for the synthesis of Grignard reagent.

**Benzyl Bromide.** Benzyl bromide was fractionated under reduced pressure (17 mm Hg) at 101°C. The middle cut was collected.

### IV. CATALYST PURIFICATION

Most of the catalysts were used as received except aluminum chloride and zinc chloride. Anhydrous aluminum chloride was sublimed at 20 mm Hg under dry nitrogen atmosphere before use in polymerization. Zinc chloride was fused under vaccum in order to remove water.

### V. TREATMENT OF REACTION SYSTEM

All glass apparatus used in model reaction and polymerization studies were dried in a 140°C oven for at least 12 hours and quickly assembled while still hot. The reaction system was closed to the atmosphere with septum caps. The reaction vessel was connected to both a dry nitrogen source and a vaccum pump, and was evacuated under a
flame and subsequently purged with dry nitrogen. The evacuation, flaming and purging procedure was repeated three times. During the reaction, a small stream of dry nitrogen was kept running through the system.

VI. MODEL COMPOUND REACTION OF POLYBENZYL

A. Preparation of Dibenzyldibenzene (DBB) Isomers:

The pure isomers of DBB were prepared by two routes: (1) by reacting 1,4-, 1,2-, or 1,3-bis(chloromethyl)benzene with benzene and (2) by reacting benzyl chloride with diphenylmethane and separating the isomers by preparative GC.

1. Method (1):
(a) p-Dibenzyldibenzene (p-DBB).

2.5 ml of TiCl₄ and 40 ml of benzene was transferred into 60 ml of cold ethyl chloride and the solution was subsequently cooled to -78°C in a dry-ice-isopropanol bath. A cold solution of 2.01 g (11.4 mmole) of 1,4-bis(chloromethyl)benzene in 30 ml of ethyl chloride was added slowly with stirring into the benzene solution. After 60 minutes, the reaction was terminated with 5 ml cold methanol. The solution was consecutively washed with
water and extracted with carbon tetrachloride several times. After carbon tetrachloride was evaporated from the extracted solution, p-DBB was recrystallized from acetone.

The analysis of this product by GC on a column of 10% Carbowax 20M on Chromosorb W showed no other impurity present.

Elementary Analysis: Found: C, 93.04%; H, 6.96%
Calcd: C, 93.02%; H, 6.98%

NMR Spectrum in CS₂: δ (relative intensity, multiplicity, assignment) 3.85 (2H, s, \(-\text{CH}_2\)-), 6.85 (4H, s, disubstituted aromatic ring), 7.10 (10H, s, monosubstituted aromatic ring).

IR Spectrum in CS₂: cm\(^{-1}\) (intensity, assignment) 3030 (s, aromatic C-H), 2910 (s, \(-\text{CH}_2\)-), 1660-2000 (w, substituted aromatic ring), 1075 & 1032 (w, m, monosubstituted aromatic), 1023 (m, p-disubstituted aromatic ring), 839 (m, p-disubstituted aromatic ring).

The NMR and IR spectra match completely to the spectra reported in the literature (81,82).

(b) o-Dibenzylbenzene (o-DBB).

o-DBB was synthesized from reacting 1,2-bis-(chloromethyl)benzene with excess of benzene by the same procedure described above.
Elementary Analysis: Found: C, 92.91%; H, 6.93%
Calcd: C, 93.02%; H, 6.98%

NMR Spectrum in CS$_2$: $^6$ (relative intensity, multiplicity, assignment) 7.00-7.15 (14H, m, aromatic rings), 3.85 (2H, s, -CH$_2$-).

IR Spectrum in CS$_2$: cm$^{-1}$ (intensity, assignment)
3030 (s, aromatic C-H), 2910 (s, -CH$_2$-), 1660-2000 (w, substituted aromatic), 1075 & 1032 (w, m, monosubstituted aromatic), 1050 (w, o-disubstituted aromatic).

(c) m-Dibenzylbenzene (m-DBB).

m-DBB was also synthesized by reacting 1,3-bis(chloromethyl)benzene with excess of benzene by the same procedure described above.

Elementary Analysis: Found: C, 92.97%; H, 6.92%
Calcd: C, 93.02%; H, 6.98%

NMR Spectrum in CS$_2$: $^6$ (relative intensity, multiplicity, assignment) 6.85-7.18 (14H, m, aromatic rings), 3.84 (2H, s, -CH$_2$-).

IR Spectrum in CS$_2$: cm$^{-1}$ (intensity, assignment)
3030 (s, aromatic C-H), 2910 (s, -CH$_2$-), 1666-2000 (w, substituted aromatic), 1090 (m, m-disubstituted aromatic), 1750 & 1032 (w, m, monosubstituted aromatic ring), 1905 (w, m-disubstituted aromatic).
2. Method (2):

It is the same procedure as described in Section VI-B-(1). In method (2), excess diphenylmethane was reacted with benzyl chloride in the presence of TiCl$_4$ at the room temperature. The product containing a mixture of DBB isomers was separated by the preparative GC on a column of 30% Carbowax 20M on anaprep ABS at 220°C. The isolated isomers have the same NMR and IR spectra and the same retention time on GC as those prepared from method (1).

B. Model Compound Reactions:

The model compound reactions were carried out at different temperatures and in different solvents by using two types of catalysts, Lewis acid and Ziegler-Natta type catalysts. The conditions of these reactions are shown in Table II-2. Only M-10 and M-19 will be described in the following sections.

1. Lewis Acid Catalyst.

Reaction M-10 was carried out in a 100 ml three-neck flask equipped with a nitrogen inlet outlet and a magnetic stirring bar operated by a submersible magnetic stirrer. The reaction system was treated as described in
Table II-2
Model Compound Reaction of Benzyl Chloride and Diphenylmethane

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp., °C</th>
<th>Time, min</th>
<th>b Isomer Distribution, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB-1</td>
<td>AlCl₃</td>
<td>C₂H₅Cl</td>
<td>-125</td>
<td>30</td>
<td>67 25 8</td>
</tr>
<tr>
<td>MB-2</td>
<td>AlCl₃</td>
<td>C₂H₅Cl</td>
<td>-78</td>
<td>180</td>
<td>47 43 10</td>
</tr>
<tr>
<td>MB-3</td>
<td>DEAC/TiCl₄</td>
<td>C₂H₅Cl</td>
<td>-125</td>
<td>30</td>
<td>54 29 16</td>
</tr>
<tr>
<td>MB-4</td>
<td>DEAC/TiCl₄</td>
<td>C₂H₅Cl</td>
<td>-65</td>
<td>30</td>
<td>53 27 20</td>
</tr>
<tr>
<td>MB-5</td>
<td>DEAC/TiCl₄</td>
<td>CH₃NO₂</td>
<td>23</td>
<td>40</td>
<td>50 38 11</td>
</tr>
<tr>
<td>MB-6</td>
<td>MoCl₅</td>
<td>C₂H₅Cl</td>
<td>-125</td>
<td>90</td>
<td>47 49 4</td>
</tr>
<tr>
<td>MB-7</td>
<td>SbF₅</td>
<td>C₂H₅Cl</td>
<td>-125</td>
<td>10</td>
<td>41 50 9</td>
</tr>
<tr>
<td>MB-8</td>
<td>SbF₅/HSO₃F</td>
<td>SO₂</td>
<td>-78</td>
<td>10</td>
<td>61 12 27</td>
</tr>
<tr>
<td>MB-9</td>
<td>SbF₅</td>
<td>SO₂</td>
<td>-78</td>
<td>30</td>
<td>53 18 29</td>
</tr>
<tr>
<td>MB-10</td>
<td>MoCl₅</td>
<td>SO₂</td>
<td>-78</td>
<td>60</td>
<td>51 41 8</td>
</tr>
<tr>
<td>MB-11</td>
<td>AlCl₃</td>
<td>SO₂</td>
<td>-68</td>
<td>20</td>
<td>46 45 9</td>
</tr>
<tr>
<td>MB-12</td>
<td>TiCl₄</td>
<td>CH₃NO₂</td>
<td>22</td>
<td>180</td>
<td>50 29 21</td>
</tr>
</tbody>
</table>

a DEAC: Diethylaluminum Chloride.

b Isomer: Dibenzylbenzenes.
Section V. 0.1 g (7 mmole) of fresh AlCl$_3$ was transferred into the flask in a dry bag. The flask was immersed in a dry-ice-isopropanol cooling bath, and 30 ml of ethyl chloride was condensed in the flask. With stirring, 1 ml (9 mmole) of diphenylmethane was quickly injected into the flask, and the solution immediately turned brown. A solution of 0.25 ml (2 mmole) of benzyl chloride in 10 ml of ethyl chloride was cooled to -78°C in a 25 ml flask equipped with a septum cap, a nitrogen gas inlet and a small section of Teflon tubing running into the three-neck flask. The monomer solution was pumped through the Teflon tubing into the three-neck flask by applying a positive nitrogen pressure. The reaction was terminated in 180 minutes with 2 ml of cold methanol. Ethyl chloride was evaporated from the solution by warming up the flask to room temperature. The solution was washed with dilute HCl solution and extracted with carbon tetrachloride three times. Carbon tetrachloride was evaporated from the extracted solution at the room temperature, and the residual solution was subjected to the isomer distribution analysis as described in Section VI-B-3.

2. Ziegler-Natta Catalyst (M-19).

In reaction M-19, 0.44 ml (4 mmole) of TiCl$_4$ and
1 ml (2 mmole) of diethylaluminum chloride solution (34.25 weight % in n-hexane) were injected from separate syringes into a dry 50 ml three-neck flask provided with a Teflon stirrer blade and septum caps, in which two needles were inserted to serve as the inlet and outlet of nitrogen gas. A dark-brown precipitate was observed to form immediately after two catalyst solutions came in contact. The catalyst suspension was aged for 30 minutes at room temperature, and 25 ml of ethyl chloride was condensed into the flask with stirring. The contents were cooled to -78°C in a dry-ice-isopropanol bath, and 1.9 ml (16 mmole) of diphenylmethane was added quickly into the vigorously stirred catalyst solution. The flask was cooled to -125°C in a n-pentane-liquid nitrogen bath, and 0.5 ml (4 mmole) of benzyl chloride in 10 ml of ethyl chloride, pre-cooled to -125°C, was transferred into the flask by the method described in the previous section. The reaction was terminated after 180 minutes with cold methanol. The solution was washed and extracted by the same way as illustrated in the previous section.

3. Analysis of Isomer Distribution.

The reaction product was analyzed by GC using a
column of 10% Carbowax 20M on Chromosorb W at 215°C. The isomer distribution of DBB was obtained from the relative peak area of each isomer. The retention time of para-, meta- and ortho-DBB are 46.0, 32.5 and 29.0 min., respectively. The response of the GC (thermal conductivity detector) on the ratio of the o-, p-, and m- of DBB was calibrated by injecting a mixture of the three pure DBB isomers. The areas of the corresponding peaks were measured and the ratios are recorded in Table II-3. The results show that the ratio of the peak areas can be used directly to determine the mole ratio of isomers.

Table II-3
Comparison of the Mole Ratio of DBB Isomers with the Ratio of the Peak Area in the GC

<table>
<thead>
<tr>
<th>Mole Ratio of DBB</th>
<th>Ratio of the Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>p : o : m</td>
<td>p : o : m</td>
</tr>
<tr>
<td>61.2 28.5 10.3</td>
<td>60.8 29.1 10.1</td>
</tr>
<tr>
<td>49.7 32.1 18.2</td>
<td>49.0 32.4 18.6</td>
</tr>
</tbody>
</table>

VII. POLYMERIZATION OF BENZYL CHLORIDE

Benzyl chloride was polymerized in different solvents under different temperatures by using different
catalysts. The details of the reaction conditions are given in Table II-4. Two polymerization reactions (PB-6 and PB-10A) carried out under different catalyst and solvent systems other than those mentioned in Section VI-B were chosen to be described in the following sections.

**Polymer PB-6.** The reaction system was treated as described in Section V. Into 100 ml four-neck flask equipped with a Teflon blade, septum cap, nitrogen gas inlet and outlet, was condensed 40 ml of SO\(_2\) at salt-ice slush temperature. 0.2 ml of SbF\(_5\) (2.9 mmole) and 5 ml of HSO\(_3\)F were injected in the flask, and the solution turned brown. With stirring, the solution was cooled to -78°C in a dry-ice-isopropanol bath, and 3 ml of benzyl chloride (26 mmole) in 10 ml of SO\(_2\) was transferred in slowly by the method described in Section VI-B-1. The solution turned red and remained unchanged in color throughout the reaction. After one hour, the reaction was terminated with cold methanol, and the red color disappeared and a white precipitate appeared. The suspension was then poured into 250 ml of methanol for complete precipitation of the polymer. The polymer suspension was filtered through a 25-50 μm sintered glass filter, and the filter cake was washed consecutively with methanol, NaOH dilute solution, water, and methanol. After drying in the vacuum oven at room temperature for 24 hours, 2.2 g (93.6%) of the polymer was
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer Conc., mmole</th>
<th>Catalyst &amp; Conc., mmole</th>
<th>Solvent</th>
<th>Temperature °C</th>
<th>Time min.</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-1</td>
<td>20.0</td>
<td>TiCl4: 0.20 DeAC: 0.10</td>
<td>bMeCl</td>
<td>-112 to -105</td>
<td>20</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-97 to -90</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>PB-2</td>
<td>20.0</td>
<td>TiCl4: 0.20 DeAC: 0.10</td>
<td>cEtCl</td>
<td>-131 to -25</td>
<td>180</td>
<td>94.3</td>
</tr>
<tr>
<td>PB-3</td>
<td>8.9</td>
<td>TiCl4: 0.09 DeAC: 0.05</td>
<td>EtCl</td>
<td>-78</td>
<td>5</td>
<td>13.2</td>
</tr>
<tr>
<td>PB-4</td>
<td>20.0</td>
<td>TiCl4: 0.09 DeAC: 0.05</td>
<td>EtCl</td>
<td>-130</td>
<td>120</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-130 to -50</td>
<td>480</td>
<td></td>
</tr>
<tr>
<td>PB-5</td>
<td>13.0</td>
<td>TiCl4: 0.09 DeAC: 0.05</td>
<td>EtCl</td>
<td>-130</td>
<td>600</td>
<td>60.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-130 to room temp.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB-6</td>
<td>25.0</td>
<td>SbF5/HSO3F: 25.3</td>
<td>SO2</td>
<td>-78</td>
<td>60</td>
<td>66.7</td>
</tr>
<tr>
<td>PB-7</td>
<td>94.0</td>
<td>AlCl3: 1.88 EtCl</td>
<td>-130</td>
<td>20</td>
<td>65.9</td>
<td></td>
</tr>
<tr>
<td>PB-8A</td>
<td>37.6</td>
<td>DEAC: 0.94 EtCl</td>
<td>-78</td>
<td>30</td>
<td>87.3</td>
<td></td>
</tr>
<tr>
<td>PB-8B</td>
<td>37.6</td>
<td>DEAC: 0.94 EtCl</td>
<td>-78</td>
<td>60</td>
<td>87.3</td>
<td></td>
</tr>
<tr>
<td>PB-9</td>
<td>37.6</td>
<td>TiCl4: 0.376 EtCl</td>
<td>-78</td>
<td>1040</td>
<td>17.3</td>
<td></td>
</tr>
<tr>
<td>PB-10A</td>
<td>37.6</td>
<td>TiCl4: 0.376 dNM</td>
<td>26</td>
<td>720</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>PB-10B</td>
<td>37.6</td>
<td>TiCl4: 0.376 NM</td>
<td>25</td>
<td>2880</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td>PB-11</td>
<td>25.0</td>
<td>SbF5: 2.5 SO2</td>
<td>-78</td>
<td>60</td>
<td>100.0</td>
<td></td>
</tr>
</tbody>
</table>

a DEAC: Diethylaluminum Chloride.
b MeCl: Methyl Chloride.
c EtCl: Ethyl Chloride.
d NM: Nitromethane.
obtained.

Analysis: Found: C, 93.28%; H, 6.47%
Calcd: C, 93.34%; H, 6.66%

$\bar{M_n} = 2926$ (in benzene at 50°C)

**Polymer PB-10.** The reaction system was treated as described in Section V. 0.41 ml (3.7 mmole) of TiCl$_4$ in 50 ml of nitromethane was transferred with a hypodermic syringe into a 100 ml three-neck flask equipped with a magnetic stirrer bar, a septum cap, a nitrogen inlet and outlet. 4.3 ml (34.7 mmole) of benzyl chloride in 10 ml of nitromethane was injected slowly into the flask by using a hypodermic syringe. The yellow solution turned dark green after 10 minutes. At the same time, HCl was detected in the gas outlet by wet litmus paper. After 12 hours of reaction at room temperature, the stirrer bar was stopped by the highly viscous, brown material formed at the bottom of the flask. The upper solution was dark green in color but clear. The reaction was terminated with methanol. Both the solution and the tacky substance at the bottom of the flask turned yellow. The solvent was evaporated under reduced pressure at room temperature, and the tacky yellow polymer was dissolved in THF and was precipitated in either cold n-hexane or cold methanol. In the latter case only a tacky yellow polymer was obtained, while in the former case, a powdered polymer was obtained. The precipitation was
repeated twice in cold \text{n}-hexane, and 0.5 g (14.8\%) of polymer in the form of a yellow powder was obtained.
\[M_n : 1554.\]

VIII. POLYMERIZATION OF 2,5-DIMETHYL BENZYL CHLORIDE

2,5-Dimethylbenzyl chloride was polymerized with diethylaluminum chloride and titanium tetrachloride as catalyst. The polymerization reactions were carried out at different temperatures and solvents as shown in Table II-5. Only polymerization of PDMB-2 will be described in the following sections.

Polymer PDMB-2. The reaction system was treated as described in Section V. 0.02 ml (0.2 mmole) of TiCl\textsubscript{4} and 0.04 ml (0.13 mmole) of diethylaluminum chloride solution (40\% \text{n}-heptane solution) were injected with a micro-syringe into a 50 ml flask containing 2 ml \text{n}-hexane. The flask was equipped with a magnetic stirrer bar and a septum cap. The solution was aged for 30 minutes at room temperature with stirring. The flask was kept under the nitrogen atmosphere by running nitrogen gas in and out of the flask through two hypodermic needles inserted into the septum cap. After 10 ml of \text{n}-hexane was added in the flask, the solution was cooled to 0\degree C in a ice-water bath. 2.4 ml (17.7 mmole) of 2,5-dimethylbenzyl chloride was added
Table II-5
Polymerization of 2,5-Dimethylbenzyl Chloride

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer Conc. mmole</th>
<th>Catalyst mmole</th>
<th>Solvent</th>
<th>Temp. °C</th>
<th>Time min.</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMB-1</td>
<td>17.7</td>
<td>0.20 0.10</td>
<td>n-Hexane</td>
<td>-64</td>
<td>60</td>
<td>84</td>
</tr>
<tr>
<td>PDMB-2</td>
<td>17.7</td>
<td>0.20 0.13</td>
<td>n-Hexane</td>
<td>0</td>
<td>30</td>
<td>31</td>
</tr>
<tr>
<td>PDMB-3</td>
<td>17.7</td>
<td>0.20 0.13</td>
<td>EtCl</td>
<td>-64</td>
<td>15</td>
<td>37</td>
</tr>
<tr>
<td>PDMB-4</td>
<td>13.3</td>
<td>0.20 0.10</td>
<td>EtCl</td>
<td>0</td>
<td>40</td>
<td>75</td>
</tr>
<tr>
<td>PDMB-5</td>
<td>17.7</td>
<td>0.20 0.13</td>
<td>TCE</td>
<td>-78</td>
<td>20</td>
<td>64</td>
</tr>
<tr>
<td>PDMB-6</td>
<td>17.0</td>
<td>0.29 0.16</td>
<td>TCE</td>
<td>-78 to 2</td>
<td>600</td>
<td>71</td>
</tr>
<tr>
<td>PDMB-7</td>
<td>17.0</td>
<td>0.20 0.10</td>
<td>TCE</td>
<td>26</td>
<td>30</td>
<td>--</td>
</tr>
<tr>
<td>PDMB-8</td>
<td>14.8</td>
<td>0.36 ----</td>
<td>TCE</td>
<td>-78 to 26</td>
<td>40</td>
<td>--</td>
</tr>
<tr>
<td>PDMB-9</td>
<td>7.4</td>
<td>0.14 0.07</td>
<td>Bulk</td>
<td>26</td>
<td>10</td>
<td>--</td>
</tr>
</tbody>
</table>

a DEAC: Diethylaluminum Chloride.
b EtCl: Ethyl Chloride
c TCE: Trichloroethylene.
dropwise into the flask, and a yellow precipitate formed immediately. After 30 minutes, the reaction was terminated with methanol, and the precipitate turned white. The product was poured into 100 ml methanol to make sure that precipitation of the polymer was complete. The polymer was filtered and washed several times with dilute HCl and methanol. 0.8 g (31% of white polymer was obtained after 24 hours of drying under vaccum at room temperature.

IX. MODEL COMPOUND REACTION OF POLY-α-METHYLBENZYL

A. Preparation of 1,1-Diphenylethane (DPE).

DPE was prepared by the hydrogenation of 1,1-diphenylethylene. 26.1 g (0.145 mole) of 1,1-diphenylethylene was dissolved in 100 ml of 95% alcohol in a Parr pressure bottle. 374 mg of 10% palladium in charcoal was added to the solution. After this mixture was well shaken, another portion of 160 ml 95% of alcohol was added. The hydrogenation was completed after one hour at 40 psi hydrogen pressure. The catalyst was removed by filtration and the solvent was removed by use of a rotatory evaporator. The final solution was then distilled under vaccum (1 mm Hg) at 93°C. 25.9 g of DPE was obtained. The analysis of this compound by GC on a column of 10% Carbowax 20M on Chromosorb W showed no impurity present. The IR spectrum
is identical to the spectrum reported (93).

B. Preparation of Bis(α-phenylethyl)benzene (BPEB) Isomers.

The BPEB isomers were prepared by reacting α-chloroethylbenzene with excess 1,1-diphenylethane under two different reaction conditions: (a) TiCl₄/nitromethane/26°C and (b) SbF₅/SO₂/-78°C. The procedures are the same as described in Section IX. Each isomer of BPEB was isolated by preparative GC on a column of 30% Carbowax 20M on Anaprep AES at 230°C. The content of ortho-isomer is so low that the quantity of the sample collected is far less than the amount needed for characterization.

1. p-Bis(α-Phenylethyl)benzene (p-BPEB).

NMR Spectrum in CDCl₃: δ (relative intensity, multiplicity, assignment) 7.07 (10H, s, monosubstituted aromatic rings), 7.01 (4H, s, disubstituted aromatic ring), 3.98 (2H, q, -CH), 1.50 (6H, d, -CH₃).

IR Spectrum Neat: cm⁻¹ (intensity, assignment) 3042 (s, aromatic C-H), 2980 & 2950 (s, m, -CH₃), 2890 (m, -CH), 1070 and 1040 (w, m, monosubstituted aromatic), 1030 (m, p-disubstituted aromatic), 850 (s, p-disubstituted aromatic).
2. **m-Bis(α-Phenylethyl)benzene (m-BPEB).**

NMR Spectrum in CDCl₃: δ (relative intensity, multiplicity, assignment) 6.90-7.24 (14H, m, aromatic ring), 4.04 (2H, q, -CH), 1.57 (6H, d, -CH₃).

IR Spectrum Neat: cm⁻¹ (intensity, assignment) 3042 (s, aromatic C-H), 2980 & 2950 (s, m, -CH₃), 2890 (m, -CH), 1666-2000 (w, substituted aromatic), 1068 & 1040 (w, m, monosubstituted aromatic), 1090 (w, m-disubstituted aromatic), 904 (w, m-disubstituted aromatic).

C. **Model Compound Reactions.**

The reaction procedure is the same as described in Section VI-B-1, except that α-chloroethylbenzene and DPE were used as the reactants. Some reactions of α-chloroethylbenzene with DPM were also carried out under the same procedure. The reaction conditions for the model compound reactions are shown in Table II-6 and Table II-7.

The isomer distribution was analyzed by GC using a column of 10% Carbowax 20M on Chromosorb W at 208°C. The retention time of BPEB isomers are 84 min. (para-), 51 min. (meta-) and 42 min. (ortho-). The relative peak area of the isomers is a direct measure of the isomer distribution.
Table II-6

Model Compound Reactions of α-Chloroethylbenzene and 1,1-Diphenylethane

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp. °C</th>
<th>Time min.</th>
<th>Isomer Distribution, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC-1</td>
<td>TiCl₄</td>
<td>CH₃NO₂</td>
<td>26</td>
<td>60</td>
<td>p 93.7 o 1.2 m 5.1</td>
</tr>
<tr>
<td>MC-2</td>
<td>MoCl₅</td>
<td>CH₃NO₂</td>
<td>26</td>
<td>60</td>
<td>p 93.9 o 1.2 m 4.9</td>
</tr>
<tr>
<td>MC-3</td>
<td>ZnCl₂</td>
<td>CH₃NO₂</td>
<td>25</td>
<td>90</td>
<td>p 93.7 o 1.3 m 5.0</td>
</tr>
<tr>
<td>MC-4a</td>
<td>SbF₅</td>
<td>SO₂</td>
<td>-78</td>
<td>5</td>
<td>p 41.5 o 0 m 58.5</td>
</tr>
<tr>
<td>MC-4b</td>
<td>SbF₅</td>
<td>SO₂</td>
<td>-78</td>
<td>20</td>
<td>p 37.1 o 0 m 62.9</td>
</tr>
<tr>
<td>MC-4c</td>
<td>SbF₅</td>
<td>SO₂</td>
<td>-78</td>
<td>60</td>
<td>p 34.7 o 0 m 65.3</td>
</tr>
<tr>
<td>MC-4d</td>
<td>SbF₅</td>
<td>SO₂</td>
<td>-78</td>
<td>90</td>
<td>p 28.6 o 0 m 71.4</td>
</tr>
<tr>
<td>MC-5</td>
<td>AlCl₃</td>
<td>C₂H₅Cl</td>
<td>-78</td>
<td>60</td>
<td>p 98.8 o 0.5 m 0.7</td>
</tr>
</tbody>
</table>
### Table II-7

Model Compound Reaction of α-Chloroethylbenzene and Diphenylmethane

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp. °C</th>
<th>Time min.</th>
<th>Isomer Distribution, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD-1</td>
<td>AlCl₃</td>
<td>CH₃NO₂</td>
<td>25</td>
<td>30</td>
<td>p 92.3 o 2.4 m 5.3</td>
</tr>
<tr>
<td>MD-2</td>
<td>TiCl₄</td>
<td>CH₃NO₂</td>
<td>25</td>
<td>30</td>
<td>p 91.4 o 4.6 m 4.3</td>
</tr>
<tr>
<td>MD-3</td>
<td>SbF₅</td>
<td>CH₃NO₂</td>
<td>25</td>
<td>60</td>
<td>p 90.3 o 3.4 m 6.3</td>
</tr>
<tr>
<td>MD-4</td>
<td>SnCl₄</td>
<td>CH₂Cl₂</td>
<td>25</td>
<td>60</td>
<td>p 90.7 o 4.7 m 4.6</td>
</tr>
<tr>
<td>MD-5</td>
<td>AlCl₃</td>
<td>C₂H₅Cl</td>
<td>-78</td>
<td>30</td>
<td>p 96.8 o 0.6 m 2.6</td>
</tr>
<tr>
<td>MD-6</td>
<td>SbF₅</td>
<td>SO₂</td>
<td>-78</td>
<td>10</td>
<td>p 41.2 o 0 m 58.8</td>
</tr>
<tr>
<td>MD-7</td>
<td>SbF₅/HSO₃F</td>
<td>SO₂</td>
<td>-78</td>
<td>10</td>
<td>p 40.7 o 0 m 59.3</td>
</tr>
<tr>
<td>MD-8</td>
<td>SbF₅/SnCl₂</td>
<td>SO₂</td>
<td>-78</td>
<td>10</td>
<td>p 33.2 o 0 m 66.8</td>
</tr>
</tbody>
</table>
X. POLYMERIZATION OF α-CHLOROETHYL BENZENE

The polymerization reaction carried out on α-chloroethylbenzene under different conditions are listed in Table II-8. Only the polymerizations of PMB-2 and PMB-7 will be described in the following sections.

Polymer PMB-2. The reaction system was treated as described in Section V. 26 ml (1.91 mole) of α-chloroethylbenzene and 140 ml of CCl₄ was transferred into a 500 ml three-neck flask provided with a Teflon stirrer blade and two septum caps. Two hypodermic needles inserted into the septum caps served as a nitrogen gas inlet and outlet. 2.1 ml (19.1 mmole) of TiCl₄ in 10 ml of CCl₄ was injected slowly into the monomer solution with stirring. The color of the solution changed from yellow to dark brown after 10 minutes. Additional amount of TiCl₄, 0.5 ml and 1.0 ml, were added into the solution after 6 hours and 8 hours of reaction, respectively. After 19 hours, 20 ml of the solution was withdrawn, and methanol was added to terminate the reaction. Sample PMB-2A was the polymer suspended in the solution and PMB-2B was the tacky polymer which adhered to the bottom of the flask. The reaction of the remaining solution was terminated with methanol after 26 hours. Samples PMB-2C and PMB-2D were the reprecipitated polymers obtained from the material suspended in the solution.
### Table II-8

Polymerization of α-Chloroethylbenzene

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer mmole</th>
<th>Catalyst mmole</th>
<th>Solvent</th>
<th>Temp. °C</th>
<th>Time hrs.</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMB-1</td>
<td>2.54</td>
<td>TiCl₄: 25.4</td>
<td>Nitromethane</td>
<td>25</td>
<td>9</td>
<td>43</td>
</tr>
<tr>
<td>PMB-2</td>
<td>1.91</td>
<td>TiCl₄: 19.1</td>
<td>CCl₄</td>
<td>25</td>
<td>16</td>
<td>19</td>
</tr>
<tr>
<td>PMB-3</td>
<td>0.50</td>
<td>AlCl₃: 61.0</td>
<td>EtCl</td>
<td>-78</td>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>PMB-4</td>
<td>1.00</td>
<td>AlCl₃: 10.0</td>
<td>EtCl</td>
<td>-78</td>
<td>3</td>
<td>19</td>
</tr>
<tr>
<td>PMB-5</td>
<td>2.00</td>
<td>AlCl₃: 22.0</td>
<td>EtCl</td>
<td>-125</td>
<td>8</td>
<td>11.7</td>
</tr>
<tr>
<td>PMB-6</td>
<td>2.00</td>
<td>AlCl₃: 70.0</td>
<td>EtCl</td>
<td>-125</td>
<td>4.5</td>
<td>100</td>
</tr>
<tr>
<td>PMB-7</td>
<td>1.00</td>
<td>AlCl₃: 10.0</td>
<td>EtCl</td>
<td>-125</td>
<td>3</td>
<td>30</td>
</tr>
</tbody>
</table>

*a EtCl: Ethyl Chloride.*
and that adhering to the bottom of the flask, respectively. The polymers were dissolved in CHCl₃ and precipitated from cold methanol. A 19% yield of the polymer was obtained after drying in a vacuum oven for about 24 hours. The ratio of PMB-2D to PMB-2C was approximately 4 to 1.

Analysis: PMB-2D

Found: C, 92.02%; H, 7.09%
Calcd: C, 92.31%; H, 7.69%
Mn: PMB-2D, 4361; PMB-2C, 1193

Polymer PMB-7. 27.4 ml (2.0 mole) of α-chloroethylbenzene was transferred into a 500 ml three-neck flask containing 100 ml of ethyl chloride at -78°C. The flask was equipped with a Teflon stirrer blade and two septum caps. A hypodermic needle was inserted into each septum cap to serve as nitrogen gas inlet and outlet. The monomer solution was cooled to -125°C by immersing the flask in a n-pentane-liquid nitrogen slush bath. 9.4 g (7.05 mole) of freshly prepared AlCl₃ was dissolved in 200 ml of ethyl chloride at -78°C in a 250 ml round-bottom flask equipped as described in Section VI-B-1. The flask was then cooled to -125°C in a n-pentane-liquid nitrogen slush bath and the catalyst solution was added slowly into the monomer solution over a 4-hour period. The solution was stirred vigorously throughout the reaction. The reaction was terminated with cold methanol a half-hour after the catalyst had been added,
and a white precipitate was observed to form. The suspension was then poured slowly into 2 l of cold methanol for complete precipitation of the polymer, and the product was filtered, washed with dilute HCl and methanol. After drying in a vacuum oven for 30 hours, 21.56 g (100%) of a white polymer was obtained. The polymer was fractionated by adding 100 ml of methanol dropwise into a 3% solution of the product in CHCl₃ with vigorous stirring. Sample PMB-7H was obtained from the first precipitated product and PMB-7L was the precipitate of the first filtrate. The relative ratio of PMB-7H to PMB-7L was 3 to 2.

Analysis: Found: PMB-7H: C, 91.65%; H, 7.65%

PMB-7L: C, 91.87%; H, 7.77%

Calcd: C, 92.31%; H, 7.69%

XI. COUPLING REACTIONS

A. Preparation of the Di-Grignard Reagents.

The reaction system was treated as described in Section V. Into a 500 ml flask, 200 ml of THF was added to preheated magnesium turnings (4.86 g, 0.2 mole). After several pieces of iodine were added, 20.4 g (86.4 mmole) of dibromobenzene in 20 ml of THF was added slowly into the reactor from a dropping funnel. The solution was refluxed for 24 hours under a nitrogen atmosphere. A portion of the
sample was withdrawn from the solution for acid-base titration, and refluxing was continued for another 24 hours. The yield of Grignard reagent measured from the titration after both 24 and 48 hours of reaction products was 54.7%.

B. Model Compound Reaction.

1.5 ml (12.9 mmole) of benzyl bromide was dissolved in 30 ml of THF in a 150 ml flask, and the solution was heated to reflux by using a warm water bath. 20 ml of Grignard reagent solution was added dropwise into the refluxing solution from a dry syringe. After 24 hours of refluxing, the reaction was quenched by injecting 2 ml of water into it. The solution was washed with water several times. The organic layer was analyzed by GC on a column of 10% Carbowax 20M on Chromosorb W. In addition to the major peak, which had the same retention time as pure \( \mathbf{a} \)-dibenzylbenzene, there was a smaller peak with shorter retention time which is believed to be 4-{benzylbromobenzene}, the reaction product of mono-Grignard reagent and benzyl bromide. No further investigation was made to identify this compound. The ratio of the two peak areas was about 3 to 1, which indicates that the yield of di-Grignard reagent described in the previous section was approximately 47%.
C. Coupling of Polybenzyl with Di-Grignard Reagent.

0.37 g of polymer PB-6, which analyzed as containing $3.44 \times 10^{-5}$ mole chloride, was dissolved in 10 ml of THF in a 50 ml three-neck flask. The solution was warmed to reflux after 0.15 ml of the di-Grignard reagent was added. After 24 hours of refluxing, the reaction was terminated with 1 ml of methanol, and the solution was poured into 100 ml of methanol. The polymer which precipitated was filtered, redissolved in THF, and reprecipitated by pouring this solution slowly into a vigorously stirred excess of methanol. The polymer was filtered, washed with water several times, and dried in a vacuum oven for one day. The entire amount of polymer was completely recovered in this process, and no weight loss was observed.

D. Model Compound Reaction of the Coupling Process.

Benzyl magnesium bromide was prepared by the method described previously. The calculated amount of p-dibromobenzene in THF was added slowly from a dropping funnel into the benzyl magnesium bromide solution with stirring. After 24 hours, the reaction was terminated by pouring the solution into ice-water. The organic layer was analyzed by GC on a column of Carbowax 20M on Chromosorb W. The major peak had the same retention time as that of a
known sample of dibenzyls, and no p-dibenzylbenzene peak was observed. This major component isolated by preparative GC showed the same IR and NMR spectra as did the standard dibenzyls.

XII. COMPLEXATION STUDIES

A. Sulfur Dioxide As a Complexing Agent.

In a typical reaction, 0.3 g (4.6 mole) of SO₂ was condensed into a cold (-15°C) preweighted 25 ml round-bottom flask equipped with a Teflon coated stirrer bar and septum cap. The amount of SO₂ condensed was measured by weight difference of the flask before and after addition of SO₂. 10 ml of pre-cooled n-hexane was added slowly into the flask from a hypodermic syringe. 0.24 ml (2.0 mmole) of benzyl chloride and 0.65 ml of a 1:1 mole ratio mixture of p-xylene and toluene was added to the SO₂ solution with stirring. The magnetic stirrer bar was operated by a submersible magnetic stirrer (Henry Troemner, Inc.). The flask was immersed in a ice-water bath and 0.22 ml (2.0 mmole) of TiCl₄ was injected into the flask. The solution turned yellow immediately. After 30 minutes, the reaction was terminated by addition of 1 ml of methanol. The mixture was consecutively washed with water and extracted with chloroform three times. The chloroform was evaporated
and the residual solution was analyzed by GC on a column of 3% SE 30 on Areopak 30 at 195°C. The relative area of the peaks of benzylated p-xylene and toluene was used to calculate the mole ratio of p-xylene and toluene reacted. The peaks were identified from known sample of benzylated toluene and benzylated p-xylene which were obtained by reacting benzyl chloride with large excess of toluene and p-xylene, respectively.

A control was carried out for each reaction to prevent an error caused by the measurement of p-xylene and toluene among different runs, since the amount of p-xylene and toluene reacted depended upon the initial concentration of these two reagents. It was obvious that any transferring and measuring error of these reagents would cause confusion on the comparison of the final results between different runs. Table II-9 shows the results from reactions carried out at the same p-xylene to toluene ratio without complexing reagents. Only Run No. 4 and 5, in which the same batch of p-xylene and toluene solution were used, give the same results. To prevent this error, a control without complexing reagent was needed for each run.

B. Tetranitromethane (TNM) As a Complexing Agent.

The general procedure and the amounts of the
Table II-9

Comparison of the Mole % Reacted of p-Xylene and Toluene for Different Runs

<table>
<thead>
<tr>
<th>Runs No.</th>
<th>Mole % Reacted p-Xylene</th>
<th>Mole % Reacted Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>82</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>74</td>
<td>26</td>
</tr>
<tr>
<td>5</td>
<td>74</td>
<td>26</td>
</tr>
</tbody>
</table>

Reagents used are the same as previously described. Different ratios of TNM to p-xylene and toluene were used in this study. TNM was added to the mixture of p-xylene and toluene, and a yellow color developed immediately. The solution was stirred for 30 minutes before n-hexane was added. After the solution was cooled to 0°C, TiCl₄ was added and the color turned to light brown, while the control remained unchanged.

XIII. CHARACTERIZATION

A. Molecular Weight.

Number average molecular weight were measured with Hewlett Packard Vapor Pressure Osmometer, Model 302,
either in benzene at 50°C or chloroform at 37°C depending on the solubility of the polymers. These analyses were provided by the Microanalytical Laboratory at the University of Massachusetts. Weight average molecular weights, molecular weight distributions of the polymer samples were measured on the Waters Associates Gel Permeation Chromatograph in 1,2,4-tetrachlorobenzene at 140°C and 80°C. Polystyrene standards were used for calibration.

B. **Elementary Analysis.**

Elementary analyses for carbon and hydrogen were run on a Coleman Carbon-Hydrogen Analyzer. Chlorine contents were analyzed by chloride Titrator from American Instrument. Oxygen was analyzed by Unterzaucher Pyrolysis over hot carbon to produce CO and subsequently analyzing CO by GC. All elementary analyses were provided by the Microanalytical Laboratory in the University of Massachusetts.

C. **Nuclear Magnetic Resonance Spectroscopy (NMR).**

The NMR spectra were recorded on a Varian A-60 NMR spectrometer with tetramethylsilane as internal standard. Either carbon disulfide or deuterated chloroform was used as solvent for the spectra of the model compounds.
Spectra of polymer samples were prepared in deuterated chloroform. The peaks of aromatic ring protons of poly-α-methylbenzyl (PMB) samples were expanded 10 times by using a sweep width 50 cps instead of 500 cps. The ratios \( R \) of the peak areas for disubstituted aromatic ring protons at 7.04 \( \delta \) relative to that for monosubstituted aromatic ring protons at 7.15 \( \delta \) were measured by the cut-and-weigh method. The number of branches in PMB samples were then calculated by using the following equation:

\[
R = \frac{4D - X}{(X + 1) \times 5}
\]

\[
D = \overline{DP} - (X + 1)
\]

where \( D \) = number of disubstituted aromatic ring on the polymer chain; \( \overline{DP} \) = average degree of polymerization; \( X \) = number of branch units.

D. IR Spectroscopy.

IR spectra were recorded on a Perkin Elmer Grating IR Spectrometer model 257. The spectra of the model compounds and other organic compounds were obtained either in solution in carbon disulfide or neat. The spectra of polybenzyl and poly-α-methylbenzyl samples were obtained on KBr discs, which were prepared by pressing well-ground
mixture of 5 mg of polymer and 50 mg of dry KBr in a Wilkes IR cell.

The degree of branching of polybenzyl was qualitatively determined by the ratio of the absorptivity at 1032 cm\(^{-1}\) (C-H bending of monosubstituted aromatic ring) to that at 2910 cm\(^{-1}\) (C-H streching), and by the ratio of absorptivity at 1023 cm\(^{-1}\) (C-H bending of \(p\)-disubstituted ring) to that at 2910 cm\(^{-1}\).

E. **UV Analysis.**

UV spectra (300-500 m\(\mu\)) were recorded on a Cary 14 Spectrophotometer. The spectra of polymer samples were obtained in toluene solution with a concentration of 10-20 mg/1 ml.

F. **Thermal Gravimetric Analysis.**

Thermal gravimetric analysis was performed on a DuPont Thermal Gravimetric Analyzer. The sample was heated at 5\(^\circ\)C/min. in air. The thermal stability of the polymer was judged from the temperature at which the sample had shown a 5\% weight loss.

G. **Gas Chromatography.**

A Varian Aerograph Gas Chromatograph 1520 was used
in the determination of the purity of monomers and for the analysis of the isomer distributions in model compound reactions. A preparative attachment was used for the preparation of pure model compounds. The column used for the analytical purpose was made of 5\(\frac{1}{4}\)" x 1/4" stainless steel tubing containing either 10\% Carbowax 20M on 60/80 Chromosorb W or 10\% SE 30 on 100/50 Aeropak 30. The column used for the preparative purpose was made of 20' x 1/4" aluminum tubing containing 30\% Carbowax 20M on 30/60 Anaprep ABS. Both the analytical and preparative gas chromatography analyses were obtained with a thermal conductivity bridge as the detector and helium gas as the carrier. Isothermal conditions were used for most operations. Only in the case of monomer and solvent analysis was the oven temperature programmed at 10\°C/min. for the high boiling compounds and 5\°C/min. for the low boiling compounds.

H. Melting Point Measurement.

A Perkin-Elmer Differential Scanning Calorimeter Model DSC 1B was used to determine the melting temperature of the crystalline polymer. A heating rate of 10\°C/min. was used in all measurements. The instrument was calibrated on either tin or indium samples, depending on the melting
point of the polymer sample. The melting point was taken as the peak temperature of the endotherm. Samples for the investigations on the effect of the thermal annealing on melting point and crystallinity were prepared under a N₂ atmosphere either in a constant temperature oil bath or by annealing directly in the DSC. Melting points of polymer samples were also determined by the disappearance of birefringence when the samples were heated at 10°C/min. on a Mettler FP1 & 2 hot stage mounted on a polarizing microscope.

I. Glass Transition Temperature.

The glass transition temperature, \( T_g \), was also determined by DSC analysis, generally at a heating rate of 10°C/min., but other heating rates were used to investigate the effect of the heating rate on \( T_g \). The \( T_g \) was recorded as the midpoint of the baseline shift on the DSC thermogram. The peak area was measured by the cut-and-weigh method. The response of the instrument was calibrated for a series of samples from the peak area and peak temperature of the samples of PB-10A. The results in Table II-10 show that the peak temperature and peak area are not affected by the sample size used. The instrument was calibrated by using naphthalene and \( p \)-nitrotoluene as standards.
Table II-10
Effect of Sample Size on the Peak Area and Peak Temperature of DSC Analysis

<table>
<thead>
<tr>
<th>Sample Weight (mg)</th>
<th>Peak Area/mg of Sample</th>
<th>Peak Temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.3</td>
<td>53.4</td>
<td>339</td>
</tr>
<tr>
<td>10.5</td>
<td>55.4</td>
<td>339</td>
</tr>
<tr>
<td>8.3</td>
<td>54.6</td>
<td>339</td>
</tr>
</tbody>
</table>

Samples for the annealing studies were prepared in one of two ways, either (1) when the annealing temperature was above room temperature, the samples were annealed directly in the DSC; or (2) when the annealing temperature was at room temperature, the samples were annealed under storage conditions. The samples were heated above their glass transition temperatures and subsequently quenched on a cold metal block surface. The annealing time was then recorded after the quenched samples have been brought up to the desired annealing temperature.

J. Compatibility.

The compatibility of poly-α-methylbenzyl and polybenzyl with polystyrene was examined by the phase separation and glass transition of solvent-cast film. The
films were prepared by casting a CHCl₃ or THF solution of 1:1 weight ratio of two polymers on a smooth glass surface.

K. Crystallinity.

A North American Philips X-ray diffractometer was used to investigate the crystallinity of the polymers. The powder samples were pressed into the hole of the sample holder, and the picture was taken by using nickle-filtered CuKα radiation. Crystallinity was also qualitatively evaluated with a polarizing microscope equipped with a Mettler hot-stage.
CHAPTER THREE
RESULT AND DISCUSSION

I. INTRODUCTION

Polybenzyls prepared from the polycondensation of benzyl chloride and its derivatives have been studied by many investigators as described in the literature review in Chapter I. Most of the polymers obtained were amorphous and apparently highly branched. (14,42) Because of the rather complicated structure of these branched polybenzyls, the characterization of this type of polymer is very difficult. Thus past investigations on the effect of polymerization conditions on polymer structure based upon the results of various methods of characterization of the polymers have been inexact and sometimes uncertain. Because of this, in the present work initial studies were made on a model reaction conducted at different reaction conditions to attempt to obtain a simple and clear picture of the effect of the reaction conditions, substitution distribution and thereby, alternately, on polymer structure. This study was also extended for the effect of conditions for substituted benzyl chlorides (i.e., 2,5-dimethylbenzyl chloride and α-chloroethylbenzene) on the structure of their polymers. The results of these model compound studies were then used to correlate the structures and properties of the respective
polymers.

II. MODEL COMPOUND REACTIONS

In order to produce a completely linear, para-disubstituted polybenzyl by the self-benzylation of benzyl chloride itself, substitution must occur only at the para-position of either the monomer units (A) or polymer chain-ends (B). Benzylation at ortho- or meta-positions of monomers or polymer chain-ends (C) and at the disubstituted aromatic nucleus of the internal units (D) will form irregular and branched structures. Therefore, the degree of

\[
\begin{align*}
\text{ClCH}_2\text{-} & \quad \text{CH}_2\text{-} \\
\text{ClCH}_2\text{-} & \quad \text{CH}_2\text{-} \\
\text{C}_1\text{-} & \quad \text{C}_2\text{-} \\
\end{align*}
\]
branching and the amount of irregular structures depend upon the extent of the substitution of type (C) and (D).

Assuming the products are kinetically controlled, the relative rates of the above substitution reactions at the different positions on the aromatic ring can be estimated from measuring the substitution distribution of a model reaction, in this case of diphenylmethane with benzyl chloride which gives a mixture of dibenzylbenzene (DBB) isomers as illustrated in Equation 3-1. If one assumes that the substitution along the polymer chain (D) occurs at about the same rate as ortho-substitution in the model reaction, then 100% para-substitution (100% para-DBB) is needed for both linearity or stereoregular structure in order to get crystalline polymers.

\[
\begin{align*}
\text{C} & \text{-CH}_2\text{-C} + \text{C} & \text{-CH}_2\text{Cl} & \xrightarrow{\text{Cat.}} & \text{C} & \text{-CH}_2\text{-C} & \text{CH}_2
\end{align*}
\]

\text{Eq. 3-1}

\(\sigma-, \pi- \text{ and } m\)-Dibenzylbenzene. (DBB)

A. Model Compound Reactions of Polybenzyl.

The model compound reactions of polybenzyl were carried out, as described in detail in Chapter II, by treating benzyl chloride with excess of diphenylmethane with different catalysts, in various solvents, at different tem-
temperatures as summarized in Table II-2. Under the experimental condition employed, exclusive mono-benzylolation reactions took place, and no detectable amount of higher substituted products was found by GC analysis. The reaction mixture was analyzed for substitution distribution by GC, and the isomer distribution of DBB is also given in Table II-2. The peak assignments and accuracy of the GC analysis was established with mixtures of known composition of authentic DBB samples as described in Chapter II.

Before applying the isomer distribution data for the study of the effect of reaction conditions on the substitution, precautions had to be taken to make sure that no isomerization reactions occurred during the model compound reactions. Isomerization (i.e., thermodynamic control) of dialkylbenzenes under the alkylating condition is a general phenomenon in most of the Friedel-Crafts alkylation reactions (5). The isomer distribution obtained under this condition depends on the reaction time and on the quantity of catalyst present in the reaction mixture. For example, in a previously reported investigation of methylation of toluene, the isomer distribution was found to vary from 56% o-, 10% m- and 34% p-xylene to 18% o-, 60% m- and 22% p-xylene when the reaction time was changed from one minute to several hours. (83) That is more m-xylene was formed as the reaction time became longer. It was suggested that
m-xylene is thermodynamically favored over o- and p-xylene (83). However, Olah and coworkers (84) reported that no isomerization reaction was observed in the benzylation of aromatic compounds with benzyl chloride in the presence of aluminum chloride in nitromethane solvent. Under these conditions, the products were presumably formed from a kinetically-controlled reaction with no appreciable thermodynamically-controlled isomerization of the alkylates. It was suggested that the reaction proceeded through a π-complex type transition state as the substrate rate-determining step, followed by a δ-complex type of activation state which determines isomer distribution (84).

The non-isomerization during benzylation using AlCl₃ as catalyst was confirmed in the present study by treating p-DBB with AlCl₃, under benzylation conditions, for 3 hours. The final reaction solution analyzed by GC did not show the presence of any o-DBB, m-DBB or disproportion products of p-DBB. The same results are also found for the other conditions; i.e., for AlCl₃/ethyl chloride/-78°C, TiCl₄/nitromethane/25°C and SbF₅/HSO₃F/SO₂/-78°C.

As mentioned previously, a linear polybenzyl can only be obtained when 100% para-substitution in the basic reaction is achieved. Reaction MB-1 in Table II-2 shows that only 67% of para-substitution is obtained under the conditions used by Kennedy and Isaacson. Therefore, it is
reasonable to expect that linear, crystalline polybenzyl will not be obtained under the conditions. However, the results of reactions MB-1 and MB-2 in Table II-2 show that the temperature does have some effect on the para-isomer content as observed by Kennedy and Isaacson, (10), who found that temperature played an important role in determining the linearity of polybenzyl and that the lower temperature gives higher para-content. This temperature effect was also observed by Finocchiaro and coworkers (37) in the benzylation of toluene. They found that the para-isomer content increased from 52% to 66% as the reaction temperature was lowered from -10°C to -130°C.

The lower ortho-isomer content in reaction MB-1 compared to that in reaction MB-2 can be explained by the increasing importance of steric hindrance as the temperature decreased. In contrast to the results for reactions MB-1 and MB-2, temperature had almost no effect on the isomer distribution in reactions MB-3 and MB-4. This could be due to the heterogeneous nature of the catalysts causing the isomer distribution to be mainly controlled by the surface structure of the catalysts. The isomer distribution also varied with the different catalysts used in the model reactions. The para-isomer content obtained in ethyl chloride solution at -125°C decreased in the order of AlCl₃ > TiCl₄ > DEAC > MoCl₅. However, the order changed to SbF₅/HSO₃F >
SbF₅ > MoCl₅ > AlCl₃ when the reactions were carried out in SO₂ solution at -78°C. The effect of the solvent on the isomer distribution is believed to stem from the ability of the solvent to solvate and stabilize the electron-deficient transition state (85).

B. Model Compound Reactions of Poly-α-methylbenzyl.

The model compound reactions for poly-α-methylbenzyl were carried out by treating α-chloroethylbenzene with the excess of diphenylmethane or 1,1-diphenylethane as illustrated in Equations 3-2 and 3-3, respectively. The reaction conditions and isomer distributions from these model compound reactions are summarized in Table II-6 and Table II-7. The analysis of the isomer distribution was described in details in Chapter II. The para-isomer content of these model compound reactions were much higher than those from the reaction of benzyl chloride with diphenylmethane. The
results in Table III-1 show that an additional methyl substitution on the methylene group of benzyl chloride caused a tremendous increase in \textit{para}-isomer content, from 50\% to 91\%, even at room temperature. As one more methyl group was substituted on the methylene group of diphenylmethane (i.e., with 1,1-diphenylethane) as shown in Table II-7, \textit{para}-isomer content increased even higher and reached 99\% at -78\^{\circ}C.

Only a small effect on the content of \textit{para}-isomer was observed with different catalysts in nitromethane at room temperature, and the order of increase in the content of \textit{para}-isomer was SbF$_5$, SnCl$_4$ < ZnCl$_2$, MoCl$_5$, TiCl$_4$ < AlCl$_3$. The high \textit{para}-content of the model compound reactions indicated in Tables II-6 and II-7 shows that the steric effect is the predominate factor in the control of the isomer distribution. The steric effect of these model compound reactions can also be understood from the unusually low content of \textit{ortho}-isomer. This is simply because the \textit{ortho}-positions of diphenylmethane and 1,1-diphenylethane are more sterically hindered than are the \textit{meta}- and \textit{para}-position of those two aromatic compounds. The slightly lower content of \textit{meta}-isomer in some of the model compound reactions in Tables II-6 and II-7 than those from the reaction of benzyl chloride and diphenylmethane indicates that \textit{\alpha}-chloroethylbenzene has higher position selectivity in the
Table III-1
Steric Effect on the Isomer Distribution of Model Compound Reactions

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp. °C</th>
<th>a Isomer Distribution %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph-CH₂-Cl + Ph-CH₂-Ph</td>
<td>TiCl₄</td>
<td>CH₃NO₃</td>
<td>22</td>
<td>50  29  16</td>
</tr>
<tr>
<td>Ph-CH₂-C1 + Ph-CH₂-Ph CH₃</td>
<td>TiCl₄</td>
<td>CH₃NO₃</td>
<td>25</td>
<td>91.4 4.6 4.3</td>
</tr>
<tr>
<td>Ph-CH₂-Cl + Ph-CH₂-Ph</td>
<td>AlCl₃</td>
<td>C₂H₅Cl</td>
<td>-78</td>
<td>47  43  10</td>
</tr>
<tr>
<td>Ph-CH₂-C1 + Ph-CH₂-Ph CH₃</td>
<td>AlCl₃</td>
<td>C₂H₅Cl</td>
<td>-78</td>
<td>96.8 0.6 2.6</td>
</tr>
</tbody>
</table>

a Isomer: ![Chemical Structure]

Table III-2
Isomer Distribution of the Model Compound Reaction of Benzyl Chloride with Diphenylmethane at Different Reaction Time

<table>
<thead>
<tr>
<th>Catalyst/Solvent</th>
<th>Temp., °C</th>
<th>Time, min</th>
<th>a Isomer Distribution, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbF₅/SO₂</td>
<td>-78</td>
<td>5</td>
<td>50  40  10</td>
</tr>
<tr>
<td>SbF₅/SO₂</td>
<td>-78</td>
<td>30</td>
<td>48  42  9</td>
</tr>
<tr>
<td>SbF₅/SO₂</td>
<td>-78</td>
<td>600</td>
<td>50  39  11</td>
</tr>
</tbody>
</table>

a Isomer: Dibenzylbenzenes
substitution of aromatic compound than does benzyl chloride.

An isomerization reaction, which did not occur in the model compound reactions of benzyl chloride and diphenylmethane, was observed in the model compound reaction of α-chloroethylbenzene in the presence of either SbF$_5$ or SbF$_5$/HSO$_3$F and in SO$_2$ solvent at -78°C. The characteristic of the isomerization reaction was the presence of a higher content of meta-isomer, and this content increased with time as described previously. That is, the rather high contents of the meta-isomer in reactions MC-4, MD-6, MD-7, and MD-8 are believed to be the result of isomerization. As the reaction time increased, the content of the meta-isomer increased and the content of the para-isomer decreased.

The isomerization in these model compound reactions could have been caused either by SbF$_5$ or SO$_2$ or both. However, as shown in Table II-7, no isomerization was observed in reaction MD-3 when nitromethane instead of SO$_2$ was used as solvent. Moreover, the reaction temperature in MD-3 was much higher than that used in the former reactions in which isomerization was observed. Usually, the higher the reaction temperature, the greater will be the tendency for substituted aromatic compounds to isomerize (36). Thus, it is reasonable to believe that the isomerization is not caused by SbF$_5$ itself but rather by SO$_2$ or by a combination of SbF$_5$
and S\textsubscript{0}\textsubscript{2}.

Under the same catalyst and solvent system (i.e., SbF\textsubscript{5} and S\textsubscript{0}\textsubscript{2}) no isomerization was observed in the model compound reaction of benzyl chloride and diphenylmethane as indicated in Table III-2. These results tend to indicate that the isomerization can only occur when \(\alpha\)-chloroethylbenzene and S\textsubscript{0}\textsubscript{2} are involved in the reaction. It has been reported that the tendency for dealkylation increases in the sequence of primary < secondary < tertiary alkyl group (86). Therefore, \(\alpha\)-phenylethyl substituents should have a higher tendency to isomerize than benzyl substituents especially under the influence of strong solvating solvent such as S\textsubscript{0}\textsubscript{2}

III. POLYBENZYL

A. Polymerization of Benzyl Chloride.

Table II-4 lists the reaction conditions for the polymerization of benzyl chloride with various catalysts and solvents at different temperatures. The data obtained from the characterization of the polymers are tabulated in Table III-3.

The polymerization temperature varied from room temperature to -130°C. The temperature control at -130°C was operated by an automatic temperature controller as
Table III-3
Properties of Polybenzyls from Polymerization of Benzyl Chloride

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Appearance Powder Color</th>
<th>Solubility</th>
<th>a</th>
<th>Solubility</th>
<th>b</th>
<th>(M.P. c Tg °C)</th>
<th>Mn</th>
<th>d</th>
<th>%C</th>
<th>d</th>
<th>%H</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-1</td>
<td>white</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td>76</td>
<td></td>
<td></td>
<td>85.5</td>
<td>6.54</td>
<td></td>
</tr>
<tr>
<td>PB-2</td>
<td>white</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td>(145)</td>
<td></td>
<td></td>
<td>90.0</td>
<td>6.68</td>
<td></td>
</tr>
<tr>
<td>PB-3</td>
<td>white</td>
<td>75</td>
<td></td>
<td></td>
<td></td>
<td>78</td>
<td></td>
<td></td>
<td>89.8</td>
<td>6.90</td>
<td></td>
</tr>
<tr>
<td>PB-4</td>
<td>white</td>
<td>55</td>
<td></td>
<td></td>
<td></td>
<td>69</td>
<td></td>
<td></td>
<td>88.9</td>
<td>6.70</td>
<td></td>
</tr>
<tr>
<td>PB-5</td>
<td>yellow</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>66</td>
<td></td>
<td></td>
<td>88.2</td>
<td>6.34</td>
<td></td>
</tr>
<tr>
<td>PB-6</td>
<td>off-white</td>
<td>&gt; 99</td>
<td></td>
<td></td>
<td></td>
<td>73</td>
<td></td>
<td></td>
<td>2926</td>
<td>93.28</td>
<td>6.47</td>
</tr>
<tr>
<td>PB-7</td>
<td>white</td>
<td>&gt; 99</td>
<td></td>
<td></td>
<td></td>
<td>69</td>
<td></td>
<td></td>
<td>6216</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB-8A</td>
<td>white</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>68</td>
<td></td>
<td></td>
<td>3108</td>
<td>92.30</td>
<td>6.45</td>
</tr>
<tr>
<td>PB-8B</td>
<td>white</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>66</td>
<td></td>
<td></td>
<td>3032</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB-9</td>
<td>white</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>65</td>
<td></td>
<td></td>
<td>1286</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB-10A</td>
<td>yellow</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>61</td>
<td></td>
<td></td>
<td>1554</td>
<td>92.79</td>
<td>6.12</td>
</tr>
<tr>
<td>PB-10B</td>
<td>yellow</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>65</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB-11</td>
<td>off-white</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>66</td>
<td></td>
<td></td>
<td>3730</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a PB-1 to PB-5 in xylene; PB-6 to PB-11 in benzene.

b Measured from DSC thermogram.

c Measured from DSC thermogram.

d Theoretical value, %C: 93.34; %H: 6.66.
described in Figure 3-1a. The variation in reactor temperature was approximately ± 1°C by this system, but the automatic temperature controlling system was not used in the polymerization of polymers PB-1, PB-2 and PB-4. As a result the temperature ranges in these polymerization reactions were quite large.

Color formation throughout the polymerization reactions were observed in every run. The color observed varied from orange to red to brown. In most of the polymerization reactions, except when TiCl₄ was used as the catalyst, color developed immediately after the addition of catalyst. At the very low reaction temperature of -130°C, no color development was observed, as for example for polymer PB-5 even at 10 hours after the addition of TiCl₄. However, at -78°C, a light brown color was observed 60 minutes after the addition of TiCl₄ in ethyl chloride. At room temperature, a dark green color developed only 10 minutes after the addition of TiCl₄ in nitromethane. TiCl₄ is considered to be a weak Friedel-Crafts catalyst than the other catalysts listed in Table II-4.

B. Polymer Solubility and Crystallinity.

All polymers obtained after precipitating from methanol were white powders, except PB-5, PB-6, PB-10, and PB-11, which were yellow or off-white powders. The solubi-
Figure 3-1a. Low temperature controlling system: A. liquid N₂ storage; B. vacuum-jacketed transfer line (glass); C. rubber connection; D. reinforced plastic shaft; E. liquid N₂ cooling coil (copper); F. shield; G. temperature controlling probe; H. reactor; I. Dewar flask; J. plastic foam; K. Fisher electro hosecock; L. Precision Temperature Controller (Bayley Instrument Co.).
lity of the polymers varied with the conditions of the polymerization. Low solubility in xylene or benzene was found when TiCl₄/DEAC was used as catalyst, although most of the polymers were soluble on refluxing in benzene, toluene, diphenylmethane and THF. THF and xylene were found to be the most effective solvents for these polymers.

The insoluble fractions of polymers PB-1, PB-2, PB-3, and PB-4 did not show any crystallinity by DSC and X-ray diffraction analysis. This observation tends to indicate that the insolubility of these polymers was not due to the higher crystallinity of these polymers, but more likely was due to a highly branched, globular-like structure (47) in which the solvent cannot penetrate easily as shown in the Figure I-1 in Chapter I. The insoluble polymers also did not show any sign of flow after the samples became soft in the temperature range of 220°C to 300°C, although it would appear from the mechanism of the benzylolation reaction that there is no possibility of crosslinking in polybenzyl prepared from benzyl chloride (67). Thus, this reasoning is taken as another indication that the insolubility of these polymers is not likely due to the crosslinking or crystallinity but is more likely due to the formation of a globular-like structure of the polymers caused by extensive branching at high molecular weights. This type of structure would, most likely, be incapable of extensive swelling under the
action of a solvent, and as the molecular weight of the polymer increased, the ratio of the surface area wetted by solvent to mass would probably decrease rapidly.

The soluble polymers have rather low molecular weights, and they are not globular-like structures, so they can be penetrated by solvent molecules easily. Furthermore, for less branched polymers, like PB-6, PB-7 and PB-11, the structure of the polymer molecules is even less likely to be of the globular type, and the minimum molecular weight at which insolubility occurs should be higher for these less branched polymers than for more branched polymers.

Untreated, virgin samples of polymer PB-2 showed a slight crystallinity from X-ray diffraction analysis and also showed a small endotherm peak at 145°C on the DSC thermogram. However, after the polymer sample was fractionated with boiling p-xylene, no crystallinity was observed on either the soluble or insoluble fractions by either DSC or X-ray diffraction analysis, and no visible change in the polymer structure was observed after fractionation from the IR spectra. Annealing of the soluble and insoluble fractions at 125°C for 20 hours still did not generate any crystallinity. It is believed, therefore, that only a very small portion of the polymer molecules of PB-2 have a rather linear structure, and even these still contain some branches, which give raise to difficulties in recrystallization.
C. Glass Transition Behavior.

The glass transition temperature of polybenzyl, which was recorded from the second heating cycle of the DSC measurements, ranged from $61^\circ C$ to $78^\circ C$ as indicated in Table III-3. The glass transition temperature of the amorphous polymers apparently varied with the molecular weight and with the type of branches, but it is difficult to separate the influence of these two factors based on the results in Table III-3.

An apparently endothermic peak in the DSC thermogram was observed in the glass transition region during the first heating cycle as illustrated in Figure 3-1. This apparent first order transition combined with the glass transition phenomenon has also been observed in several other amorphous polymers; e.g., in PVC (87), poly(ethylene terephthalate) (88, 89), polystyrene and poly(methyl methacrylate), etc. (89). Several explanation have been proposed to account for this observation, and two of these are the equilibrium theory (90) and the local ordering theory (87, 91).

In the equilibrium theory, it is postulated that a relatively small number of "holes" are frozen in the glass state. On a subsequent fast heating, the equilibrium number of the holes at the transition is "overshot", since there is
Figure 3-1 DSC Thermogram of Polybenzyl sample. First (—) and second (---) heating cycles are superposed.

Figure 3-2 The effect of annealing at room temperature on the area of the endothermic peaks at the glass transition region of polybenzyls. DSC heating rate of $10^\circ C/\text{min}$.

*Peak Area(mg) : Measured by cut and weight method.
not enough time for equilibrium to be established, and the glass returns to the equilibrium via a path which appears endothermic, thereby giving raise to a maximum at the point of infection.

On the other hand, local ordering theory states that the motion of individual chain segments below the glass temperature can lead to the formation of comparatively stable structural units in the form of a local alignment of chains, similar to the concept of a fringed-micelle crystallite. However, the size of this local order is too small to be detected by X-ray diffractometry. According to this model, as the glass temperature is approached, a disturbing influence of gross chain mobility develops, leading to structure breakdown.

The peak areas and the temperatures of the endothermic peaks in the glass transition regions of some of the polybenzyls were observed to be affected by the annealing below $T_g$. Figure 3-2 shows that the effect of annealing time at room temperature on the area of the endothermic peak of polymers PB-6, PB-7, PB-10, and PB-11. The initial rates of the increase of area versus time for polymers PB-6 and PB-11 were higher than those for polymers PB-7 and PB-10. Since polymers PB-6 and PB-11 were less branched than polymers PB-7 and PB-10 (as will be discussed in the next section), the results in Figure 3-2 tend to indicate that
higher branched polymer molecules reached their equilibrium state more easily, in terms of the equilibrium theory, or found it easier to form some kind of local order, in terms of local ordering theory. Since more branches on the polymer molecules will result in a higher free volume and, hence, a higher segmental mobility, it is reasonable to expect that the higher branched polybenzyls can reach on equilibrium state easier or faster than the lower branched molecules. On the other hand, if a local order does exist, it is probably formed by alignment of the branched units, which being more linear are presumably more flexible than the main backbone.

The effect of annealing time on the temperature of the apparent endothermic peak is illustrated in Figure 3-3. The temperature of the apparent endothermic peak increased with the annealing time. As shown in Figure 3-3, the temperature increase was 16°C which was higher than those of polymers PB-1, PB-7, and PB-10, which were 12, 10 and 10°C, respectively. The area of the apparent endothermic peak was affected not only by the annealing time but also by annealing temperature as shown in Figure 3-4. The plot of peak area versus annealing temperature at 12 hours annealing time in Figure 3-5 indicates that peak area increased with temperature and reached a maximum, then decreased to zero as the annealing temperature approached the
Figure 3-3 DSC thermograms of polymer PB-6 annealed at room temperature for various annealing periods. Heating rate of 10°C/min.
Figure 3-5. The plot of annealing temperature versus the area of endothermic peak in the glass transition region of PB-2 (soluble portion) at annealing time of 25 hours.

*Peak Area (mg) : Measured by cut and weight method.

Figure 3-4. The Effect of annealing temperature on the area of endothermic peak in the glass transition region of PB-2 (soluble portion).
glass transition region. This peculiar phenomenon has also been observed by Ali and Sheldon (89) on poly(ethyl methacrylate), poly(ethylene terephthalate), and other polymers. However, no reasonable explanation can be made for it on the base of the equilibrium theory or the local ordering theory.

Table III–4 shows the effect of heating rate on the temperatures of the apparent endothermic peaks. A correction was made for the lag of the actual temperature of the sample behind the indicated temperature which is inherent in the instrument at the faster scanning rates. This correction was based on the extent of the elevation of the measured temperature of the first order transition of naphthalene observed with the corresponding increase in heating rate. The peak temperatures after correction showed increases with increased heating rate. These results suggest that the apparent endothermic peak had a second order transition nature. Therefore, it is likely that any local order or crystallization which would have a first-order transition nature, was not the source of the endothermic peaks.

D. Thermal Stability of Polymers.

Thermal gravimetric analyses for some of the polymer samples are given in Figure 3-6. Two types of thermal
Table III-4

Effect of Heating Rate on the Temperature of the Endothermic Peaks in the Glass Transition Region of Polymer PB-10A

<table>
<thead>
<tr>
<th>Heating Rate °C/min</th>
<th>Weight of Sample mg</th>
<th>Peak Temp., °K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Observed</td>
</tr>
<tr>
<td>5</td>
<td>8.4</td>
<td>330.0</td>
</tr>
<tr>
<td>10</td>
<td>8.5</td>
<td>333.5</td>
</tr>
<tr>
<td>20</td>
<td>8.5</td>
<td>338.5</td>
</tr>
<tr>
<td>40</td>
<td>8.5</td>
<td>344.0</td>
</tr>
</tbody>
</table>

Table III-5

Correlation of Chlorine Content of Polybenzyl Samples with Isomer Distribution of Model Compound Reactions

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Cl, Mole Fraction</th>
<th>Mn</th>
<th>^aIsomer Distribution of Model Compound Reactions, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>PB-7</td>
<td>0</td>
<td>6216</td>
<td>67</td>
</tr>
<tr>
<td>PB-8A</td>
<td>0</td>
<td>3108</td>
<td>--</td>
</tr>
<tr>
<td>PB-11</td>
<td>0</td>
<td>3730</td>
<td>53</td>
</tr>
<tr>
<td>PB-10A</td>
<td>0.035</td>
<td>1554</td>
<td>50</td>
</tr>
<tr>
<td>PB-6</td>
<td>0.270</td>
<td>2926</td>
<td>61</td>
</tr>
</tbody>
</table>

^a Isomer: Dibenzylbenzenes.
Figure 3-6. TGA thermograms of PB-6, PB-11(---), PB-7(---) and PB-10A(---) at a heating rate of 5°C/min. in air.
curves are seen in Figure 3-6, one with a single-step degradation pattern and the other with a two-step degradation. Polymers give a single-step thermal curve are believed to be more regular in structure and those which are more branched give the two-step thermal curve (42). The temperature at which a 5% weight loss occurred was also found to be higher for the more linear polymers (PB-6 and PB-11) than for the more highly branched polymers (PB-7 and PB-10), as indicated in Table III-6.

E. Side Reactions.

Polybenzyl prepared from benzyl chloride theoretically should contain a single chloromethyl group for every polymer molecule. However, the elementary analyses of the polymer samples, as indicated in Table III-5 showed that the chloride contents were lower than the theoretical value. The loss of chloromethyl group through side reactions during the polymerization reaction would result in the termination of the polymerization at one end of the polymer chain. Possible side reactions during which could occur the polymerization would include either anthracene formation by the terminal chloromethyl group or hydrolysis by moisture present in the polymerization system.

The formation of anthracene in polybenzyl, as
Table III-6
Correlation of Data of Polybenzyl Samples with Isomer Distribution of Model Compound Reactions

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp. °C</th>
<th>TGA °C</th>
<th>A1032 cm⁻¹</th>
<th>A1023 cm⁻¹</th>
<th>a Isomer Distribution of Model Compound Reaction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-6</td>
<td>SbF₅/HSO₃F</td>
<td>SO₂</td>
<td>-78</td>
<td>470</td>
<td>0.272</td>
<td>0.556</td>
<td>61 12 27</td>
</tr>
<tr>
<td>PB-11</td>
<td>SbF₅</td>
<td>SO₂</td>
<td>-78</td>
<td>470</td>
<td>0.300</td>
<td>0.460</td>
<td>53 18 29</td>
</tr>
<tr>
<td>PB-7</td>
<td>AlCl₃</td>
<td>C₂H₅Cl</td>
<td>-125</td>
<td>400</td>
<td>0.387</td>
<td>0.467</td>
<td>67 25 7</td>
</tr>
<tr>
<td>PB-10A</td>
<td>TiCl₄</td>
<td>CH₃NO₂</td>
<td>26</td>
<td>385</td>
<td>0.398</td>
<td>0.433</td>
<td>50 29 21</td>
</tr>
</tbody>
</table>

a Isomer: Dibenzylbenzenes.
illustrated in Equation 3-4, has been reported before (74, 96) and was suggested to be due to ortho-substitution at either the monomer or the end group of the polymer molecules followed by a second ortho-substitution with that substituent as is shown in Equation 3-4. In this case, an increase in anthracene formation would result in a decrease in chloromethyl group content and consequently a decrease in the chloride content.

![Chemical Structure](image)

Equation 3-4 shows that dihydroanthracene can only be formed if a benzylation reaction occurs at the ortho-position relative to chloromethyl group of the substrate, in either the monomer or polymer chain end. Therefore, it is expectable that the reaction condition which gives raise to a higher content of ortho-isomer in the model compound reaction would result in a higher possibility of formation of anthracene terminal groups and, hence, a low chlorine content. Table III-5 indicates that a good correlation exists between the chlorine content of the polymers and the content of the ortho-isomer in the model compound reactions.
UV absorption in the region of 325-400 μm in poly-
benzyl has been used by Montaudo and coworkers (49) as the
evidence of the presence of anthracene terminal group in the
polymer chain. Similar UV absorption patterns in the region
325-400 μm were also obtained in the present work for poly-
mers PB-7, PB-8A, PB-9, and PB-10A, but not in polymers
PB-6 and PB-11 in toluene solution (10 mg/ml). Anthracene
terminal group in polymers PB-6 and PB-11 can be explained
from the low content of ortho-isomer in the model compound
reaction as shown in Table III-5.

Chlorine atom of the chloromethyl group can also
be displaced by water to form a hydroxymethyl group. Al-
though the reaction apparatus and the solvents were dried
thoroughly, as described in the Experimental Section, one
still cannot rule out the possibility of the existence of
traces of water in the reaction system. However, no hydroxyl
group were detected in the polymer samples from the IR ana-
lysies.

F. Characterization of Polymer Structure.

High resolution nuclear magnetic spectra of the
soluble polymer samples are quite simple, the resonance
absorption at 7.04 δ due to the aromatic protons and an-
other at 3.88 δ due to the methylene protons. However, the
peaks, for the aromatic proton, were rather broad. The NMR spectrum of polymer PB-6 reproduced in Figure 3-6a shows that the resonance absorption for the aromatic protons ranged from 6.5 to 7.15 which not only covers the absorption region of protons in the para-substituted aromatic rings but also covers those in the ortho-, meta- and multiple substituted rings. It is believed, therefore, that the NMR spectra of these polybenzyls would be more complicated if a higher magnetic field NMR instrument is used, and only under this condition the NMR spectra could be used for the characterization of the regularity of the polymer molecules.

Characterization of the degree of branching and para-substitution in polybenzyls was mainly obtained from the IR analysis. The absorption peak at 810 cm\(^{-1}\) is generally considered to be characteristic of para-substituted aromatic nuclei. Peaks in 770 to 730 and 710 to 690 cm\(^{-1}\) region, are considered to be indicative of mono-substituted aromatic nuclei. However, the IR spectra of polybenzyl samples (e.g., polymers PB-6 and PB-7 in Figures 3-7 and 3-8, respectively) show that the 810 cm\(^{-1}\) peak is not well resolved and cannot be used for measuring the degree of para-substitution of these polymers.

In the IR spectra of the model compounds (i.e., for o-, p- and m-dibenzylbenzene) a well resolved region from 1000 to 1100 cm\(^{-1}\) assignable to C-H in-plane bending
Figure 3-6a. NMR spectrum of PB-6 in CDCl₃.

Figure 3-7. IR spectrum of PB-6. (KBr disc)

Figure 3-8. IR spectrum of PB-7. (KBr disc)
was found, and it can be used for the characterization of polymer branching. The characteristic peaks for para-, ortho- and meta-substituted aromatic nuclei are 1023, 1050 and 1090 cm\(^{-1}\), respectively, as illustrated in Figures 3-9, 3-10 and 3-11. An absorption peak at 1032 cm\(^{-1}\), which appeared in the IR spectrum of diphenylmethane (Figure 3-12) as well as in o-, p-, and m-dibenzylbenzenes but not in the compensated spectra, Figures 3-13, 3-14 and 3-15, is attributed to the monosubstituted aromatic nucleus.

The relative contents of para-substitution in the polymer molecules was estimated from the ratio of 1025 cm\(^{-1}\) to 2910 cm\(^{-1}\) peaks. The absorption at 2910 cm\(^{-1}\) is due to C-H stretching of methylene group. The relative amount of monosubstitution was estimated from the ratio of 1032 cm\(^{-1}\) to 2910 cm\(^{-1}\) peaks. The absorption peaks at 1050 and 1090 cm\(^{-1}\) for ortho- and meta-substituted aromatic nuclei were rather weak and it was not possible to use these peaks for calculating the content of ortho- and meta-polymers.

The results of the measurements of thermal stability and degree of branching of the polymers and the isomer distribution from model compound reaction studies are collected together in Table III-6. The higher the ratios of 1032 cm\(^{-1}\)/2910 cm\(^{-1}\) peaks, the higher the degree of branching, while conversely the higher the 1023 cm\(^{-1}\)/2910 cm\(^{-1}\) peak ratio, the higher the linearity of the polymer.
Figure 3-9. IR spectrum of 1,4-dibenzylbenzene in CS$_2$.

Figure 3-10. IR spectrum of 1,2-dibenzylbenzene in CS$_2$. 
Figure 3-11. IR spectrum of 1,3-dibenzylbenzene in CS$_2$.

Figure 3-12. IR spectrum of diphenylmethane in CS$_2$. 
Figure 3-13. Portion of the IR spectrum of 1,4-di-benzylbenzene compensated by diphenylmethane.

Figure 3-14. Portion of the IR spectrum of 1,2-di-benzylbenzene compensated by diphenylmethane.

Figure 3-15. Portion of the IR spectrum of 1,3-di-benzylbenzene compensated by diphenylmethane.
The results in Table III-6 reveal that high branching as indicated by IR analysis and low content of para-substitution as indicated from model compound reaction studies, result in low thermal stabilities (low TGA temperature), and in addition the TGA thermal curves of these polymers (Figure 3-6), as discussed previously, show different degradation patterns. It is concluded from this reasoning, therefore, that polymers PB-7 and PB-10 are more highly branched than polymers PB-6 and PB-11.

The isomer distributions from the model compound reactions in Table III-6 show that the contents of the ortho-isomer increase with the degree of branching of the polymer, and the content of para-isomer in the model compound reaction correlated with the degree of para-substitution on the polymer chains determined by IR, except polymer PB-7. The model compound reaction of polymer PB-7 gives the highest para-isomer content (67%) among the model compound reactions carried out at different conditions and, hence, polymer PB-7 should have the most linear structure. However, TGA and IR analysis indicated that polymer PB-7 had higher branching than polymers PB-6 and PB-11.

The conflict between the model compound reaction data and the results of polymer characterization can in this case be explained as follow. The degree of branching does not depend only on the degree of para-substitution of the
model compound reaction but also on the degree of ortho-substitution. Because branching on the para-substituted aromatic nuclei of the polymer chains can be considered to be related to the amount of ortho-substitution in the model compound reaction, the higher the ortho-isomer distribution in the model reaction, the more the aromatic nuclei of the internal repeating units of the polymer chains are going to be substituted. This will result in a lower total para-substitution content of polymer molecules than those predicted from the model compound reaction studies; instead the units would show the IR characteristics of 1,2,5-trisubstitution. Because polymer PB-7 should have a higher content of the ortho-isomer from the related model compound reaction than polymers PB-6 and PB-11, it is reasonable to expect that polymer PB-7 would have a higher branching and lower para-content than polymers PB-6 and PB-11.

Another possible cause for the higher structural regularity of polymers PB-6 and PB-11 than PB-7 is complexation of SO2 with the aromatic nuclei of the polymer molecules. This mechanism will be discussed more detail in the next section. As indicated in Table II-4, polymers PB-6 and PB-11 were prepared in SO2 solution while polymer PB-7 was not. The formation of a π-complex between aromatic nuclei and electron acceptors, such as SO2, will result a decrease in the reactivity of aromatic nuclei toward electrophilic
substitution. The equilibrium constants of π-complex formation for disubstituted aromatic nuclei are higher than those for monosubstituted aromatic nuclei. Therefore, π-complex formation along the polymer chain should be more prevalent than on the chain end, and as a result, benzylolation along the polymer chain will be suppressed which could result a less branched polymer.

G. Complexation Studies.

As mentioned previously in Chapter I, one of the reasons for branch-formation in polybenzyl is that the alkyl-disubstituted aromatic nuclei are more active toward electrophilic substitution than monosubstituted aromatic nuclei. Thus, if the reactivity of the disubstituted and monosubstituted aromatic nuclei can be reversed by some means, it should be possible to reduce the degree of branching of the polymers.

It has been reported that some electron acceptors, like \( \text{SO}_2 \) (92) and tetranitromethane (TNM) (93), can form π-complexes with aromatic compounds. The equilibrium constant for these π-complexes for a given acceptor, depends upon the π-basicity of the aromatic compounds within a series of the latter. The equilibrium constants of toluene relative to that of \( \text{p-xylene} \), for comparative with \( \text{SO}_2 \) and with TNM, are
given in Table III-7. As indicated in Table III-7, \( p \)-xylene, which has a higher \( \pi \)-basicity than toluene, has a higher

<table>
<thead>
<tr>
<th>Donor</th>
<th>( \text{SO}_2 )</th>
<th>Acceptor</th>
<th>( \text{TNM} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.59</td>
<td></td>
<td>0.14</td>
</tr>
<tr>
<td>( p )-xylene</td>
<td>1.00</td>
<td>1.00</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) 25°C in \( \text{CCl}_4 \) (92).

\( b \) 20.8°C in \( \text{CCl}_4 \) (93).

equilibrium constant of \( \pi \)-complex with both \( \text{SO}_2 \) and \( \text{TNM} \).

Since the formation of a \( \pi \)-complex of this type will cause a decrease in the basicity or nucleophilicity of the aromatic compound, and consequently cause a decrease in electrophilic substitution reactions such as benzylation, it is to be expected that the reactivities of toluene and \( p \)-xylene toward benzylation will change after formation of the \( \pi \)-complex. Using \( p \)-xylene as an analogue for the repeating units of polymer chains and toluene for the polymer chain end, it can be expected that branching attacks on the repeating units of polymer chains could then be suppressed by complexation and a lower branched polymer molecules could be obtained.
Model compound reactions of complexation studies were conducted by reacting benzyl chloride with a mixture of toluene and p-xylene which resemble the monosubstituted and disubstituted aromatic nuclei of the polymer chains, respectively. The results of the model compound reactions are collected in Table III-8. The analysis of reaction products and the necessity of conducting a control for each run are described in detail in the Experimental Section. From the data in Table III-8, it is seen that the mole ratio for benzylation of p-xylene relative to toluene decreased from 3.5 to 1.8 after S02 was added to the mixture of toluene and p-xylene. In the case of TNM as the complexing agent, the ratio decreased from 4.6 to 2.0. These results do show that the relative reactivity of p-xylene was decreased and the relative amount of toluene reacted was increased by about two fold after the addition of the complexing agents. Thus, it is to be expected, in the case of polymerization, that benzylation along the polymer chains could be reduced by a similar amount when complexing agents were present.

H. Coupling Reaction.

As mentioned in the previous section, the repeating units on the polymer chains have a higher inherent reactivity than either the chain ends or the monomer and, hence,
Table III-8

Effect of Complexation on the Reaction of Benzyl Chloride with 
\( p \)-Xylene and Toluene

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Acceptor</th>
<th>( \text{Donor}=p\text{-Xylene} )</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>( c ) ( p\text{-Xylene Reacted} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a 1</td>
<td>Control</td>
<td>1/1</td>
<td>n-Hexane</td>
<td>TiCl(_4)</td>
<td>3.5</td>
</tr>
<tr>
<td>d</td>
<td>( \text{SO}_2 )</td>
<td>1/1</td>
<td>n-Hexane</td>
<td>TiCl(_4)</td>
<td>1.8</td>
</tr>
<tr>
<td>b 2</td>
<td>Control</td>
<td>1/1</td>
<td>n-Hexane</td>
<td>TiCl(_4)</td>
<td>4.6</td>
</tr>
<tr>
<td>e, f</td>
<td>TNM</td>
<td>1/1</td>
<td>n-Hexane</td>
<td>TiCl(_4)</td>
<td>2.0</td>
</tr>
</tbody>
</table>

\( a \) Reaction temperature, \( 0^\circ \text{C.} \)
\( b \) Reaction temperature, \( -15^\circ \text{C.} \)
\( c \) Analyzed by GC.
\( d \) Mole ratio of \( \text{SO}_2/\text{benzyl chloride}/p\text{-xylene} = 1.5/1/1. \)
\( e \) Mole ratio of TNM/\( \text{benzyl chloride}/p\text{-xylene} = 6/1/1. \)
\( f \) TNM: Tetraniitromethane.
the probability of branching will increase as the polymer chain grows. Thus, the lower the molecular weight of the polymer, the lower should be the number of branches per polymer chain. It should be possible, therefore, to prepare more linear polymer of a given molecular weight by first preparing and isolating relatively low molecular weight polymers with one chloromethyl group per chain, and then coupling these polymers through chloromethyl groups, by using a bis(Grignard) aromatic reagent, to form a higher molecular weight product without increasing the number of branches per unit length of polymer molecules. The details

\[
2 \text{ (Polymer)} - \text{CH}_2\text{Cl} + \text{BrMg} - \text{MgBr} \rightarrow \text{(Polymer A)} - \text{CH}_2 - \text{CH}_2
\]

of the coupling reactions used and the preparation of Grignard reagents are described in Experimental Section.

In order to examine the feasibility of the coupling reaction, a model reaction was conducted by reacting benzyl bromide with a bis(Grignard) reagent prepared from \(p\)-dibromobenzene. The reaction products after terminating with water were analyzed by GC. The major peak in the GC analysis has the same retention time as that of \(p\)-dibenzylbenzene. There was also a small peak present which was approximately \(1/3\) the size of the major peak, with a retention time shorter than that of \(p\)-dibenzylbenzene but longer than benzene or toluene. This small peak is probably 4-bromodi-
phenylmethane, which would be the reaction product of benzyl bromide with the mono-Grignard reagent of $p$-dibromobenzene present as a result of conversion in the preparation of \textit{bis}(Grignard) reagent.

The coupling reaction of polybenzyl and di-Grignard reagent was conducted in THF at reflux temperature for 24 hours. The less branched PB-6 sample was chosen as the polymer for coupling. The total weight of the polymer, before and after the coupling reaction, was determined to make sure no polymer loss occurred during the recovery. The $M_n$ of the polymer was found to increase from 2926 to 3867 after coupling. The degree of para-substituted aromatic nuclei measured from the ratio of $I_{1023}/I_{2910}$ from IR spectra also increased from 0.556 to 0.607. The relatively small increase in the $M_n$ of the coupled polymer can be explained by the fact that the di-Grignard reagent contained some mono-Grignard reagent, which reacts with chloromethyl groups but does not cause coupling of two polymer chains. Another reason, which may account for the low molecular weight of coupled polymer, is the probable low chloromethyl content, as indicated by the low chlorine content, of the starting polymer. Elementary analysis of polymer PB-6 shows that it only contained 0.33 mole % of chlorine, indicating that only 1/3 of the polymer chains were capable of being coupled by the \textit{bis}(Grignard) reagent.
I. Film-Forming and Compatibility.

Polymer films prepared by molding at 90°C were all brittle and cracked during preparation, presumably because of the low molecular weights of these polymers. However, films prepared from polymer PB-11 did not crack as badly as those of polymer PB-7, although the molecular weight of the latter was twice as high as that of the former. This result could be due to a higher branched structure in polymer PB-7.

Film cast from a chloroform solution of a poly-blend containing a 1 to 1 weight ratio of polymer PB-7 and polystyrene showed almost no phase separation. The DSC thermogram of this film was rather difficult to understand, because no visible change on the baseline of the thermogram indicative of a glass transition was observed.

IV. POLY-2,5-DIMETHYLBENZYL

A. Polymerization of 2,5-Dimethylbenzyl Chloride.

The preparation of poly-2,5-dimethylbenzyl prepared from 2,5-dimethylbenzyl chloride is illustrated in Equation 3-4a. Because of two additional methyl groups substituted on the aromatic nucleus in this monomer compared to benzyl chloride, it is expected to show more steric control

\[
\begin{align*}
n \text{CH}_3 \text{CH}_2 \text{Cl} & \xrightarrow{\text{Catalyst}} \left[ \text{CH}_3 \text{CH}_2 \right]_n + n \text{HCl} \\
\end{align*}
\]
in the benzylation reaction. The 6-position on the aromatic ring of 2,5-dimethylbenzyl chloride, as shown in Equation 3-4a, is more steric hindered than the 3- and 4-positions, while with substitution at 3-position will cause extreme crowding of -CH₂ group at 1-position. Thus, it is expected that the benzylation will occur mostly at 4-position. More important, as the polymer chain grows, further substitution on the aromatic nucleus of the repeating units is sterically hindered by the presence of the two methyl groups on the aromatic nucleus and branching is less likely.

The data for the polymerization of 2,5-dimethylbenzyl chloride at various reaction conditions are collected in Tables II-5 and III-9. The polymerization reactions were carried out at different temperatures with a combination of TiCl₄ and DEAC as catalyst except polymer PDMB-8, in which TiCl₄ alone was used as catalyst. Trichloroethylene (TCE) was used as solvent in some of the polymerization reactions, because of its low freezing point (-84°C) and the fact that it is a better solvent for poly-2,5-dimethylbenzyl polymers than ethyl chloride.

No polymerization reactions were observed when the catalyst solution was prepared by adding TiCl₄ and DEAC chloride separately into TCE at -78°C. However, the polymerization reactions did occur as the temperature was raised above 0°C, as shown for polymer PDMB-6 in Table II-5. Polymerization reactions also occurred when the catalyst solutions
Table III-9
Properties of Poly-2,5-dimethylbenzyls Obtained from the
Polymerizations of 2,5-Dimethylbenzyl Chloride

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solubility in Benzene, %</th>
<th>M.P., °C</th>
<th>C%</th>
<th>H%</th>
<th>Cl%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMB-1</td>
<td>61</td>
<td>s 140-180, i 225-248</td>
<td>s 89.03</td>
<td>8.61</td>
<td>1.44</td>
</tr>
<tr>
<td>PDMB-2</td>
<td>100</td>
<td>150-214</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PDMB-3</td>
<td>100</td>
<td>200-265</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PDMB-4</td>
<td>91</td>
<td>s 140-210, i &gt; 300</td>
<td>s 84.15</td>
<td>8.26</td>
<td>2.01</td>
</tr>
<tr>
<td>PDMB-5</td>
<td>72</td>
<td>s 153-191, i 193-205</td>
<td>s 89.68</td>
<td>9.78</td>
<td>---</td>
</tr>
<tr>
<td>PDMB-6</td>
<td>88</td>
<td>s 172-263, i 242-331</td>
<td>s 89.28</td>
<td>8.34</td>
<td>---</td>
</tr>
<tr>
<td>PDMB-7</td>
<td>--</td>
<td>151-185</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PDMB-8</td>
<td>--</td>
<td>167-265</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PDMB-9</td>
<td>--</td>
<td>273-307</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

a All polymer samples are white powders.
b s: fraction soluble in refluxing benzene.
c i: fraction insoluble in refluxing benzene.
were prepared either by adding TiCl₄ and DEAC separately into TCE at room temperature, as in the case of polymer PDMB-7, or by adding TCE into premixed TiCl₄ and DEAC at -78°C as for polymer PDMB-5.

During the addition of TiCl₄ into TCE at -78°C, formation of some yellow crystals in the solution was observed. The crystals did not seem to be polymeric material and disappeared as the temperature increased, or as soon as they came in contact with cold methanol. No attempt was made to identify these yellow crystals. However, the above observations indicate that the yellow crystals probably were a complex compound of TiCl₄ and TCE. This complex was stable at -78°C and but showed no catalytic activity for the polymerization. At higher temperature, the complex presumably was unstable and TiCl₄ was released and its catalytic activity for the polymerization was resumed.

B. Crystallinity.

The polymers obtained under all the polymerization conditions were crystalline as described in Table III-9. Polymers PDMB-7 and PDME-8 were obtained as crystalline products even though the polymerization reaction was run at room temperature. It is believed, therefore, that steric hindrance on the aromatic nucleus is far more important than other
factors (such as temperature, catalyst, etc.) as far as control of branching in the polybenzyl is concerned. The X-ray diffraction patterns of these polymers, which had different melting points, were the same. The d-spacing obtained from the X-ray diffraction patterns were: 6.52 (strong), 5.03 (strong), 4.12 (strong), 3.40 (weak), and these values are very close to those reported in the literatures for poly-2,5-dimethylbenzyl polymers (12,14).

The melting points of poly-2,5-dimethylbenzyl polymers, measured by DSC analysis, varied from 140°C to 300°C as indicated in Table III-9. The polymers, PDMB-1, 2, 5 and 7, with relatively low melting points between 140°C and 191°C were believed to be mixtures of oligomers (24), but the results of annealing studies of polymer PDMB-7 in Table III-10, for example, indicated that its melting point could be increased from 150-185°C to 238-255°C (recorded as temperature range of the endothermic peak from DSC analysis). This observation tends to indicate that the low melting points of these polymers was not due to the presence of oligomers but rather to of crystalline imperfections.

Table III-10 also shows that the melting points of the polymers can be increased by as much as 70°C depending upon the initial melting points of the polymers. This large variation in the melting points, and the related rather large increases in the melting points of some of the polymers after annealing, can be explained on the basis of
Table III-10

Effect of Annealing at 140°C on the Melting Points of Poly-2,5-dimethylbenzyls

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Original M.P., °C</th>
<th>a Annealed M.P., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMB-1</td>
<td>124-131</td>
<td>170-187</td>
</tr>
<tr>
<td>PDMB-4</td>
<td>140-210, 235-255</td>
<td>b 276-313</td>
</tr>
<tr>
<td>PDMB-7</td>
<td>151-185</td>
<td>238-255</td>
</tr>
<tr>
<td>PDMB-8</td>
<td>162-236</td>
<td>237-276</td>
</tr>
<tr>
<td>PDMB-9</td>
<td>273-307</td>
<td>248-290</td>
</tr>
</tbody>
</table>

a Samples were sealed in DSC pans, heated to 240°C in an oil bath, cooled to 140°C and held 161 hours.

b Annealed at 140°C for 28 hours directly in DSC.
chain stiffness of these polymers which inhibits crystallization and makes longer annealing time necessary for the development of more perfect crystals.

An interesting melting behavior of the soluble portion of polymer PDMB-4 was observed when the sample was thermally treated in different ways as illustrated in Figure 3-16. The area of peak A decreased while that of peak B increased as the sample was annealed at 140°C for 14 hours. On a subsequent quenching of the sample in air, peak B disappeared but peak A remained almost unchanged. A new peak, C, was observed after the sample was cooled slowly from 270 to 140°C and annealed for 28 hours. However, peak A and B did not appear on the DSC thermogram. Further treatment of the sample by quenching in air resulted in a reappearance of peaks A and B but a decrease in the area of peak C.

Peak A which can be easily formed by quenching in air may be from a less perfect crystalline structure, and the crystalline perfections of the three endotherms is, therefore, believed to increase in the order A < B < C.

C. IR Spectra.

The infrared absorption of poly-2,5-dimethylbenzyl is illustrated in Figure 3-18 by a typical spectrum from
Figure 3-16. Endothermic peaks in DSC thermogram of PDMB-4 recorded at heating rates of 10°C/min. The samples were treated as following before each run:

I. Original sample.
II. Annealed 14 hours at 140°C.
III. Quenched in air after II (without annealing).
IV. Heated to 274°C, cooled at 10°C/min. to 230°C, and then at 5°C/min. to 140°C before annealing 28 hours.
V. Quenched in air after IV (without annealing).
soluble portion of polymer PDMB-5. Aromatic and alkyl C-H stretching peaks in the region 3100-2850 cm$^{-1}$ are well resolved. The region 2000-1670 cm$^{-1}$ contains 3 peaks and the central peak appears as a shoulder of the peak at right hand side. This region of the spectrum is reproduced in Figure 3-17 and compared with the same region of the spectra of low molecular weight model compounds having 1,2,4- (or 1,2,5-) tri- and 1,2,4,5-tetrasubstitution (99) as shown in Figure 3-17. It is quite clear from Figure 3-18 that the polymer molecules contain 1,2,4- (or 1,2,5-) trisubstitution as well as 1,2,4,5-tetrasubstituted aromatic nuclei, and the former correspond to the chain-ends while the latter to repeating units of the polymer molecules. The absorptions at 880 and 818 cm$^{-1}$ correspond, respectively to the C-H bending of 1,2,4,5-tetrasubstituted and 1,2,4- (or 1,2,5-) trisubstituted aromatic rings (100). An estimate of the relative molecular weights of poly-2,5-dimethylbenzyl from the ratio of absorptions at 880 and 818 cm$^{-1}$ will be discussed later.

D. Solubility.

Poly-2,5-dimethylbenzyls, like some of the poly-
1,2,4,-Trisubstituted benzenoid compound.

1,2,4,5-Tetrasubstituted benzenoid compound.

Polymer PDMB-5

Figure 3-17. Schematic representation of 5-6 region in the IR spectra for substituted benzenoid compounds and polymer PDMB-5.

Figure 3-18. IR spectrum of polymer PDMB-5. (KBr disc)
benzyls, have poor solubility in common organic solvents. Most of the polymers, except polymers PDMB-2 and PDMB-3, are partially soluble in boiling xylene, benzene, tetrachloroethylene and diphenylmethane, etc. The solubility of the polymers in refluxing benzene or p-xylene are recorded in Table II-9. The DSC analysis of the insoluble samples of these polymers, except for PDMB-4, shows melting peaks from 225 to 331°C. The result suggests that the insoluble polymers are of relatively high crystallinity presumably because of regular structures. That is, the insolubility of the polymers caused by the globular-like structure, as in the case of some of the insoluble polybenzyl samples, can apparently be ruled out, and both molecular weight and crystallinity are more likely the main causes of the observed poor solubility of these polymers.

It is rather difficult to differentiate between these two factors because attempts at molecular weight measurements were unsuccessful due to the insolubility of these polymers. However, relative molecular weight differences between the polymers can be estimated from the ratio of IR absorption peaks 880 and 818 cm$^{-1}$, which corresponds to the tetrasubstituted and trisubstituted aromatic nuclei, respectively, as discussed above. It is assumed that ratio of I880/I818, the higher is the relative molecular weights of the samples, and the data in Table III-11 shows that the
insoluble fractions generally show a higher ratio of I880/I818 than the soluble one. Nevertheless, the poor film forming ability of those insoluble polymers suggests that their molecular weight cannot be higher than that of poly-\(\alpha\)-methylbenzyl, sample PMB-6H, which had a good film forming ability at molecular weight of 9981.

The validity of using the I880/I818 ratio for estimating relative molecular weight of the poly-2,5-dimethylbenzyl has been examined by measuring the molecular weights of soluble fractions of the polymers by GPC. The results in Table III-12 generally show a good agreement between the \(\overline{Mn}\) and I880/I818 values with the exception of polymer PDMB-4.

The number average molecular weights, \(\overline{Mn}\), of poly-2,5-dimethylbenzyl samples in Table III-12 were obtained by \(\overline{An} \times Q\) (102), where \(\overline{An}\) is number average molecular angstrom length of polymer chains and \(Q\) is the molecular weight per angstrom length of polymers. \(\overline{An}\) was calculated directly from the gel permeation chromatograms of the polymer samples by using polystyrene samples as standards. The angstrom length of the polymer chain unit of poly-2,5-dimethylbenzyl in a fully extended conformation is 4.3 Å (94) and the molecular weight of this length is 118. Thus, \(Q\) value of poly-2,5-dimethylbenzyl calculated from the ratio of 118/4.3 is 27.
Table III-11
Ratio 1880 cm\(^{-1}\)/1818 cm\(^{-1}\) Measured from the Infrared Spectra of the Soluble and Insoluble Fractions of Some of Poly-2,5-dimethylbenzyls

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PDMB-1</th>
<th>PDMB-4</th>
<th>PDMB-5</th>
<th>PDMB-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Soluble</td>
<td>0.43</td>
<td>0.45</td>
<td>0.71</td>
<td>0.58</td>
</tr>
<tr>
<td>Insoluble</td>
<td>0.88</td>
<td>0.88</td>
<td>0.77</td>
<td>0.78</td>
</tr>
</tbody>
</table>

\(^a\) Soluble in refluxed benzene.

Table III-12
Comparison of Ratio 1880 cm\(^{-1}\)/1818 cm\(^{-1}\) with \(\overline{Mn}\) Calculated from GPC Analysis

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(a) An, A</th>
<th>(b) (Q, A^{-1})</th>
<th>(\overline{Mn})</th>
<th>(1880/1818)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMB-5</td>
<td>166</td>
<td>27</td>
<td>4482</td>
<td>0.71</td>
</tr>
<tr>
<td>PDMB-6</td>
<td>88</td>
<td>27</td>
<td>2376</td>
<td>0.58</td>
</tr>
<tr>
<td>PDMB-2</td>
<td>66</td>
<td>27</td>
<td>1782</td>
<td>0.50</td>
</tr>
<tr>
<td>PDMB-4</td>
<td>86</td>
<td>27</td>
<td>2322</td>
<td>0.45</td>
</tr>
</tbody>
</table>

\(^a\) Measured from gel permeation chromatogram by using polystyrene as standards.

\(^b\) Estimated from monomeric chain length and weight.
E. Side Reactions.

No anthracene terminal group have been detected from the UV spectra of polymers PDMB-1 and PDMB-4 (soluble fractions) in toluene solution (12 mg/ml) at the region 300-500 m\(\mu\). This result is not surprising because the ortho-position to the chloromethyl group in the monomer or on polymer chain endgroup is sterically hindered, and benzyla
tion at the ortho-position to form anthracene terminal group,

![Chemical structure](image1)

as illustrated in Equation 3-4, should be inhibited. The relatively high chlorine content of polymer PDMB-1 (1.44 for soluble fraction) and PDMB-4 (2.78 for insoluble fraction) compared to those of polybenzyls also supports the conclu
sion that little or no anthracene formation occurs in these polymer molecules.

V. POLY-\(\alpha\)-METHYLBENZYL

A. Polymerization of \(\alpha\)-Chloroethylbenzene.

Poly-\(\alpha\)-methylbenzylbenzene was prepared from the polycondensation of \(\alpha\)-chloroethylbenzene, with either TiCl\(_4\)
or AlCl₃ as catalyst, as illustrated in Equation 3-5. Tables II-8 and III-13 tabulate the polymerization reaction

\[
\begin{align*}
n \begin{array}{c}
\text{Catalyst} \\
\end{array} \\
\end{align*}
\begin{array}{c}
\text{CH}_3 \\
\text{C-Cl} \\
\text{H} \\
\end{array}
\rightarrow
\begin{array}{c}
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{C} \\
\text{H} \\
\end{array} \right]_n \\
\end{array} + \text{HCl}
\]

Eq. 3-5

conditions and the data obtained from the characterization of the polymers. The yield of the polymerization reactions was found to be dependent on the catalyst/monomer ratio, i.e., the yield increased with the catalyst/monomer ratio as indicated in polymers PMB-3 and PMB-4; PMB-5, PMB-6 and PMB-7.

The polymers prepared at -78 and -125°C with AlCl₃ as catalyst were white powders, while those prepared at room temperature with TiCl₄ as catalyst was tan or off-white in color. The polymerization reactions in nitromethane solution showed a phase separation of the polymer from the solution, which was not observed in the other reaction conditions. Precipitation of the polymer would be expected to reduce or inhibit the reactivities of the chloromethyl end-groups by preventing their reacting with catalyst molecules.

Thus, the molecular weight of the polymer PMB-1 prepared in nitromethane solution was low as indicated in Table III-13. Low molecular weights of polymer prepared in nitromethane solution was also observed for polybenzyls, for
## Table III-13

Properties of Poly-\( \alpha \)-methylbenzyls Obtained from Polymerization of \( \alpha \)-Chloroethylbenzene

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Color</th>
<th>( M_n )</th>
<th>M.P., °C</th>
<th>( T_g ), °C</th>
<th>Crystallinity</th>
<th>e 9C%</th>
<th>H%</th>
<th>Cl%</th>
<th>O%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMB-1</td>
<td>tan</td>
<td>1549</td>
<td>55</td>
<td></td>
<td>-</td>
<td>92.0</td>
<td>7.4</td>
<td>0.08</td>
<td>0</td>
</tr>
<tr>
<td>PMB-2D</td>
<td>off-white ((2777))</td>
<td>4361</td>
<td>101</td>
<td>-</td>
<td>92.02</td>
<td>7.09</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMB-3</td>
<td>white</td>
<td>1929</td>
<td>55</td>
<td>-</td>
<td>91.0</td>
<td>7.0</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMB-4</td>
<td>white</td>
<td>2983</td>
<td>72</td>
<td>-</td>
<td>90.5</td>
<td>7.0</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMB-5</td>
<td>white</td>
<td>4513</td>
<td>190</td>
<td>93</td>
<td>91.57</td>
<td>7.62</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMB-6</td>
<td>white</td>
<td>6250</td>
<td>198</td>
<td>95</td>
<td>+</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMB-6L</td>
<td>white</td>
<td>3460</td>
<td>171</td>
<td>87</td>
<td>+</td>
<td>91.87</td>
<td>7.77</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PMB-6H</td>
<td>white</td>
<td>9981</td>
<td>211</td>
<td>101</td>
<td>+</td>
<td>91.65</td>
<td>7.65</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>PMB-7</td>
<td>white</td>
<td>4289</td>
<td>173</td>
<td>85</td>
<td>-</td>
<td>91.2</td>
<td>6.7</td>
<td>0.47</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) PMB-2D is 4/5 fraction of polymer PMB-2 (see Experimental Section).

\( b \) \( M_n \) of PMB-2 is estimated from PMB-2C and PMB-2D (see Experimental Section).

\( c \) Measured from DSC.

\( d \) Measured from X-ray diffraction.

\( e \) Theoretical value: C: 91.6%; H: 7.7%; Cl: 0.7% for \( M_n = 5000 \).
example, for PB-1 in Table III-3. These two polymers had almost the same molecular weights and molecular weight distribution as shown in Table III-14. This result indicated that these two polymers have similar solubilities in nitromethane, and the polymer molecules precipitated out and stopped growing when the degree of polymerization reached 15-17. On the other hand, carbon tetrachloride was a good solvent for poly-α-methylbenzyl, and the molecular weight of polymer PMB-2 prepared in CCl₄ solution was much higher than that of polymer PMB-1.

The precipitation effect of the polymer on the molecular weight was examined by an attempted further polymerization of polymer PMB-1. This polymer was dissolved in a large quantity of CCl₄ and the polymerization was re-initiated with TiCl₄. If the low molecular weight of polymer PMB-1 was due to precipitation of the polymer as suggested, further reaction of the polymer in dilute CCl₄ solution should be possible resulting in an increase in the molecular weight of the polymer. However, the polymer showed only a slight increase in the molecular weight, from 1549 to 1742, after 65 hours of reaction at room temperature. This slight difference in molecular weight can be attributed to low chlorine content of the original polymer, because the elementary analysis of polymer PMB-1 showed only 0.08 weight % of the chlorine present. This result means that
Table III-14
Mn and Molecular Weight Distribution of Poly-α-methylbenzyl, PMB-1, and Polybenzyl, PB-10A, Prepared in Nitromethane Solution at Room Temperature

<table>
<thead>
<tr>
<th>Polymer</th>
<th>a Mn</th>
<th>b Mn/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMB-1</td>
<td>1549</td>
<td>1.02</td>
</tr>
<tr>
<td>PB-10A</td>
<td>1554</td>
<td>1.03</td>
</tr>
</tbody>
</table>

*a Measured by VPO.

*b Measured by GPC.

Table III-15
Chemical Shifts of Protons in NMR Spectra of Poly-α-methylbenzyls

<table>
<thead>
<tr>
<th>Protons</th>
<th>a Chemical Shift, δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic ring</td>
<td></td>
</tr>
<tr>
<td>Monosubstituted</td>
<td>7.15</td>
</tr>
<tr>
<td>Disubstituted or Trisubstituted</td>
<td>≥ 7.04</td>
</tr>
<tr>
<td>Methyl</td>
<td>1.5</td>
</tr>
<tr>
<td>Methyldyne</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*a Relative to TMS, 60 MHz spectra.
only 3.5% of the polymer chains had chloromethyl groups which could be reacted with TiCl₄ for further polymerization, and hence an increase in the molecular weight under these conditions will be small.

B. Side Reactions.

The chlorine content of poly-α-methylbenzyl was very low compared to the theoretical value, as was also observed in polybenzyl polymers. The elementary analysis of poly-α-methylbenzyl prepared either at room temperature, i.e., PMB-1, or at -125°C, i.e., PMB-6 did not contain any oxygen by elementary analysis. Thus, the low chlorine content of this polymer was apparently not caused by termination of the reaction by the moisture in the reaction system.

Anthracene formation which occurred in some of the polybenzyls has not been observed in poly-α-methylbenzyl according to UV analysis, presumably because of low ortho-substitution tendency, as indicated in model compound reactions. It is more likely that the low chlorine content was due to indane formation during the polymerization.

The indanyl structure has been observed in some of the cationic polymerizations of styrene (97) and its derivatives, e.g., with α-methylstyrene (98) as illustrated in Equation 3-6. Fritz and Ress (23) in the polymerization of
2-chloroisopropylbenzene derivatives to aryleneisopropylidene

\[
\begin{align*}
\text{R} & \text{C} - \text{C} - \text{R} \rightarrow \text{R} & \text{C} - \text{C} - \text{R} \\
\text{aryl} & \text{ene} & \text{isopropylidene} \\
\end{align*}
\]

Eq. 3-6

polymers also suggested the formation of indanyl structure as shown in Equation 3-7. Indane formation in Equation 3-8 was believed to occur by the normal addition reaction of \(\alpha\)-methylstyrene with an aryleneisopropyl carbonium ion followed by cyclization.

\[
\text{Cl} + \text{HCl}
\]

The existence of styrene in the \(\alpha\)-chloroethylbenzene monomer has been described in the Experimental Section.
Although the styrene content in the monomer was reduced to 0.6-0.8%, it still could have caused a significant amount of indane formation in the polymerization. In addition to the original presence of styrene, more styrene could have been formed by dehydrochlorination of α-chloroethylbenzene during the polymerization reaction to cause even higher indane formation.

C. Measuring the Degree of Branching.

NMR spectra of poly-α-methylbenzyl prepared at high and low temperatures are reproduced in Figures 3-19 and 3-20. The relatively well resolved spectra of these polymers compared to those of the polybenzyls is presumably due to the less branched structure of the former polymers. In Figure 3-19 the portion of the spectrum assigned to the methyl protons is resolved into two peaks, while the resonance peak of methyne protons is a quartet. Two resonance peaks of aromatic protons come from disubstituted and monosubstituted aromatic rings. The chemical shifts relative to TMS for the resonance peaks are listed in Table III-15.

The number of branches, X, of poly-α-methylbenzyls can be calculated from the NMR data and the molecular weight of the polymer by using the following equation.

\[
\frac{\text{Peak Area of } 7.04}{\text{Peak Area of } 7.15} = \frac{4D - X}{(X + 1) \times 5}
\]

where \( D = DP-(X+1) \)
Figure 3-19. NMR spectrum of PMB-6L in CDCl₃.

Figure 3-20. NMR spectrum of PMB-1 in CDCl₃.
The ratio of peak areas at 7.04 δ to 7.15 δ is equal to the ratio of the protons in disubstituted and tri-substituted aromatic rings to those in the monosubstituted rings. The relative number of disubstituted and multisubstituted aromatic rings can be obtained by subtracting the number of monosubstituted aromatic rings, \((X + 1)\), from the average degree of polymerization, \(\bar{DP}\). Because for each branch the number of protons on the aromatic rings will be reduced by one, the total number of protons on the disubstituted aromatic rings is equal to \((4D - X)\). The results of this calculation for estimating the degree of branching of poly-\(\alpha\)-methylbenzyls are collected in Table III-16.

Different molecular weight fractions of polymer PEB-6 in Table III-16 show the different numbers of branches per polymer molecule. The high molecular weight fraction, polymer PMB-6H, has a higher number of branches per polymer molecule than low molecular weight fraction, polymer PMB-6L. This is simply because the probability of the branching is increased as the polymer chains become longer as discussed in the Introduction Section.

D. Effect of Polymerization Conditions on the Degree of Branching.

The effect of polymerization temperature on the
Table III-16
Degree of Branching of Poly-\(\alpha\)-methylbenzyls Measured from NMR and Molecular Weight Data

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(7.15 \delta)</th>
<th>(7.04 \delta)</th>
<th>X=Branches</th>
<th>Branches/10 Monomer units</th>
<th>(M_n)</th>
<th>(DP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMB-1</td>
<td>0.52</td>
<td>3.20</td>
<td>2.1</td>
<td>1549</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>PMB-2D</td>
<td>0.44</td>
<td>11.7</td>
<td>2.8</td>
<td>1193</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>PMB-3</td>
<td>0.38</td>
<td>3.23</td>
<td>1.7</td>
<td>1929</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>PMB-4</td>
<td>0.19</td>
<td>1.51</td>
<td>0.52</td>
<td>2983</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>PMB-5</td>
<td>0.063</td>
<td>0.56</td>
<td>0.13</td>
<td>4513</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>PMB-6</td>
<td>0.059</td>
<td>1.70</td>
<td>0.28</td>
<td>6253</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>PMB-6L</td>
<td>0.051</td>
<td>0.30</td>
<td>(\approx 0.0)</td>
<td>3460</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>PMB-6H</td>
<td>0.056</td>
<td>3.08</td>
<td>0.31</td>
<td>9981</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>PMB-7</td>
<td>0.096</td>
<td>1.68</td>
<td>0.52</td>
<td>4289</td>
<td>41</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) The ratio of peak areas of \(7.15 \delta\) to \(7.04 \delta\).
degree of branching of the polymers, as indicated in Table III-17, reveals that the polymers prepared at higher temperature generally have a higher degree of branching as expected. The results are in agreement with the temperature effect on the isomer distribution of the model compound reaction of poly-α-methylbenzyl as discussed previously.

There are some differences in the degree of branching of the polymers prepared at the same reaction temperature, such as polymers PMB-3 and PMB-4; PMB-5, PMB-6 and PMB-7. The differences in the degrees of branching is caused by the different catalyst/monomer ratio in the polymerization reaction. A higher catalyst/monomer ratio in the polymerization reaction results in a polymer with a higher degree of branching, except in the case of polymer PMB-7. The high degree of branching at high catalyst/monomer ratios can be explained by the fact that at higher ratios, more active species are created and the chance of selective benzylolation is decreased; consequently, the degree of branching will be increased.

The exceptional high degree of branching of polymer PMB-7 at a very low catalyst/monomer is attributed to the different polymerization procedure used in which the order of the addition of the reactants was changed. In the polymerization of PMB-7, the monomer solution was added dropwise into the catalyst solution while in the other
Table III-17
Effect of Temperature and Catalyst/Monomer Ratio in the Polymerization of α-Chloroethylbenzene on the Degree of Branching of the Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temp. °C</th>
<th>Catalyst Monomers</th>
<th>Degree of Branching, Branches/10 Monomer Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMB-1</td>
<td>25</td>
<td>1/100</td>
<td>2.1</td>
</tr>
<tr>
<td>PMB-2D</td>
<td>25</td>
<td>1/100</td>
<td>2.8</td>
</tr>
<tr>
<td>PMB-3</td>
<td>-78</td>
<td>1/8</td>
<td>1.7</td>
</tr>
<tr>
<td>PMB-4</td>
<td>-78</td>
<td>&lt; 1/100</td>
<td>0.52</td>
</tr>
<tr>
<td>PMB-5</td>
<td>-125</td>
<td>1/100</td>
<td>0.13</td>
</tr>
<tr>
<td>PMB-6</td>
<td>-125</td>
<td>1/33</td>
<td>0.28</td>
</tr>
<tr>
<td>PMB-7</td>
<td>-125</td>
<td>1/100</td>
<td>0.52</td>
</tr>
</tbody>
</table>
polymerizations, such as for PMB-6, the order of addition of the reactants was reversed. The addition of monomer solution into the catalyst solution results in a very high catalyst/monomer ratio at early stage of the addition of monomer, a ratio which is much greater than the total catalyst/monomer ratio. The degree of branching of polymer PMB-7 is, therefore, expected to be higher than it should be from the reaction conditions.

E. Effect of Degree of Branching on the Properties of Polymers.

The effect of degree of branching on some of the properties of poly-α-methylbenzyl is tabulated in Table III-18.

1. Crystallinity.

Crystallinity was not detected in the polymer samples prepared at room temperature and at -78°C; i.e., polymers PMB-1, PMB-2, PMB-3 and PMB-4, showed no crystallinity either by X-ray diffraction or by DSC analysis. Annealing of these polymer samples at 180°C under N₂ for 72 hours still did not show any endothermic peaks on the DSC thermograms. Examination of the birefringence of these polymer samples before and after annealing also showed no visible change. The only
Table III-18
Effect of Branching on Some of the Properties of Poly-α-methylbenzyls

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Degree of Branching, Branches/10 Monomer Units</th>
<th>a Crystal-(\text{linity})</th>
<th>b M.P.</th>
<th>c TGA °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMB-1</td>
<td>2.1</td>
<td>-</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>PMB-2D</td>
<td>2.8</td>
<td>-</td>
<td>No</td>
<td>415</td>
</tr>
<tr>
<td>PMB-3</td>
<td>1.7</td>
<td>-</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>PMB-4</td>
<td>0.52</td>
<td>-</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>PMB-5</td>
<td>0.13</td>
<td>+</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>PMB-6</td>
<td>0.28</td>
<td>+</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>PMB-6L</td>
<td>0.0</td>
<td>+</td>
<td>Yes</td>
<td>437</td>
</tr>
<tr>
<td>PMB-6H</td>
<td>0.31</td>
<td>+</td>
<td>Yes</td>
<td>465</td>
</tr>
<tr>
<td>PMB-7</td>
<td>0.52</td>
<td>-</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

a From X-ray diffraction.

b Endothermic peak in DSC thermogram.

c Temperature of 5% weight loss (heating rate, 5°C/min. in air).
crystalline polymers were those prepared at -125°C, i.e., polymer PMB-5, PMB-6 and PMB-7. Polymer PMB-7 only showed a small melting endothermic peak at 173°C on DSC thermogram, but there was no indication of crystallinity from the X-ray diffraction analysis, which suggests that polymer PMB-7 must have a very low degree of crystallinity.

As indicated in Table III-18, polymer PMB-7 had a relatively high degree of branching as compared to polymers PMB-5 and PMB-6 and its degree of branching was close to that of PMB-4, which was amorphous polymer. Thus, the maximum limit of the degree of branching for poly-α-methylbenzyl in order to have a crystalline polymer is approximately 0.5 branches/10 monomer units. Polymers PMB-3 and PMB-4 which did not show any crystallinity, however, had a very high content of para-isomer (98.8%), in the model compound reactions, as shown in MC-5 in Table II-6. It is rather difficult to believe that the polymers obtained under conditions which should generate such high para-isomer content according to the model compound reaction, are not crystalline because they contain too many branches. Apparently the deviation of the result of model compound reactions from that of polymerization is attributable to an oversimplified assumption made about the model compound reaction. No concentration differences between the repeating units and chain-ends of the polymer molecules was assumed in the model compound
reaction. In the polymerization reaction, the number of repeating units is higher than chain-ends and therefore, the degree of branching of the polymer is higher than that predicted from the results of the model compound reactions.

The d-spacings of these crystalline polymers calculated from the X-ray diffraction spectra are 5.73 (strong), 4.98 (strong), 3.85 (medium). No difference in d-spacings of crystalline polymers with different melting points was observed. The melting points of the crystalline polymers measured from the DSC analysis as indicated in Table III-13, varied from 171 to 211°C. An attempt to correlate the difference in the melting points of the polymers with their structures was found to be unnecessary because the difference in the melting points of the polymers could be eliminated by annealing as can be seen by a comparison of polymers PMB-6H and PMB-6L in Table III-19. The melting point of polymer PMB-6L was increased from 171 to 219°C by annealing and reached the value of the melting point of the high melting polymer PMB-6H. The annealed samples also showed an increase in crystallinity from the fact that the relative intensity of the amorphous hallow in the X-ray diffraction spectra decreased as the polymer samples were annealed.

Two endothermic peaks on the DSC thermogram of the annealed samples of polymer PMB-6L and PMB-6H were observed as indicated in Table III-19. The temperature increase of the
low temperature endothermic peak at different annealing temperatures was greater than that of the high temperature endothermic peak. The change in the temperatures of high temperature endothermic peaks was rather small. There was a tendency, as shown in Table III-19, for the low temperature endothermic peak to approach the high temperature endothermic peak at annealing temperature and time increased. This result indicates that these two types of endothermic peaks may represent the same type of polymer crystalline structure but with different degree of perfection. This conclusion is also supported from the identical X-ray diffraction patterns of annealed and unannealed samples of PMB-6L and PMB-6H.

2. Thermal Stability.

The thermal stabilities of polymers PMB-2, PMB-6L and PMB-6H, as based on the on-set temperature of 5% weight loss in the thermal gravimetric analysis, is shown in Table III-18. The results indicate that the higher branched polymer PMB-2 had a lower thermal stability than lower branched polymer PMB-6L, and this is in agreement with the conclusion drawn from the studies of polybenzyls.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>M.P., °C Before Annealing</th>
<th>M.P., °C, After Annealing after Annealing for</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>14 hrs., 150°C</td>
</tr>
<tr>
<td>PMB-6L</td>
<td>171</td>
<td>165, 190</td>
</tr>
<tr>
<td>PMB-6H</td>
<td>211</td>
<td>169, 201</td>
</tr>
</tbody>
</table>

*a* Annealed in DSC.

*b* Annealed in oil bath.

*c* Annealed in hot press.

A qualitative comparison of the solubilities of poly-α-methylbenzyls with their \( M_n \) values and degrees crystallinity are shown in Table III-20. Chloroform was the most effective solvent among those listed in the table. Polymers prepared at \(-125^\circ C\) (i.e., polymers PMB-5, PMB-6 and PMB-7) was insoluble in \( CCl_4 \), THF and toluene, while those prepared at \(-78^\circ C\) and room temperature (i.e., polymers PMB-1, PMB-2, PMB-3, and PMB-4) were very soluble in these three solvents. The low solubility of polymers PMB-5, PMB-6 and PMB-7 was presumably due to their crystalline nature, and this result can be understood from a comparison of the solubilities of the noncrystalline and crystalline polymers of the approximately the same molecular weights; e.g., PMB-2D vs. PMB-5 or PMB-7 in Table III-20. The effect of crystallinity on the solubility of the polymers can also be demonstrated by the different solubilities of the quenched and annealed samples of polymer PMB-6H. The quenched sample of polymer PMB-6H which showed complete darkness under cross polars on a polarizing microscope, was, therefore, apparently amorphous, and was very soluble in \( CHCl_3 \), while its annealed sample which showed brightness under the polarizing microscope was insoluble in \( CHCl_3 \).

The globular-like structure which was suggested as the main reason for the poor solubility of some of the polybenzyls (40) presumably cannot exist in the branched
Table III-20
Relationship between the Solubility and Molecular Weight or Crystallinity of Poly-α-methylbenzyls

<table>
<thead>
<tr>
<th>Polymer</th>
<th>CHCl$_3$</th>
<th>CCl$_4$</th>
<th>THF</th>
<th>Toluene</th>
<th>$\overline{M_n}$</th>
<th>$^d$ Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMB-1</td>
<td>a vs</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>1549</td>
<td>-</td>
</tr>
<tr>
<td>PMB-2D</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>4361</td>
<td>-</td>
</tr>
<tr>
<td>PMB-3</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>1929</td>
<td>-</td>
</tr>
<tr>
<td>PMB-4</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>2983</td>
<td>-</td>
</tr>
<tr>
<td>PMB-5</td>
<td>b s</td>
<td>c is</td>
<td>is</td>
<td>is</td>
<td>4513</td>
<td>+</td>
</tr>
<tr>
<td>PMB-6</td>
<td>s</td>
<td>is</td>
<td>is</td>
<td>is</td>
<td>6253</td>
<td>+</td>
</tr>
<tr>
<td>PMB-6L</td>
<td>s</td>
<td>is</td>
<td>is</td>
<td>is</td>
<td>3460</td>
<td>+</td>
</tr>
<tr>
<td>PMB-6H</td>
<td>s</td>
<td>is</td>
<td>is</td>
<td>is</td>
<td>9981</td>
<td>+</td>
</tr>
<tr>
<td>PMB-7</td>
<td>vs</td>
<td>is</td>
<td>is</td>
<td>is</td>
<td>4289</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ vs: very soluble.

$^b$ s: soluble.

$^c$ is: insoluble.

$^d$ From X-ray diffraction.
poly-\(\alpha\)-methylbenzyl. The reason is that polymer PMB-2D, which had the highest degree of branching among the polymers listed in Table III-20, only had 2.8 branches per ten repeating units and this value would be much too low for the type of globular-like structure proposed for the polybenzyls. That is, the estimated degree of branching for a globular-like structure would be approximately one branch in every repeating unit. The non-globular-like structure of branched poly-\(\alpha\)-methylbenzyls caused the good solubility of these polymers in common solvents when amorphous.

F. Effects of \(\bar{M}_n\) and Degree of Branching on Tg.

The glass transition temperature, Tg, of various poly-\(\alpha\)-methylbenzyls are given in Table III-13. When Tg is plotted as a function of molecular weight in Figure 3-21, it appears that Tg levels off at a molecular weight of about 4000-5000. This molecular weight effect on Tg is quite common and been reported for many vinyl polymers (88), like polystyrene, polymethylmethacrylate, etc. This type of molecular weight dependency is easily understood on the basis of the free-volume theory of the Tg phenomenon. That is, lowering the molecular weight of the polymer increases the concentration of end groups, which results in a higher free-volume and consequently lowers the Tg. However, as
Figure 3-21. The effect of molecular weight on $T_g$ of branched poly-$\alpha$-methylbenzyl polymers.

( ) : Degree of branching; number of branches per 10 monomer units.
reported for other polymers, the degree of branching also appears to have some effects on the $T_g$ values. This can be seen from the relatively high $T_g$ values of two polymers with high degree of branching (2.8 and 2.1) as shown in Figure 3-21. As mentioned in Chapter I, the effect of branching on the $T_g$ depends on the type of branching, namely, whether the branches are star-type or comb-type structures. The $T_g$ of star-type polymers, with many branches crowding at branching points, is higher than that of comb-type polymer of the same molecular weight (10). Thus, one can conclude on this basis that the structure of the higher branched polymers PMB-1 and PMB-2 was probably closer to that of a star-type than comb-type structure or at least it can be tentatively concluded that the distribution of branches on the polymer chains was much concentrated in one region rather than evenly distributed along the polymer chains.

G. Film-Forming and Compatability.

The film-forming ability of poly-$\alpha$-methylbenzyls is generally better than that of the polybenzyls and the poly-2,5-dimethylbenzene, mainly because poly-$\alpha$-methylbenzyls have a lower degree of branching. However, films prepared from all poly-$\alpha$-methylbenzyls were still brittle, except for polymer PMB-6H. The quenched amorphous film (0.2 mm thick) of polymer PMB-6H
was clear and very strong and could be stretched 20 times its original length at 150°C by applying a weight of 7 grams. The stretched film showed a complete brightness under the polarizing microscope. It is believed that this brightness was not due to the crystallinity but rather to the orientation, because no crystallinity was detected by x-ray diffraction in this film.

The compatibility of several poly-α-methylbenzyl samples with polystyrene was investigated by casting films from CHCl₃ or THF solutions of 1 : 1 weight ratio of polystyrene and polymer PMB-2, PMB-4, PMB-6L or PMB-6H. Phase separation was observed in polymer PMB-6L and PMB-6H but not in PMB-2 and PMB-4. The main difference between these two sets of polymers was crystallinity, not the molecular weight. Thus, it is believed that the crystalline nature of polymer PMB-6L and PMB-6H was the main reason of the incompatibility of these polymers with polystyrene.
CHAPTER FOUR
SUMMARY

Polybenzyl, poly-2,5-dimethylbenzyl and poly-\(\alpha\)-methylbenzyl were prepared from the polycondensation of benzyl chloride, 2,5-dimethylbenzyl chloride and \(\alpha\)-chloroethylbenzene respectively, with either Friedel-Crafts or Ziegler-Natta catalyst in various kinds of solvents at different temperatures (i.e. room temperature to \(-130^\circ C\)). Crystalline poly-2,5-dimethylbenzyl samples were obtained in all systems examined in this work, but crystalline poly-\(\alpha\)-methylbenzyl and polybenzyl samples were prepared only at a polymerization temperature of \(-125^\circ C\). The crystallinity of polybenzyl sample was much lower than that of poly-\(\alpha\)-methylbenzyl sample. The result indicate that the steric effect of the monomers is far more important in controlling crystallinity (or degree of branching) than other factors, i.e., temperature, catalyst and solvent. This conclusion is also supported by the results from model compound reactions of polybenzyl (i.e., diphenylmethane with benzyl chloride) and poly-\(\alpha\)-methylbenzyl (i.e., 1,1-diphenylethane or diphenylmethane with \(\alpha\)-chloroethylbenzene). The para-isomer content of the model compound reactions increased significantly from 47% to 97% as benzyl chloride was replaced by \(\alpha\)-chloroethylbenzene. It was found that crystalline
poly-α-methylbenzyl could be obtained when the degree of branching was approximately 0.5 branches / 10 monomer units.

The number of branches, \( X \), of poly-α-methylbenzyl samples was calculated from the NMR absorption of aromatic protons and the degree of polymerization. The degree of branching of polybenzyl was characterized by IR but not by NMR due to its ill resolved spectra. The ratio of 1025 cm\(^{-1}\)/2910 cm\(^{-1}\) and 1032 cm\(^{-1}\)/2910 cm\(^{-1}\) from IR absorption spectra were used for estimating the degree of branching. The degree of branching of polybenzyl samples correlated very well with the isomer distribution from the model compound reactions. The higher the para-isomer content from the model compound reactions, the greater the ratio of 1023 cm\(^{-1}\)/2910 cm\(^{-1}\) peaks, that was, the higher the degree of linearity. However, there is some discrepancy between para-isomer content from the model compound reactions and the degree of linearity of the polymers. This is because the ortho-isomer content is the main factor controlling the degree of branching, or degree of linearity. Thus the model compound reactions which have high para- and low ortho-content correlate with polymerization to give a higher linear and less branched polymer.

Isomer contents of the model compound reactions also correlated very well with the degree of branching of poly-α-methylbenzyl polymers prepared under the corresponding
conditions. Nevertheless, the amount of para-isomer content of the model compound reactions was higher than the amount of para-disubstitution in the polymer chains. This is attributed to the oversimplified assumption of the polymerization mechanism based on the model compound reaction that there is no concentration differences between the repeating units and chain-ends of the polymer molecules.

No isomerization in the model compound reactions was observed in most of the reaction systems except in α-chloroethylbenzene/SbF$_5$/(HSO$_3$F)/SO$_2$.

In the polymerization of α-chloroethylbenzene, the catalyst/monomer ratio was found to affect the degree of branching of the polymers. The higher the catalyst/monomer ratio, the greater the degree of branching of the polymers. The catalyst/monomer ratio also affected the polymer yield with the higher the ratio, the greater the yield.

The low molecular weights (1000-7000) of these three types of polymers were attributed to the precipitation of the polymers and the side-reactions of the polymer molecules during polymerization. When a better solvent was used to conduct a polymerization, higher molecular weight polymer was achieved. Reinitiation of a polymerization in a better solvent resulted in an increase of molecular weight of the polymer.

The lower values of chlorine contents than those
of the expected number of endgroups in polybenzyl and poly-
α-methylbenzyl polymers were due to the side-reactions
occurring during the polymerizations. Anthracene terminal
groups were present in most of the polybenzyl polymers
which were prepared under conditions corresponding to a
high ortho-isomer content in the model compound reactions.
Polymer samples, PMB-6 and 11 prepared under conditions
giving low ortho-isomer content in the model compound reac-
tion, did not show any anthracene terminal groups. No
anthracene terminal groups was found in poly-2,5-dimethyl-
benzyl, presumably because the ortho-position to the chloro-
methyl group in the monomer or on polymer chain endgroup is
sterically hindered and formation of anthracene terminal
group is inhibited. Anthracene terminal groups were not
found in the poly-α-methylbenzyl polymers. The low chlorine
contents in these polymers were attributed to indane forma-
tion during polymerization. Indane formation was believed
to be caused by the existence of styrene in the monomer or
by the formation of styrene during polymerization.

One way to reduce the degree of branching of the
polymers is to reverse the reactivity of the disubstituted
and monosubstituted aromatic nuclei by forming π-complexes
with some electron-acceptors (i.e., S02, tetranitromethane).
The results of model reactions of toluene and p-xylene with
benzyl chloride showed that the relative reactivity of
p-xylene to toluene was decreased about two fold after the addition of complexing agents.

A higher molecular weight polybenzyl could be obtained without an increase in the number of branches per unit length of polymer molecules by coupling through chloromethyl groups of polymer molecules using a bis-(Grignard) aromatic reagents.

The solubilities of polybenzyl and poly-2,5-dimethylbenzyl polymers prepared in this work were generally poor. The poor solubility of some of polybenzyl samples was apparently caused by the globular-like structure. However, in poly-2,5-dimethylbenzyl polymers, the poor solubility was attributed to the high crystallinity of the polymers. This is also true of crystalline poly-α-methylbenzyl polymers.

The melting points of polymers varied from 140 to 300°C for poly-2,5-dimethylbenzyl samples and 171 to 211°C for poly-α-methylbenzyl samples. An attempt to correlate the difference in the melting points of the polymers with their structure was not successful because the melting points could be increased tremendously through simple annealing (i.e., 70°C for PDMB-7). Identical X-ray diffraction pattern
for the same types of polymers with different melting points indicated that the polymers did not have different type of crystalline structure but rather had a different degree of crystalline perfection.

DSC thermograms of polybenzyl samples showed an endothermic peak in the glass transition region. The area of this peak increased with annealing time when annealed below Tg. The initial rate of increase of the peak area was higher for higher branched polymers. This observation was explained by equilibrium theory and local ordering theory. The area of the endothermic peak also increased with the annealing temperature to a maximum, then decreased to zero as the temperature approached Tg. The Tg of poly-α-methylbenzyl samples increases with the Mn of the polymers as expected, and leveled off at a molecular weight of 4000-5000. The Tg values of some of the polymers increased with degree of branching. This result indicates that the structure of these branched polymers is a star-type structure, or at least the distribution of branches on the polymer chains is concentrated in one region.

The high branched polybenzyl and poly-α-methylbenzyl polymers had lower thermal stabilities based on TGA analysis. Two types of thermograms were observed, one with a single-step degradation pattern and the other with a two-step degradation pattern. Polymers exhibit a single-step pattern were found to be more regular in structure.
CHAPTER FIVE
SUGGESTIONS FOR FUTURE WORK

Complexation to toluene and \( p \)-xylene with electron-acceptors, such as \( \text{SO}_2 \) or tetranitromethane, resulted in a decrease of reactivity of \( p \)-xylene toward benzylation by benzyl chloride. Polymerizations of benzyl chloride in the presence of \( \text{SO}_2 \) (i.e., PB-6 and PB-11) also gave a less branched polymers. It is recommended that further study on the complexation is necessary for the improvement of linearity of the polymers. The studies should involve a search for stronger complexing agents, an evaluation of the optimum concentration for use of complexing agents, and the effect of catalyst on the complexation of these agents with aromatic nuclei.

Model compound reactions of the polymerizations in this work did not take into account the concentrations of di- and monosubstituted aromatic nuclei. This leads to some deviations in predicting the corresponding degree of branching of polymers. Therefore, a study of the model compound reactions of toluene, \( o \)- and \( p \)-xylene is recommended.

Another suggestion for further work is to investigate the effect of reaction conditions on the loss of chlorine from the polymer endgroup, because it appears that side reactions causing the loss of chlorine were the main reason
for the formation of only low molecular weight polymers. Metathetic catalysts suggested by Fritz and coworker (23) should also be employed in these polymerizations.

Finally, characterization of the polymer by combination of pyrolysis gas chromatography and mass spectrometry will be helpful to confirm the results obtained from IR and NMR analyses.
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