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## Synthesis and characterization of polybutadiene-containing polyurethanes.

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SYNTHESIS AND CHARACTERIZATION OF  
POLYBUTADIENE-CONTAINING POLYURETHANES

A Thesis Presented

By

MARK B. ROSSMAN

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

MASTER OF SCIENCE

February 1981

Polymer Science and Engineering

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POLYBUTADIENE-CONTAINING POLYURETHANES

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A great deal of assistance was supplied by Christine Brunette, whose results for the mechanical, thermal, and spectroscopic analyses are presented throughout. Her suggestions and discussions provided much valuable information which is greatly appreciated.

## ABSTRACT

### Synthesis and Characterization of Polybutadiene-Containing Polyurethanes

February 1981

Mark B. Rossman

B.S. - University of Massachusetts

M.S. - University of Massachusetts

Directed by: Prof. William J. MacKnight  
Prof. Robert W. Lenz

Several segmented polyurethanes have been synthesized, based on a variety of hydroxyl-terminated polybutadienes (HTPB), two of which included a free radically polymerized, branched polybutadiene with an average functionality of 2.1, and a hydrogenated derivative. The third was an anionically polymerized, high vinyl content polybutadiene with an average functionality of 1.9. Polyurethanes were prepared in bulk, without added catalyst, by a two-step process, where first the HTPB was endcapped with an excess of 2,4-toluene-diisocyanate followed by chain extension by 1,4-butanediol. Series of samples of varying hard segment (urethane) content were prepared by this method.

Structure-property relationships for these materials were studied by mechanical, thermal, and spectroscopic methods. Results indicated that the polyurethanes were well phase separated. The complete absence of hydrogen bonding within the soft segments, due to the all hydrocarbon nature of the butadiene backbone, promotes this phase sep-

aration. In this way, the extent of hydrogen bonding, which occurs only in the hard segment domains, is an indication of the degree of phase separation in these systems.

Synthesis of model hydroxy-telechelic prepolymers via a Grignard coupling reaction was also investigated. This novel route to linear, difunctional oligomers showed some success, and further modification of the procedure may produce materials suitable for preparation of polyurethanes.

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# C H A P T E R I

## INTRODUCTION

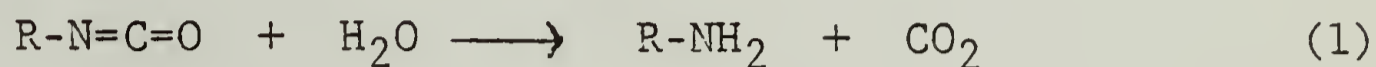
Since their development in Germany during the 1920's and 1930's, the polyurethanes have become one of the most rapidly growing classes of materials today. Two major factors leading to this growth are the wide range of applications and versatility of these polymers. Formulations for fibers, foams, coatings, plastics, and elastomers are available, based on a wide range of raw materials and components. It has been estimated (1) that polyurethane demand in the western hemisphere alone will grow 9% annually over the next five years. Solid polyurethane elastomers are widely utilized as engineering materials due to their good toughness, wear properties, tear strength, and abrasion and chemical resistance. This work is concerned with one particular class of these polyurethane elastomers.

The basic chemistry of the polyurethanes is that of the highly reactive isocyanate group. Their reaction with active hydrogen-containing compounds such as alcohols or

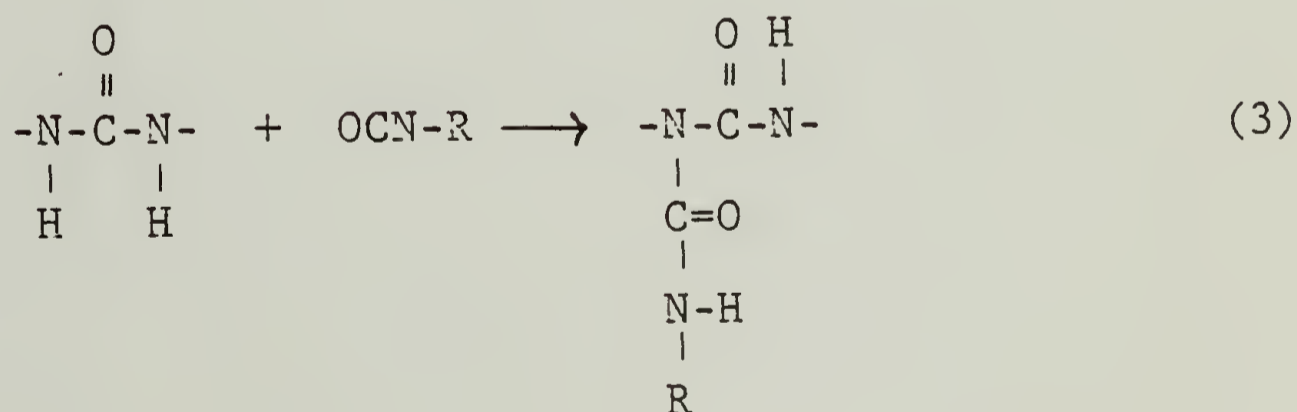
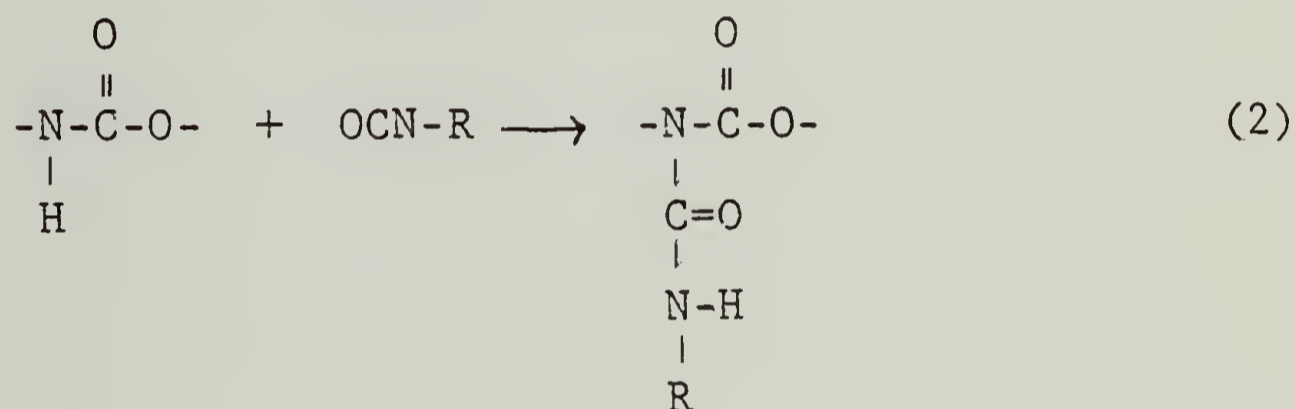
amines, leads to the formation of urethane,  $\begin{array}{c} \text{O} \\ \parallel \\ -\text{N}-\text{C}-\text{O}- \\ | \\ \text{H} \end{array}$ , or

urea,  $\begin{array}{c} \text{O} \\ \parallel \\ -\text{N}-\text{C}-\text{N}- \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$  groups, respectively. For the case of poly-

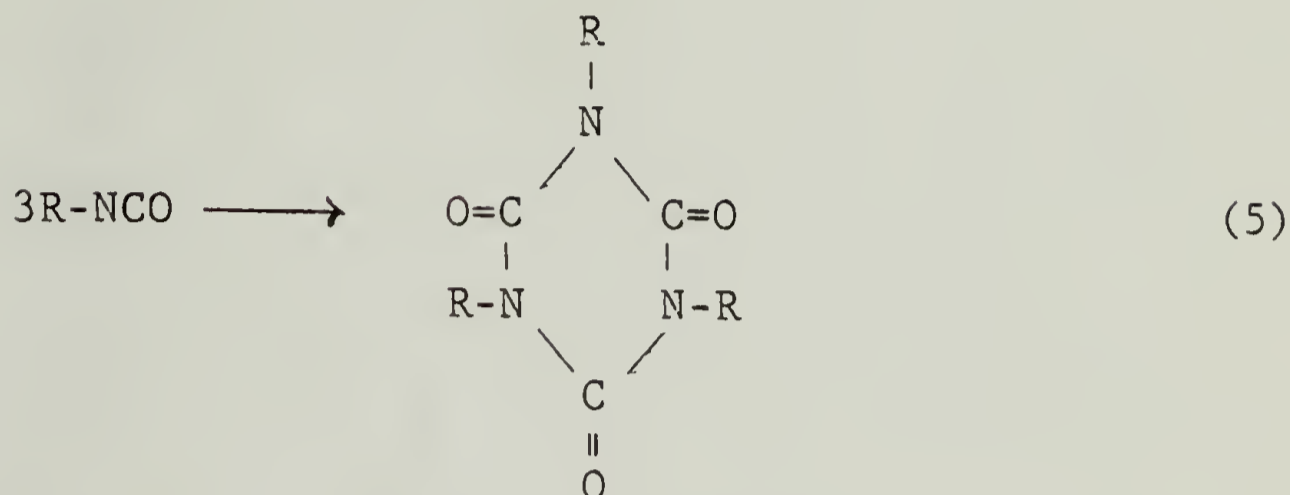
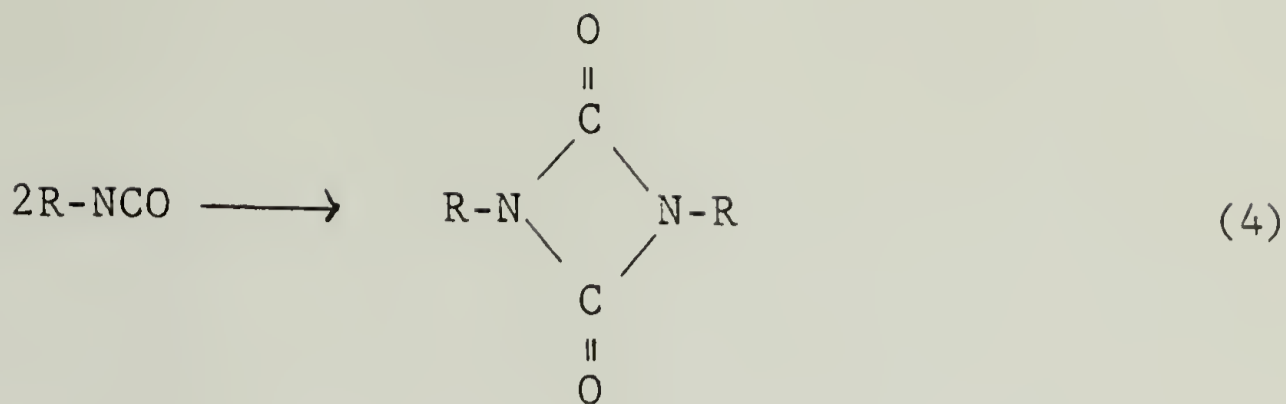
functional reactants, high polymers containing urethane and/or urea segments are produced. Other important reactions are also possible. Reaction of isocyanate with water produces an amine and carbon dioxide (eq. 1), the latter



being incorporated as a blowing agent formed in situ in a typical foam formulation. Excess free isocyanate can react with active hydrogen in already formed urethane and urea groups to form allophanate (eq.2) and biuret (eq. 3)

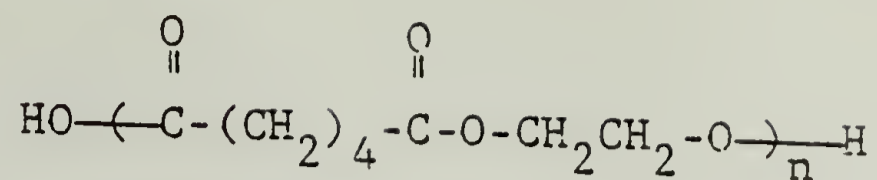


linkages, respectively. Dimerization and trimerization is also possible, especially in the presence of specific catalysts (eqs. 4 and 5).



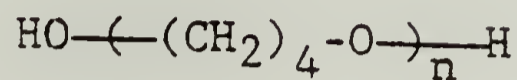
In most cases, homopolymers produced from the reaction of diisocyanates with diols are not the most useful polyurethanes. Instead, block copolymers which incorporate moderate molecular weight polyols in the polymer backbone are used. The most common of these are hydroxyl-terminated polyethers and polyesters with molecular weights in the range from about 1000 to 10,000. These usually liquid polyols are produced as intermediates in the polyurethane synthesis. Some typical polyols are shown in figure 1. Two systems are generally used to prepare polyurethanes of this type. In the two-shot method, the polyol is first end-capped with an excess of the diisocyanate to give an isocyanate end-capped prepolymer. This prepolymer is then converted to high molecular weight by use of a low molecular weight diol or diamine chain extender. In the one-

## POLYESTERS :

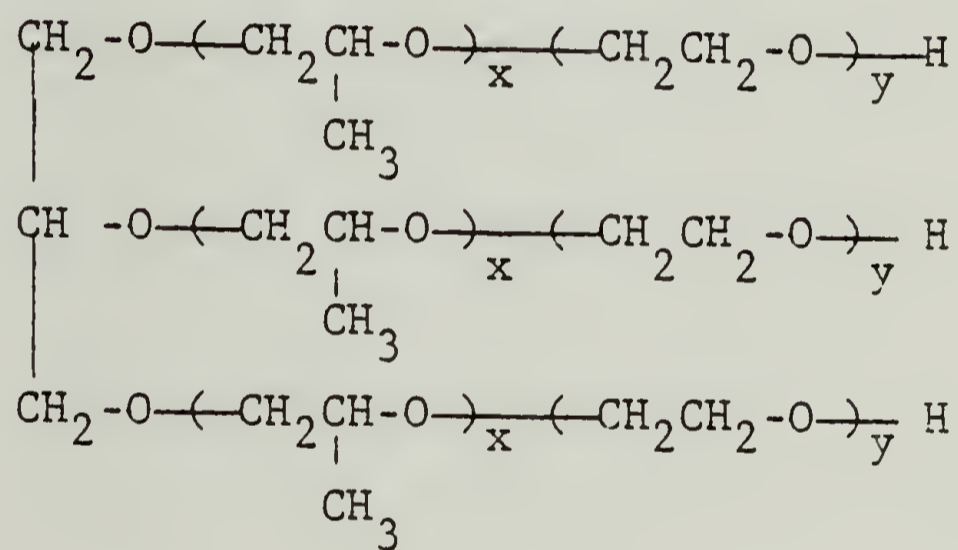


Spandex, Lycra

## POLYETHERS :



Polytetramethylene oxide (PTMO)

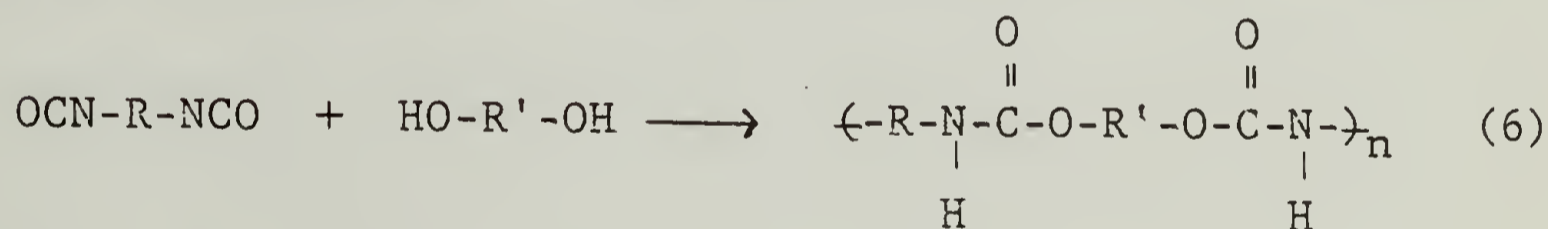


Polypropylene oxide endcapped with polyethylene oxide (block copolymer); initiated with glycerol.

Fig. 1. Typical polyols used in polyurethane synthesis.

shot method, polyol, diisocyanate, and chain extender are mixed together in one step. Such a system is used in the reaction injection molding (RIM) process now used commercially, in which polyol and chain extender stored within one chamber are mixed with diisocyanate and catalyst stored in another chamber. The reactions are typically catalyzed by tertiary amines or organotin compounds. By proper choice of catalyst, side reactions can be controlled. Catalysts for isocyanate reactions have been reviewed (2).

Urethane elastomers so produced are segmented polymers consisting of alternating hard and soft blocks. The hard blocks are formed in the chain extension step where sequences of diisocyanate and diol or diamine chain extender are built up (eq. 6). The soft blocks consist of



the long, flexible polyol chains. The combination of the usually amorphous, flexible soft blocks with the rigid, sometimes crystalline hard blocks gives rise to many of the properties of these materials.

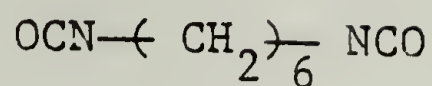
It is now generally accepted that many of the properties of these polyurethanes are due to microphase separation of the hard and soft domains (3). The rigid hard domains, dispersed in a soft segment matrix, serve to reinforce the elastomeric matrix by acting as tie down points

or filler particles. In this way, the elastomer behaves like a crosslinked rubber at temperatures up to the softening point of the hard segment domains. Above this point, thermoplastic flow is possible in the case of linear polyurethanes.

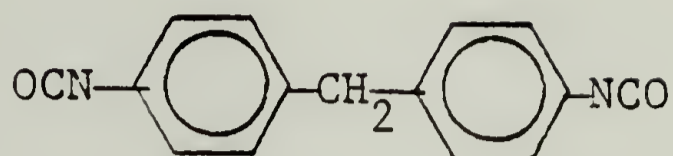
Because of the diversity of components which are used for producing polyurethanes, there is a large number of different combinations of components which can be used. An almost endless array of systems consisting of different polyols, diisocyanates, and chain extenders is possible. Of these, some are more important than others, of course. Most of the previous work on polyurethanes has been concerned with systems incorporating a polyether or polyester soft segment, these materials being the most important commercially. Of the available diisocyanates, 4,4'-diphenyl-methane diisocyanate (MDI) and toluene diisocyanate (TDI; 2,4 and 2,6-isomers) are the most common of the aromatic diisocyanates (fig. 2) and have received the most attention. A variety of techniques have been used to study the properties of MDI based polyurethanes (4 - 7),

Much of the previous work on segmented polyurethanes has dealt with materials based on symmetrical diisocyanates, such as MDI and 2,6-TDI. Schneider and others (8 - 11) have studied polyurethanes based on toluene diisocyanates to determine the effects of asymmetric placement of isocyanate groups on polyurethane structure and properties.

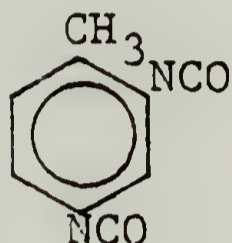
## ISOCYANATES:



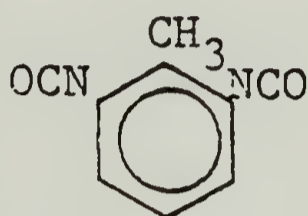
Hexamethylene  
diisocyanate



4,4'-diphenylmethane  
diisocyanate (MDI)  
(also polymeric  
and saturated  
forms)



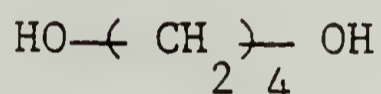
2,4



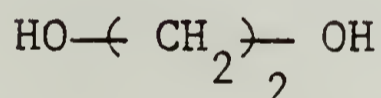
2,6

Toluene diisocyanate  
(TDI - two isomers)

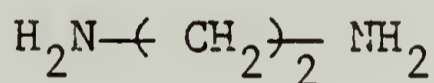
## CHAIN EXTENDERS:



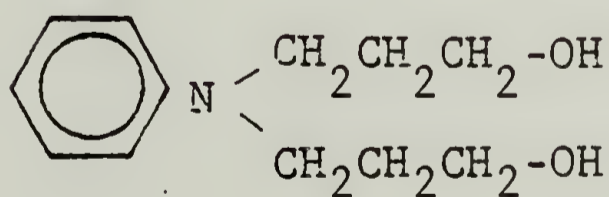
1,4-butanediol



Ethylene glycol



Ethylene diamine



Hydroxy propyl aniline

Fig. 2. Common diisocyanates and chain extenders used in polyurethane synthesis.

Using the two isomers of TDI, 2,4-TDI and 2,6-TDI, samples with hard segments containing asymmetric and symmetric isocyanate placement, respectively, were prepared. It was found that the 2,6-TDI samples showed crystallinity in the hard segment, while the 2,4-TDI samples did not. Infrared analysis (9) was used to determine the extent of phase separation and the role of hydrogen bonding in determining properties. It was shown that the 2,4-TDI samples showed extensive phase mixing and poorly defined domain structure due to the amorphous nature of the hard segments. Dynamic mechanical studies of similar samples were done by Senich and MacKnight (12). In all of these cases, interurethane hydrogen bonding plays a part in the organization of the hard segment domains. An interesting question which arises is to what extent do hydrogen bonding and phase separation affect the properties of these materials.

In recent years, there has been increasing interest in segmented polyurethanes based on polybutadiene soft segments. The low moisture permeability (13) of these materials makes them more suited for certain applications than the more conventional polyether or polyester based polyurethanes, despite inferior abrasion resistance and tensile and tear strength (14). One useful application of the polybutadiene-based materials is as electrical potting and encapsulating compounds (13).

In light of the earlier work on phase segregated poly-

urethane systems already referred to, one very interesting feature of the polybutadiene-containing polyurethanes is the complete elimination of hydrogen bonding to the soft segment due to the hydrocarbon nature of the butadiene backbone. By restricting hydrogen bonding to the hard segments only in this way, phase segregation is promoted. As such, these materials provide a system for studying the role played by microphase separation in determining polyurethane properties, in the absence of inter-phase hydrogen bonding.

Many other factors which would also affect polyurethane properties have been investigated. Seefried and others have done studies on the variation of soft segment molecular weight for MDI polyurethanes with polyester soft segments (15, 16). Mechanical studies of the effects of composition on relaxation properties of MDI based polyurethanes were done by Huh and Cooper (7). Studies have also been done on polyurethanes with hard blocks of controlled molecular weight distribution and no hydrogen bonding (17). Legasse has done studies of the morphology and transition behavior of butadiene based polyurethanes (18). The influence of butadiene soft segment molecular weight on mechanical properties of segmented and nonsegmented polyurethanes has been reported by Ono and coworkers (19).

Although extensive studies have been carried out on segmented polyurethanes, relatively little work has been done with polybutadiene-containing polyurethanes. Hydroxy-

telechelic polybutadienes have been in existence, and their synthesis and applications have been reviewed (20). Studies of polybutadiene based polyurethanes have been carried out by Ryan (21), and their applications have been investigated (13, 20, 21).

This work represents part of a fundamental study concerning the effects of composition and structure on the properties of segmented polyurethanes. The systems investigated consisted of hydroxyl-terminated polybutadiene (HTPB), 2,4-toluene diisocyanate (TDI), and 1,4-butanediol. As already mentioned, the incorporation of a hydrocarbon soft segment restricts hydrogen bonding to the hard segments, thereby promoting phase separation. Use of the unsymmetrical 2,4 isomer of TDI reduces the possibility of crystallinity in the hard segments, which along with the amorphous nature of the soft segment, eliminates any influence of crystallinity on properties. Therefore, in the ideal case of a linear polybutadiene-containing polyurethane, with the absence of inter-phase hydrogen bonding and crystallinity, properties will depend on the extent of phase separation and the organization of hard and soft domains.

Polyurethanes were prepared of varying hard and soft segment concentrations, and were characterized by various techniques including dynamic mechanical and tensile testing, differential scanning calorimetry, and fourier trans-

form infrared spectroscopy, as well as other methods when applicable.

## C H A P T E R    I I

# SYNTHESIS AND CHARACTERIZATION OF HYDROXY-TERMINATED POLYBUTADIENE OLIGOMERS AND DERIVATIVES

### Introduction

Background information. As has already been stated, the incorporation of a polybutadiene soft segment in a segmented polyurethane leads to many desirable characteristics in the elastomer. The most important for this study is the restriction of hydrogen bonding to the hard segments only. The all hydrocarbon backbone will also result in better hydrolytic stability than polyether or polyester based materials as well as improved low temperature properties.

Polybutadienes in general can be synthesized by a number of polymerization methods and processes (20). To be useful as a raw material for polyurethane production, certain characteristics are required. The two most important are perhaps moderate molecular weight (less than 10,000, typically) and hydroxyl (or amine) functionality. The two most useful methods for preparation of hydroxy-telechelic polybutadienes are free radical and anionic polymerization processes. For the purposes of this study, several additional characteristics are desired for the soft segment. To minimize effects due to variation in structure along the butadiene backbone, a simple, well defined struc-

ture is desired for such a model study. First, the prepolymer should be linear and preferably of all 1,4-addition products (from here on, the term prepolymer shall refer to any HTPB). Any long branches or pendant vinyl groups from 1,2-addition of butadiene monomer will have a definite effect on chain mobility and soft segment  $T_g$ . Ideally, these materials should contain exact difunctionality which would allow preparation of linear polyurethanes. Any excess functionality, which is introduced by branching, results in chemically crosslinked polyurethanes. In this case, the materials are thermosetting and characterization is extremely complicated. Molecular weight and molecular weight distribution of the hard and soft segments are also important factors in determining polyurethane properties (17). A narrow molecular weight distribution in the soft segment is most desirable in this case.

In general, the characteristics desired for the polybutadiene soft segments in this work are those which produce the least complicated systems to be studied. In the ideal case, the prepolymer should be linear with exact difunctionality, narrow molecular weight distribution, and all 1,4-addition butadiene segments (preferably trans). Unfortunately, it would be extremely difficult if not impossible to prepare such a model prepolymer, and so available materials must be used or new materials synthesized to approach the characteristics of a model soft segment.

Commercial materials. Of the commercially available hydroxy-terminated polybutadienes, two were found to be useful and were used in the synthesis of phase separated polyurethanes. In each case, some desired properties were available at the expense of others, as will be seen.

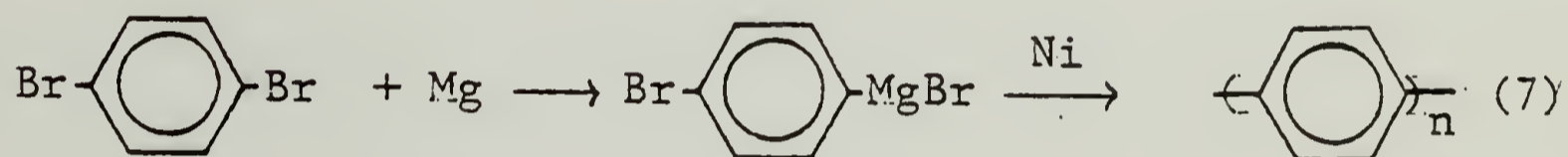
ARCO Poly-bd. HTPB produced by free radical polymerization with hydrogen peroxide initiator was obtained from The ARCO Chemical Company. Due to the free radical process used in the manufacture, transfer reactions lead to branched polymers (24) and result in an average functionality greater than two. This is especially the case in the presence of high initiator concentration, as is needed to obtain the moderate molecular weight desired. In addition, there is little control over microstructure and molecular weight distribution will be rather broad in these polymers. The polyurethanes prepared from these materials will be crosslinked and thermosetting, and therefore will most likely be insoluble and difficult to characterize.

JSR HTPB. Anionically polymerized HTPB was obtained from The Japan Synthetic Rubber Company. In this case, the prepolymer was linear, and soluble polyurethanes could be prepared which are free of urethane crosslinks.

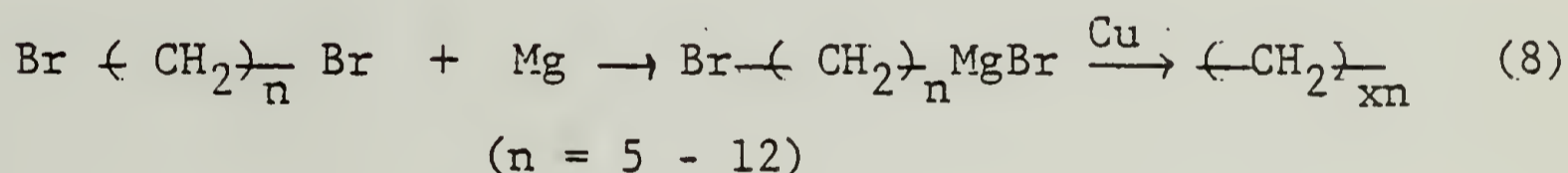
Hydrogenation of HTPB. In addition to using these commercial prepolymers as received, catalytic hydrogenation of the ARCO HTPB was carried out using palladium on activated carbon catalyst. The hydrogenated prepolymer,

as well as the two commercial HTPB's, were converted into polyurethanes, as will be discussed.

Grignard synthesis. In an attempt to prepare prepolymers that are more well defined than those obtained commercially, the synthesis of linear, difunctional, hydroxy-telechelic hydrocarbon oligomers was carried out. This procedure is based on a Grignard coupling reaction of  $\alpha, \omega$ -dibromo-n-alkanes using copper catalysts. Yamamoto and others (26, 27) have reported the use of transition metal compounds to catalyze the coupling of aromatic and aliphatic dibromo compounds to give linear polyphenylene (eq. 7) and poly-



methylene (eq. 8) type polymers. Preparation of several



linear polymethylenes was reported. In each case, ir spectra were shown to be essentially that of high density polyethylene. Also, analysis for bromine showed that both ends of the polymer chains were bromine terminated. This method was thereby seen as a possible route to linear, difunctional hydroxy-telechelic prepolymers.

A modification of this method was attempted to prepare

a linear polymethylene with hydroxyl endgroups. Instead of using an A-B type polycondensation as described by Yamamoto, an A-A, B-B system was used in hopes of producing hydroxyl functionality. The reaction scheme used was an extension of that described previously, as shown in figure 3. The product, a linear, hydroxyl-terminated polymethylene, would correspond to a completely hydrogenated, linear polybutadiene. An attempt was also made to produce an oligomer with unsaturation by starting with an unsaturated dibromo compound, 1,4-dibromo-2-butene.

### Experimental

#### Characterization of commercial HTPB.

NMR and IR. Proton and carbon-13 nmr of the polybutadienes were obtained on a Perkin Elmer R-32 90 MHz and a Varian CFT-20 spectrometer, respectively. Infrared measurements were made on a Nicolet 7199 Fourier Transform Infrared spectrometer. All nmr measurements were made in chloroform solution with TMS internal reference. IR spectra were obtained from films cast from chloroform solution onto KBr disks.

Functionality determination. The hydroxyl values of the HTPB's were determined by a procedure suggested by ARCO Chemical Co. (25). The hydroxyl groups were acetylated with an excess of acetic anhydride in pyridine. The amount of reagent which reacts with the sample was determined by ti-

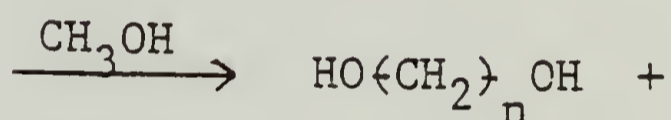
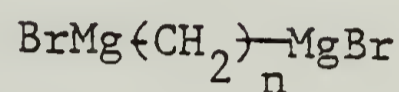
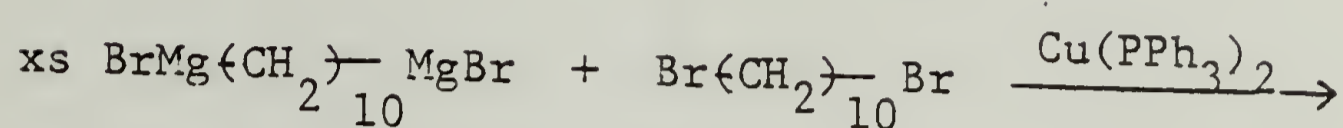


Figure 3. Reaction scheme for synthesis of hydroxyl-terminated polymethylene via a Grignard coupling reaction.

trating the excess hydrolyzed anhydride and resulting acetic acid with alcoholic potassium hydroxide. The hydroxyl value was reported as the milliequivalents of hydroxyl groups per gram of material. The average functionality was then determined by multiplying the number of equivalents per gram by the molecular weight of the HTPB. For each HTPB, three samples and one blank determination were run.

#### Hydrogenation of ARCO R-45M HTPB.

Materials. ARCO R-45M HTPB was used as received. Spectrophotomic grade toluene (Fisher Scientific Co.) was used without further purification. Palladium on activated carbon catalyst was obtained from Alfa Chemical Co. and was used as received.

Procedure. Hydrogenation was carried out at room temperature in a Parr 2 litre high pressure reactor bomb. 100 g. of ARCO R-45M HTPB was dissolved in 500 ml. of toluene in a 2 litre glass reaction sleeve. Approximately 0.5 g. of palladium on carbon catalyst was added and the sleeve was placed in the bomb chamber, which was equipped with a mechanical stirrer and gas inlet and outlet valves. The bomb was assembled and was then connected to a hydrogen cylinder. The reaction sleeve was flushed for 15 minutes with a slow flow of  $H_2$  gas. The bomb was then pressurized with  $H_2$  to a starting pressure of 470 psi. The stirrer was engaged and the reaction was allowed to run for about

20 hours. Initially, a substantial pressure drop was observed in about the first two hours, after which the pressure decreased at a slower rate. The stirring was stopped when the pressure reached 140 psi, and the remaining gas was vented out of the reactor. The bomb was dismantled, and the reactor sleeve was allowed to stand for a day to allow most of the catalyst residues to settle. The solution was then filtered by suction through Celite filter aid to remove the catalyst residues, and the solvent was then removed under vacuum on a rotary evaporator, isolating the hydrogenated prepolymer. The product was noticeably more viscous than the starting material. The yield was 91.9 g.

Characterization of hydrogenated HTPB. The extent of hydrogenation was determined by proton nmr (28). The fraction of butadiene units hydrogenated, F, was calculated as:

$$F = \frac{1 - 2R}{1 + 2R} ,$$

where R is the total integral due to the protons on residual double bonds (5.4 ppm) divided by the total integral due to methylene groups (1.3 and 2.0 ppm). Proton nmr spectra of the hydrogenated and non-hydrogenated prepolymers are shown in figure 4. Functionality determination and infrared analysis were also carried out.

#### Grignard coupling reaction of $\alpha, \omega$ -dibromoalkanes.

Materials. Tetrahydrofuran (Aldrich Chemical Co.,

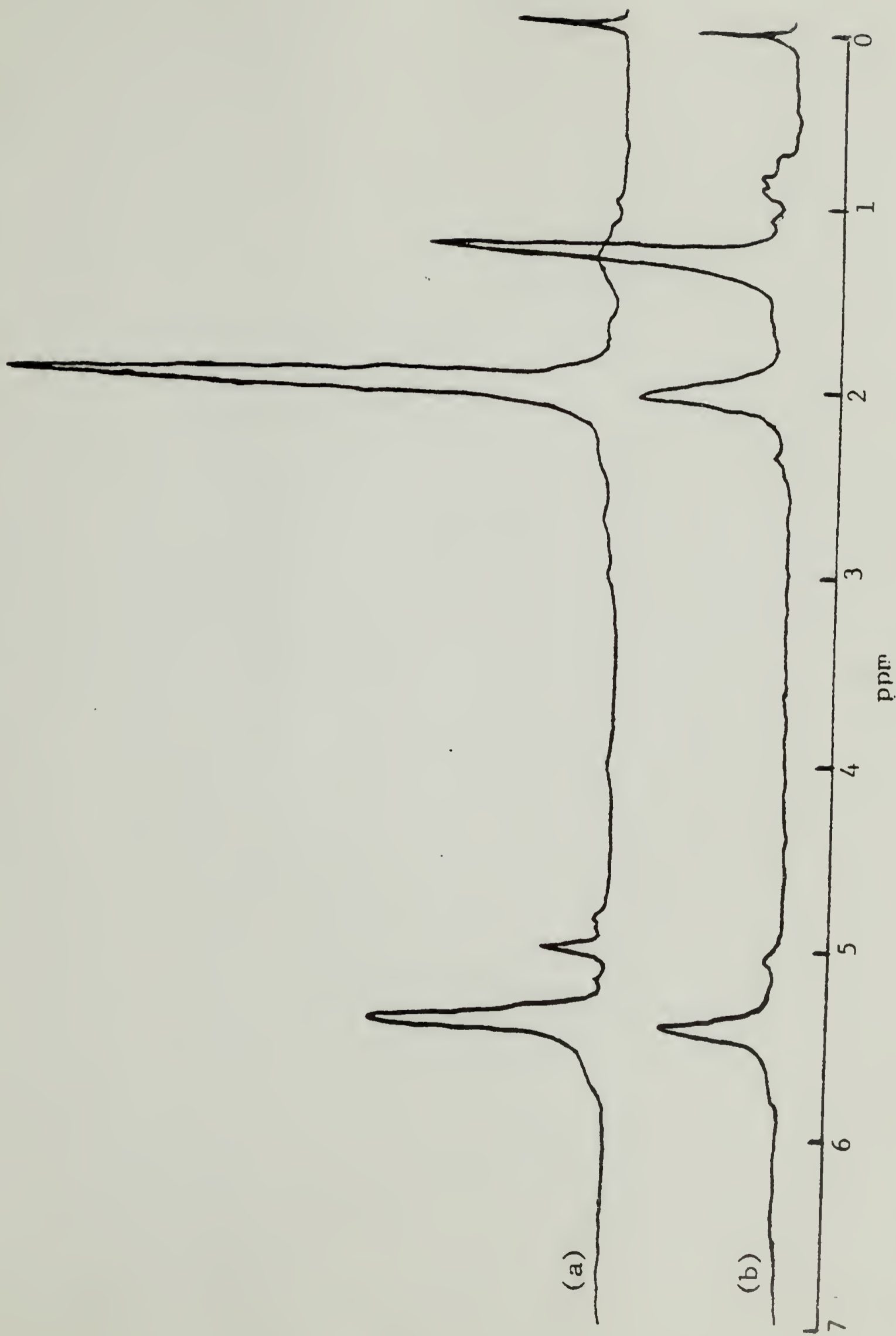


Figure 4. Proton nmr spectra of non-hydrogenated (a) and hydrogenated (b) HTPB.

99+%) was dried over calcium hydride for 24 hours and then distilled and stored under argon. 1,10-dibromodecane and magnesium (Aldrich) were used as received. The catalyst,  $\text{CuBr}(\text{PPh}_3)_2$  ( $\text{PPh}_3$  = triphenyl phosphine) was prepared as described previously (29). Ethylene oxide (Linde Div., Union Carbide Corp.) was used as received, dispensed as a liquid from a pressurized cylinder.

Procedure. 3.3 g. (0.13 mole) of magnesium turnings were placed in a three-neck round bottom flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel. All glassware had been oven dried overnight prior to setting up. Argon was passed through the system, during which time the whole apparatus was flamed out. When cool, 20 g. (0.067 mole) of 1,10-dibromodecane was added to the dropping funnel, followed by addition of 100 ml. of THF, the transfer of THF being done by use of a double-ended transfer needle to prevent any exposure to air or moisture. The dropping funnel was shaken to dissolve the monomer in the THF.

A small amount of the THF solution of monomer was then added to the magnesium in the flask. In some cases, reaction started with stirring only, as evidenced by the evolution of heat and small bubbles appearing on the surface of the magnesium. When the reaction would not start on its own, the flask was externally warmed by use of a heat gun, after which the reaction would begin and continue on its own.

With the reaction underway, THF would begin to reflux, and the monomer solution was added dropwise to the reaction mixture with stirring, the rate of addition maintained about the same as the rate of THF reflux. During this time, the reaction mixture turned slightly yellow. When all monomer had been added, the mixture was stirred for an additional three hours, after which heat was applied to continue refluxing of THF for another three hours. The flask was then allowed to cool to room temperature, maintaining argon flow. Only a small amount of unreacted magnesium metal remained.

At this time, 15.7 g. (0.052 mole) of 1,10-dibromodecane was dissolved in 100 ml. of THF in the dropping funnel as before. 0.10 g. of  $\text{CuBr}(\text{PPh}_3)_2$  was added to the reaction mixture followed by addition of the monomer solution from the dropping funnel with stirring under argon flow. After a short while, the mixture turned dark, and small amounts of white precipitate could be noticed. The polymerization was allowed to continue overnight. The mixture was then heated to reflux, at which point the precipitated polymer dissolved. An inlet tube extending below the level of the reaction mixture was added to the flask, the other end of which was connected to an ethylene oxide cylinder. A dry ice/acetone cold finger was added to the top of the condenser. A small amount of ethylene oxide was allowed to pass through the solution, followed by addition of 5 ml. of methanol. The reaction mixture was

stirred as it cooled to room temperature and was then poured into 800 ml. of methanol to give a fine, white precipitate. The precipitate was collected over a glass filter, and was then reprecipitated from hot toluene. The product was isolated by suction filtration and was washed several times with methanol, then dried under vacuum at 60°C overnight to give a fine, white powder. The powder had a melting range of 93° - 103°C, and the yield was 6.9 g. (41% yield, based on the amount of carbon taken into the polymer).

ANAL: Calc. C: 85.7, H: 14.3 Found C: 81.6, H: 14.3, Br: .86

### Results and Discussion

Commercial HTPB. The properties of the two commercial HTPB's, whether supplied by the manufacturer or independently determined, are presented in tables 1 and 2. In the case of the ARCO R-45M, the hydroxyl value of 0.75 meq./g. corresponds to an average functionality of 2.1 hydroxyl groups per molecule, using the molecular weight given as 2800. This excess functionality leads to the production of polyurethanes which contain urethane crosslinks. The microstructure consists of both cis and trans 1,4-addition products as well as 1,2-sequences (fig. 5a), as confirmed by ir analysis (14),

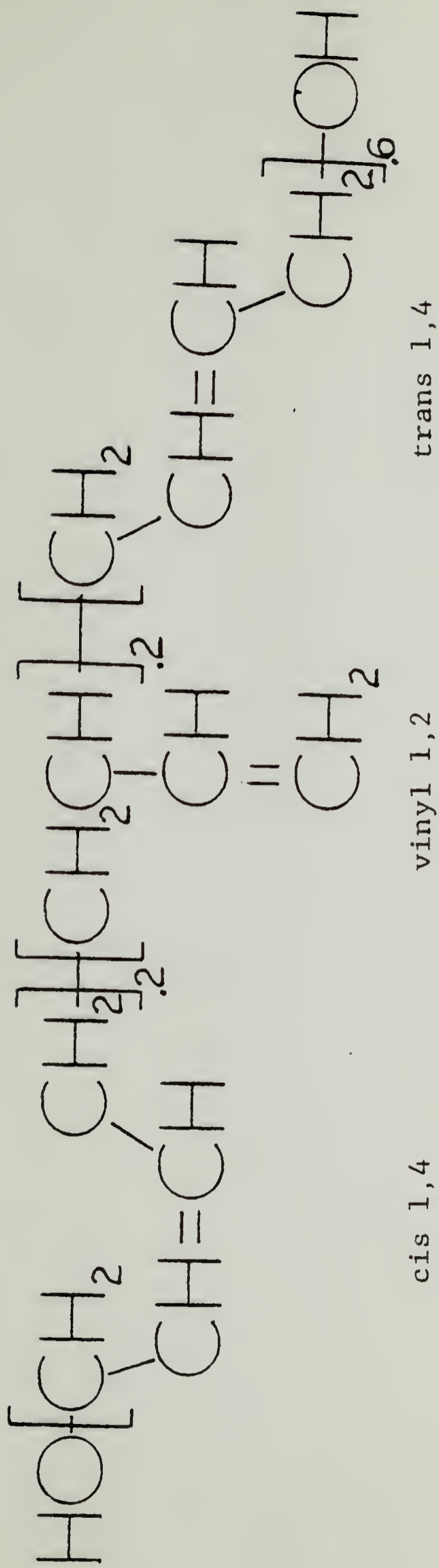
The JSR HTPB, with molecular weight given as 2120, was found to contain approximately 55% 1,2-addition se-

Molecular weight	2800
Hydroxyl value	0.75 meq./g.
Average functionality	2.1
Microstructure: cis-1,4	20%
trans-1,4	60%
vinyl-1,2	20%

Table 1. Properties of ARCO R-45M HTPB

Molecular weight	2120
Hydroxyl value	0.91 meq./g.
Average functionality	1.9
Microstructure: cis & 1,4 trans	45%
vinyl-1,2	55%

Table 2. Properties of JSR HTPB



(a)

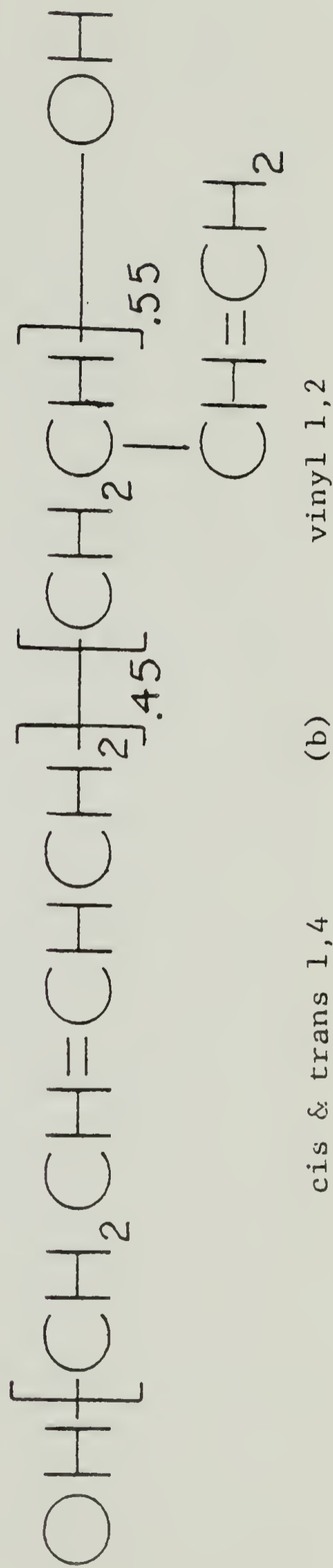


Figure 5. Structures of commercial HTPB's: a) ARCO R-45M, b) JSR HTPB.

quences from ir analysis (30) and nmr (fig. 6). The hydroxyl value was determined to be 0.91 meq./g., which corresponds to an average functionality of 1.9 hydroxyl groups per molecule, which may have been reasonably expected for an anionic polymerization. In this case, the polybutadiene was linear, and polyurethanes devoid of chemical urethane crosslinks could be produced. The JSR HTPB structure is shown in figure 5b.

Hydrogenated HTPB. The product from the hydrogenation of the ARCO R-45M was much more viscous than the starting material, evidenced by a greater resistance to flow, almost to a point where it could be called a soft, sticky solid. It was also somewhat opaque. The functionality was found to be the same as the non-hydrogenated material (31), assuming the slight change in molecular weight due to the hydrogenation to be negligible. The extent of hydrogenation was determined by two methods. An estimate of hydrogen consumed in the reaction was made based on the pressure drop in the system. This was suspected to be unreliable due to possible leakage of  $H_2$  during the reaction. A more definite determination, made using proton nmr (28), showed that 65% of the butadiene units were hydrogenated. Infrared results (14) showed that hydrogenation preferentially took place in the pendant vinyl groups, as could be expected since these groups should be more accessible for reaction. This is consistent with the results of

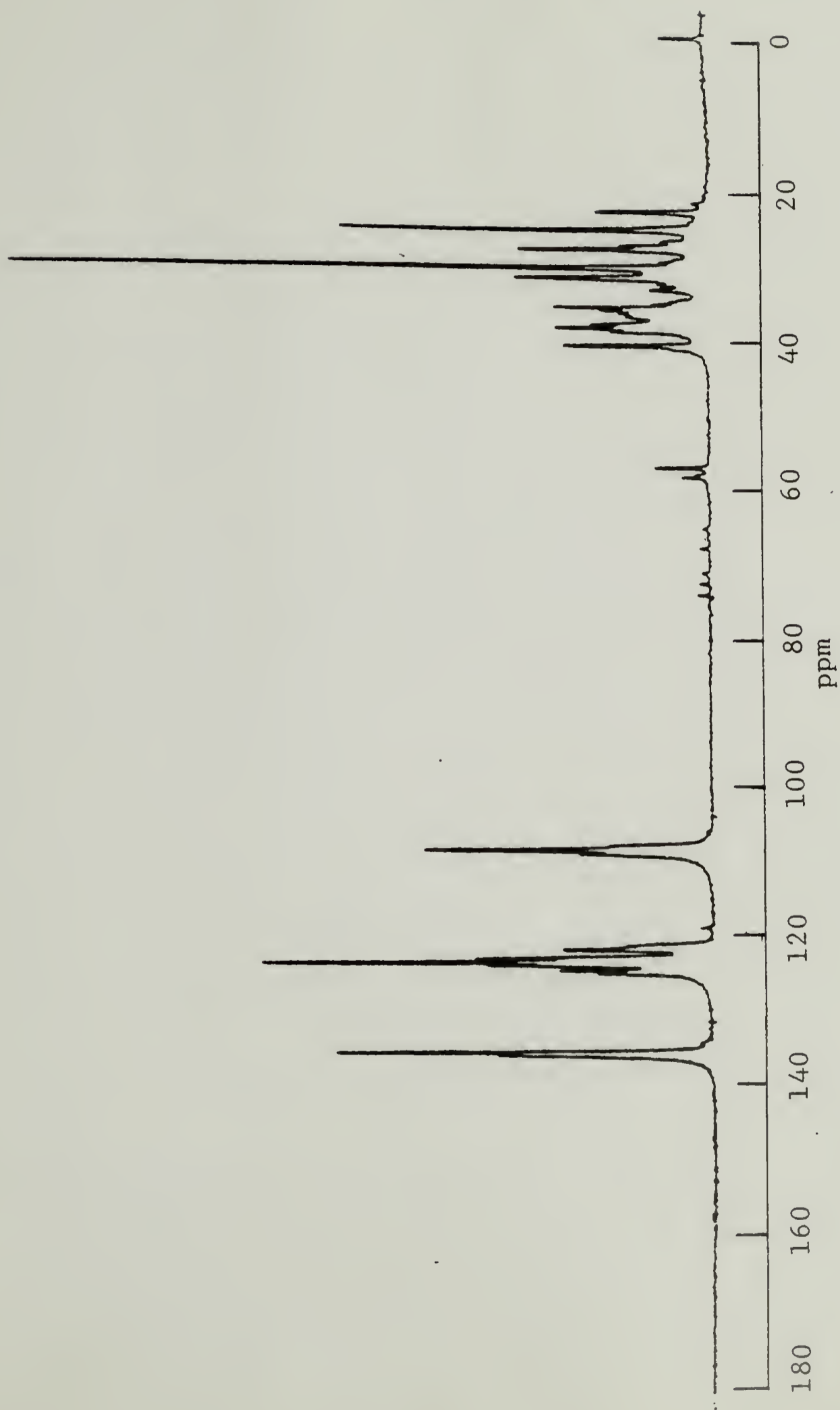


Figure 6. Carbon-13 nmr spectrum of JSR HTPB.

Mango and Lenz, who showed that the rate of hydrogenation of the pendant vinyl double bonds was greater than that of the internal double bonds (32). In addition, it was seen that hydrogenation in the 1,4-units preferentially took place in the cis units.

The hydrogenated product was actually a copolymer consisting of polymethylene, poly-1-butene, and residual polybutadiene (cis and trans 1,4 and vinyl 1,2) sequences (fig. 7). Crystallization may be possible if long enough sequences of methylene units are present. Some evidence of crystallinity was seen by ir measurements (14), but the random placement of the hydrogenated vinyl groups probably precludes any extensive crystallinity in these prepolymers.

Grignard synthesis. The product from the Grignard coupling reaction of 1,10-dibromodecane was a white powder with a melting range of  $93^{\circ} - 103^{\circ}\text{C}$ . 1,10-dibromodecane was chosen as monomer because this starting material gave favorable results in the original work, and it was readily available. Samples were also prepared by the same method as used by Yamamoto for comparison. The melting ranges of these products were generally in the same range as that for the hydroxyl-terminated samples. In each case, the ir spectrum of the products was essentially that of high density polyethylene, showing bands at 2910, 2845, 1470, 1460, 725, and  $715\text{ cm}^{-1}$  (fig. 8). In addition, a band in the OH stretch region was evident for the hydroxyl-terminated sam-



$$x = \sim .35$$

$$y + z = \sim .65, \quad y > z$$

Figure 7. Structure of product from hydrogenation of ARCO HTPB.

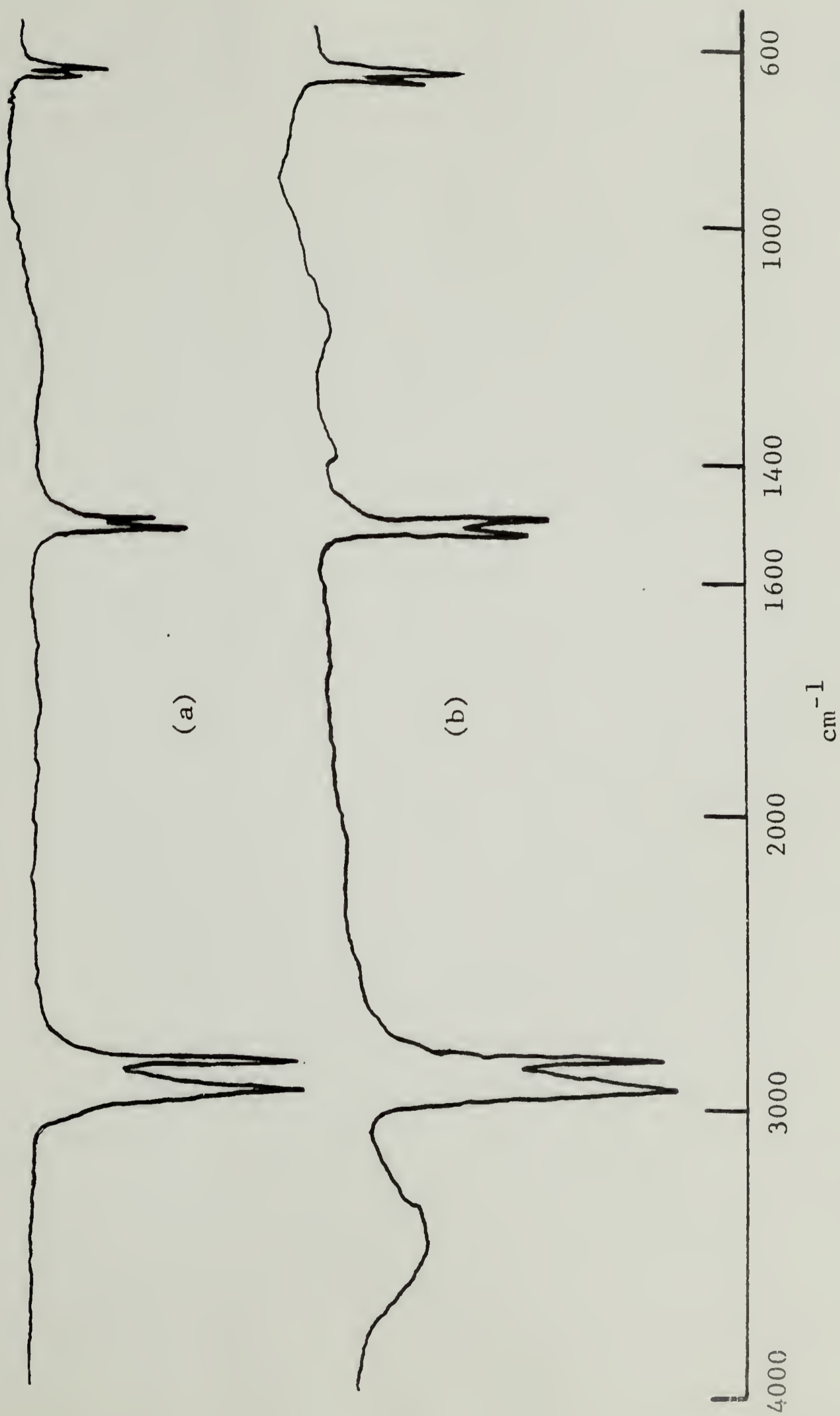


Figure 8. Infrared spectra of products from Grignard coupling of 1,10-dibromodecane: (a) Br terminated, (b) OH terminated.

ple. This result, along with microanalysis for bromine, showed that at least some of the polymethylene molecules were hydroxyl-terminated. The molecular weight of the samples was estimated to be in the range of 2000 to 3000, based on end group analysis. The exact extent of endgroups bearing hydroxyl groups is still open to question, and whether or not these materials may be useful for polyurethane synthesis is yet to be determined.

### Conclusions and Suggestions for Further Work

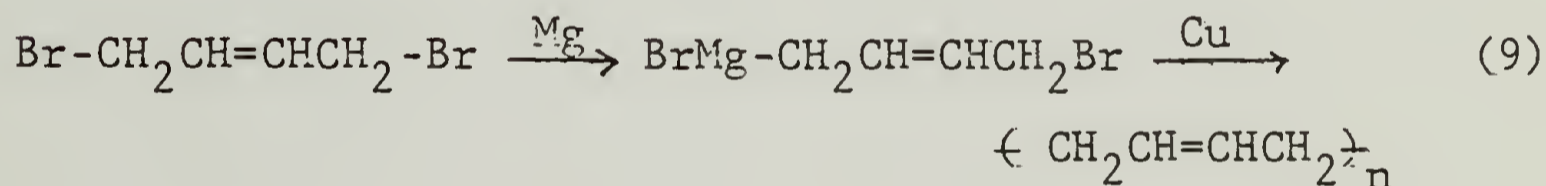
Despite the lack of certain desirable properties in the commercially available HTPB's, these materials provide a potentially useful component for polyurethane systems. Despite the inferior mechanical properties realized in the final cured polymer, these materials still show a number of advantages over polyether and polyester based polyurethanes, as has already been noted.

It appears that, of the conventional polymerization methods, the anionic mechanism is potentially the most useful for synthesizing model soft segments. The anionically polymerized JSR HTPB closely approaches the characteristics of such a model compound. Choice of an initiator system which promotes 1,4-addition of butadiene, if possible, would solve many of the current problems.

The effect of hydrogenation of the prepolymer is still under investigation. Theoretically, hydrogenation

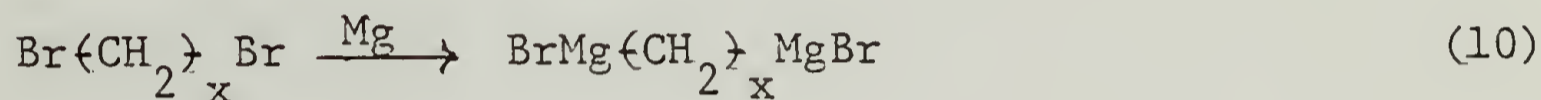
should serve to improve the oxidative stability of the cured polyurethanes by reducing the amount of unsaturation present. Further work should be done to produce a series of prepolymers of varying extent of hydrogenation, perhaps using a different catalyst system than that used here. A facile reaction at room temperature would be most desirable to minimize any degradation of the prepolymer or loss of functionality.

The Grignard synthesis, as a novel approach to tailored prepolymers, could potentially be used to produce model compounds on a laboratory scale. Of great interest would be polymerization of an unsaturated monomer, such as 1,4-dibromo-2-butene, which by this method would give linear, 1,4-polybutadiene (eq. 9). Experiments were attempted us-



ing this monomer, with inconclusive results. An indistinguishable brown, viscous mass resulted, giving some indication that some coupling and build-up of molecular weight may have been accomplished. It appears that in the presence of the catalyst, side reactions between Grignard groups and unsaturated groups of the monomer may occur, thereby terminating the coupling reaction and neutralizing reactive Grignard groups. The initial Grignard reaction between

the monomer and magnesium should proceed without much trouble to a reasonable extent, as has been shown in the similar case of allyl bromide (33). In addition, by co-reacting the unsaturated monomer with a saturated dibromoalkane, oligomers could be synthesized which correspond to hydrogenated polybutadienes of various extents of residual unsaturation, up to 100% hydrogenation. By choice of proper components, lengths of saturated sequences between unsaturation points could be controlled (eq. 10),



## C H A P T E R   I I I

### PREPARATION AND CHARACTERIZATION OF POLYURETHANES

#### Introduction

Several segmented polyurethane films were prepared by a two-step batch reaction process. The method used is based on that described by Pigott and coworkers (34) with minor variations. The components used included one of the commercial HTPB oligomers or the hydrogenated derivative, 2,4-toluene diisocyanate, and 1,4-butanediol. In all samples, no catalyst was added to the reaction mixture to eliminate any presence of catalyst residues in the final polymer.

In the first step of the preparation, the respective HTPB was endcapped with an excess of diisocyanate, the amount of the excess determining the concentration of hard segment in the final polymer. As such, series of samples were prepared for each prepolymer by varying the molar ratio of NCO to OH equivalents in the HTPB, usually in 4:1, 6:1, and 8:1 ratio increments. The final composition contained a 5% molar excess of isocyanate over total hydroxyl groups (from both HTPB and diol chain extender) to promote allophanate formation.

In the second step, the isocyanate end-capped prepolymer was chain extended with 1,4-butanediol to produce

the final cured polyurethane. In all, three series of polyurethane samples were prepared, one each based on the ARCO HTPB, the JSR HTPB, and the hydrogenated HTPB. Each sample of the three series was characterized by various methods, including dynamic mechanical and tensile testing, differential scanning calorimetry, and fourier transform infrared spectroscopy.

To aid in the infrared analysis, a sample consisting of pure hard segment was also prepared from TDI and butanediol in a solution polymerization. In addition, a representative polyurethane sample was prepared from a deuterated butanediol,  $\text{DO}(\text{CH}_2)_4\text{OD}$ . This sample has the unique characteristic of containing deuterium in the urethane groups contained completely in the hard segment only (fig. 9), assuming no exchange of hydrogen for deuterium takes place. The urethane deuterium which was present in the chain extender can be differentiated from the urethane hydrogen which was originally present in the prepolymer by ir analysis. It is possible that in this way, further analysis could be performed concerning the nature of the phase boundaries in these systems.

### Experimental

#### Preparation of polyurethane films.

Materials. Liquid hydroxyl-terminated polybutadiene (HTPB) prepolymers were obtained from ARCO Chemical Co.

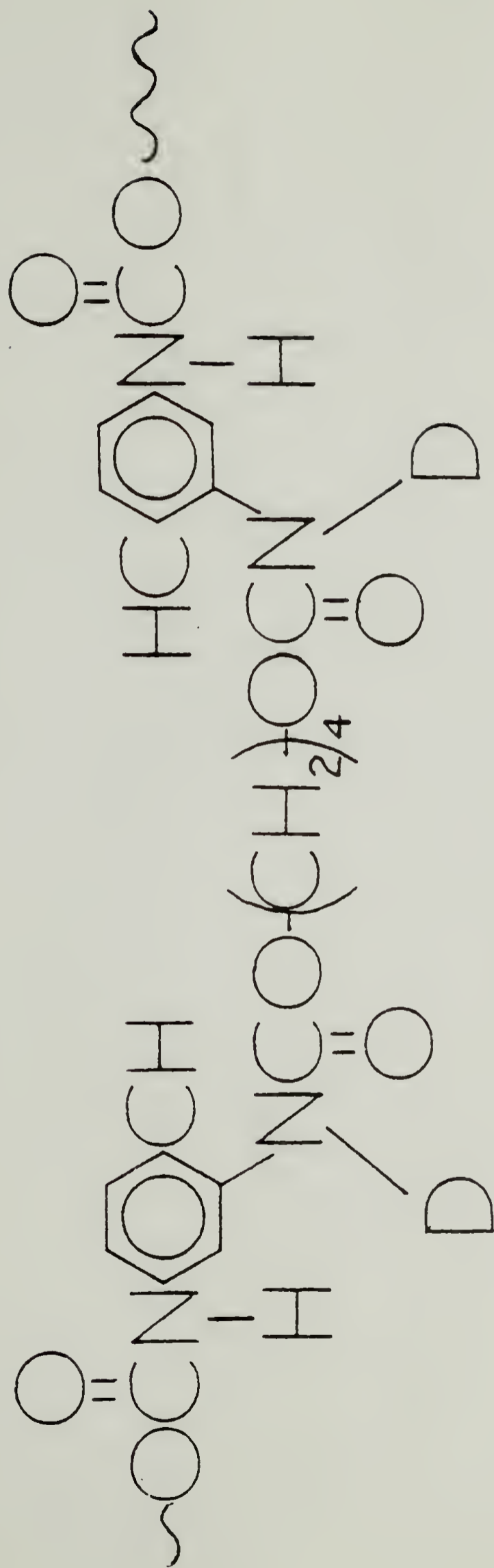


Figure 9. Hard segment unit from chain extension with deuterated butanediol.

(R-45M) and Japan Synthetic Rubber Co. (JSR). These materials were used as received, and with the ARCO R-45M, one hydrogenated derivative was used.

2,4-toluene diisocyanate (Aldrich Chemical Co.) consisted of 97% of the 2,4-isomer and was distilled under reduced pressure, then stored under nitrogen before use. 1,4-butanediol (Aldrich) was used without further purification.

Procedure. For a typical sample, 10.6 g. (0.01 eq.) of JSR HTPB was accurately weighed into a 100 ml. reaction kettle which was equipped with a paddle stirrer and vacuum connection. The kettle was assembled and placed into a controlled constant temperature oil bath. The prepolymer was then degassed and the temperature was raised to 120°C. Degassing was continued under vacuum at 120°C with stirring for one hour.

5.4 g. (0.06 eq.) of 2,4-TDI was accurately weighed and added through a rubber septum into the reaction kettle by syringe. To insure accurate weights of diisocyanate (and diol chain extender), the syringes used for transferring each component were weighed before and after the addition, to account for any material left in the syringe. The amount of TDI added was determined by the desired hard segment/soft segment ratio for the particular sample. The endcapping reaction was carried out at 120°C with stirring under constant nitrogen flow for one hour.

When the endcapping step was complete, the temperature was lowered to 80°C, and 2.3 g. (0.05 eq.) of 1,4-butanediol, which had been accurately weighed, was added by syringe. The amount of butanediol added was calculated to allow for a 5% molar excess of NCO equivalents over the total hydroxyl equivalents in the sample. This addition was followed by rapid stirring of the reaction mixture which, after a few seconds, turned milky white. The reaction kettle was then degassed briefly by applying vacuum to remove any trapped gas, and the mixture was poured into a teflon-lined mold, 15 mil thick. The sample was then compression molded in air at 120°C for approximately 17 hours under slight pressure. All samples were allowed to stand for at least one week in an inert atmosphere before testing.

#### Synthesis of pure hard segment.

Materials. 2,4-TDI and 1,4-butanediol were the same as used in the polyurethane film preparation. Dimethyl sulfoxide and methyl iso-butyl ketone were used without further purification.

Procedure. 2.5 g. (0.029 eq.) of 2,4-TDI was dissolved in 80 ml. of a 1:1 mixture (by volume) of DMSO and methyl iso-butyl ketone in a 250 ml. round bottom flask equipped with a magnetic stirrer, thermometer, and argon inlet. The flask was placed in an oil bath and the temperature was raised to 75°C as argon was passed over the solution.

1.2 g. (0.027 eq.) of 1,4-butanediol was added dropwise to the solution with stirring. After the addition was complete, the temperature was raised to 95°C and was maintained between 95°C and 100°C for three hours with continuous stirring. A small amount of methanol was then added to insure complete reaction of isocyanate, and the flask was cooled to room temperature. The solution was poured into 800 ml. of distilled water, resulting in the formation of two layers. After separating the layers, the precipitated polymer was filtered and washed several times with methanol. The product was dried overnight under vacuum at 60°C to give a fine, white powder.

#### Measurements.

Dynamic mechanical analysis. Measurements were carried out using a Vibron Dynamic Viscoelastometer (Toyo Measuring Instrument Co.) model DDV II at a fixed frequency of 11 Hz. Samples were tested at a temperature range from -130°C to 150°C with a heating rate of 1.5 deg./min. under a dry nitrogen atmosphere.

Tensile testing. Stress-strain data were obtained on an Instron Model TM-SM table model universal testing instrument at an extension rate of 40 mm./min. Samples were die cut from the polyurethane sheet 0.015 inches thick with a gage length of 1.5 inches long and 0.12 inches wide. For cyclic stress-strain experiments, a single sample was exposed to increasing amounts of prestrain. The sample was

extended by increments up to 20%, allowed to relax at zero load for 5 minutes, extended to 40%, and so on. Data was obtained at 0, 20, 40, 60, and 80% of the extension at break. All data reported are averages of at least five tests on different samples.

Thermal analysis. Soft segment glass transition temperature measurements were made with a Perkin Elmer DSC-2, purged with helium and cooled with liquid nitrogen. Runs were made on polymer samples of 15 mg, at a heating rate of  $20^{\circ}\text{C}/\text{min.}$  and an attenuation of 2 mcal./sec. The higher temperature runs were carried out on a DSC-2 equipped with a two stage mechanical refrigeration unit. Scans were conducted from  $240^{\circ}\text{K}$  to  $420^{\circ}\text{K}$  at  $20^{\circ}\text{C}/\text{min.}$  with an attenuation of 2 mcal./sec. Glass transition temperatures were determined as the temperature corresponding to one half of the increase in heat capacity at the transition. Penetrometer analyses were also carried out using a Perkin Elmer TMS-1 on samples of 50 mil thickness, with a probe weight of 25 g., heating rate of  $10^{\circ}\text{C}/\text{min.}$ , and an attenuation of 0.5 mil/inch. Transition temperatures were estimated as the intersection of the two lines tangent to the curve preceeding and following the region of softening.

Infrared analysis. Spectra of the various prepoly-  
mers were obtained from films cast from chloroform solution on KBr disks. In the case of the insoluble polyurethanes, a small amount of the reaction mixture was pressed

between two KBr disks or teflon coated aluminum plates, which in most cases produced films thin enough for spectroscopic analysis. Infrared spectra ( $400 - 4000 \text{ cm}^{-1}$ ) were obtained with a Nicolet 7199 Fourier Transform Infrared Spectrometer. It is not this author's intention to discuss the infrared analysis further, but only to make reference to the results for completeness (14, 30).

### Results and Discussion

In all, three series of polyurethanes were prepared, one each based on the ARCO HTPB, the hydrogenated HTPB, and the JSR HTPB. Typically, each series consisted of three samples of varying amounts of hard segment content, as determined by the amount of excess TDI added. Using the functionality of the respective prepolymer, the amount of 2,4-TDI to add was calculated to produce ratios of NCO equivalents to OH equivalents in the prepolymer of 4, 6, and 8 to 1. The amount of diol chain extender to be added was then calculated to produce an overall 5% molar excess of isocyanate in the sample. The sample compositions and corresponding hard segment (urethane) contents are shown in table 3. A representative structure of a typical polyurethane is shown in figure 10, indicating hard segment and soft segment components, the soft segment alternatively consisting of either the ARCO HTPB, the hydrogenated HTPB, or the JSR HTPB.

<u>Sample #</u>	<u>Prepolymer</u>	<u>Composition (HTPB/TDI/BD)</u>		<u>Wt. % Hard Segment</u>
		<u>equiv.</u>	<u>grams</u>	
R-50	ARCO HTPB	1/4.2/3.1	72.7/19.7/7.5	27.2
R-51	ARCO HTPB	1/6.5/5.3	62.1/26.6/11.3	37.9
R-52	ARCO HTPB	1/8.4/6.9	56.2/30.7/13.1	43.8
HY-50	Hyd. HTPB	1/4.1/2.9	73.7/19.3/7.0	26.3
HY-51	Hyd. HTPB	1/6.4/5.2	63.5/25.6/10.9	36.5
HY-52	Hyd. HTPB	1/8.3/7.3	56.6/29.8/13.6	43.4
J-1	JSR HTPB	1/2.1/1.2	82.0/14.0/4.0	18.0
J-2	JSR HTPB	1/3.0/1.9	75.2/18.7/6.1	24.8
J-3	JSR HTPB	1/4.1/3.0	68.2/23.0/8.8	31.8
J-4	JSR HTPB	1/6.2/5.0	58.3/29.4/12.3	41.7
J-5	JSR HTPB	1/8.4/7.2	50.3/34.4/15.3	49.7
J-6	JSR HTPB	1/10.0/8.8	45.7/37.4/16.9	54.3

Table 3. Sample compositions for polybutadiene-containing polyurethanes.

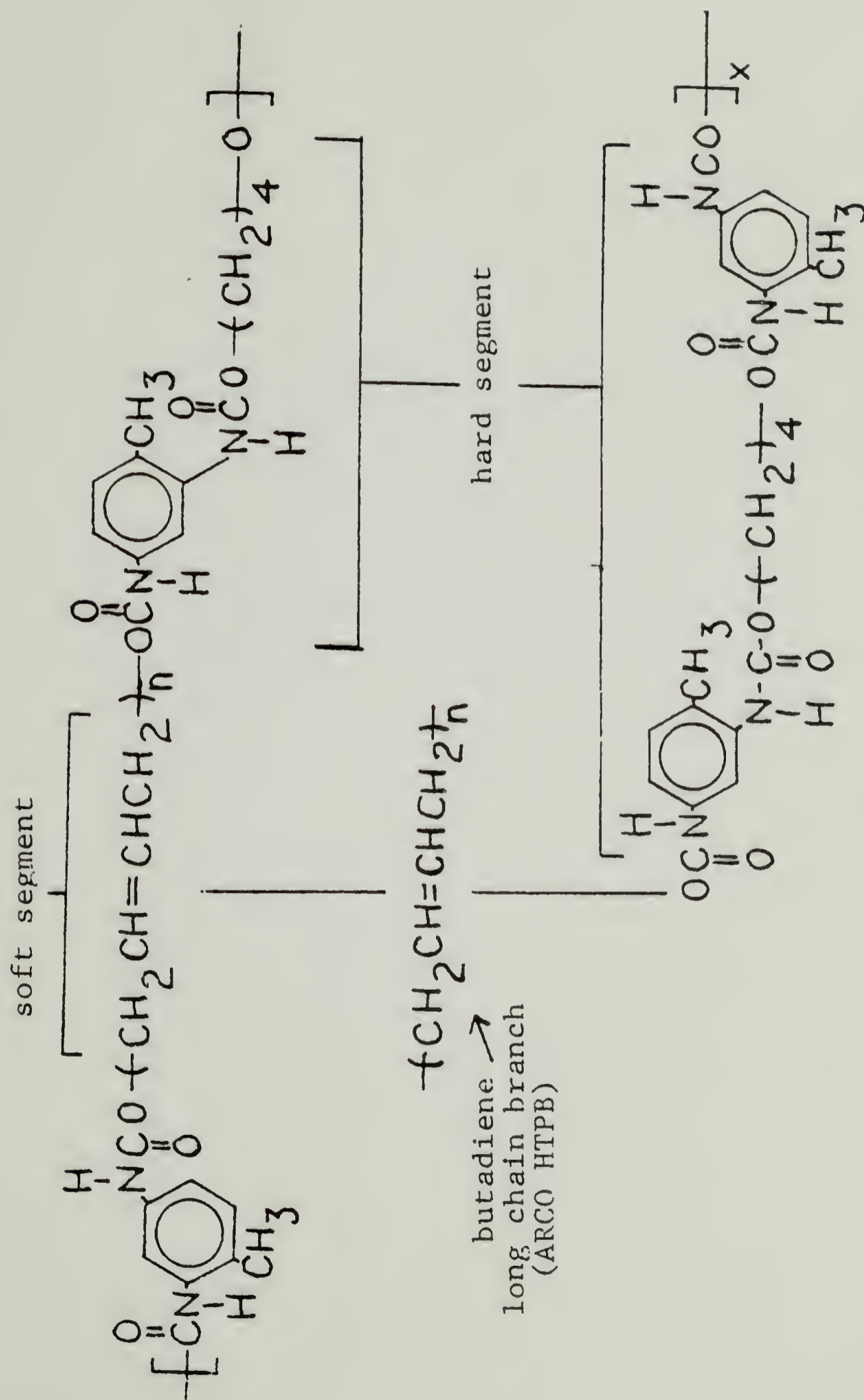


Figure 10. Typical structure of a butadiene-containing polyurethane.

The dissimilar reactivities of the isocyanate groups in 2,4-TDI preclude the occurrence of hard segment sequences consisting of only a single TDI unit where each isocyanate group has reacted with one prepolymer molecule (fig. 11). In the first step of the polyurethane synthesis, once the more reactive isocyanate group (that which is para to the methyl group) reacts with the hydroxyl of the polyol, the reactivity of the remaining isocyanate group is greatly diminished, thereby preventing further reaction at this stage (35). Therefore, after the first step is complete, only isocyanate endcapped polybutadiene and free TDI are present in the reaction mixture, with no real build up of molecular weight.

In the second step of the synthesis, the chain extension step, molecular weight is built up by the reaction of the short chain diol with both the isocyanate endcapped polybutadiene and the free diisocyanate. The length of the hard segment sequences will be determined largely by the amount of excess free diisocyanate in the sample, leading to the desired hard segment content (also referred to as urethane weight per cent). Due to a number of factors, it is most likely that the hard segment sequence lengths will be polydisperse, ranging from one diol molecule reacted with two isocyanate terminated prepolymer molecules up to hard segments consisting of several sequences of alternating TDI - butanediol units (fig. 11).



It is also possible to have reaction leading to pure hard segment, consisting of TDI and butanediol only. One reason for these occurrences is that the reactivity of a functional group is most probably independent of the size of the molecule to which it is attached, as is the case in typical step growth polymerizations (36). Therefore, the manner in which the different species of difunctional molecules react is essentially random. In addition, there is a problem of incompatibility between the highly polar isocyanate and the hydrocarbon soft segments. In this case, insufficient mixing may lead to a separation of the two phases before the reactive groups have completely reacted, leaving some low molecular weight adducts consisting of pure hard segment and unextended soft segment.

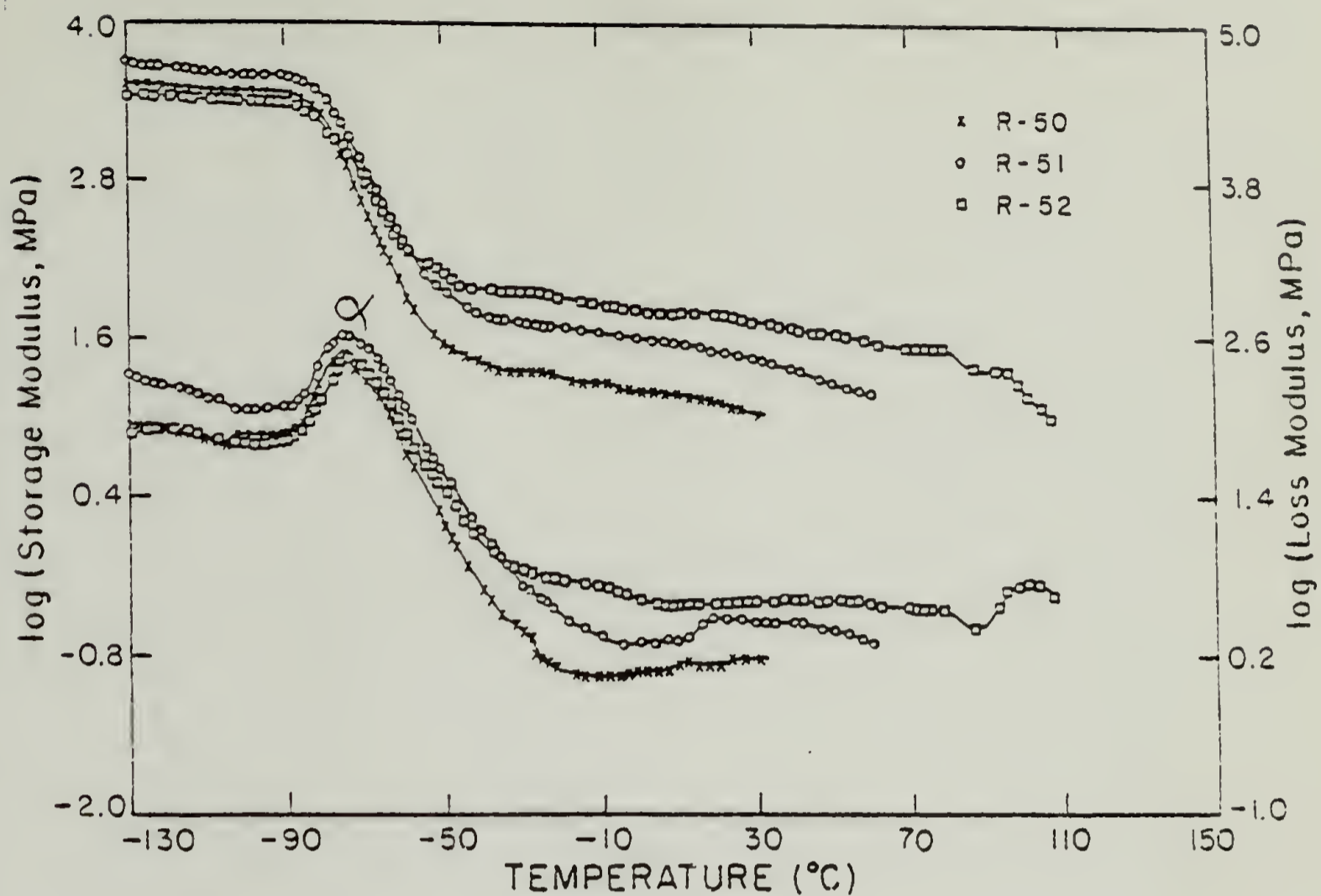
Polyurethanes based on ARCO HTPB. For the polyurethanes prepared from the non-hydrogenated and hydrogenated ARCO HTPB, all of the samples were found to be thermosetting, as they were insoluble in the usual urethane solvents (DMSO, DMF, etc.). Since this indicates a rather complex network for these systems, many useful characterization methods were not possible, particularly those requiring dissolution of the polymer.

Dynamic mechanical analysis. The results for the dynamic mechanical and tensile properties of the HTPB (ARCO) and the hydrogenated HTPB based polyurethanes are shown in table 4. Figure 12 shows the temperature dependence of

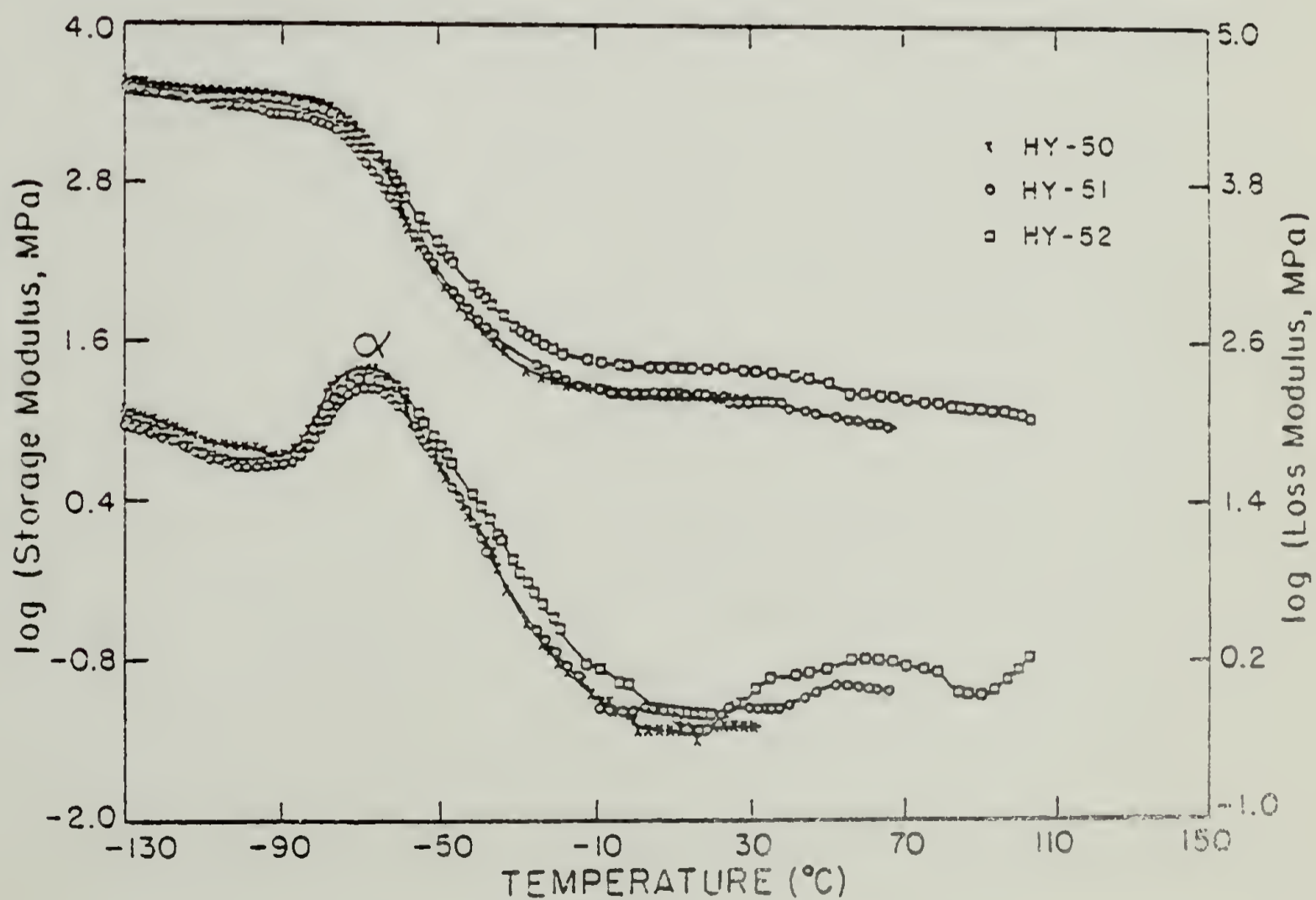
Sample #	Composition (HTPB/TDI/BD) (eq.)	Dynamic Mechanical		Tensile Stress (psi)	Ultimate Elongation %
		From E'' <sub>max</sub>	T <sub>g</sub> (°C) From tan $\delta$ <sub>max</sub>		
R-50	1/4.2/3.1	-74.4	-64.8	570	340
R-51	1/6.5/5.3	-73.5	-63.2	1390	230
R-52	1/8.4/6.9	-73.7	-64.8	1410	150
HY-50	1/4.1/2.9	-69.5	-54.5	1220	410
HY-51	1/6.4/5.2	-69.5	-53.1	1350	380
HY-52	1/8.3/7.3	-68.8	-53.7	1920	260

Table 4. Dynamic mechanical and tensile data for ARCO HTPB and hydrogenated HTPB based polyurethanes.

Figure 12. Temperature dependence of the storage and loss modulus for (a) ARCO HTPB based polyurethanes, and (b) hydrogenated ARCO HTPB based polyurethanes.



(a)



(b)

the storage modulus and loss modulus for the two series of polyurethanes at each composition. In each case, a major relaxation ( $\alpha$ ) occurs, at about  $-74^{\circ}\text{C}$  for the unsaturated samples (fig. 12a) and at  $-69^{\circ}\text{C}$  for the hydrogenated samples (fig. 12b). This transition is accompanied by a decrease in modulus from about 1000 to 10 MPa, and is associated with the glass transition of the soft segments. It can be seen that this temperature is independent of composition, and the  $T_g$  of the butadiene in the polyurethane is only about  $7^{\circ}\text{C}$  higher than that of the free polybutadiene. These facts indicate that these systems are well phase separated. A hard segment transition, which was evident in DSC data, could not be discerned from the dynamic mechanical results.

Tensile testing. The results of tensile testing on the two series of polyurethane films prepared from the ARCO HTPB and hydrogenated HTPB are shown in table 4. In both cases, the initial modulus increased, as seen in figure 13, as the less mobile hard segments tended to establish rigidity in the sample. By the same means, the stress level increased with hard segment content within each series. In addition, the ultimate elongation decreased with increasing hard segment for both series.

With one exception, the initial modulus and stress at break were higher in the hydrogenated HTPB based samples, as was the ultimate elongation. This result indicates

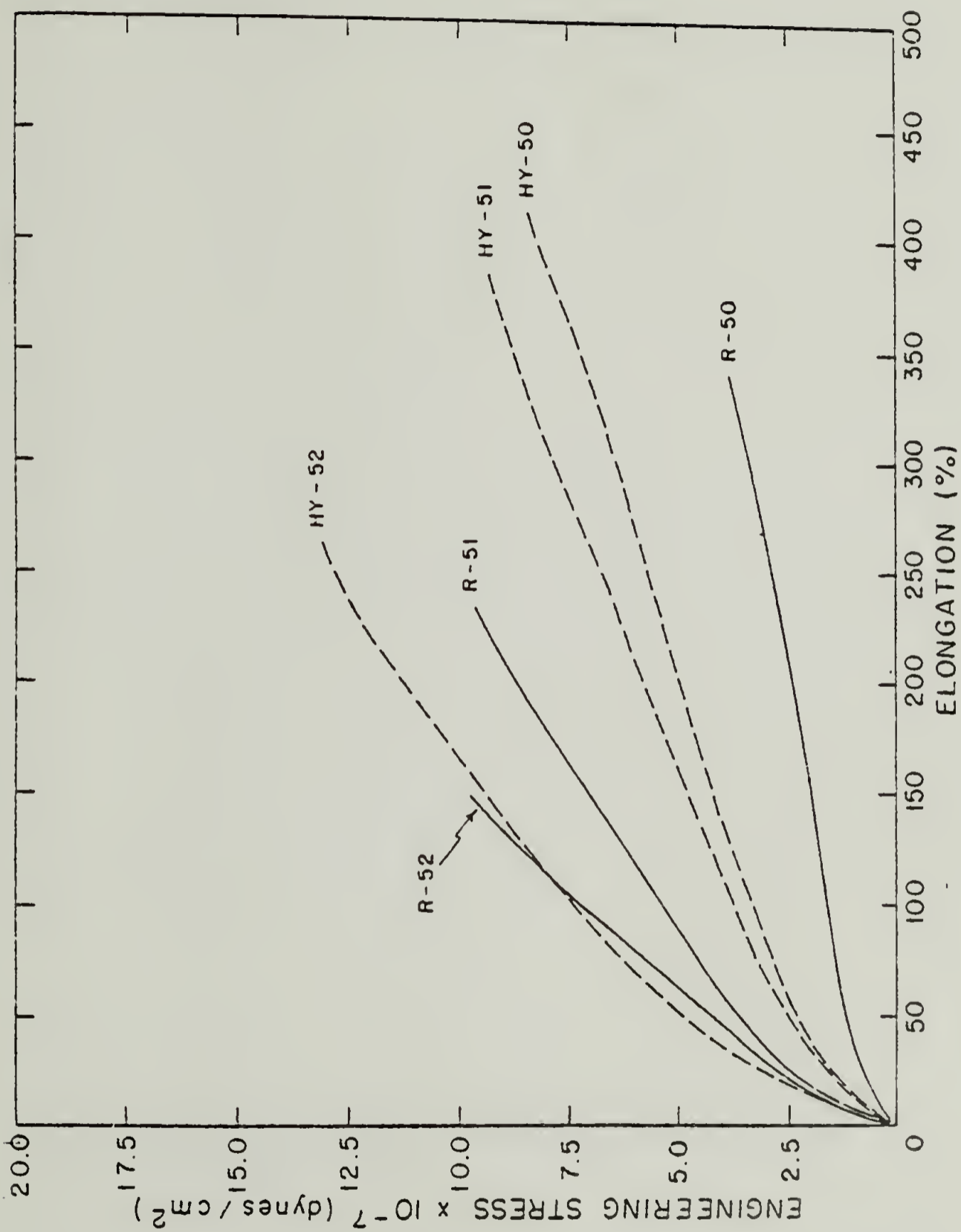


Figure 13. Stress-strain plots of ARCO HTPB based polyurethanes: solid line - non-hydrogenated, dashed line - hydrogenated HTPB.

increased toughness in these materials. Cyclic Instron tests indicated stress softening in these samples. This type of behavior is typical of phase separated materials.

Thermal analysis. The soft segment  $T_g$  values for the unsaturated polyurethanes were found to be  $-65^{\circ}\text{C}$  to  $-72^{\circ}\text{C}$  by DSC and  $-68^{\circ}\text{C}$  by TMA. Hard segment transitions were evident at  $35^{\circ}\text{C}$  to  $40^{\circ}\text{C}$  and at  $65^{\circ}\text{C}$  to  $75^{\circ}\text{C}$ . The presence of two hard segment  $T_g$ 's may be due to domains of different hard segment sequence lengths.

The soft segment  $T_g$  for the hydrogenated HTPB based samples was found to  $-70^{\circ}\text{C}$ , compared to a  $T_g$  of  $-81^{\circ}\text{C}$  for the original hydrogenated prepolymer.

Polyurethanes based on JSR HTPB. The samples prepared from the JSR HTPB were found to be soluble in DMF at elevated temperatures. This substantiated the fact that the prepolymer was linear and therefore no urethane crosslinks were present in the final cured polyurethane. Reversible allophanate crosslinks should be broken at the solution temperatures ( $>80^{\circ}\text{C}$ ). One characterization method made possible by the solubility of these materials was high resolution carbon-13 nmr at elevated temperatures. Unfortunately, it was found that the polymer had undergone some degradation at the temperatures necessary for dissolution during the long times needed to accumulate sufficient data for acquisition of a spectrum. Attempts were made using DMF solvent with a  $\text{D}_2\text{O}$  external lock at  $80^{\circ}\text{C}$  with little success.

A total of six samples were prepared based on the JSR HTPB ranging from TDI/OH equivalents in the prepolymer of 2:1 up to 10:1. The compositions are shown in table 3.

Dynamic mechanical and tensile testing. The dynamic mechanical and tensile results for the JSR HTPB based polyurethanes are presented in table 5. For each sample composition, a major relaxation occurred at about  $-55^{\circ}\text{C}$  to  $-57^{\circ}\text{C}$ , which is associated with the glass transition of the soft segment. In addition, upper relaxations were noticed in all but the lowest hard segment sample. The three samples of highest hard segment content (J-4, J-5, J-6) showed two upper relaxations. This may be an indication that two distinct sizes of hard segment domains are present as a result of differences in hard segment sequence lengths (fig. 11). Similar results were obtained from DSC measurements.

Perhaps the most important observation which can be made from the stress-strain data shown in table 5 is the occurrence of a phase inversion, at which point the polyurethane goes from an elastomeric material to one which behaves more like a brittle plastic. The sample with the highest hard segment content (J-6) was most likely composed mainly of a mixture of the hard and soft segment homopolymers. The phase inversion appears to occur at about 40% hard segment content. At this point, the system could be considered as going from rigid hard domains embedded in an amorphous soft segment matrix to a system in which the hard

<u>Sample #</u>	<u>Composition (HTPB/TDI/BD) (eq.)</u>	<u>Dynamic Mechanical</u>		<u>Tensile Stress (psi)</u>	<u>% Elongation</u>	<u>% Recovery</u>
		<u>Soft</u>	<u>Hard</u>			
J-1	1/2.1/1.2	-57	-	410	1000	95
J-2	1/3.0/1.9	-56	20	600	1620	90
J-3	1/4.1/3.0	-55	20	480	1160	89
J-4	1/6.2/5.0	-56	35, 76	624	430	87
J-5	1/8.4/7.2	-57	56, 91	390	70	82
J-6	1/10.0/8.8	-56	60, 93	390	15	(brittle)

Table 5. Dynamic mechanical and tensile data for JSR HTPB based polyurethanes.

domains become dominant in determining properties. At this point, the material takes on the characteristics of a plastic, as a greater concentration of hard segment is present.

### Conclusions and Suggestions for Furthur Work

The polyurethane films prepared from the various prepolymers in general appearance showed good clarity and homogeneity. The method of evacuating the reaction kettle after the chain extension step was very effective for producing films which were free of bubbles. There is still a definite problem in mixing the chain extender with the isocyanate endcapped prepolymer, as the incompatibility between the two may very likely lead to incomplete mixing before the reaction is complete. This could be a contributing factor in producing a mixture of two homopolymers as well as polydispersity in the hard segments. These problems may be resolved by carrying out the polymerization in solution, but in this case the structure and morphology of the products would probably change drastically. The final structure of the polyurethane is also probably a function of the reaction temperatures and times, and small changes in either could alter the final properties.

In the case of each prepolymer used, the polyurethanes produced showed evidence of phase separation based on the mechanical and thermal data. The lack of phase mixing can be attributed to the complete absence of interphase hydrogen bonding, since crystallinity is not a factor in either

phase. The JSR HTPB based polyurethanes could conceivably be considered to be phase separated to a greater extent, since influence of urethane crosslinks is not a factor as it is in the ARCO HTPB based materials. This may be indicated in part by the mechanical results, where the distinct hard segment (upper) transitions show a trend as hard segment content increases. The higher relaxation temperatures found for the higher hard segment polymers could be a result of better domain organization.

As an extension of this investigation, other diene and hydrocarbon rubbers, such as isoprene, chloroprene, and isobutylene could be incorporated as a soft segment. It is likely that similar problems as encountered with the polybutadiene prepolymers will occur, especially in the case of free radically polymerized materials. However, the effect of soft segment structure could be studied in this way. In addition, prepolymers of various molecular weights could be used to better define the effects of that parameter. Hydrogenation could also be carried out on other diene prepolymers for comparison.

It would also be interesting to prepared samples based on the polybutadiene soft segments using MDI as the endcapping agent instead of TDI. Since incorporation of MDI in the hard segments leads to crystalline domains, the effect on properties could be investigated. Also, the MDI based polybutadiene-containing polyurethane properties could be

compared to other MDI based systems.

A very important characterization method made possible by the solubility of the JSR HTPB based materials is high resolution carbon-13 nuclear magnetic resonance spectroscopy. By treating the two phase polyurethane as a block copolymer consisting of alternating hard and soft blocks, a determination of the sequence lengths of each block could be made. A number of investigations have been made on polyester and polyether urethanes using nmr techniques (37-39), and similar methods could be used for the polybutadiene based systems. High resolution proton nmr would also be used to accurately determine the composition of each polyurethane, which would aid in the sequence length analysis.

The synthesis of model, monodisperse, known sequence length hard segments should also be investigated. This could be done by selectively reacting monofunctional hydroxyl and isocyanate bearing compounds followed by regeneration of functional groups, for example, nitration of an aromatic ring followed by hydrogenation and phosgenation to give isocyanate functionality. Series of similar reactions could be used to build up hard segments of known, monodisperse sequence lengths. Many factors, such as side reactions and insolubility of adducts would have to be overcome before such a procedure would be successful.

## REFERENCES

1. Chemical and Engineering News, June 30, 1980, American Chemical Society, p. 12.
2. J. H. Saunders and K. C. Frisch, "Polyurethanes," Interscience, Part I, 1962 and Part II, 1964.
3. G. M. Estes, S. L. Cooper and A. V. Tobolsky, J. Macromol. Sci., C4(2), 313 (1970).
4. S. B. Clough and N. S. Schneider, J. Macromol. Sci., Phys., 2, 553 (1968).
5. R. W. Seymour and S. L. Cooper, Macromolecules, 6, 48 (1973).
6. C. E. Wilkes and C. S. Yusek, J. Macromol. Sci., Phys., 7, 579 (1973).
7. D. S. Huh and S. L. Cooper, Polym. Eng. Sci., 11, 369 (1971).
8. N. S. Schneider, C. S. Paik Sung, R. W. Matton, and J. L. Illinger, Macromolecules, 8, 62 (1975).
9. C. S. Paik Sung and N. S. Schneider, Macromolecules, 8, 68 (1975).
10. N. S. Schneider and C. S. Paik Sung, Polym. Eng. Sci., 17, 73 (1977).
11. C. S. Paik Sung and N. S. Schneider, Macromolecules, 10, 452 (1977).
12. G. A. Senich and W. J. MacKnight, "A Dynamic Mechanical Study of Phase Segregation in Toluene Diisocyanate Block Polyurethanes," in S. L. Cooper and G. M. Estes, eds., Multiphase Polymers, ACS, 1979, p. 97.
13. C. Arnold Jr., J. Elastomers Plastics, 6, 238 (1974).
14. C. M. Brunette, W. J. MacKnight, S. L. Hsu and N. S. Schneider, Polym. Eng. Sci., in print.
15. C. G. Seefried, J. V. Koleske and F. E. Critchfield, J. Appl. Polym. Sci., 19, 2493 (1975).

16. C. G. Seefried, et. al., J. Appl. Polym. Sci., 19, 2503 (1975).
17. H. N. Ng, A. E. Allegrezza, R. W. Seymour and S. L. Cooper, Polymer, 14, 255 (1973).
18. R. R. Legasse, J. Appl. Polym. Sci., 21, 2489 (1977).
19. K. Ono, H. Shimada, T. Nishimuro, S. Yamashita, H. Okamoto and Y. Minoura, J. Appl. Polym. Sci., 21, 3223 (1977).
20. David M. French, Rubber Chem. and Technol., 42, 71 (1969).
21. P. W. Ryan, J. Electroplastics, 3, 57 (1971).
22. R. D. Elmore, Use of EN-7 to Encapsulate Analyzer Assemblies, PDO 6989189, Sept. 1974.
23. G. B. Wood, Evaluation of Conformal Coatings of Micro-electronic Circuitry in Fuse Applications, MDL-TR-1777, March 1977.
24. R. W. Lenz, "Organic Chemistry of Synthetic High Polymers," Interscience, New York, 1967, ch. 11.
25. Kermit Ramey, ARCO Chemical Co., AFRPL-TR-74-64, "Characterization of R-45M, Final Report".
26. T. Yamamoto, Y. Hayashi and A. Yamamoto, Bull. Chem. Soc. Japan, 51, 2091 (1978).
27. T. Yamamoto, K. Sanechika, Y. Hayashi and A. Yamamoto, J. Polym. Sci. Lett., 17, 187 (1979).
28. J. M. G. Cowie, Macromolecules, 10(5), 1124 (1977).
29. F. H. Jardine, L. Rube and A. G. Vokra, J. Chem. Soc., London, Sec. A, p. 238 (1970).
30. C. M. Brunette, W. J. MacKnight, et. al., in print.
31. E. D. Lillie, unpublished results.
32. L. A. Mango and R. W. Lenz, Makromol. Chem., 163, 13 (1973).
33. J. C. H. Hwa and H. Sims, Organic Synthesis, Coll. Vol. V, 41, p. 608.

34. K. A. Pigott, B. F. Frye, K. R. Allen, S. Steingiser, W. C. Darr and J. H. Saunders, J. Chem. Eng. Data, 5(3), 391 (1960).
35. P. Wright and A. P. C. Cumming, "Solid Polyurethane Elastomers," Maclauren, London, 1969.
36. R. W. Lenz, "Organic Chemistry of Synthetic High Polymers," Interscience, New York, 1967, p. 58, sec. 3.5.
37. H. Suzuki, H. Ono, and T. Hongo, Makromol. Chem., 132, 309 (1970).
38. H. Suzuki, J. Polym. Sci., Part A-1, 9, 387 (1971).
39. R. A. Assink, J. Polym. Sci., Phys., 15(1), 59 (1977).

## APPENDIX

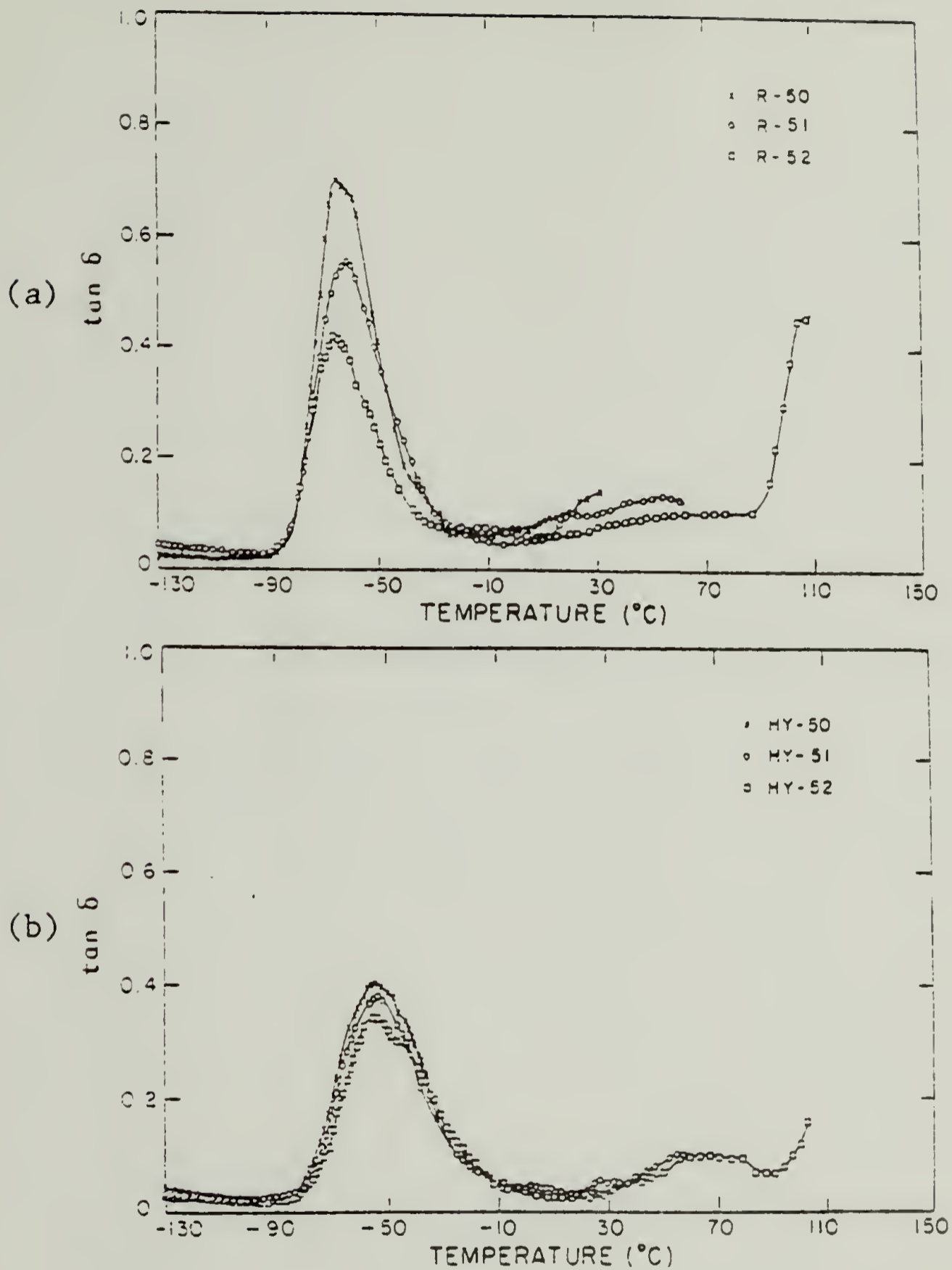


Figure 14. Temperature dependence of the loss tangent for (a) ARCO HTPB based polyurethanes, and (b) hydrogenated HTPB based polyurethanes,

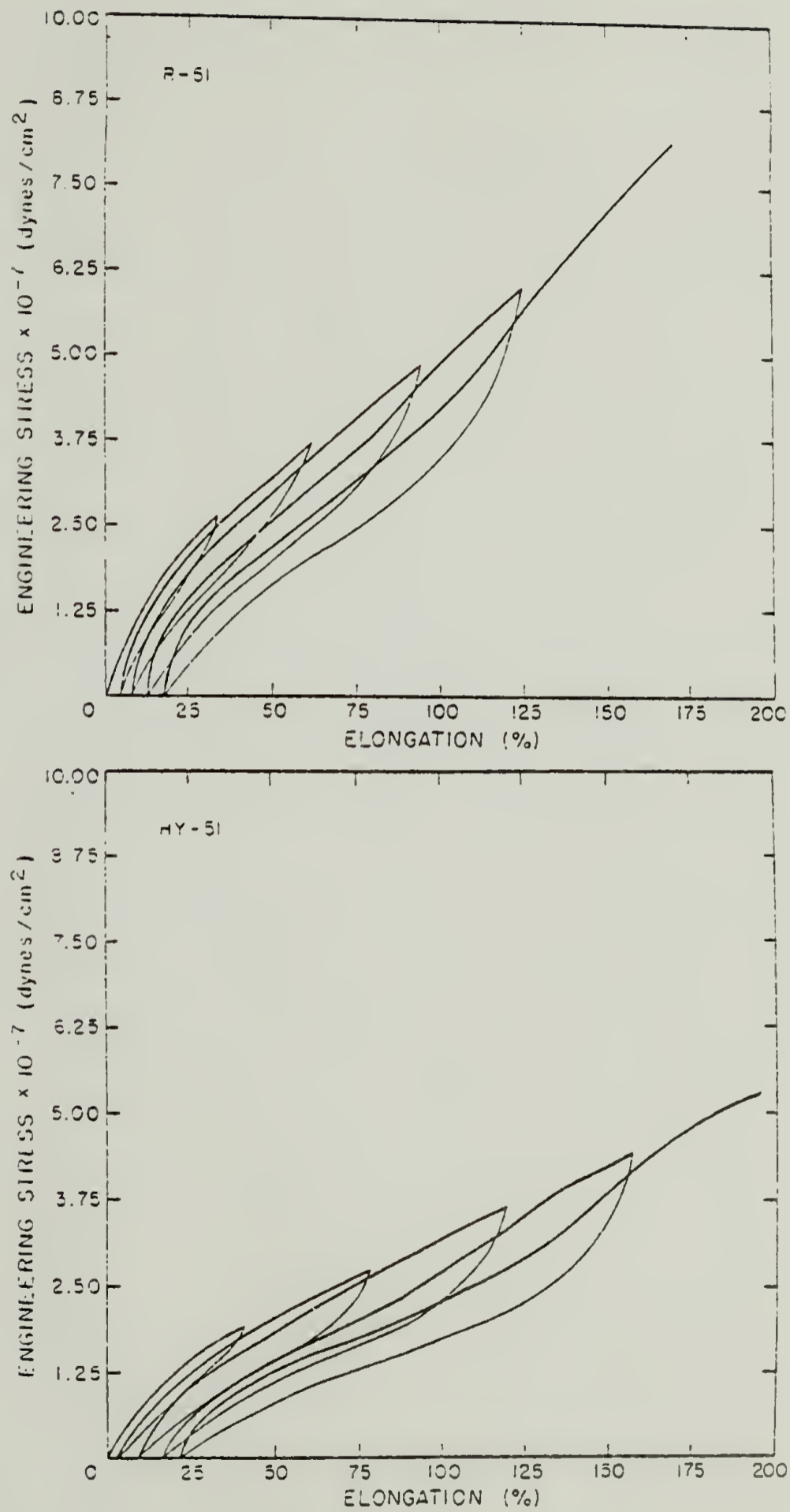
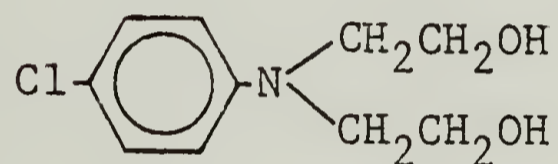
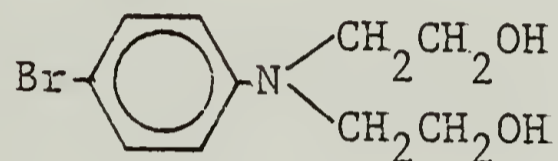


Figure 15. Cyclic stress-strain curves for samples R-51 (non-hydrogenated) and HY-51 (hydrogenated HTPB),

## ADDITIONAL POLYURETHANE SAMPLES

In addition to the three series of samples already mentioned, two series of polyurethane films were also prepared using an aniline derivative as chain extender instead of butanediol. The compounds used were *p*-bromo-N,N-bis-(2-hydroxyethyl) aniline and *p*-chloro-N,N-bis-(2-hydroxyethyl) aniline;



These materials were prepared by the reaction of either *p*-bromoaniline or *p*-chloroaniline with ethylene oxide at about 160°C. Since each of these chain extenders is a solid at room temperature, heating to the melting point (80°C - 90°C) was necessary before adding to the isocyanate endcapped prepolymer.

The polyurethane films so produced were generally of good quality and appeared homogeneous. The inclusion of bromine and chlorine in these materials could serve a number of purposes. The bromine could serve to enhance the electron density contrast in transmission electron micros-

copy studies. The chlorine will act as a chemical tag for structure studies by X-ray microanalysis. As such the preparation of these materials was surveyed only, and no further structure or property studies were conducted. Further substitution of halogen atoms on the aromatic ring may lead to materials with improved fire retardancy. The effect of any of the component changes mentioned on polyurethane structure and properties has not been investigated.

