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STRUCTURE-PROPERTY RELATIONSHIPS
IN LINEAR POLYURETHANES

A Dissertation Presented

By

BRUCE H. BENGTON

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

DOCTOR OF PHILOSOPHY

September 1985

Department of Polymer Science and Engineering

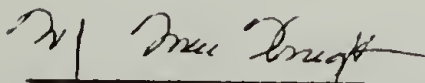
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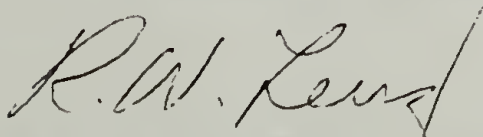
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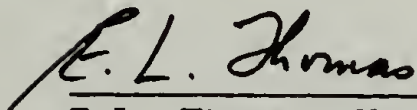
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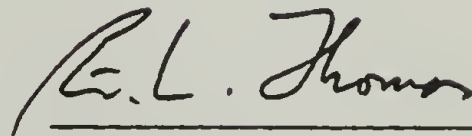
W.J. MacKnight, Chairman




R.W. Lenz, Member



E.L. Thomas, Member



E.L. Thomas
Department Head
Polymer Science and Engineering



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Thanks be to God, from Whom all blessings flow.

ABSTRACT

STRUCTURE-PROPERTY RELATIONSHIPS IN LINEAR POLYURETHANES

September 1985

Bruce H. Bengtson

B.A., North Park College

Ph.D. University of Massachusetts

Directed by: Professor William J. MacKnight

Three series of polyurethanes based on amorphous hard segments consisting of 2,4-toluene diisocyanate (TDI) and 1,4-butane diol (BDO) were prepared by solution polymerization. The soft segments used were polycaprolactone (PCL), polytetramethylene glycol (TMG), and hydroxy terminated polybutadiene (HTPBD) of 2,000 molecular weight. Hard segment length (content) was varied in each series. Thus, the effects of the soft segment type and the hard segment type and length on polyurethane properties were studied systematically. These materials were characterized by thermal analysis, dynamic mechanical analysis, and stress-strain measurements.

The HTPBD polyurethanes exhibit a two phase morphology as deduced from thermal and dynamic mechanical analysis. Most of these samples exhibited hard and soft segment glass transition temperatures (T_g). HTPBD polyurethanes are completely phase segregated, as the soft segment T_g is very close to that of the free HTPBD oligomer and is independent of hard segment type or length. Thermal history effects on the extent of phase segregation and dynamic mechanical properties are negligible.

The hard segment T_g increases with increasing hard segment length according to a Fox-Flory type relationship. From thermal analysis and mechanical studies, morphological transitions are seen to occur with increasing hard segment content. (This has been corroborated by electron microscopy studies.)

The TMG polyurethanes with hard segment contents greater than 40% also exhibit two phase behavior. The degree of phase segregation increases with increasing hard segment length, as indicated by T_g suppression of the soft segment fraction. We believe that a critical hard segment length is required for phase segregation to occur. Thermal history effects on the extent of phase segregation and dynamic mechanical properties are virtually negligible. Composition dependent morphologies are also apparent for this series.

The PCL polyurethanes are highly compatible block copolymers with each sample displaying only a single T_g . The T_g 's determined for quenched samples are in reasonable agreement with the values calculated for completely compatible systems. Crystallization of the PCL soft segments occurs for materials with less than 40% hard segments. Mechanical properties are highly influenced by sample T_g , soft segment crystallinity, and stress induced crystallization.

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C H A P T E R I

INTRODUCTION AND LITERATURE REVIEW

Segmented polyurethanes are a class of thermoplastic elastomers of great commercial importance. These materials derive most of their useful properties from the incompatibility of the hard and soft segments and subsequent phase separation into separate domains. The soft segment is usually a polyether or polyester of molecular weight between 600 and 5000 (macroglycol) possessing a glass transition temperature (T_g) well below ambient temperature. Hard segments are typically formed by the extension of an aromatic diisocyanate with a low molecular weight diol or diamine and have a T_g or melting transition above the use temperature. The hard segment domains provide physical crosslinking, act as reinforcing fillers, and are responsible for the performance of these materials at higher temperatures. The utility of polyurethanes in a variety of commercial applications is made possible by the range of possible chemical compositions for these materials. Uses for polyurethanes include hard and soft foams, fibers, films and coatings, thermoplastic elastomers, and structural materials such as automobile fenders.

POLYURETHANE SYNTHESIS

The wide range of polyurethane compositions is made possible by the ready reaction of isocyanates with compounds containing reactive hydrogens. Urethane linkages result from the reaction of an isocyanate

with an alcohol (eq. 1) or the reaction of an



amine with a chloroformate (eq 2). The former is



the reaction of choice as this method produces no by-products, such as HCl. The isocyanate may also react with an amine giving a urea linkage (eq. 3).



Under certain conditions, isocyanates will also react with the N-H group of an urethane, forming an allophonate linkage (eq 4).



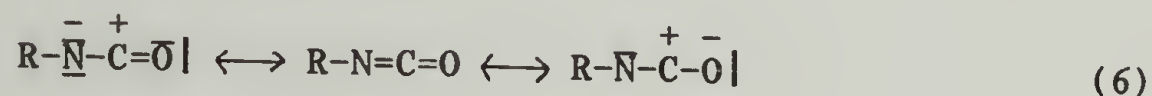
A similar reaction can occur with a urea as well, giving a biuret.



These side reactions become important at temperatures above 100°C and the allophonates and biurets decompose above 150°C. These side

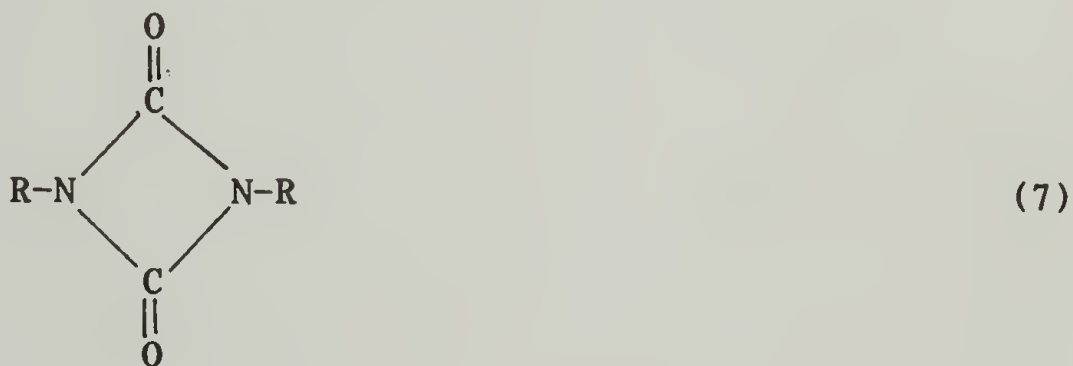
reactions often result in chain branching or chemical cross-linking in polyurethanes when a stoichiometric excess of isocyanate is used.

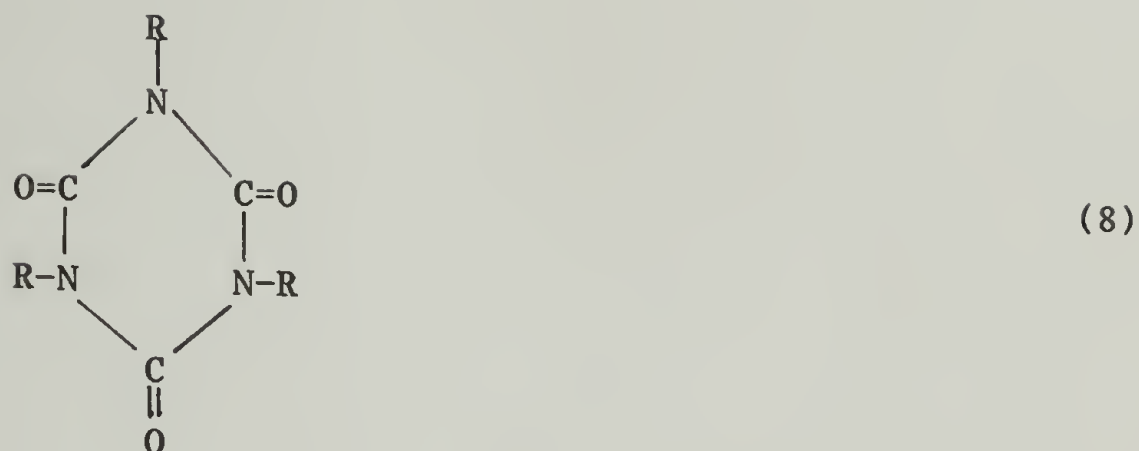
Isocyanates have a high reactivity because of their resonance structures (eq. 6), with the carbon atom obtaining a partial positive charge, making it



susceptible to nucleophilic attack, with the active hydrogen attaching to the partially negative nitrogen. The more nucleophilic the alcohol or amine, the more rapid is the formation of urethane or urea. These facile reactions can be further catalyzed by transition metal compounds, such as dibutyl tin dilaurate or organic bases such as triethylenediamine catalysts can increase the reaction rate by 3 to 4 orders of magnitude over that of the uncatalyzed reaction.

Catalysts also may cause dimers (eq. 7) or trimers (eq. 8) to form from isocyanates. The trimers of a





diisocyanate are a basic ingredient of isocyanurate foam insulation. The carbon nitrogen double bond can be opened for polymerization to nylon-1 type polymers by use of the correct catalyst and low temperatures (eq. 9).



Polyurethanes can be prepared by either solution or bulk polymerization using one or two step methods. Early studies were performed using solution methods.^{1,2} More recently the emphasis has shifted to bulk methods, as catalyzed bulk polymerizations can produce polyurethane elastomers and structural materials with suitable commercial properties. In the one step method, all the reactants are added simultaneously. Bulk one step polymerizations are used in reaction injection molding (RIM), where an entire part is formed in less than one minute reaction time. This is possible because of the rapidity

of the reaction and the absence of by-product formation. A two step polymerization is often used to isolate the soft segment chains. First the macroglycols are endcapped with an excess of diisocyanate, and then the diol is added for chain extension and the formation of the hard segments.

Camargo and others³⁻⁶ have shown that uncatalyzed (slowly reacting) systems show phase separation at low conversions leading to polymers with poor properties. This early phase separation is caused by incompatibility of either the initial reactants or oligomers produced early in the reaction. Early phase separation can occur before high polymer is formed and causes the hard segment sequence length distribution to deviate from the geometric distribution formed ideally. In the extreme case where the monomers are highly incompatible, the final product approximates a blend of hard segment copolymer and extended soft segment.^{4,6} Early phase separation has not been extensively studied so some doubt exists over the time and size scales of this phenomenon. Original work by Castro et al.⁵ indicated that the phase separation occurred at a number average hard segment length (this term is defined in the next section) of 1.3. These results agree with values obtained by DSC⁷ and other methods.³

The fact that bulk polymerization produces less than ideal products (as far as sequence length distribution is concerned) has regenerated interest in solution polymerization. The conditions are suitable for the formation of more ideal system, as the reactants and products stay in solution throughout the reaction with no phase separation. Attempts

have been made to synthesize monodisperse hard segments⁸⁻¹² to determine the minimum hard segment length necessary for phase segregation. At this time only two groups have synthesized polyurethanes with monodisperse hard segments. In the classic work by Harrel,¹ hard segments of piperazine and BDO were prepared. Fu¹² has made polymers with monodisperse 2,4-TDI/BDO hard segments and these results will be used in this thesis for comparison with similar polyurethanes with ideal hard segment length distributions.

HARD SEGMENT LENGTH DISTRIBUTIONS

Distributions and statistics are important concepts in the field of polymer science. Two of the most fundamental polymer properties are molecular weight and molecular weight distribution. Both have profound effects on the physical properties of polyurethanes. Polyurethanes are complex in regard to sequence length distributions as well as the molecular weight distribution of the copolymer. Experimental evidence indicates that the sequence length distribution of piperazine hard segments greatly influences the mechanical properties of these particular polyurethanes.¹

Several authors have examined theoretical hard segment sequence length distribution.¹³⁻¹⁷ The most useful of these is a series of calculations by Peebles,^{13,14} specifically for a polyurethane system. The main point of this effort is that under ideal conditions the distribution of hard segment lengths follows a most probable (Flory) distribution. Assumptions for this case include: (1) the reactivities

of the isocyanate groups of the diisocyanate are equal and independent of whether or not the other isocyanate has reacted, (2) the reactivity of any alcohol is independent of its molecular weight, and (3) good mixing occurs so that local stoichiometry is maintained. Under these conditions the average hard segment length for a polyurethane of composition $1/n/n-1$ (polyol/diisocyanate/diol) is n at complete conversion. The polydispersity of the hard segments would be 2.

However, these ideal conditions do not exist in most urethane systems. Specifically MDI and TDI show a marked drop in reactivity of the second isocyanate reaction; a drop to $1/3$ and $1/25$ of the original reaction rate respectively.¹⁸ This combined with the use of a two step method gives a more narrow distribution of hard segment lengths than the ideal case. A lower value of number average sequence length (\bar{S}_n) also occurs.

$$\bar{S}_n = C_1 / (C_1 - X_1) \quad (10)$$

$$\bar{S}_w / \bar{S}_n = 1 + X_1 / C_1 \quad (11)$$

where X_1 = unreacted diisocyanate, depending upon reactivity ratio and composition and $C_1 = (n-1)$ in the scheme of the preceeding paragraph.

Determination of the hard segment length and distribution in polyurethanes has not proven to be simple. Consequently, little work has been published in this area. Suzuki et al. have used selective perchloric acid degradation of a polyether poly(urea)urethane to obtain

the isolated MDI/hydrazine hard segments.^{19,20} The number average weight molecular weight determined by titration and elemental analysis was found to be lower than expected from ideal conditions. The number average sequence length of a polyester polyurethane has been determined by NMR from comparisons with model compounds.²¹ Values obtained were in agreement with calculated values. Both methods gave only number averages and not the distributions. The depolymerization technique is only applicable to a small number of systems because of possible side reactions. However, the isolated hard segments produced by this method should be able to be analyzed by GPC to determine the hard segment length distribution.

Because of this lack of experimental determination, the hard segment length and distribution are generally assumed to correspond to the ideal conditions. Studies on the effect of hard segment distribution have been limited to comparisons of mono- and polydisperse hard segments.

Harrell¹ has prepared both random and monodisperse hard segment polyurethanes from polytetramethylene glycol (TMG), piperazine, and butane diol (BDO) dichloroformate. These materials do not contain N-H bonds and therefore cannot hydrogen bond. It was shown that the monodisperse hard segment materials possessed higher recovery, tensile modulus and strength as compared to polydisperse materials of identical composition. It is not yet known if these effects would also occur in hydrogen bonded systems.

Fu¹² has synthesized polyurethanes with monodisperse TDI/BDO hard segments and soft segments of polybutadiene, TMG, and PCL. His results

will be compared to polydisperse hard segment polyurethanes of the same soft segments later in this thesis.

Monodisperse hard segments from MDI and BDO have recently been prepared by a number of workers.⁸⁻¹¹ However, no polymers from these materials have yet been reported.

PHASE SEGREGATION

Most of the usable properties of polyurethanes are a result of phase segregation. The hard segment domains act as both physical crosslinks and reinforcing filler that is well bonded to the rubber matrix. The extent of phase segregation is influenced by the chemical nature of the constituents, their stereochemistry, the length of hard and soft segments, and any interactions between hard and soft segments. Techniques such as small angle x-ray scattering (SAXS), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and electron microscopy have been used to establish the existence and/or the extent of phase segregation.²²⁻²⁶ Aside from directly imaging the microdomains by microscopy (which is very difficult to accomplish for polyurethanes) these techniques infer phase separation from a low angle interlamellar peak (SAXS) or the existence of two separate Tg's, one for soft segment and one for hard segment (DSC, DMA) and an elevated plateau modulus (DMA).

Hard segments contain more polar constituents while the soft segments are relatively less polar or even strictly non-polar. This difference in polarity is the basic origin of the segmental

incompatibility that causes phase segregation.

Interactions between hard and soft segments, usually hydrogen bonding, are also known to have a profound effect on the extent of phase segregation. Clough et al.²² studied polyurethanes with MDI/BDO hard segments and polyester and polyether soft segments. They came to the following conclusions: (1) phase segregation is more pronounced in polyether polyurethanes than in equivalent polyester polyurethane and (2) longer segment lengths are more highly phase segregated. The explanation given for the first conclusion is that the carbonyl of the polyester soft segment is a much more effective hydrogen bond acceptor than is the polyether oxygen. Hence this greater specific interaction between hard and soft segments enhances phase mixing. It is generally accepted that longer segmental lengths (molecular weights) improve the degree of phase segregation.²³⁻²⁶ A thermodynamic explanation for both effects will be presented later.

The effect of specific intradomain ionic interactions has recently been investigated by Cooper et al.²⁷⁻²⁹ They have synthesized polyurethanes with zwitterion containing hard segments and soft segments of TMG and hydroxyl terminated polybutadiene (HTPBD). In the absence of the zwitterion, the HTPBD polyurethanes are much more highly phase segregated than TMG polyurethanes, most likely due to the absence of interphase hydrogen bonding in the former. Introduction of the zwitterion creates strong ionic interactions between the hard segments. This causes more complete phase segregation in the TMG polyurethanes, as these interactions generate an additional driving force for phase

segregation. Use of different neutralizing salts causes differing degrees of hard segment interactions and phase segregation. For example, use of sodium acetate neutralizes the interchain ionic interactions and properties approach those of the nonionized material. Behaviors intermediate between the zwitterion material and the original uncharged polyurethane can be obtained with addition of different salts. The type and location of interchain specific interactions have a significant effect on the phase segregation and therefore the properties of polyurethanes.

Crystallization in either hard or soft segments provides another driving force for phase segregation. For example, Cooper et al.³⁰ have compared the phase segregation differences between crystalline MDI and non-crystalline H₁₂MDI based polyurethanes with the other constituents being identical. SAXS results indicate that the interfacial thickness of the amorphous hard segment material (H₁₂MDI) was significantly greater than for the crystalline hard segments. Observed phase segregation in the materials of Harrell¹ most likely arises from the crystalline non-hydrogen bonded hard segments.

The role of hydrogen bonding in phase segregation is not completely understood even though it is often used as a semi-quantitative measure of the extent of phase mixing.³¹ It is certain that the extent of hydrogen bonding is an important factor in phase mixing. Practically all polyurethanes are extensively hydrogen bonded. The hydrogen bond donor is the N-H group of the urethane linkage and the acceptor could be either oxygen of the urethane or ester linkages or the ether oxygen of

the soft segment. The distribution of hydrogen bonding with the various acceptors depends on many factors and is extremely difficult to determine quantitatively.³² A comparison of the extent of phase mixing calculated from DSC and infrared (hydrogen bonding analysis) results shows that the degree of phase mixing calculated from the T_g was significantly higher than that calculated from infrared analysis.^{26,33} Hydrogen bonding has been shown to influence morphological features such as crystalline chain ordering in semicrystalline polyurethanes.³⁴

The thermodynamic condition for phase separation can be obtained from the free energy of mixing.

$$\Delta G_M = \Delta H_M - T\Delta S_M \quad (12)$$

The entropy of mixing, ΔS_M , is usually small and positive for polymer systems, because the number of molecules involved is small. The heat of enthalpy of mixing can be defined by equation 13;

$$\Delta H_M = n_A \phi_B RT \chi_{AB} \quad (13)$$

where n_A is the number of moles of A, ϕ_B is the volume fraction of constituent B and χ_{AB} is the interaction parameter which characterizes the interaction energy of A with B. χ_{AB} may be expressed in terms of solubility parameters:

$$\chi_{AB} = \frac{V_r}{RT} (\delta_A - \delta_B)^2 \quad (14)$$

where V_r is a reference volume and δ_A and δ_B are the solubility parameters of A and B respectively. The solubility parameter is defined as the square root of the cohesive energy density, which for small molecules is the energy of vaporization per unit volume. These values can be experimentally determined for polymers by swelling measurements or estimated from tables of group contributions. The solubility parameter approach is applicable only in the absence of strong interactions between constituents.

As ΔS_m is small, the thermodynamic compatibility of the constituents is generally determined by the value of χ_{AB} , which determines the magnitude and sign of ΔH_M . In the simple thermodynamic analysis for phase separation, the value of χ_{AB} at the critical point is given by;

$$(\chi_{AB})_{Cr} = 1/2[1/z_A)^{1/2} + (1/z_B)^{1/2}]^2 \quad (15)$$

where z_A is the degree of polymerization of A. Phase separation occurs if $\chi_{AB} > (\chi_{AB})_{Cr}$. For simple liquids $(\chi_{AB})_{Cr} = 2$, for polymer-solvent mixtures $(\chi_{AB})_{Cr} = 1/2$, and for polymer-polymer systems $(\chi_{AB})_{Cr}$ is a small positive number.

Application of these concepts to block copolymers requires some modifications. The occurrence of covalent bonding between segments limits the number of arrangements possible, resulting in a loss of configurational entropy of mixing. Because of this, the critical molecular weight for phase separation is greater for block copolymers than for mixtures of the corresponding homopolymers.

Several theories of block copolymer microphase separation have been proposed.^{35,-41} Most are applicable only to AB or ABA type block copolymers of monodisperse segment lengths. Krause³⁰⁻⁴¹ has developed a thermodynamic treatment applicable to $(AB)_n$ multi-block copolymers. A lattice theory was used assuming a lattice coordination number of 8 and monodisperse block lengths. The free energy change on microphase separation for 1 mol of block copolymer molecules containing repeat units A and B, each having the same volume as a lattice site is:

$$\frac{\Delta G}{RT} = - \frac{3n_A v_B \chi_{AB}}{4} - \ln(v_A)^{v_A} (v_B)^{v_B} + 2(m-1)(\Delta S_d/R) - \ln(m-1) \quad (16)$$

where m is the number of blocks in the copolymer, v_A and v_B are the volume fractions of A and B, n_A is the number of A repeat units in each molecule, $(\Delta S_d/R)$ is essentially the entropy lost by immobilization of one repeat unit at the interface, and χ_{AB} is the interaction parameter.

The first term of equation 16 represents the enthalpy of mixing lost upon microphase separation assuming a sharp interface. The second term is the entropy lost upon microphase separation. The third term represents the entropy lost due to the formation of an interface. The final term occurs for copolymers with more than three blocks due to the interchangability of the identical blocks in these copolymers.

The main conclusions from the above are: 1) as the number of blocks increases in a copolymer of given length, the microphase separation becomes more difficult, 2) for constant composition and number of blocks per molecule, microphase separation becomes easier as the molecular

weight increases, and 3) for molecules having the same length and number of blocks, a copolymer with $v_A = v_B = 0.5$ undergoes microphase separation more readily than other compositions. A major problem with this method lies in the determination of a value of $(\Delta S_d/R)$. Experimentally determined values can vary from 0.85 to 3.5 for cis and trans poly 1,4-isoprene, respectively. However, the three conclusions stated above are valid and this method is very useful in demonstrating the influence of the number of blocks on microphase separation.

POLYURETHANE MORPHOLOGY

Polyurethanes generally do not possess well characterized morphologies as do AB and ABA type block copolymers. Briber has compared the large number of morphological models that have been proposed and concluded that none were sufficient to explain all the characteristics of polyurethanes.⁴² This is a result of the variety of factors affecting polyurethane morphology; such as hard and soft segment polarity, presence of crystallinity, segment length and length distribution, volume fraction of each phase, method of sample preparation, and thermal and mechanical history of the sample.

Direct imaging of the domains by electron microscopy is difficult due to the lack of a significant degree of phase contrast, and the small size of the domains with respect to specimen thickness caused by the short segmental lengths. This method is also prone to production of artifacts and a critique of polyurethane morphological electron microscopy studies has been recently published.⁴³ The morphology of

polyurethanes has been shown to be highly complicated,⁴⁴⁻⁴⁷ especially crystalline systems.⁴² Results of a study by Lunardon et al.⁴⁸ showed that three phases coexist in a crystalline polyurethane; a soft phase, a crystalline hard phase, and a mixed phase (interface).

MECHANICAL PROPERTIES

The commercial interest in polyurethanes is spurred by the variety and utility of the mechanical properties obtainable by use of different chemical systems. The mechanical properties of polyurethanes are greatly influenced by the size, shape and concentration of the hard segment domains, the deformational resistance of the hard domains, and the orientation of the segments under strain.^{49,50} Generally, the polymer morphology has the overriding influence on mechanical properties.

The hard domains in polyurethane thermoplastic elastomers increase both modulus and ultimate strength in roughly the same fashion as the particulate reinforcement of rubber occurs.⁵¹ Plastic domains increase strength by preventing catastrophic crack propagation through the material. This is accomplished by the deflection or bifurcation of cracks, cavitation (which has a stabilizing effect), and plastic deformation of the hard domains, which dissipates energy. Only two phase (or filled) elastomers exhibit toughness over extended ranges of temperature and time or strain rate. Another reinforcing phase may also arise from the orientation of the chains, resulting in strain-induced crystallization..

The effect of hard segment content on polyurethane mechanical properties is quite pronounced. At low hard segment concentrations, the polyurethane is a thermoplastic elastomer with discrete reinforcing hard segment domains. The presence of high hard segment content reverses this situation, with the soft segments serving as rubber modifiers for the polymer. It is possible to tailor the mechanical properties for various end uses by changing the hard segment concentration.

The hard segment type also has been shown to affect the mechanical behavior of polyurethanes. Hard segments with crystallinity or higher cohesiveness usually increase the mechanical properties of the material. For instance, crystalline hard segments based on MDI are used in RIM processes for production of stiff structural materials, while polyurethanes with amorphous TDI based hard segments are generally only useful in soft foam applications. Polyurethanes with urea hard segments usually have properties superior to those from urethane hard segments of similar composition (an oxygen is replaced by N-H). The more polar nature of the urea leads to more stable and well defined hard domains, resulting in enhancement of the properties.

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C H A P T E R I I
STRUCTURE-PROPERTY RELATIONSHIPS IN POLYBUTADIENE
CONTAINING POLYURETHANES

INTRODUCTION

The existence of phase segregation, caused by the clustering of hard and soft segments into separate microdomains, has been well documented for block copolymers and segmented polyurethanes.¹ Therefore physical and mechanical properties are interpreted on the basis of a two phase model. Most polyurethane studies are complicated by one or more of the following effects: (1) specific interactions between phases via hydrogen bonding, (2) crystallinity in either phase, and (3) the presence of chemical crosslinking. All three effects may influence the nature and extent of phase segregation.

These complications were avoided by using a hydroxy terminated polybutadiene (HTPBD) with exact difunctionality and a hard segment consisting of 2,4 toluene diisocyanate (TDI) and butanediol (BDO). The nonpolar soft segment precludes hydrogen bonding between hard and soft segments and its high vinyl content (55%) prevents crystallization. The asymmetric TDI prevents crystallization in the hard segment.² There is a large difference in solubility parameters between the hard and soft segments; $\delta = 8.2 \text{ (cal/cm}^3)^{1/2}$ for polybutadiene and $\delta = 12.2 \text{ (cal/cm}^3)^{1/2}$ for TDI/BDO hard segments.⁴ Therefore, a high degree of phase segregation would be expected for this polyurethane.

The polyurethanes described above were previously synthesized in

this laboratory via a two step bulk polymerization method.⁵ The HTPBD was first end-capped with TDI, followed by BDO addition. The reactants were mixed and then poured into a mold for complete curing. A 5% excess of TDI was used in all cases. As expected, highly phase segregated materials were obtained. Thus, the soft segment T_g was invariant with hard segment content and very close to that of the free HTPBD. The hard segment T_g behavior proved to be unexpectedly complicated. Two hard segment T_g 's were detected in some samples instead of a single transition. The same phenomenon has been observed in other HTPBD based polyurethanes.^{6,7} It was suggested that the two T_g 's correspond to domains of different hard segment lengths. However, it remained unclear why the hard segments would segregate into separate domains based on hard segment length.

To better understand this behavior, Xu et al.⁸ have performed fractionation studies to obtain sol-gel fractions from these samples in DMF at 70°C. The samples were completely soluble in DMF only above 85°C, possibly because of the cleavage of allophonate crosslinks that have been detected in these samples (experimental evidence to be presented later). For all samples studied, the gel fraction had a hard segment content and length, calculated from IR measurements, which was of constant value, independent of the original composition and correspondingly a single hard segment T_g . Hard segment content, length, and T_g of the sol fractions varied systematically with the original sample composition. The results suggest that a bimodal distribution of hard segment lengths occurs in these copolymers. Chen et al.⁹ followed

the bulk polymerization of these materials by optical microscopy. The reactant mixture was placed between glass slides, kept at the reaction temperature, and observed under partially crossed polars (70°).

Domains, thought to be BDO rich regions, were present at the beginning and throughout the reaction. Therefore, the final composition was thought to be controlled by the diffusion rates of the reactants between domains and by the reaction rates of the species. A model based on the observed phase separation and on the diffusion of reactants was presented to explain the formation of a bimodal distribution of hard segment lengths.

Phase separation has also been found to occur at low conversion in other polyurethane bulk polymerizations.^{10,11} Camargo et al.¹⁰ found that phase separation occurs at a short characteristic hard segment length in uncatalyzed RIM polyurethane systems. His data for the hard segment length at phase separation are in agreement with the DSC data of Hager et al.¹¹

Products formed by this bulk polymerization are generally opaque and exhibit poor mechanical properties. Molecular weights are below 10,000 and $\bar{M}_w/\bar{M}_n = 3 - 7$.¹² Furthermore, they contain allophanates, the formation of which is facilitated by the high reaction temperature and the use of an excess amount of isocyanate. To avoid the premature phase separation which occurs in the bulk reaction and the resulting poor mechanical properties, it is desirable to carry out the reaction in solution. This should allow for a homogeneous reaction mixture. Additionally, allophanate formation should be suppressed since

stoichiometry is maintained and the reaction temperature used is lower than in the bulk polymerization. The present study focuses on the solution synthesis and properties of a series of HTPBD polyurethanes. The results of DSC, dynamic mechanical, and tensile measurements on these polymers are reported.

EXPERIMENTAL SECTION

Materials

HTPBD of molecular weight 2200 was kindly supplied by the Japanese Synthetic Rubber Co. It has a functionality of 1.97 and a microstructure consisting of 55% vinyl, 35% cis and 10% trans double bonds as reported previously.⁵ 2,4-TDI (ICN: containing 5-10% 2,6 isomer) and BDO (Aldrich) were vacuum distilled, stored under N₂ and used within two months. Tetrahydrofuran (THF), HPLC grade, was refluxed overnight in the presence of isocyanate and distilled immediately prior to use. Dibutyl tin dilaurate (DBTDL) (Alfa) was used as received.

2 to 7 grams HTPBD was dissolved in 50 ml CHCl₃ in a 200 ml round bottom flask equipped with a magnetic stirrer and nitrogen inlet and outlet. The CHCl₃ was distilled off to remove any adventitious water in the azeotrope. 100 ml THF and 2 drops DBTDL catalyst were added and the solution was brought to reflux. The desired stoichiometric amount of TDI was added followed by 1 hour of reaction to endcap the HTPBD. The amount of BDO added was calculated to reach a final isocyanate/hydroxyl ratio of 1. It was added stepwise over 2-3 hours followed by 1 1/2 hrs. of reaction. The total concentration was about 10% and the solution

remained clear throughout the reaction. The polymer was precipitated and washed in distilled water and dried in vacuum for 24 hrs. at 70°C. Yields were generally better than 90%.

Measurements

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC-II equipped with a data station or chart recorder. A heating rate of 20°/min. and a sensitivity of 2 or 5 mcal/sec were used. Samples of approximately 15 mg were prepared by compression molding at 120°C for 15 min. The glass transition temperature (T_g) was taken as the mid-point of the step increase in heat capacity and values reported are averages of at least 3 scans. ΔC_p data were obtained using a TADS data station interfaced with the DSC. These data are averages of 5 separate runs.

Dynamic mechanical measurements were performed with a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA). The temperature range of -90 - 130°C was scanned at 5°/min. at 1 Hz. A double cantilever bending geometry was used. Samples 1.5 mm thick were compression molded at 150°C for 30 min.

Stress-strain data were obtained on an Instron universal testing machine at an extension rate of 1 cm/min. using a gauge length of 2.5 cm. Rectangular samples 3 mm wide were cut from 0.5 mm thick films compression molded at 120°C for 30 min. Results are averages of at least 5 different samples. Samples used in hysteresis studies are 5 mm wide strips cut from films of thickness between 0.2 and 0.4 mm.

Hysteresis results are determined at the same strain rate as before. Samples were allowed to relax for one minute at zero load between extensions. Percent hysteresis is defined as the area bounded by the loading - unloading curve divided by the area under the loading curve. These areas were measured using a planimeter.

Solvent extraction studies of the bulk polymerized urethanes were carried out by immersing two gram samples in 50 ml DMSO. Samples were extracted for two weeks twice and dried for three days at 60°C under vacuum. The soluble portion was precipitated into H₂O and analyzed by IR and NMR.

A test for the presence of allophonate groups was performed as follows: 0.75 g of bulk sample was stirred in 40 ml DMSO for one day without dissolution, 6 ml dibutylamine was added, 4 ml DMF was added to coalesce the two layers formed, and the mixture was stirred overnight. The clear solution that formed is indicative of the destruction of allophonate cross-links.¹³

RESULTS AND DISCUSSION

Bulk Studies

Further evidence for the blend nature of the bulk polymerized urethanes is provided by the extraction study. Brunette's samples, JSR-10, 55 wt % hard segment and JSR 8, 49 wt % hard segment, had weight losses of 53% and 44% respectively. The soluble portion of JSR-10 had a molecular weight of 2,600 as determined by GPC. This molecular weight corresponds to a hard segment \overline{DP}_m of 9 which is also the expected hard

segment length for this supposed copolymer. The infrared and NMR spectra of this material are identical to those for pure hard segment homopolymer with no peaks representative of the unsaturated soft segment. This contrasts with a higher temperature extraction with DMF done by Xu et al.⁸ where unsaturated soft segment is included in the extracted material. The percent weight loss is very close to the amount of hard segment in the original sample. The model of Chen et al.⁹ provides for an explanation of these data as BDO and TDI rich regions of the reaction mixture allow for the formation of low molecular weight hard segment that cannot couple with the soft segment because of low diffusion rates between reaction phases.

Reaction of JSR-6, 42 wt % hard segment, with an amine in the presence of DMSO produces a soluble polymer due to the destruction of allophonate cross-links. The solubility must result from the presence of the amine as JSR-6 is insoluble in DMSO and DMF at ambient temperature. These materials are soluble in DMF above 85°C probably due to a similar degradation of allophonates catalyzed by DMF as they are insoluble in DMSO at equivalent temperatures. DMSO and DMF have essentially the same solubility parameter, $\delta = 12.0$ and 12.1 respectively, so the difference in solubility must arise from the structure of DMF.

Hard Segment Studies

The effect of water absorption on the hard segment was studied. A compression molded film of hard segment homopolymer (GPC MW = 60,000)

was soaked in water for three weeks. Samples were analyzed by DSC to determine T_g and by TGS to determine the amount of water absorbed. From the weight loss between 100 and 200°C, the sample was calculated to be 3.2% water with the rest being hard segment. A similar sample had a T_g of 331 K (56°C) on runs that were quenched from 380 K (110°C) and T_g of 378 (105°C) after being held at 440 K (170°C) for 15 minutes. Hard segment films that have been allowed to absorb H_2O from the atmosphere foam at about 140°C during DMTA experiments so 15 minutes at 170°C should remove any water in the system. TGS curves show insignificant weight loss above 170°C until degradation starts at 300°C.

The Fox equation was used to determine a value for T_g of H_2O in these systems.¹⁴ A value of 70 K was obtained.

$$\frac{1}{T_g} = \frac{W_{H_2O}}{T_{gH_2O}} + \frac{W_{HS}}{T_{gHS}}$$

This is quite a bit (60°) lower than a value in the literature calculated directly¹⁵ or from mixtures of water and alcohols.¹⁶ Perhaps this is because the hard segment has stronger hydrogen bond acceptors, carbonyl groups, as well as donors. A sample that had been stored at ambient humidity had a T_g of 353 K (80°C) which, using the calculated T_{gH_2O} , corresponds to 1.8% water. This calculated value is in reasonable agreement with the 2% H_2O determined by TGS for a similar sample. This value will also be used later to calculate the T_g of scrupulously dried copolymer samples.

Another question of interest is whether or not different hard

segment lengths are compatible. Fu has shown that short sequences of the hard segment, $\overline{DP}_n < 6$, are compatible. To extend this study, a film of a 50:50 blend of hard segment polymer ($M_n = 60,000$) and a monodisperse hydroxyl terminated hard segment (3B, 3,BDO/2,TDI, $M_n = 620^{17}$) was prepared from THF solution. The film was extensively dried and kept in a desicator. A single T_g of 320 K (47°C) was found. This is indicative of a single phase. The value of T_g was significantly below that of 345 K (72°C) calculated with the Fox equation using T_{g3B} of 318 K (45°C) (experimental value). Calculation of T_{g3B} from the Fox equation, leaving T_{g3B} as the unknown, gives a value of 277 K (4°C). This is close to the T_g of an aceto-terminated 3B (rather than OH terminated) of 281 K (8°C). Perhaps the OH groups plasticize the polymer. This would explain the large decrease of T_g when H_2O is absorbed in the hard segment.

Polymer Characterization

The appearance of samples obtained from this solution polymerization differs from that of the bulk polymerized samples. Whereas the latter are generally yellow and opaque, the solution polymerized samples are white and produce clear films when compression molded. Solution polymerized samples are completely soluble in THF at room temperature in contrast to the low temperature insolubility of the bulk polymerized samples. The complete solubility is taken as evidence for the expected absence of allophonate crosslinks due to the low reaction temperature (68°C) and the use of exact stoichiometric amounts of reactants as well

as the homogeneous reaction conditions.

Table 2-1 presents the compositions and some characteristic properties of the samples studied. The molar ratios of reactants, HTPBD:TDI:BDO, is completely described by 1:N:(N-1) and only the value of N need be specified. Therefore, the product designation, JSR-104 indicates a material with a mole ratio of TDI to soft segment of (N) of 10.4. Molecular weights were determined from GPC data using a calibration curve for polystyrene. The general validity of this calibration for these copolymers will be discussed in Chapter IV. \overline{DP}_m is the average number of hard segments per copolymer molecule. The \overline{M}_n of the solution polymerized samples are generally an order of magnitude greater than the \overline{M}_n of the corresponding bulk polymerized samples. The poly-dispersity index ($\overline{M}_w/\overline{M}_n$) of the solution polymerized samples is about 2, which is the expected value for step growth polymerizations, while the indexes for the bulk polymerized samples range from 3 to 7. The final column gives information about the general physical appearance and the mechanical nature of these samples.

The two step solution polymerization is a procedure for which Peebles¹⁴ has devised a method to calculate the average hard block length and hence the average molecular weight of the hard blocks. The values thus calculated are included in Table 2-2.

DSC

DSC traces of some samples are presented in Figure 2-1. Single hard and soft segment T_g 's were observed for these samples confirming the two

Table 2-1
Sample Characterization of JSR Polyurethanes

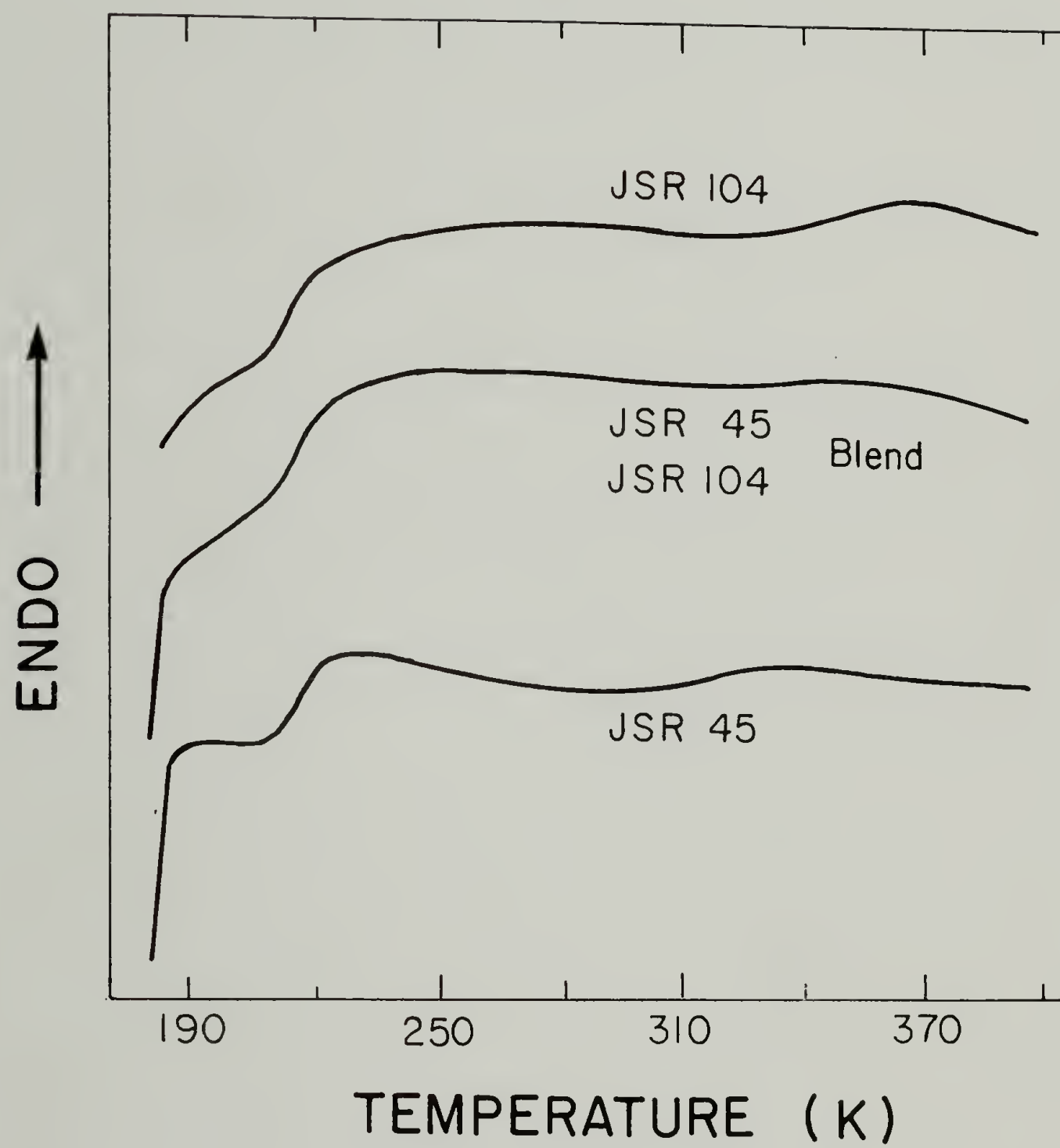
Sample	Weight Percent Hard Segment	\bar{M}_n	\bar{DP}_n	Properties
JSR-10	9	11,000	5	Viscous liquid
JSR-23	20	28,000	10	Clear, soft, very tacky rubber
JSR-33	27	23,000	10	Clear, tacky soft rubber
JSR-45	34	41,000	13	Clear, tough rubber
JSR-58	41	24,000	6	Clear, tough rubber
JSR-68	44	60,000	15	Clear, tough rubber
JSR-87	51	35,000	8	Clear, rubbery, tough
JSR-104	56	28,000	6	Clear, rubbery, tough
JSR-253	76	18,000	2	Clear, rigid

Table 2-2

Thermal Properties

Sample	Hard Segment M_n	T _g			
		Hard Segment		Soft Segment	
		DSC	DMTA	DSC	DMTA
HTPBD	0	--	---	-65	----
JSR-10	174	--	---	-58	----
JSR-23	440	--	---	-59	-32
JSR-33	781	25	55	-60	-32
JSR-45	1,098	48	65	-60	-30
JSR-58	1,440	48	68	-60	-32
JSR-68	1,795	63	99	-60	-31
JSR-87	2,207	63	91	-60	-32
JSR-104	2,656	73	99	-60	-32
JSR-253	6,576	76	103	-62	-32
Hard Segment Homopolymer	60,000	80	100	---	----

Figure 2-1 DSC traces for JSR polyurethanes.



phase nature of this system. A summary of the DSC transition temperature for the copolymers, HTPBD, and hard segment homopolymer is presented in Table 2-2 and thermal data are plotted in Figure 2-2. The soft segment T_g is independent of hard segment content and thermal history as in the bulk polymerized samples. The T_g of $-63^\circ\text{C} \pm 2^\circ$ is only 5° above that of the free HTPBD. Camberlin and Pascault¹⁹ have calculated that an increase in T_g of 4.2° of the soft segment above the corresponding homopolymer T_g corresponds to complete phase segregation. Greater differences in the T_g 's correspond to increasing amounts of phase mixing. Our results indicate that phase segregation, in these samples, is complete or very nearly so.

In contrast to the bulk polymerized samples, single hard segment T_g 's were observed in all samples. The T_g 's have been plotted versus the inverse of the hard block molecular weights (from Table 2-2) in Figure 2-3. The solid line corresponds to the experimental data and the dashed line to the calculated values of T_g using the Fox equation and W_{H_2O} and T_{gH_2O} calculated earlier. These calculated values agreed within 4° with experimentally determined T_g 's of scrupulously dried samples. The straight line is described by a relationship analogous to the Fox-Flory relationship:²⁰

$$T_g = T_g^\infty - K/\bar{M}_n \quad (1)$$

where T_g^∞ is the T_g of a hard segment block of infinite molecular weight. The experimental value of the constant is 4.6×10^4 , which is

Figure 2-2 Thermal properties of JSR polyurethanes as a function of hard segment content.

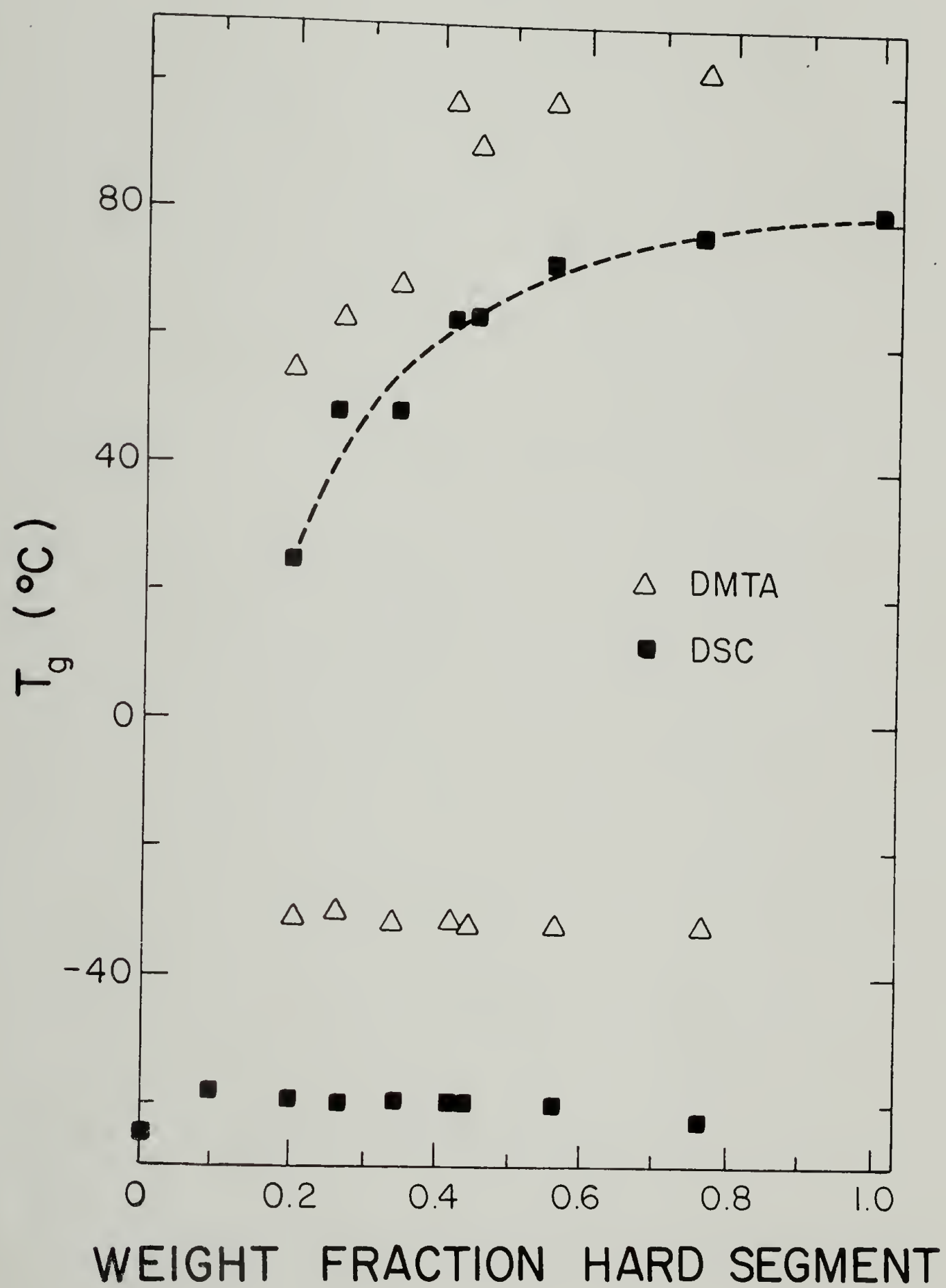
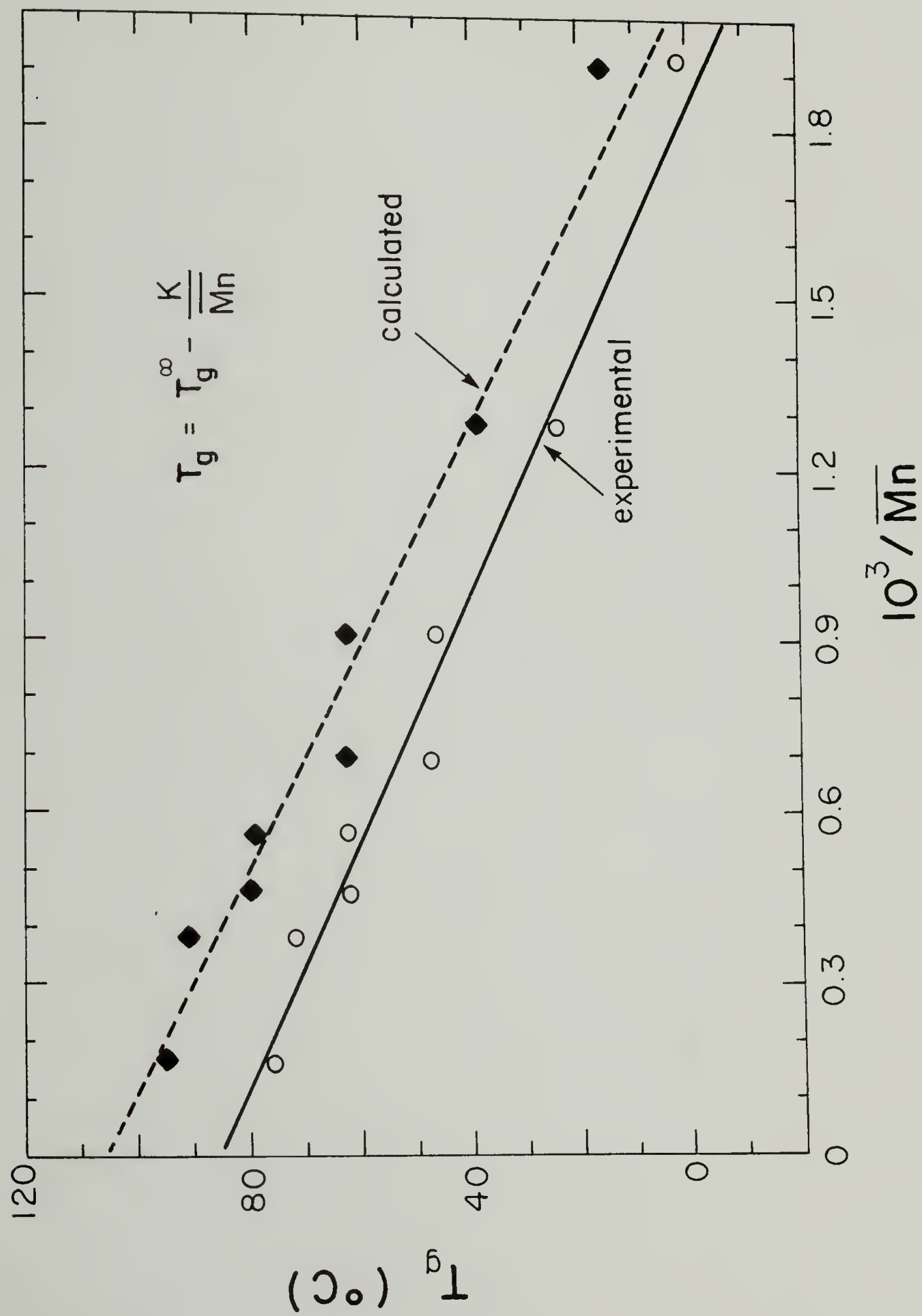


Figure 2-3 Fox-Flory relationship of the hard segment T_g 's.



in the range expected for stiff polar polymers.²¹ A linear relationship between T_g and inverse number average molecular weight of the hard segment has not been observed in other TDI/BDO polyurethane systems,²² but has been observed in a variety of diblock and triblock copolymers.²³ The Fox-Flory theory takes into account the differences of the free volumes of the chain ends and inner chain units. In our system chain ends may be neglected but a significant difference in the free volumes of inner block units and block ends is expected since this relationship holds. The HTPBD blocks attached to the ends of each hard segment block are highly mobile at these temperatures and exert little restraint on the hard block ends. Therefore, the hard block ends may behave as free chain ends.

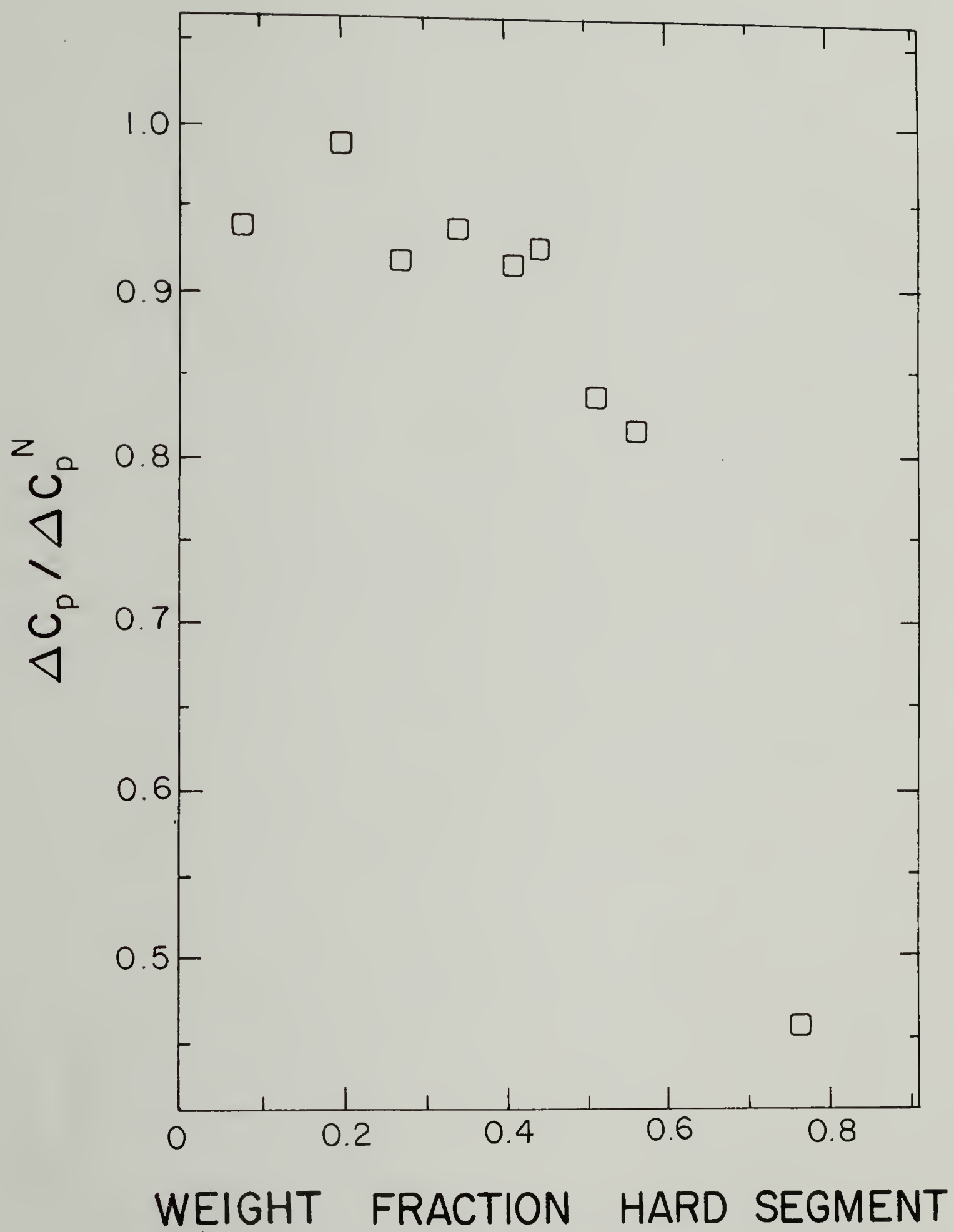
The calculated curve in Figure 2-3 is approached asymptotically at higher \bar{M}_n by a curve constructed by Fu¹⁷ for monodisperse 2,4-TDI/BDO oligomers. This difference is possibly a result of the chemical nature of the hard block endgroups. The oligomers cited here have hydroxyl endgroups which may well be associated through hydrogen bonding, thereby restricting the endgroup motion and raising their T_g 's. This effect would be proportional to the concentration of hydroxyls so that it would become negligible at higher molecular weights. A similar line constructed from Fu's data for JSR polyurethanes containing monodisperse 2,4-TDI/BDO hard segments gives T_g^∞ of 101°C and $K = 67,000$. The T_g 's of nonhydroxyl terminated oligomers also fall on this line. The agreement of T_g^∞ with that of the homopolymer is good but the value of K is increased by about 40%. Reasons for this increase are unclear as

both series are essentially completely phase segregated and the domain interfaces should be similar. The behavior of the Fox-Flory curve should be the same for mono- or polydisperse substances with equivalent number average molecular weights.

Some bulk polymerized samples displayed two hard segment T_g 's. To determine if these arise due to incompatibility of hard segments of different lengths a blend of JSR-45 (hard segment $M_n = 1098$) and JSR-104 (hard segment $M_n = 2656$) was prepared from solution and analyzed by DSC. Equal amounts by weight JSR-45 and JSR-104 were dissolved in THF and a film was cast. The DSC trace is included in Figure 2-1. As can be seen, the blend has a single T_g intermediate between that of the two constituents. This, combined with the earlier hard segment blend studies, indicates that different hard segment lengths are compatible. Therefore, the two T_g 's observed by Brunette et al.⁵ must arise from separate domains formed because of the heterogeneous nature of the bulk polymerization.

Camberlin and Pascault¹⁹ have measured the degree of phase segregation in segmented polyurethanes by measuring the heat capacity change ΔC_p at the glass transition of the soft segment. The heat capacity change ΔC_p is compared with the ΔC_p^N which is the normalized value (calculated as ΔC_p for the soft segment oligomer times weight fraction soft segment in the sample). The ratio $\Delta C_p / \Delta C_p^N$ corresponds to the fraction of soft segment that is in the relaxing phase and $1 - (\Delta C_p / \Delta C_p^N)$ is a measure of the fraction of soft segment incorporated in either the hard segment domains or in the interface. The results are shown in Figure 2-4.

Figure 2-4 Normalized heat capacity change for JSR
polyurethanes.



Three general values can be discerned, 0.95, 0.85, and 0.46. A decrease in $\Delta C_p / \Delta C_p^N$ can be considered to result from an increase in the degree of interconnectiveness of the hard domains.²⁴ The three levels of $\Delta C_p / \Delta C_p^N$ correspond to samples of three separate morphologies to be discussed later. As the morphology changes, differing fractions of soft segment are included in an interfacial region where chain motion and hence, relaxation is prevented. Incorporation of soft segment into hard segment domains is doubtful due to the huge incompatibility between hard and soft segments. The data points do generally fall on a curve calculated by assuming a constant density of spherical hard segment domains for all samples and assuming that $(r+\Delta r)/r$ is constant where r = radius of domain and Δr = interfacial thickness. However this model appears improbable as a lamellar type morphology is known to occur for some of these materials.

Contrary to the findings of Camberlin and Pascault¹⁹ for a similar soft segments and MDI/BDO hard segments, no effect of thermal history was found to occur. DSC results on Fu's materials¹⁷ also show a constant value of $\Delta C_p / \Delta C_p^N$ whether the sample was aged or was quenched from the melt.²⁵

The kinetic effect noted by Camberlin and Pascault may be a result of the crystalline hard segment used. The viscosity of the soft segments may still affect the rate of decrease of $\Delta C_p / \Delta C_p^N$.

DMTA

The relaxation behavior of several of the samples studied is

illustrated in Figures 2-5 and 2-6. As can be seen, the plots illustrate two relaxations corresponding to the two phases present in the material. The T_g values, determined at 1 Hz from the $\tan \delta$ peaks, are listed with the DSC results in Table 2-2. Consistent with the DSC results, the soft segment T_g of $-31^\circ\text{C} \pm 2^\circ$ is independent of hard segment content. The value for T_g obtained by DMTA is approximately 30° higher than the value obtained from DSC. The soft segment T_g is also characterized by a step decrease in the value of the storage modulus of 1 to 2 orders of magnitude.

The hard segment T_g varies systematically with increasing hard segment content. Samples of lowest hard segment content display only an increase in $\tan \delta$ with increasing temperature to the point of flow ($\tan \delta = 1.2$). Increasing the hard segment content leads first to a shoulder and finally, for JSR-253, a sharp peak. This increase of hard segment T_g is a result of increasing hard segment length as discussed for the DSC results. The T_g values, as with the soft segment T_g , are about 30°C higher than those determined by DSC.

Consistent with findings for other phase segregated systems,²⁶ the level of the plateau storage modulus above the soft segment T_g increases with increasing hard segment content. This effect can be attributed to an increase in the volume fraction of hard segment. The reinforcing nature of the hard segment domains is responsible for the increase in modulus.

A final point to note lies in the temperature dependence of $\tan \delta$ illustrated in Figure 2-6. As the hard segment content increases, the

Figure 2-5 Temperature dependence of E' and E'' for JSR
polyurethanes.

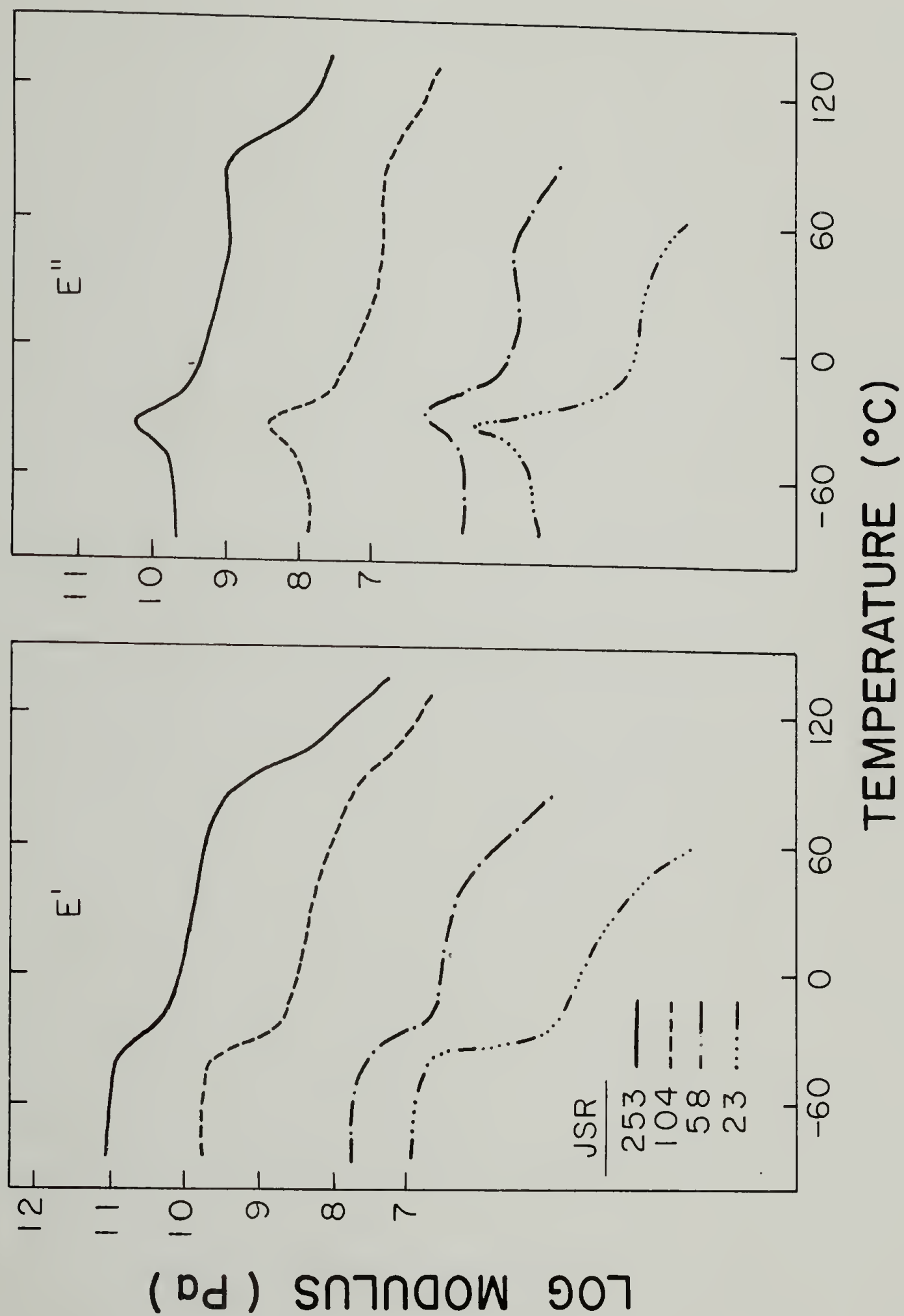
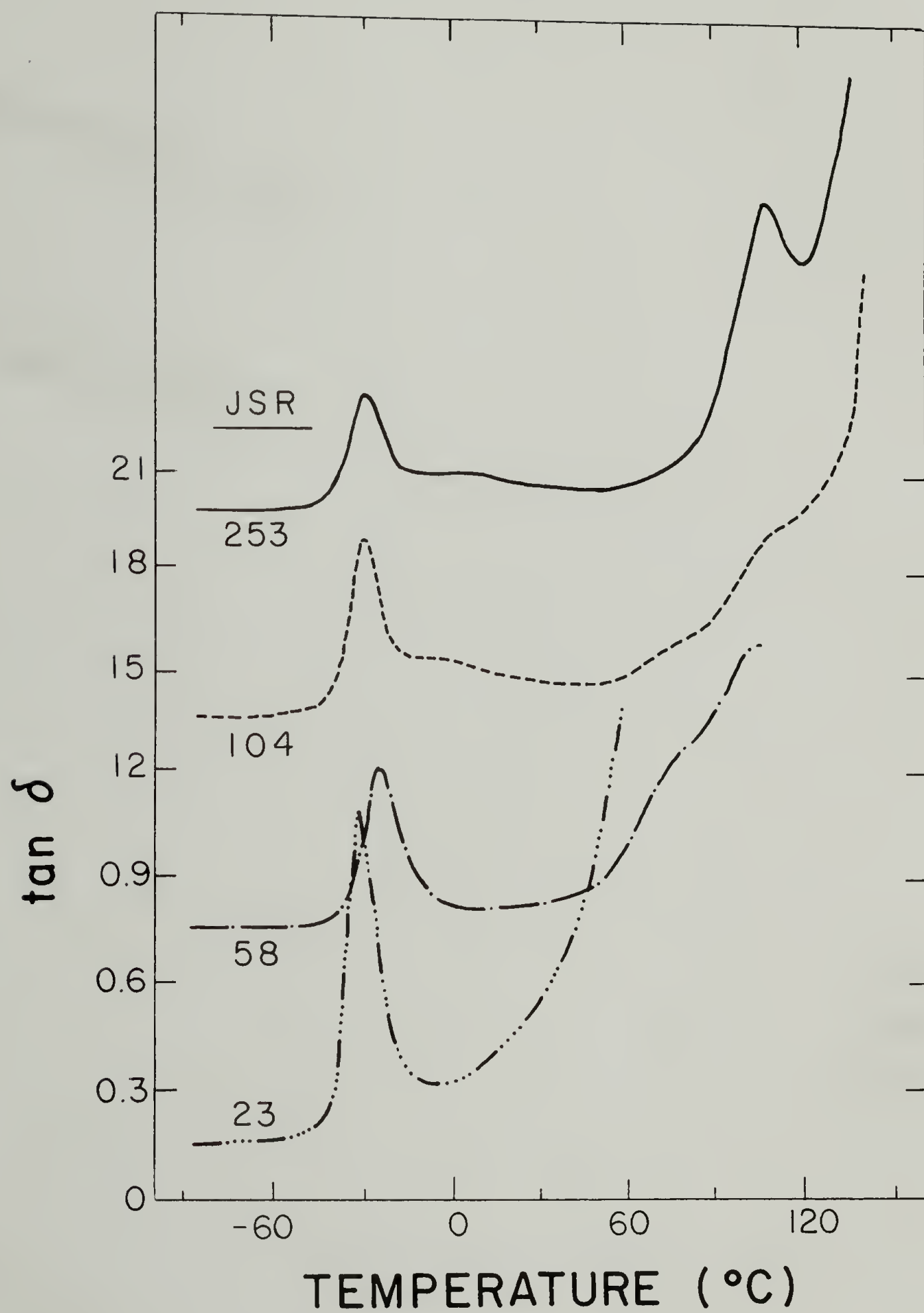


Figure 2-6 Temperature dependence of $\tan \delta$ for JSR
polyurethanes.



magnitude of the soft segment damping peak decreases while the magnitude of the hard segment shoulder or peak increases. Such changes in the damping behavior of these materials clearly reflect changes in the relative amounts of the constituent phases. The change in hard segment damping behavior between samples JSR-104 (56% hard segment) and JSR-253 (76% hard segment) suggest a change in sample morphology. JSR-253 displays a pronounced $\tan \delta$ peak of magnitude close to that of the soft segment damping peak of the lowest hard segment content sample, while JSR-104 displays only a shoulder. The plateau modulus of JSR-253 is also significantly higher than that of JSR-104 (about 0.6 order of magnitude). Given the relative volume or weight fraction hard segment of these samples, a difference in morphology would not be unexpected. Further evidence for a morphological change is presented and discussed later.

Unlike the behavior of other polyurethanes,²⁷ yet consistent with the results for other HTPBD polyurethanes,^{5-7,28} the dynamic mechanical properties of these materials are unaffected by thermal history. Samples were quenched from 130°C to -80°C and immediately retested and were also stored at room temperature for a month prior to retesting. The values for the various viscoelastic functions are essentially unchanged. This invariance of properties suggests that no thermally activated phase mixing, altering the sample morphology, occurs. The absence of thermal history effects can be attributed to the lack of urethane hydrogen bonding to the HTPBD soft segment⁵ by the hard segment N-H groups.

DMTA was performed on a bulk polymerized sample, JSR-8, and these results compare well with Brunette's Rheovibron results.⁵ Tan δ peaks at 83 and 123°C were found to be of similar magnitudes as the tan δ peaks at 56 and 91°C determined by Rheovibron. The relaxations occur at higher temperatures due to the differing heating rates and deformation geometries used but the separation of the two transitions is essentially the same. Multifrequency analyses were performed on JSR-45, JRS-104, and JSR-253 to determine the apparent activation energy of the hard segment relaxation. The value determined, 250 ± 30 kJ/mol, is in good agreement with the value of Brunette⁵ for bulk polymerized sample, 280 ± 30 kJ/mole.

A comparison of thermal and dynamic mechanical properties of these materials with the monodisperse hard segment materials of Fu¹⁷ reveal little effect of the hard segment length distribution on these properties. For instance, the soft segment Tg's (from DSC) of both series are all within 4° of -60°C and the hard segment Tg's follow similar behaviors as mentioned earlier. Dynamic mechanical spectra also show similar shapes and relaxation temperatures.

Tensile Measurements

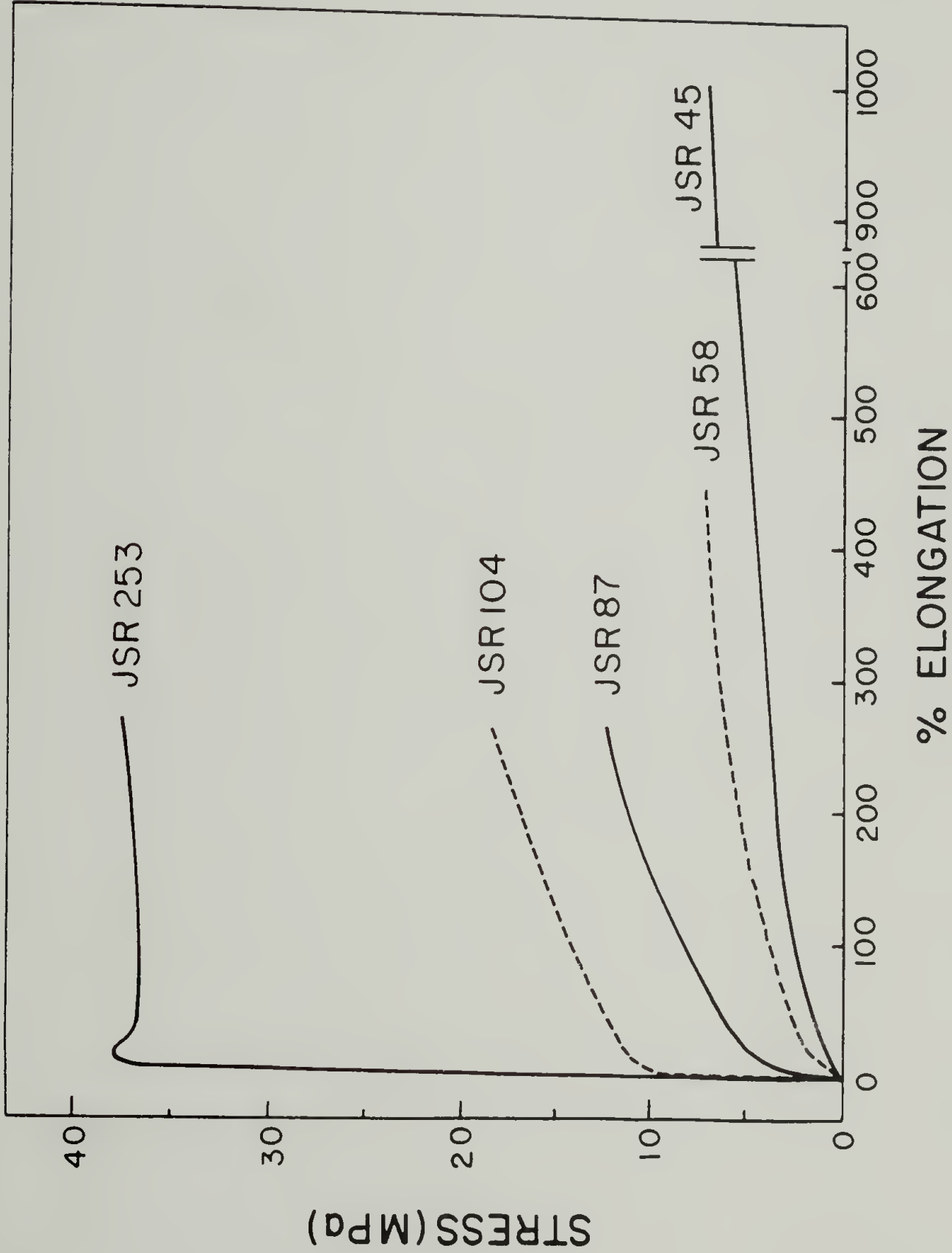
The effect of hard segment content on the stress-strain behavior of the copolymers was investigated and compared with the results of Brunette et al.⁵ for bulk polymerized samples. Results are listed in Table 2-3 and stress-strain curves are presented in Figure 2-7. Three general types of mechanical behavior are observed, depending on hard

Table 2-3

Table of Mechanical Properties

Bulk Polymerized			Solution Polymerized			Modulus MPa
Wt. fraction Hard segment	σ_B MPa	ϵ_B %	Wt. fraction Hard Segment	σ_B MPa	ϵ_B %	
0.18	2.83	1,000				
0.25	4.14	1,620	0.27	10.3	620	10
0.32	3.31	1,160	0.34	7.53	1,120	10
0.42	4.27	430	0.41	7.21	440	15
0.49	2.69	70	0.51	12.4	260	84
0.55	2.69	15	0.55	18.6	250	175
			0.76	38.6	250	450

Figure 2-7 Stress-strain behavior of JSR polyurethanes.



segment contents. Materials with hard segment contents below 45% are soft elastomers. At 76% hard segment content, they behave as a rubber toughened plastic, displaying necking and strain whitening. Intermediate compositions behave as rigid elastomers. This variation of mechanical properties is very likely caused by changes in sample morphology. When volume fractions of the two phases are similar, both phases may be continuous. The stress-strain data suggest that below 45% hard segment content the polybutadiene rubber soft segment is the continuous phase with hard segment domains acting as physical crosslinks and reinforcing filler. At 76% hard segment content, the hard segment is expected to comprise the continuous phase with domains of the elastomer toughening the material. Intermediate materials appear to be bicontinuous in nature. The deformation of bicontinuous samples proceeds in two steps: first the relatively high modulus hard segment deforms followed by the lower modulus deformation of an elastomer after the hard segment becomes discontinuous. Stress-strain curves of these materials display two greatly different slopes corresponding to the moduli of the two phases. These described morphological changes have been observed by electron microscopy²⁹ for these materials. The intermediate compositions appear to have a 'plate like' bicontinuous morphology.

Additional evidence for a morphological transition with changing composition is provided by hysteresis studies. Percent hysteresis is plotted in Figure 2-8 and the cyclic strain curves are presented in Figure 2-9. Hysteresis and permanent set in polyurethanes are thought

Figure 2-8 Percent hysteresis as a function of strain in JSR
polyurethanes.

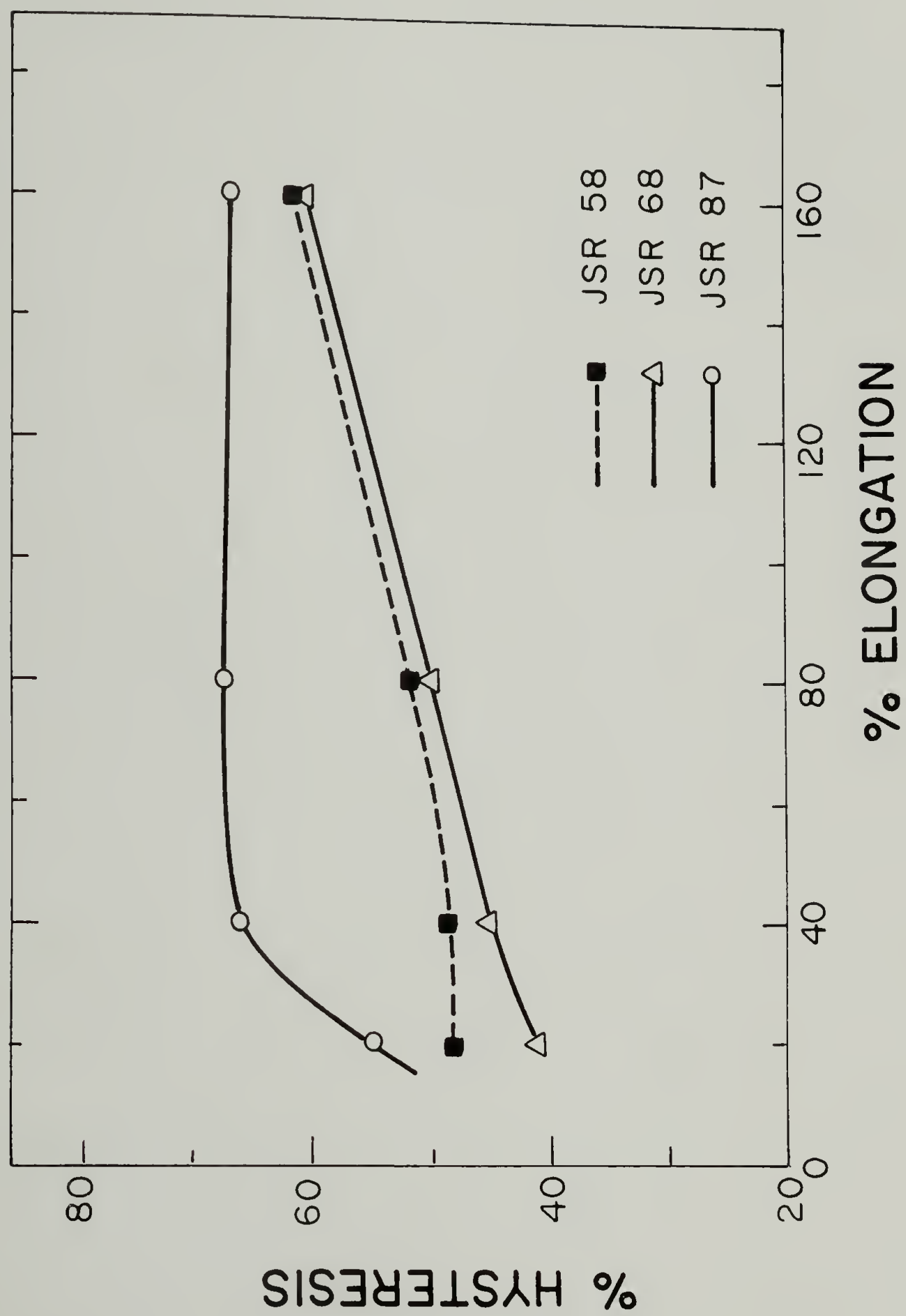
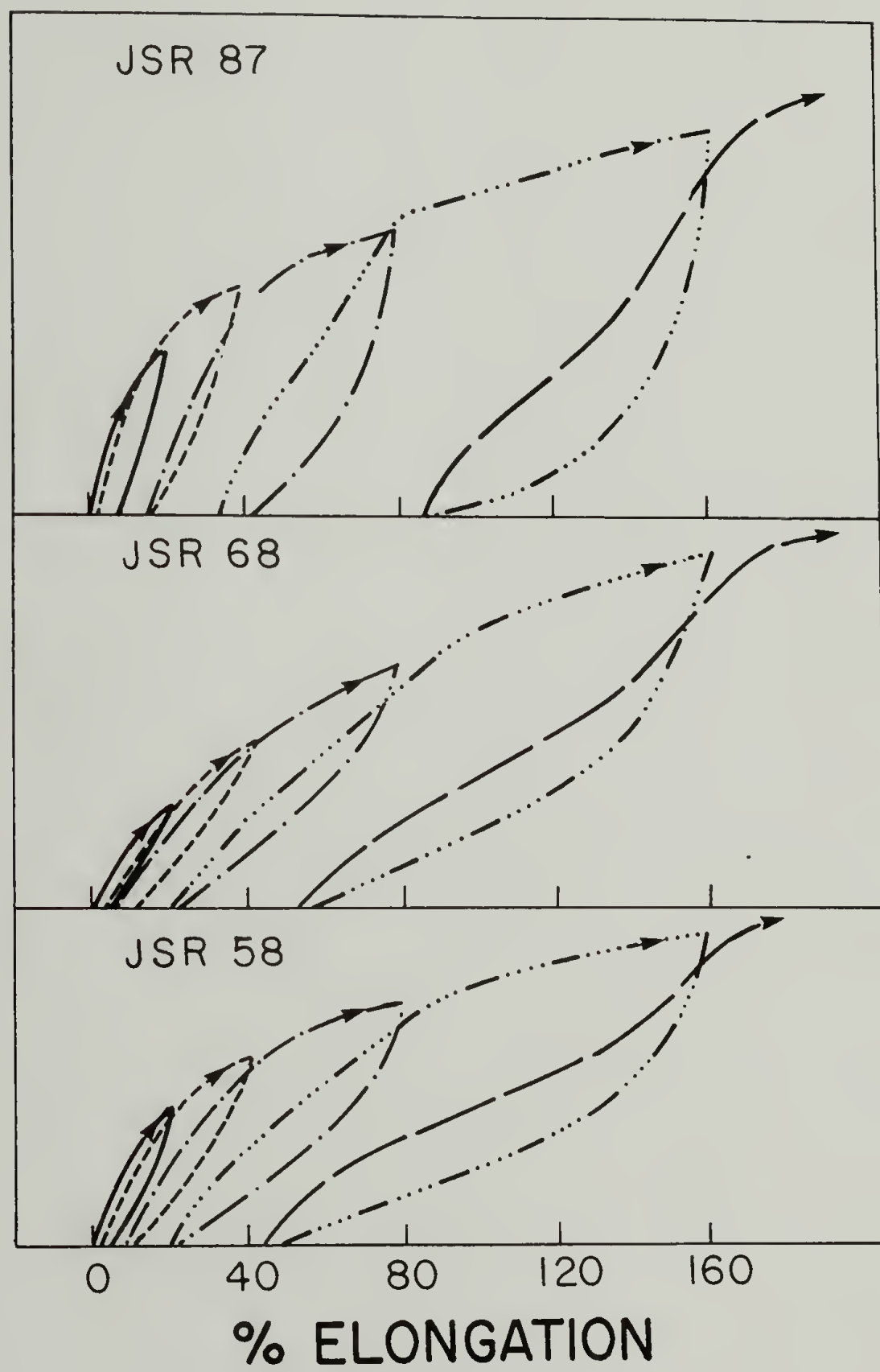


Figure 2-9 Cyclic stress-strain curves for JSR-58, JSR-68 and JSR-87.

ENGINEERING STRESS



to arise from plastic deformation of the hard domains. Original dimensions of a stretched polyurethane can be regained by heating to close to the hard segment Tg. Retraction to the original length is thought to result from 'healing' of the hard domains, restoring their original structure. The percent hysteresis has been used to help ascertain the morphology of the material, specifically as a measure of domain interconnectivity.³⁰ Non-continuous hard domains in polyurethanes should give less hysteresis than continuous or interconnected domains. The plot in Figure 2-8 shows that JSR-87 with 51% hard segments has significantly higher hysteresis than JSR-68 and JSR-58 with 45 and 42% hard segments respectively. Since the stress-strain data indicate a morphological transition between these materials, the change in percent hysteresis can be thought of as a result of the morphological transition.

Morphological changes in mechanical properties also occurred in the bulk polymerized samples.⁵ The changes in the bulk polymerized sample morphology occurred at lower hard segment contents and over a narrower range of composition than for the solution polymerized samples. Brittle low modulus plastics were obtained at hard segment contents above 45% and soft rubbers were obtained at a hard segment content below 35%.

Values for the stress and elongation at break are listed along with the values obtained for the bulk polymerized samples in Table 2-3. The same strain rate and sample cross section were used to study both series of samples. The table shows a marked difference between bulk and solution polymerized materials. The solution polymerized materials

exhibit tensile strengths which are 2 to 7 times higher than those of corresponding bulk polymerized samples and maintain high elongations at high hard segment content. These differences are the result of the different products obtained by different synthetic routes.

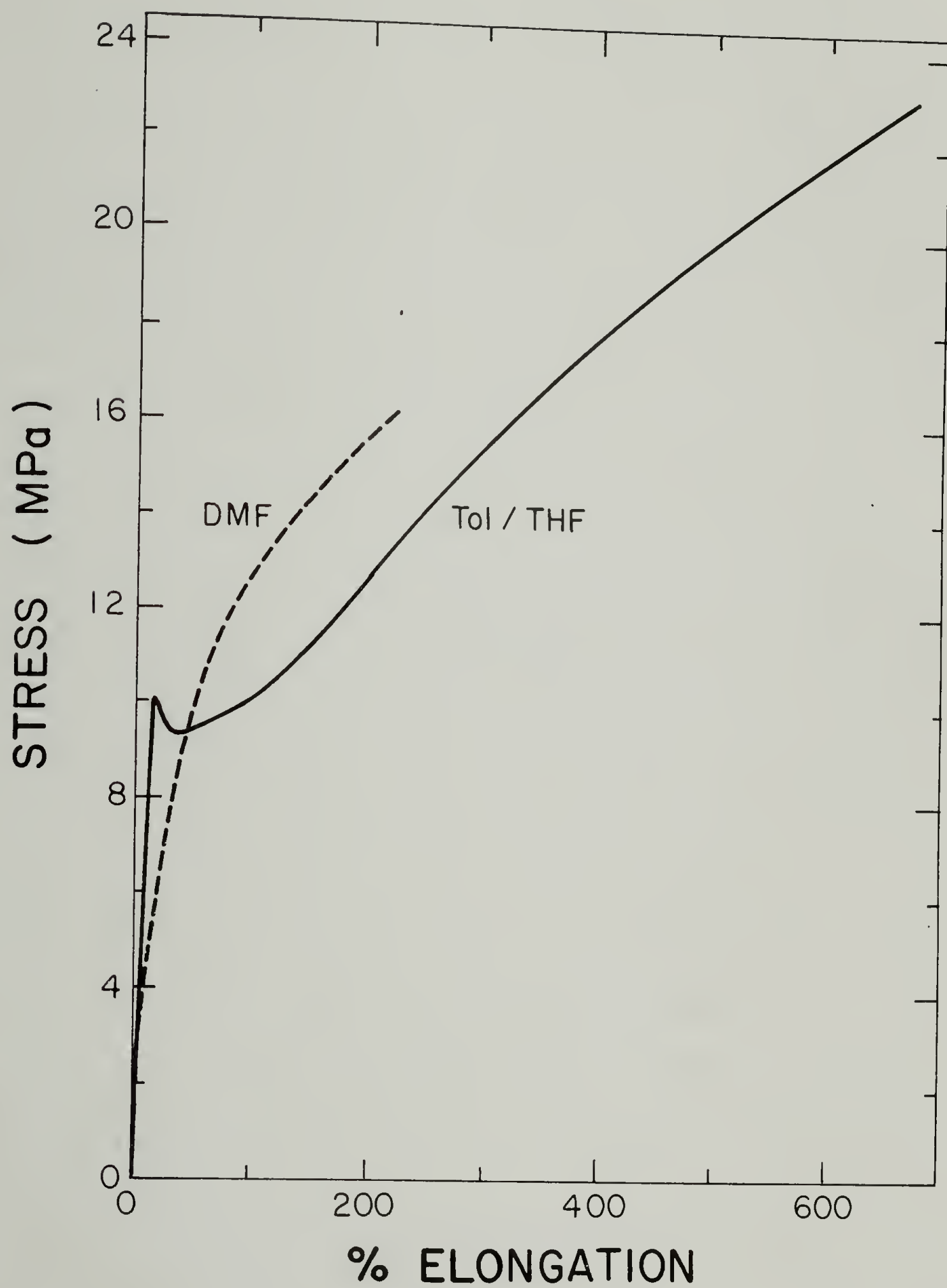
Another interesting feature of the morphology and hence, of the mechanical properties of these polyurethanes is displayed in Figure 2-10. Samples for tensile testing of JSR-87, 51% hard segments, were cast from DMF and THF/toluene (80/20) solutions and the results are shown in the figure. Sample preparation has a profound effect on the mechanical properties, as different solvents may produce different sample morphologies in block copolymers.³¹ The DMF cast sample approximates the behavior of the compression molded samples.

A final note involves the effect of the hard segment length distribution on mechanical properties of JSR containing polyurethanes. The mechanical properties of the monodisperse hard segment materials of Fu²⁰ are drastically lower than those of the polydisperse hard segment materials studied for this thesis. There are two probable reasons for this; 1) the molecular weights of Fu's materials are lower by at least a factor of two, and 2) the synthetic method used by Fu results in a significant amount of soft segment coupling, which raises the soft segment \bar{M}_n and is known to decrease polyurethane mechanical properties.³¹

CONCLUSIONS

A series of HTPBD containing polyurethanes of high molecular weight

Figure 2-10 Stress-strain behavior of JSR-87 cast from DMF and THF/toluene.



have been synthesized in solution. The value of the soft segment T_g is very close to that of the free HTPBD and independent of hard segment content indicating complete or very nearly complete phase segregation. Since the hard segments of TDI/BDO are amorphous, the driving force for phase segregation must arise from the large degree of incompatibility between the polar hard segment and nonpolar soft segment. Furthermore, in these samples there is also no opportunity for significant hydrogen bonding between hard and soft segments to enhance compatibility.

The values of the hard segment glass transition increase with the average hard segment length following a Fox-Flory type relationship. In contrast to the two hard segment T_g 's observed in bulk polymerized samples, only a single hard segment T_g occurred in the present study. This indicates that the double T_g behavior is a result of the heterogeneous nature of the bulk polymerization.

With increasing hard segment content, the properties vary from soft to rigid elastomers, and on to rubber toughened plastics. This variation in properties is caused by changes in the sample morphology which depends upon the relative fractions of hard and soft segments. Mechanical properties show marked improvement over the corresponding bulk polymerized samples. Unlike polyester and polyether urethanes, these materials evidence no change in the soft segment T_g following thermal treatment and no effect of thermal history on the mechanical properties.

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C H A P T E R I I I

STRUCTURE-PROPERTY RELATIONSHIPS IN POLYCAPROLACTONE POLYURETHANES

INTRODUCTION

Seefried et al.¹⁻⁴ have carried out systematic studies of polycaprolactone (PCL) containing polyurethanes. They varied hard segment type and content and soft segment length. Polyurethanes with MDI/BDO hard segments were found to have crystalline soft segments when the molecular weight of PCL was greater than 3000. Phase segregation was also found to increase as the PCL molecular weight increased. For polyurethanes of PCL-2000 molecular weight and TDI/BDO hard segments, T_g determined by dynamic mechanical analysis increased with increasing hard segment content. This is indicative of a compatible block copolymer. Van Bogart et al.⁵ have also compared the effects of crystalline and amorphous hard segments on the properties of PCL polyurethanes. The slightly greater compatibility of the amorphous hard segments with PCL caused an increase in the domain interfacial area. Besides hard segment crystallinity, little difference in polymer properties was found between crystalline and amorphous systems.

EXPERIMENTAL

Polycaprolactone diol was obtained from Polysciences. It had a \bar{M}_n of 2,200 and molecular weight dispersity of 1.5 as determined by GPC and a \bar{M}_n of 2060 determined by end group analysis.⁶ Pure 2,4-TDI (99+%,

Sigma) was used instead of the mixed isomer TDI used in Chapter II.

The polymerization method used was the same as in Chapter II.

Property studies were also performed as before except compression molded samples were prepared at 100°C. All DSC results were obtained by the use of the TADS system. Wide angle x-ray scattering was performed using a Statton II camera and x-rays of wavelength 1.54 Å from Copper Ka radiation. The film was placed 53.1 mm from the scattering sample.

RESULTS AND DISCUSSION

Sample Characterization

Table 3-1 lists the samples prepared, their molecular weights and qualitative physical properties. The sample nomenclature is the same as in Chapter II. Molecular weight distributions are close to 2, as for JSR materials. Materials with less than 40% hard segments are crystalline, and the higher the hard segment content the more slowly crystallization occurs. For example, PCL-50 takes about 4 days to change from a transparent material to an opaque one, while PCL-35 becomes opaque within one day of quenching. PCL-111 is a clear leathery material that slowly regains its original dimensions after stretching.

The molecular weight values obtained by GPC should have the same general validity as those for the JSR materials, since the molecular weight for the soft segment oligomer, 2200, determined by GPC agrees very well with the value determined by end group analysis, 2060.

Thermal Analysis

The thermal analysis properties for this series are summarized in

Table 3-1
PCL Polyurethane Characterization

Sample	Wt. Fraction Hard Segment	\bar{M}_n	\bar{DP}_m	Properties
PCL-32	0.25	10,000	4	Opaque, Easily torn, Leathery
PCL-34	0.28	21,000	7	Opaque, Moderately tough, Leathery
PCL-35	0.29	32,000	11	Opaque, Tough, Leathery
PCL-50	0.36	30,000	9	Opaque, Tough, Leathery
PCL-111	0.57	26,200	6	Clear, Leathery, tough
PCL-207	0.71	16,000	2	Clear, Brittle plastic
PCL-230	0.75	18,500	2.5	Clear, Brittle plastic

Tables 3-2 and 3-3. DSC curves for the initial scans are presented in Figure 3-1. Contrary to the report of Critchfield et al.³ and similar to the results of Fu,⁶ this soft segment crystallizes, as evidenced by endothermic peaks for PCL-35, PCL-34, PCL-32 and PCL-50. Combining these results with those of Fu it is safe to say that, for a copolymer of a 2000 molecular weight polycaprolactone soft segment and 2,4-TDI/BDO hard segments, the soft segment is crystalline at weight fractions of hard segments below 45%. Possible explanations for this upper limit will be discussed later. Values for the percent of polycaprolactone crystallized are included in Table 3-2. These values are computed by dividing the experimental ΔH_f by 32.21 cal/g, which is a literature value calculated for 100% crystallinity.⁷

The copolymers crystallize very slowly compared to polycaprolactone oligomers or polymers. DSC cooling traces (at 10°C/min) did not display a crystallization peak for any of the samples. It takes weeks for PCL-50 to completely crystallize. This kinetic effect may result from a lowered nucleation rate⁸ or a raised value of T_g , both of which effects should be more pronounced at higher hard segment contents. This is seen to be the case. 24 hrs after melting, PCL-50 has a ΔH_f of 0.44 compared to the long time annealed (crystallized) ΔH of 8 cal/g (i.e. 2% of the polycaprolactone is crystalline compared to 38%). For PCL-35, $\Delta H = 8.11$ cal/g after 1 day vs. 8.8 cal/g for long crystallization times (i.e. 36% vs. 39%).

From these results and Fu's, it can be inferred that there is a critical hard segment content and/or length that prevents the soft

Table 3-2
Thermal Properties of PCL Polyurethanes

Sample	T _g (°C)		T _m (°C)	ΔH _m
	Initial	Quenched		
PCL-2000	(-63) ^a	-65	50	24.1 cal/g
PCL-32	-30	-28	43	12.68
PCL-35	-6	-25	44	8.79
PCL-50	3	-16	44	7.99
PCL-111	23	18	--	--
PCL-207	41	39	--	--
PCL-230	40	46	--	--

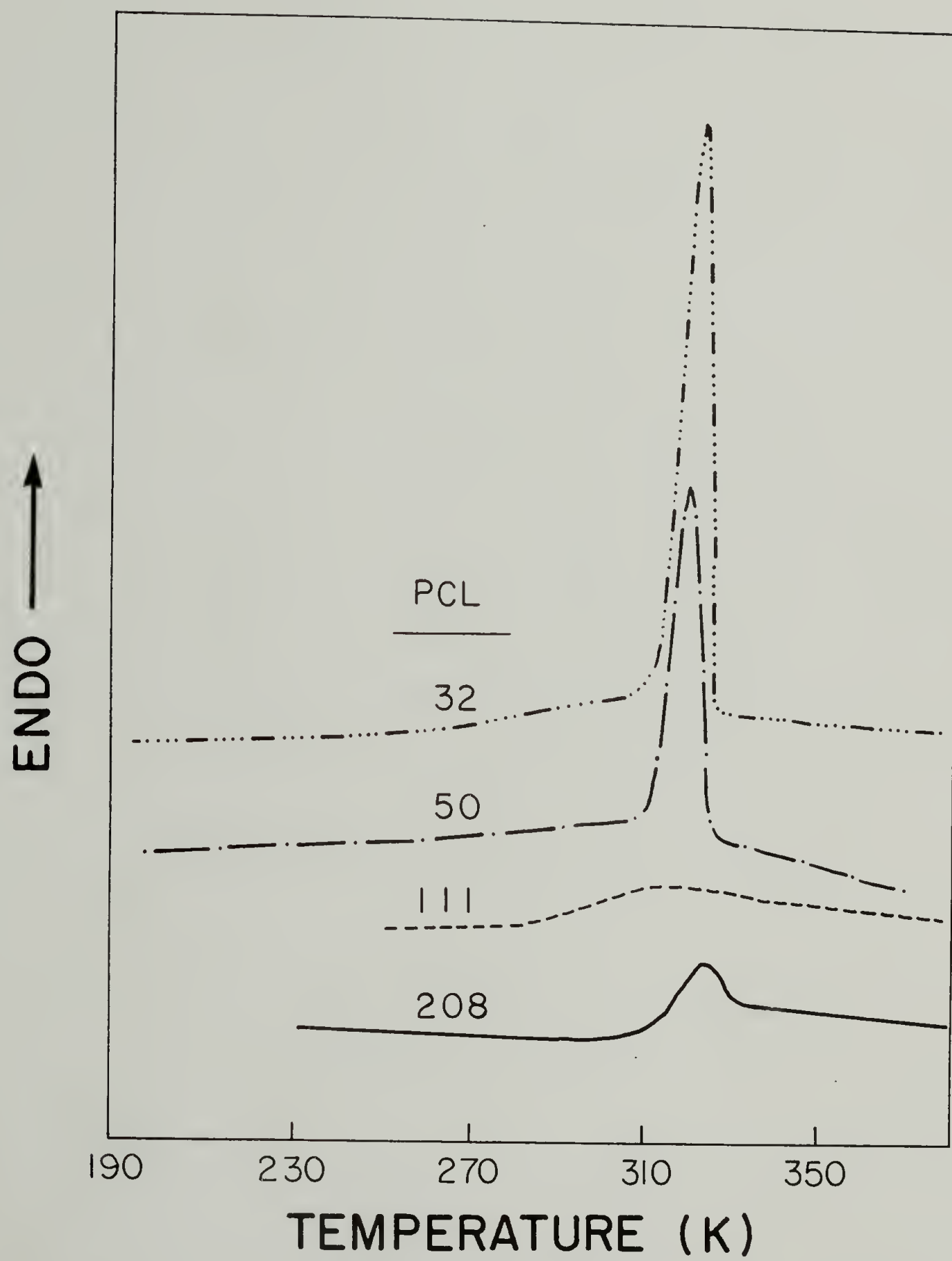
^aSmall transition.

Table 3-3

Thermal Analysis Results as a Function of Time Following
Quenching for PCL-50

Crystallization Time	T _g experimental (K)	T _g Calculated (K)	ΔH Cal/g	% PCL Crystallinity
Quenched	257	248	----	0
1 day	254		0.42	2
2.1 d	255	250	1.13	5.3
3.2 d	257		1.96	9.2
4 d	263		2.84	13
5 d	264	254	3.47	16
6 d	264		5.57	26
7 d	267		6.16	29
8 d	268		6.62	31
10 d	268	262	7.08	33
12.1 d	---		6.60	31
14 d	---		7.07	33
15.3 d	270	263	7.12	34
19.8 d	273		7.61	36
47 d	276	265	7.99	38

Figure 3-1 DSC traces for aged PCL polyurethanes.



segment from crystallizing. Judging from our data, this critical content is 44% hard segment content; below this the soft segment crystallizes. Fu found that at phase separation of two amorphous phases occurs at 48% hard segment. At 55% and above, both initial and quenched runs show essentially the same single T_g behavior. At about 50% composition, the soft and hard segments have equivalent molecular weights and perhaps this hard segment length decreases the mobility of the soft segments, thereby preventing crystallization. This high molecular weight may also provide for demixing by reducing the entropy gained on mixing to below a critical value to induce phase mixing in this system. Above 55% hard segment content, phase separation doesn't occur even after 8 months. Perhaps this can be explained by the high viscosity of the longer hard segments which will prevent demixing.

A study of percent crystallinity and T_g vs. time was conducted for PCL-50 and the results are listed in Table 3-3 and displayed in Figures 3-2 and 3-3. Values expected for T_g are included in Table 3-3 and were calculated using the percent of soft segment crystallinity and the Fox equation:⁹

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

where W_1 and W_2 are the weight fractions 1 and 2 in the relaxing phase and T_{g1} and T_{g2} are the T_g 's of the pure materials (-65°C and 105°C for polycaprolactone and 2,4-TDI/BDO hard segment respectively). The fraction of crystallized soft segment was subtracted so the calculations

Figure 3-2 Percent crystallinity vs. crystallization time for
PCL-50.

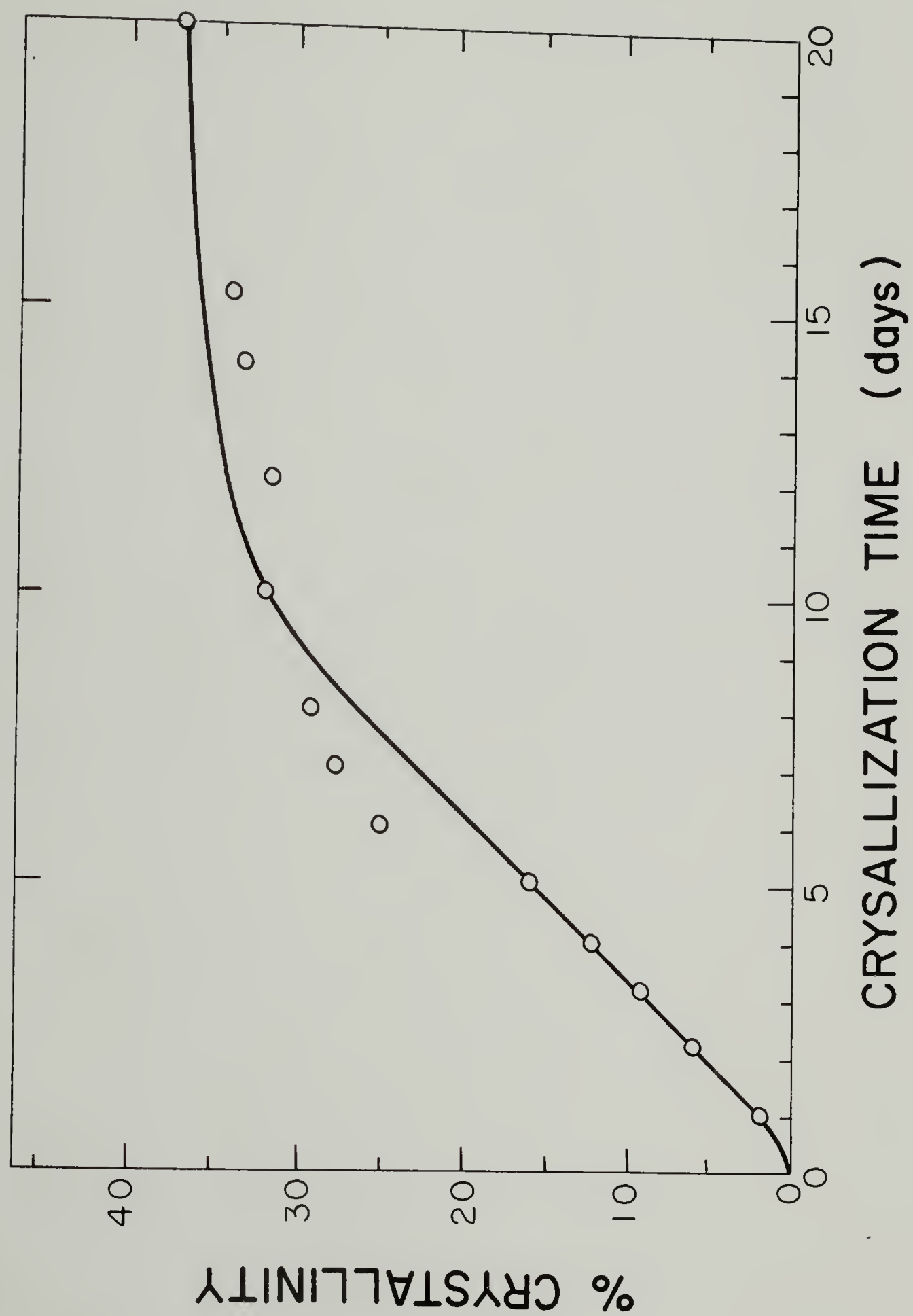
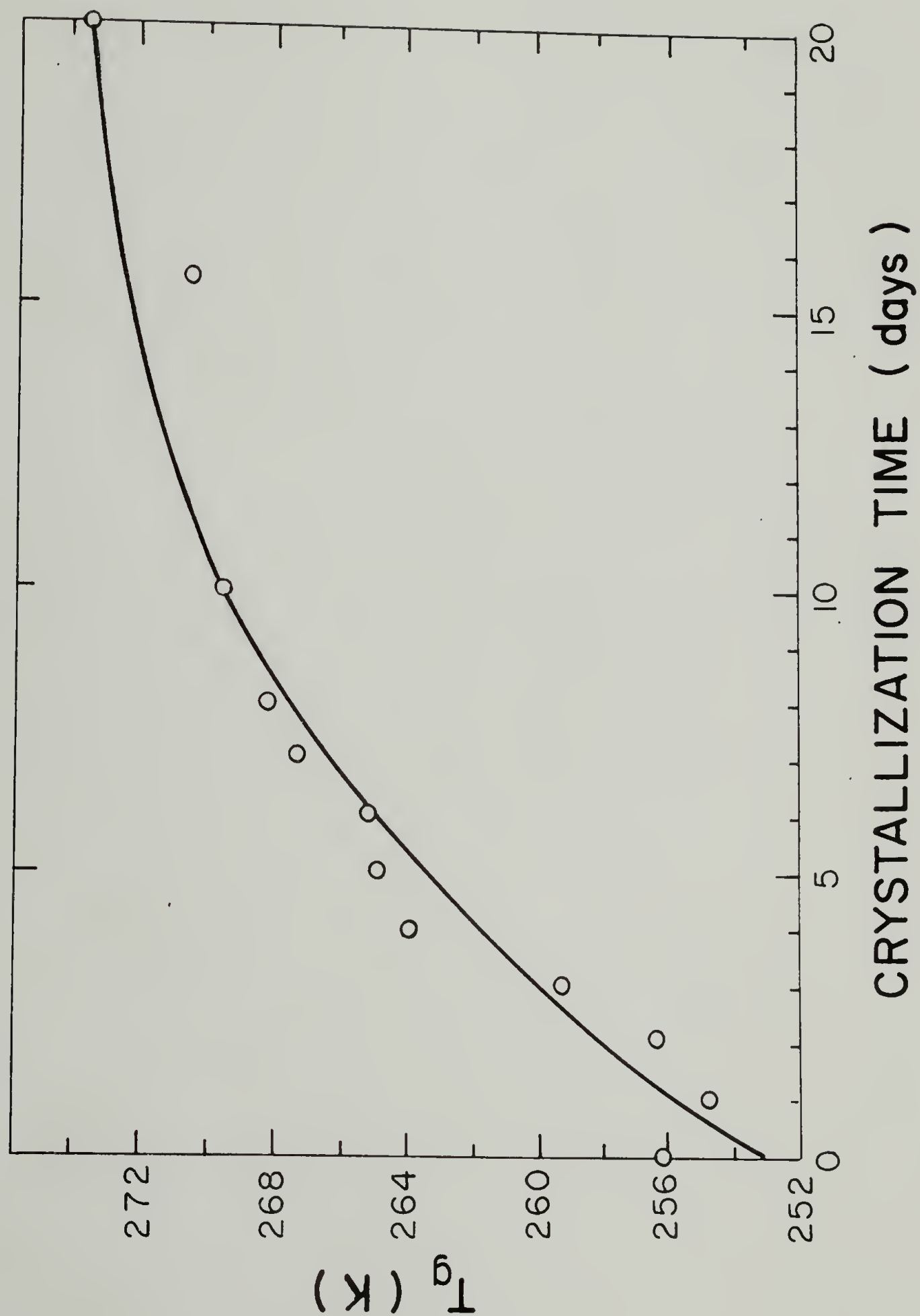


Figure 3-3 Tg vs. crystallization time for PCL-50.



strictly apply to only the amorphous phase.

A typical Avrami style S shaped % crystallization vs. time curve was obtained (Figure 3-2). The slope of the linear portion is 3.6%/day. The T_g increases monotonically with crystallization time as shown in Figure 3-3. This is to be expected, as the development of crystallinity provides physical cross-links and increases the relative fraction of the higher T_g material in the amorphous phase. The experimental values of T_g generally lie roughly 8°C above the values calculated from the Fox equation. A possible reason for this will be presented shortly.

Quenched samples exhibit only a single T_g. Figure 3-4 displays the DSC traces, and the values of T_g are contained in Table 3-2 and displayed as a function of hard segment content in Figure 3-5. T_g increases as the hard segment content increases similarly to the results of Seefried et al.³ Values of T_g calculated from the Fox equation are displayed as a solid curve in Figure 3-5. The experimental values of T_g lie slightly above this line, and significantly above the dashed line calculated from the Fox equation using the requisite T_g values of Fu's aceto-terminated hard segments of the appropriate molecular weight of the hard segment. This discrepancy can be explained by consideration of an empirical equation obtained by Schneider to describe the increase in a polyurethane polyester soft segment T_g.¹⁰ The equation calculates the effect on T_g of hydrogen bonding between the ester carbonyl and the N-H of the urethane which can act as a virtual crosslinks:

$$\frac{(T_g - T_g^0s)}{T_g^0s} = \frac{K X_c}{1-X_c}$$

Figure 3-4 DSC traces for quenched PCL polyurethanes.

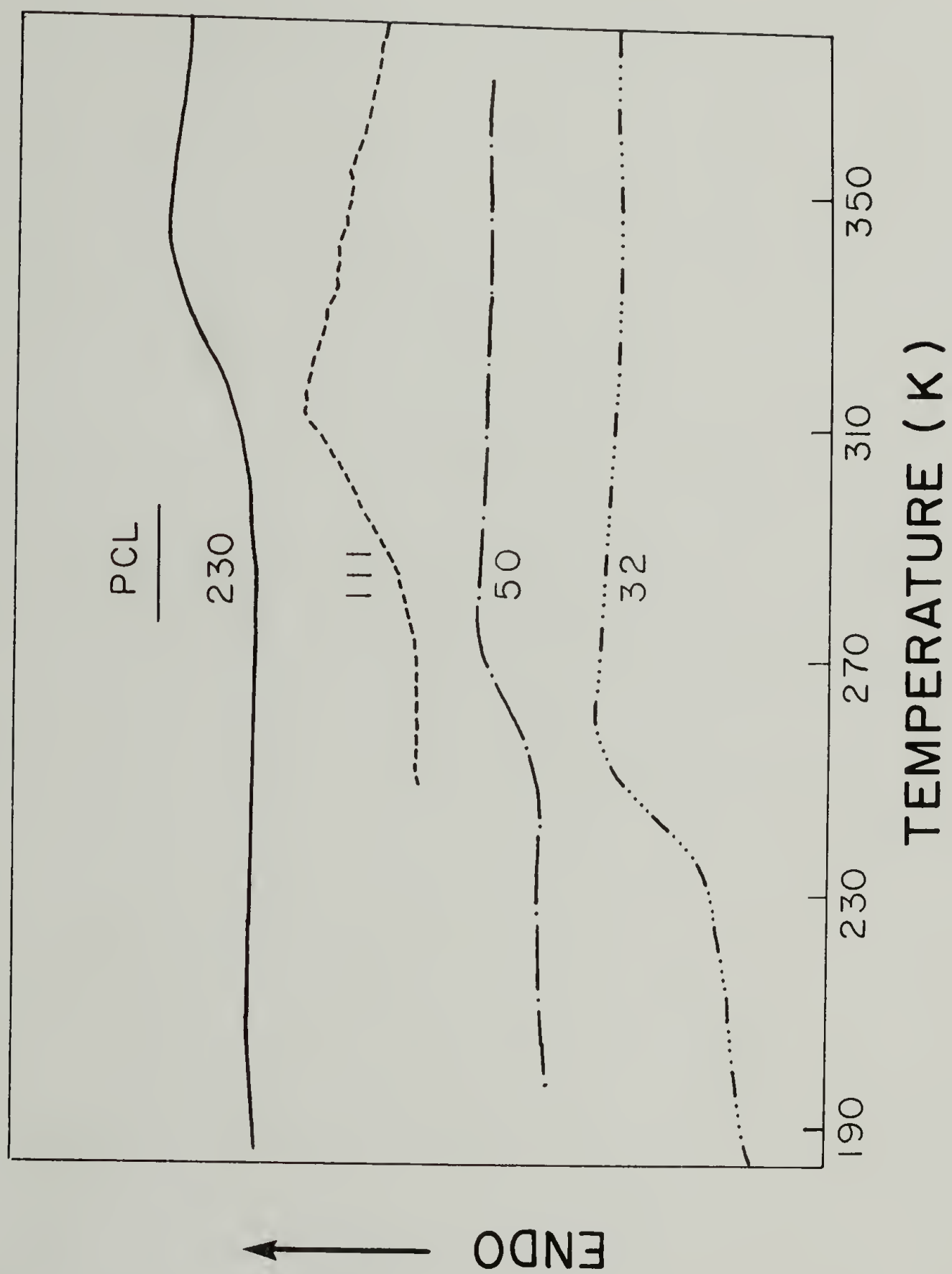
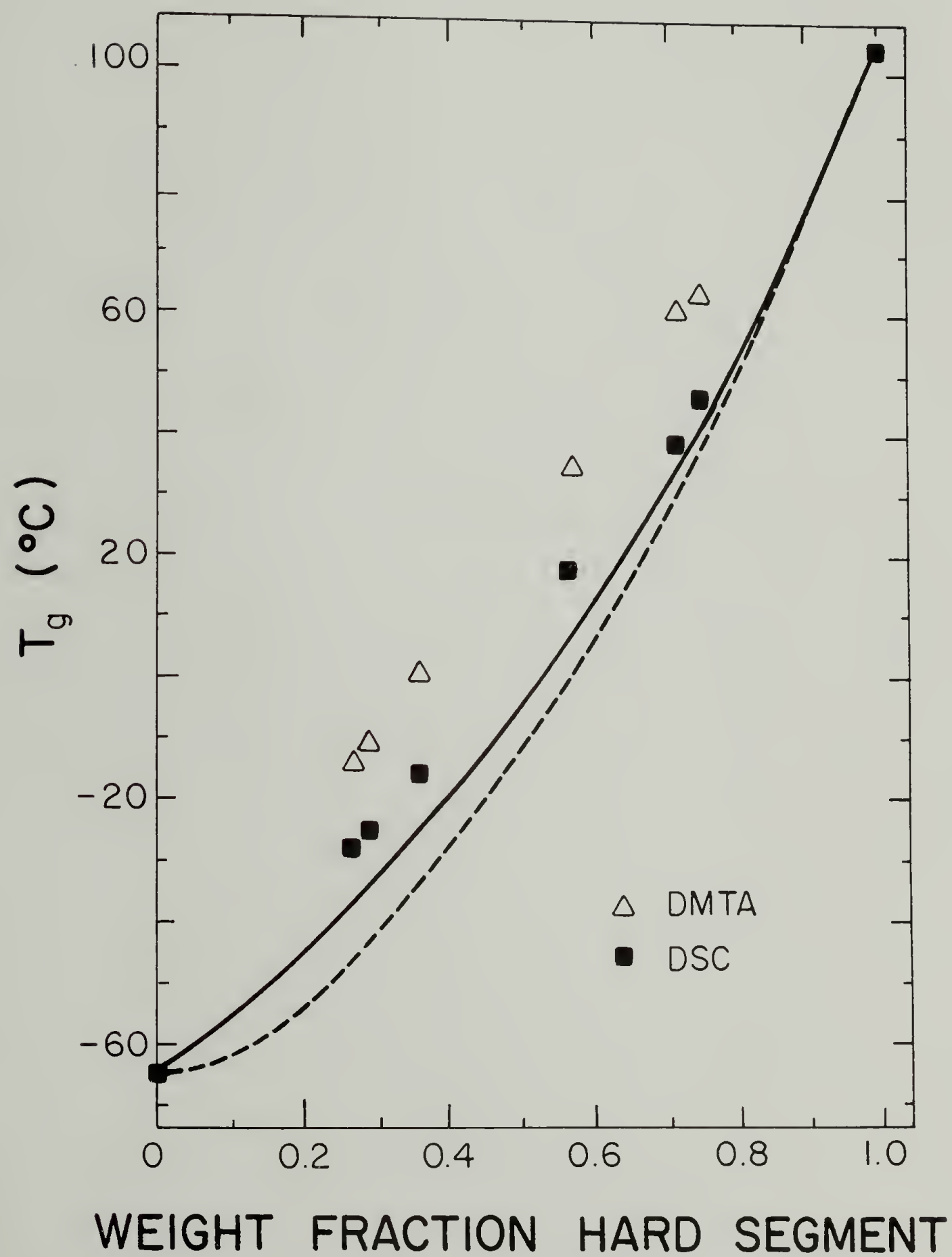


Figure 3-5 Thermal properties of quenched PCL polyurethanes as a function of hard segment content.



where T_g is the experimental T_g , T_g^0 is the T_g of the pure soft segment, X_c is the mole fraction of carbonyls effectively crosslinked by hydrogen bonding, and K is a constant in the range of 1.2 and 1.5. As with the data of Fu,⁶ the discrepancy between the experimental values and the calculated ones is greater at higher hard segment contents. This is consistent with the theory of Schneider as the amount of hydrogen bonding must be a function of the total N-H content.

A study of the compatibility of hard and soft segments was also carried by Thermal Analysis on 50:50 blends of hard and soft segments of different molecular weights. Blends were cast from THF solution, dried and examined by DSC. The first blend studied consisted of high molecular weight PCL ($M_n \sim 40,000$) and 2,4 hard segment ($M_n \sim 50,000$). The melting point of pure PCL-700 was 70°C with a percent crystallinity between 68 and 79%. (These values are in general agreement with the literature⁷ values of 63°C and 70% crystallinity.) Quenched scans exhibit a lower T_m by about 10°C (61°C) and a reduced PCL crystallinity of 50% and no exothermic recrystallization peak. The blend of PCL-700/hard segment exhibited a melting peak at 62°C, 8 degrees lower than the PCL-700 and with a crystalline fraction PCL of 59%. The Fox equation predicts a T_g of 18°C for this assumingly compatible system (when calculating the weight fraction PCL, the crystalline fraction was subtracted). There appears to be a T_g in this general region for the blend but an exact calculation of the T_g mid-point is difficult due to the change in baseline associated with the crystalline peak. Using onset T_g values the calculated value for a compatible T_g is 14°C, which

is 5° above the onset of a shift in the baseline. Given the M_n and differences in the solubility parameters of these two materials, one would expect incompatibility, as the molecular weights are greater than the critical phase separation value for styrene-butadiene block copolymers. The critical molecular weight for phase separation of homopolymers is even lower than for block copolymers. The reason for this unexpected compatibility is most likely the presence of specific interactions between the polar groups of these polymers.

Polycaprolactone is known to be compatible with a variety of other polymers due to the interactions of the carbonyl with other dipoles.¹¹ Extensive opportunity exists for hydrogen bonding between the two as discussed earlier. There also is still a significant driving force for crystallization of PCL. The melting point depression is an indication of compatibility, as well.

Blends of low molecular weight constituents, PCL-2000 and 7B ($M_w = 1674$), also display a degree of compatibility. The T_m of PCL is decreased and in quenched samples a recrystallization peak and large T_g are found. Obviously the constituents are sufficiently mixed in the melt to preclude the rapid crystallization observed for the PCL-2000. However, the T_g is well below the calculated value and there exists no hard T_g though this T_g might be hidden by the melting peak.

DMTA

Dynamic mechanical thermal analysis results for these copolymers are listed in Table 3-4 and displayed in Figures 3-6 through 3-9. The

Table 3-4

DMTA Results for PCL Polyurethanes

	<u>tan δ Peak ($^{\circ}$C)</u>		<u>log E'' Peak ($^{\circ}$)</u>	
	Initial	Quenched	Initial	Quenched
PCL-32	21	-14	-1	-25
PCL-35	24	-11	2	-23
PCL-50	31	1	12	-13
PCL-111	32	35	13	17
PCL-207	55	61	39	45

Figure 3-6 Temperature dependence of E' and E'' for crystalline
PCL polyurethanes.

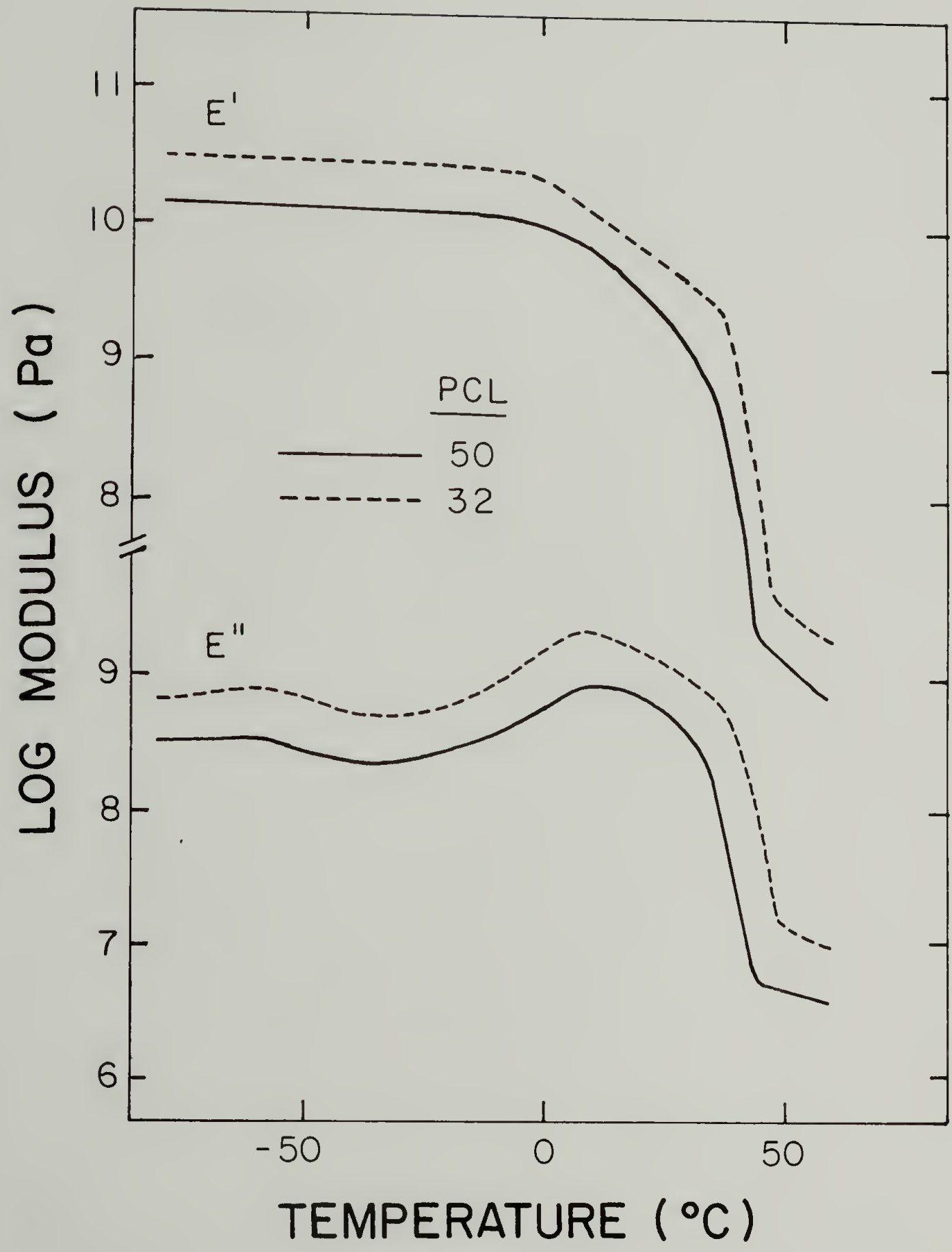


Figure 3-7 Temperature dependence of $\tan \delta$ for crystalline PCL polyurethanes.

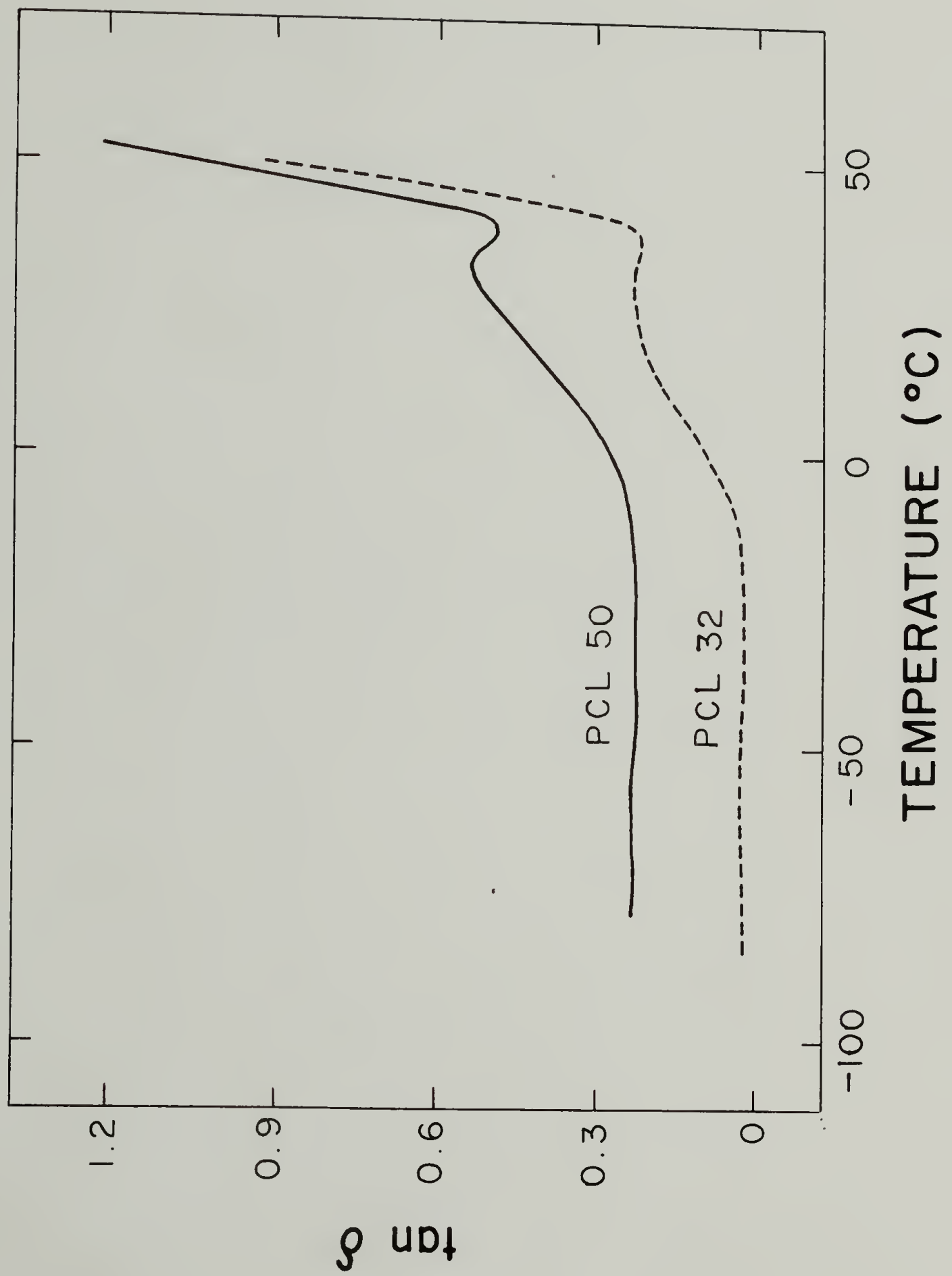


Figure 3-8 Temperature dependence of E' and E'' for quenched PCL polyurethanes.

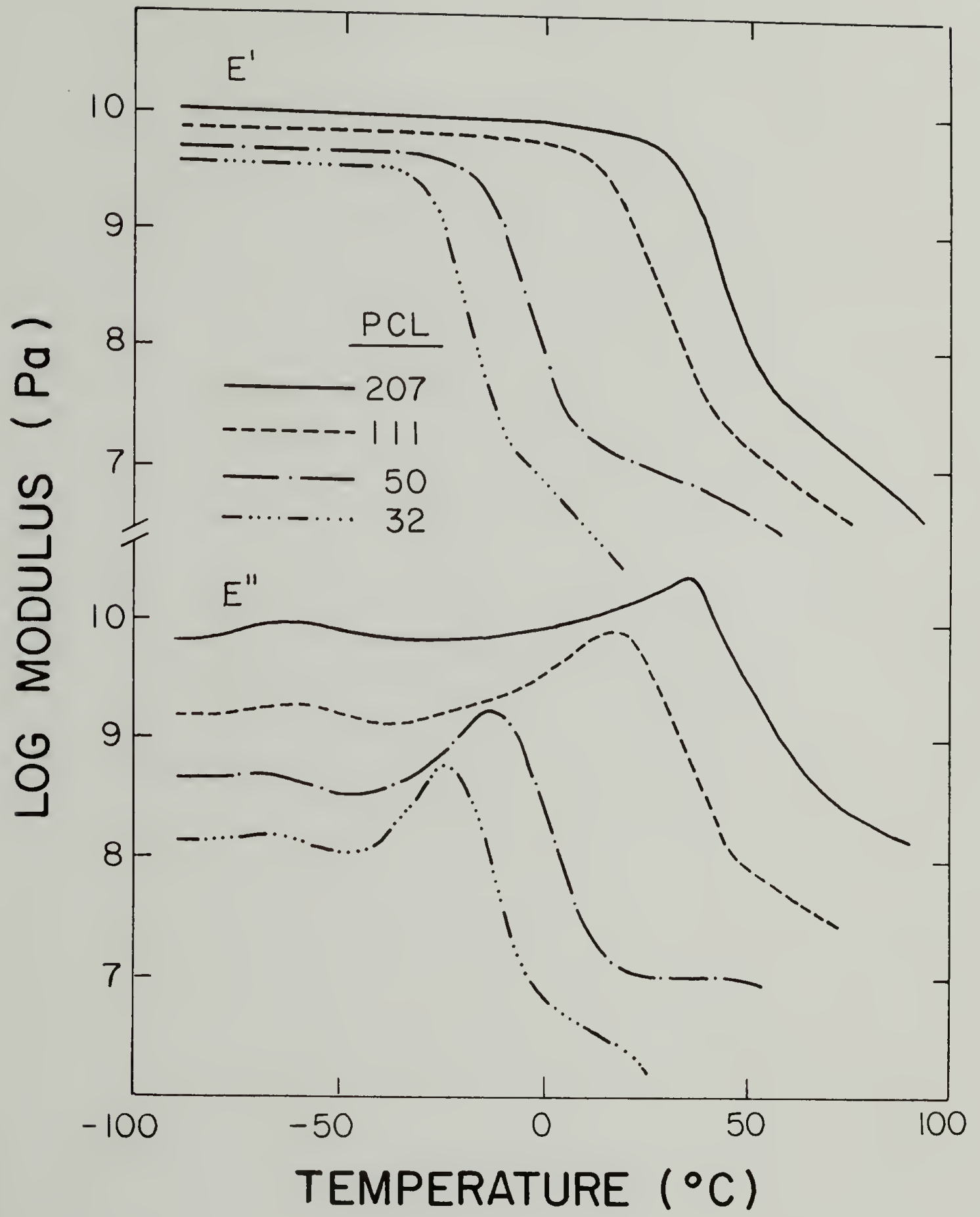
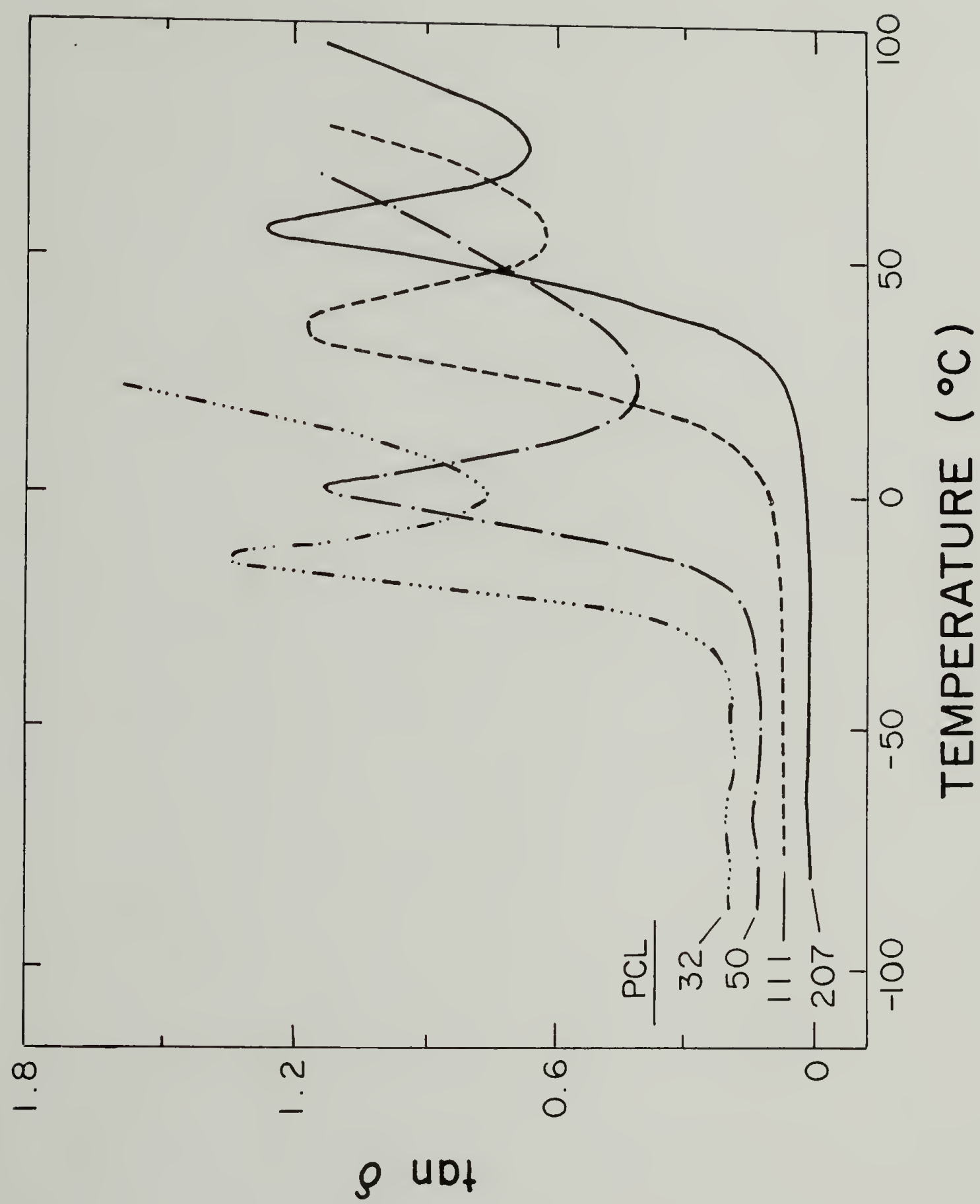


Figure 3-9 Temperature dependence of $\tan \delta$ for quenched PCL
polyurethanes.



results are in good agreement with the DSC results and data for quenched samples are included in Figure 3-5 (triangles). These data bracket those of Critchfield et al.³ for the $\tan \delta$ peaks from similar samples of 31, 42, and 49% hard segment content with $\tan \delta$ peaks at -10, 10, and 20°C respectively. The temperature of the relaxation determined by this method lies about 25°C above the value of T_g determined by DSC for the same sample as with the JSR series.

Aged samples of low hard segment content also display two phase behavior by DMTA. Figures 3-6 and 3-7 show the data for aged samples. As with the DSC results, both a T_g and melting are apparent. The melting is evidenced by the precipitous drop in storage and loss moduli, E' and E'' , and the sharp increase in $\tan \delta$ between 31 and 38°C for all the crystallized samples. This melting region is in close agreement with a melting point determined by Critchfield et al. for a polyurethane with a 3000 molecular weight polycaprolactone soft segment and MDI/BDO hard segment.¹ It is apparent from the gradual drop in the storage modulus in the glass relaxation region that the crystalline soft segments provide some reinforcement of the material above the amorphous T_g .

A small low temperature loss peak occurs around -70°C for all the samples. This peak likely results from a short segmental relaxation of the soft segment. Other workers have reported a crankshaft type relaxation for polycaprolactone polyurethanes around -100°C.⁵ The other copolymers studied in this dissertation, with identical hard segments, do not display this peak.

A comparison of DMTA data from PCL-50 with that from a chemically identical copolymer containing monodisperse hard segments prepared by Fu is shown in Figure 3-10. These two copolymers, PCL-50 and PCL-4B, are identical except for the distribution of hard segment lengths in PCL-50. As can be seen from Figure 3-10, both materials have essentially identical behavior. Scans from quenched PCL-50 and PCL-48 are superimposable. Therefore, as far as dynamic mechanical properties are concerned, the hard segment length distribution has no effect on the behavior of this material.

Morphology

Contrary to the reports in the literature for this system,³ these materials evidence soft segment crystallinity. Copolymers containing less than 40% hard segment content show strong WAXS peaks of identical d spacings as listed in Table 3-5.

Mechanical Properties

Similar to the other copolymers studied, a range of tensile behavior is also evidenced by this series as displayed in Figure 3-11 and Table 3-6. Copolymers with high hard segment content are very brittle, so much so that it was impossible to cut test specimens (there was a similar problem with the hard segment homopolymer). These materials have a T_g around 40 - 45°C. A material with a T_g around 20°C, PCL-111, displays markedly different behavior, that of an elastomer. The reason for this difference in mechanical properties is the relationship between

Figure 3-10 Comparison of dynamic mechanical properties of PCL-50 and PCL-4B.

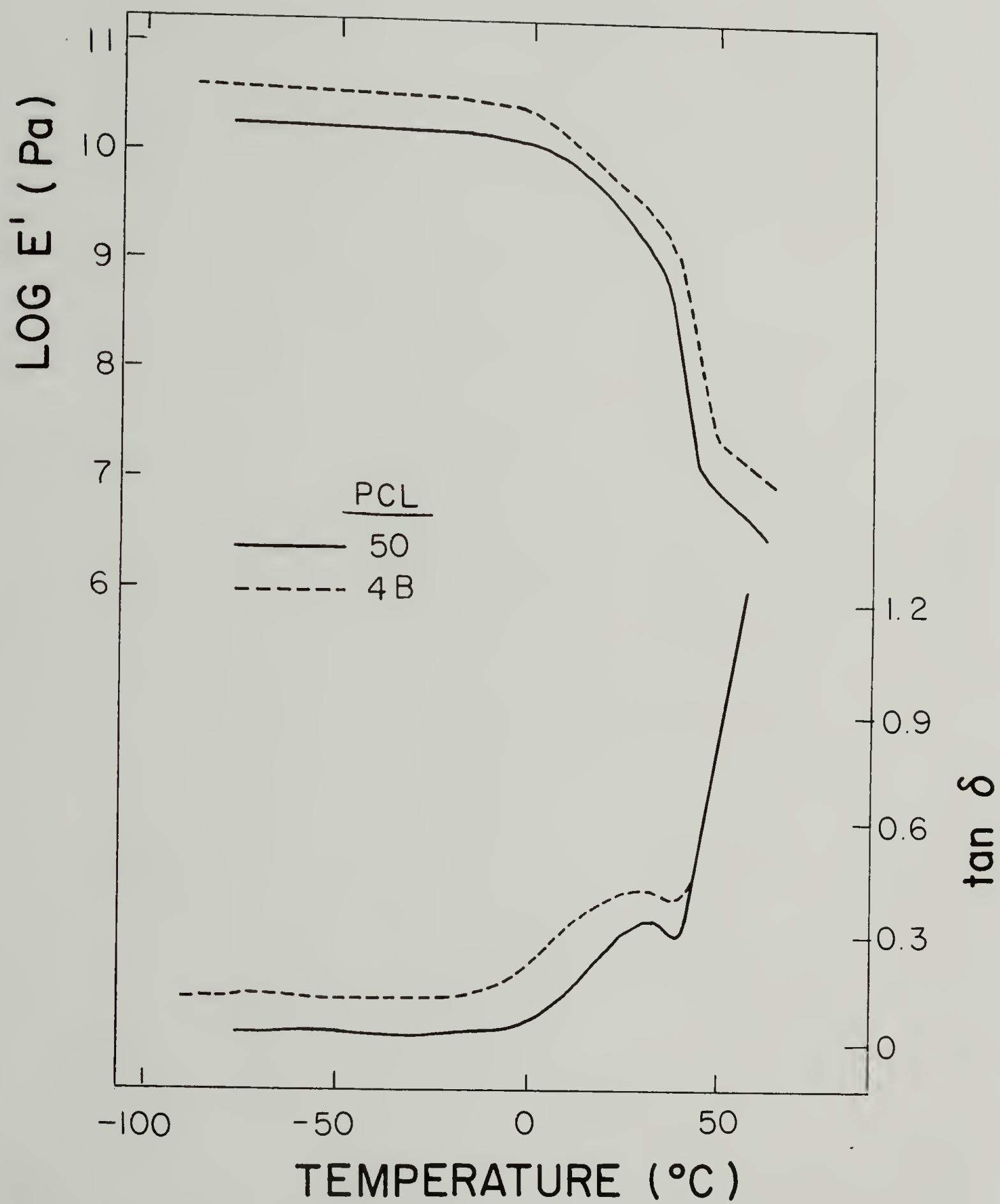


Table 3-5
X-Ray Results
d-Spacings Å

PCL Oligomer	3.75	4.15	a
PCL-32	3.73	4.08	a
PCL-50	3.76	4.18	a
Literature Values ⁵	3.75	4.14	4.57

^aAmorphous halo.

Figure 3-11 Stress-strain behavior of PCL polyurethanes.

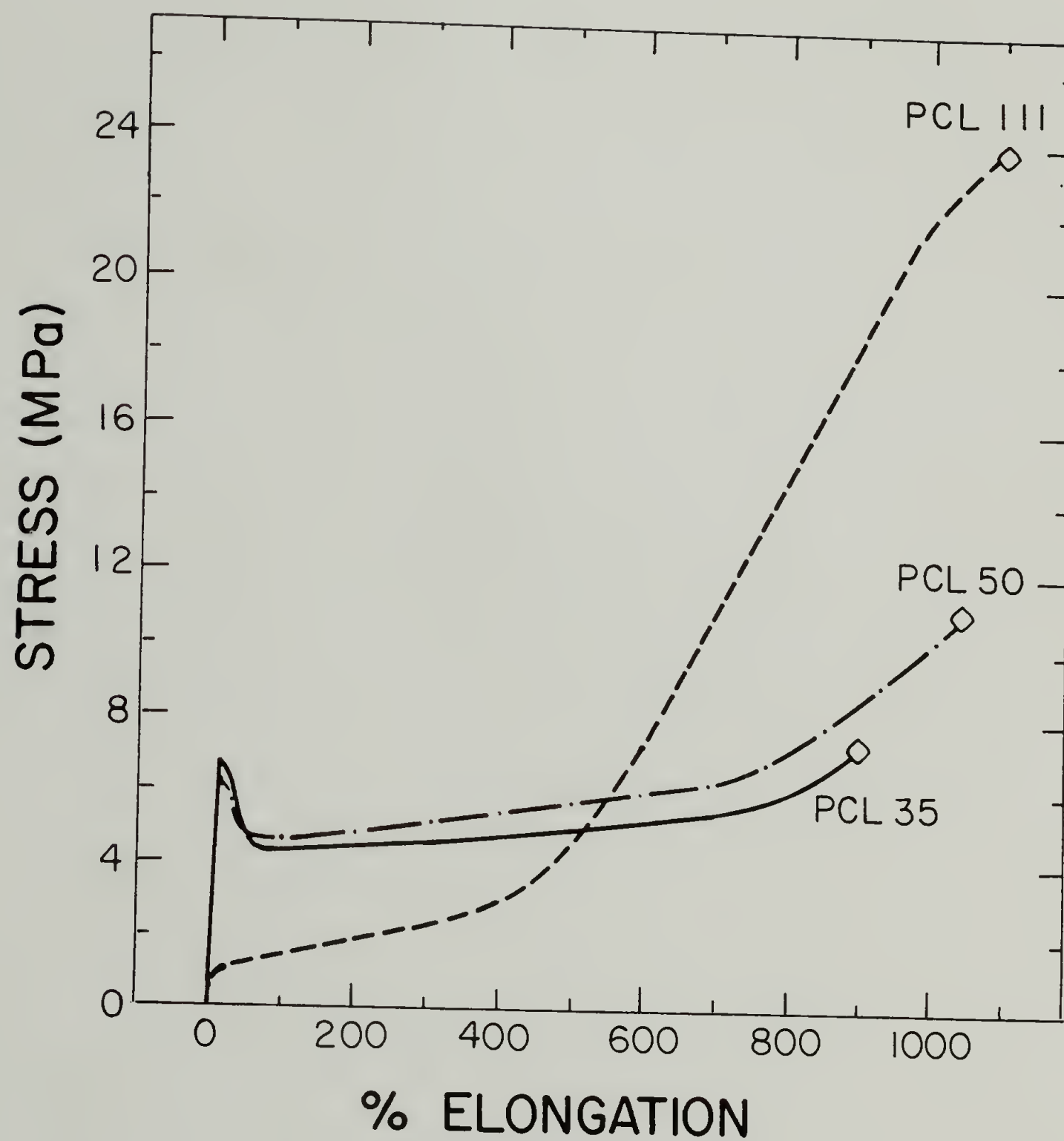


Table 3-6

Mechanical Properties

	Wt. Fraction Hard Segment	M_n	σ_B (MPa)	$E_B\%$	σ_{yield}	Modulus (MPa)
PCL-32	0.27	10,000	3.9	20	5.6	80
PCL-34	0.28	21,000	5.8	300	5.8	100
PCL-35	0.29	32,000	7.3	900	7.3	130
PCL-50	0.36	30,700	11.0	1,140	6.3	110
PCL-111	0.57	26,200	23.8	1,100	---	20

the temperature of testing or handling and the T_g of the material. The T_g of PCL-111 is slightly below the ambient testing temperature and hence PCL-111 is a rubbery material. Since their T_g 's are above ambient temperature, PCL-207 and PCL-230 are glassy materials.

Crystalline samples exhibit necking, drawing, and appear to stress crystallize. Samples have a steady value of stress from the end of the yielding region to about 700%, where there is a slight upturn in the stress-strain curve along with a whitening of the sample. This upturn is probably due to the reinforcing nature of the stress induced crystallization, as polycaprolactone polyurethanes are known to stress crystallize.

The evidence for stress induced crystallization of PCL-111 is more pronounced. Both the upturn with stress-strain curve and the amount of sample whitening are greater than for PCL-50. If one heats a clear sample at about 400% elongation, which is close to the onset of strain induced crystallization at 500%, the clear sample becomes white. This does not occur when heated at 200% elongation. Instead, the sample cross section contracts and the sample draws like a non-crosslinked rubber. This liquid-like behavior occurs because the testing temperature has been raised significantly above the T_g of this non-crosslinked amorphous material. This material, PCL-111 56% hard segment, recovers to its original dimensions in about 20 minutes following elongation to 600%.

The crystalline samples show qualitatively similar results to those of Fu, but have higher ultimate strengths and yield stresses. These

differences most likely arise from the higher degree of soft segment extension (that is the linkage of the soft segments by TDI alone) in Fu's samples, thereby raising the molecular weight of the soft segments. An increase in soft segment from 2000 molecular weight is known to lower the mechanical properties of polyurethanes.² The copolymer molecular weight differences are minimal and should not be a significant factor in this difference.

Another feature of interest is the effect of molecular weight on the mechanical properties of these polyurethanes. Figure 3-12 shows the stress-strain curves of essentially chemically identical samples with differing molecular weights. The most pronounced effect of molecular weight is on the elongation at break, increasing from 20% at 10,000 molecular weight to 300% at 20,000 to 900% at 30,000. The initial modulus increases from 80 to 90 to 130 MPa respectively and the yield stress increases slightly when the molecular weight changes from 20,000 to 30,000.

A final feature of interest is the large amount of hysteresis. Figure 3-13 shows the hysteresis behavior of PCL-111. The percent hysteresis is between 85 and 90% up to a pre-strain level of 130% elongation. This could be a result of the slow recovery rate due to the proximity of the material T_g to the experimental temperature. The relaxation time necessary for complete recovery of the original dimensions is 20 minutes. The crystalline materials also display a similarly high hysteresis, both those of this study and those with monodisperse hard segments.⁶ As these materials exhibit necking, a

Figure 3-12 Effect of molecular weight on PCL polyurethane
mechanical properties.

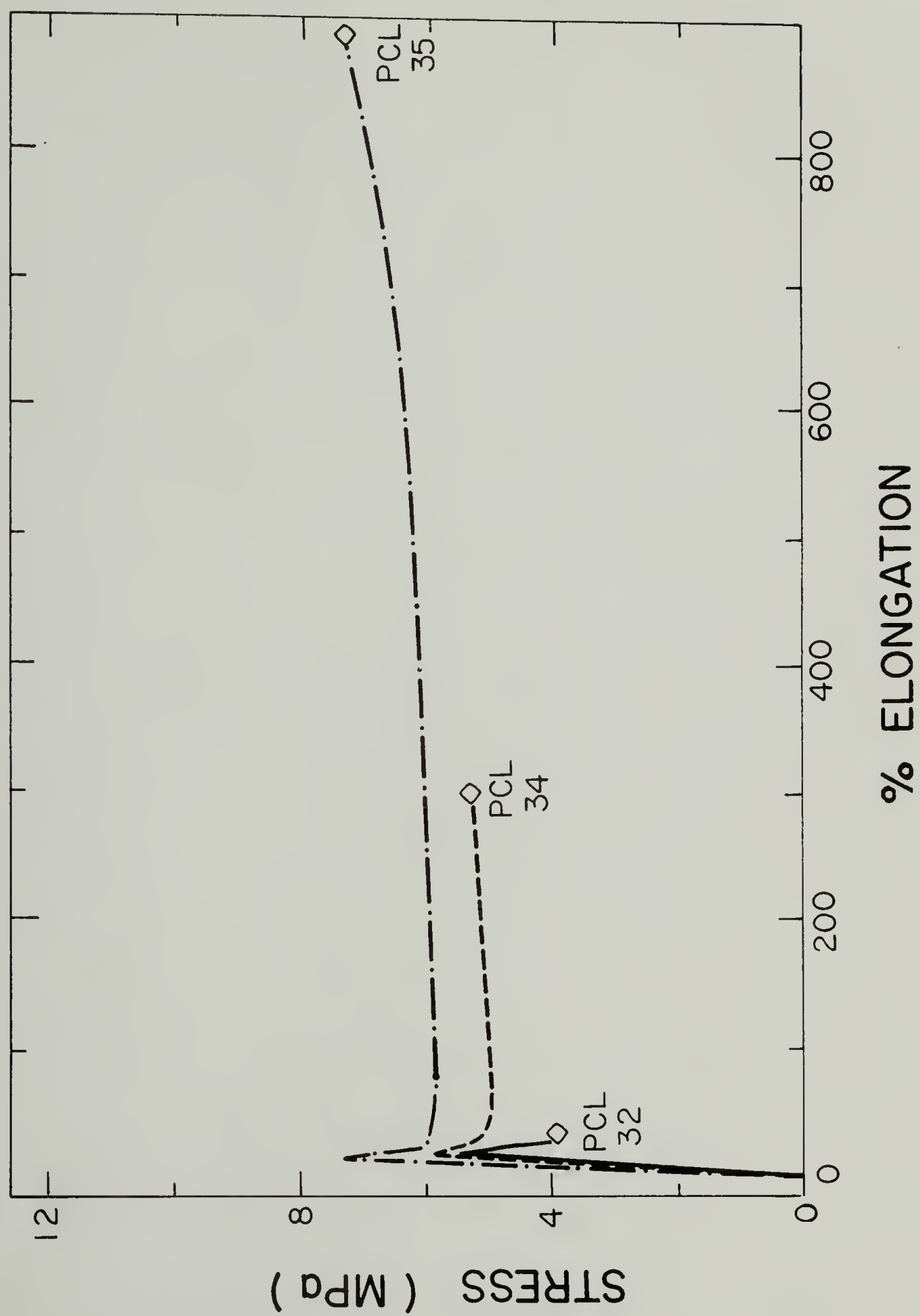
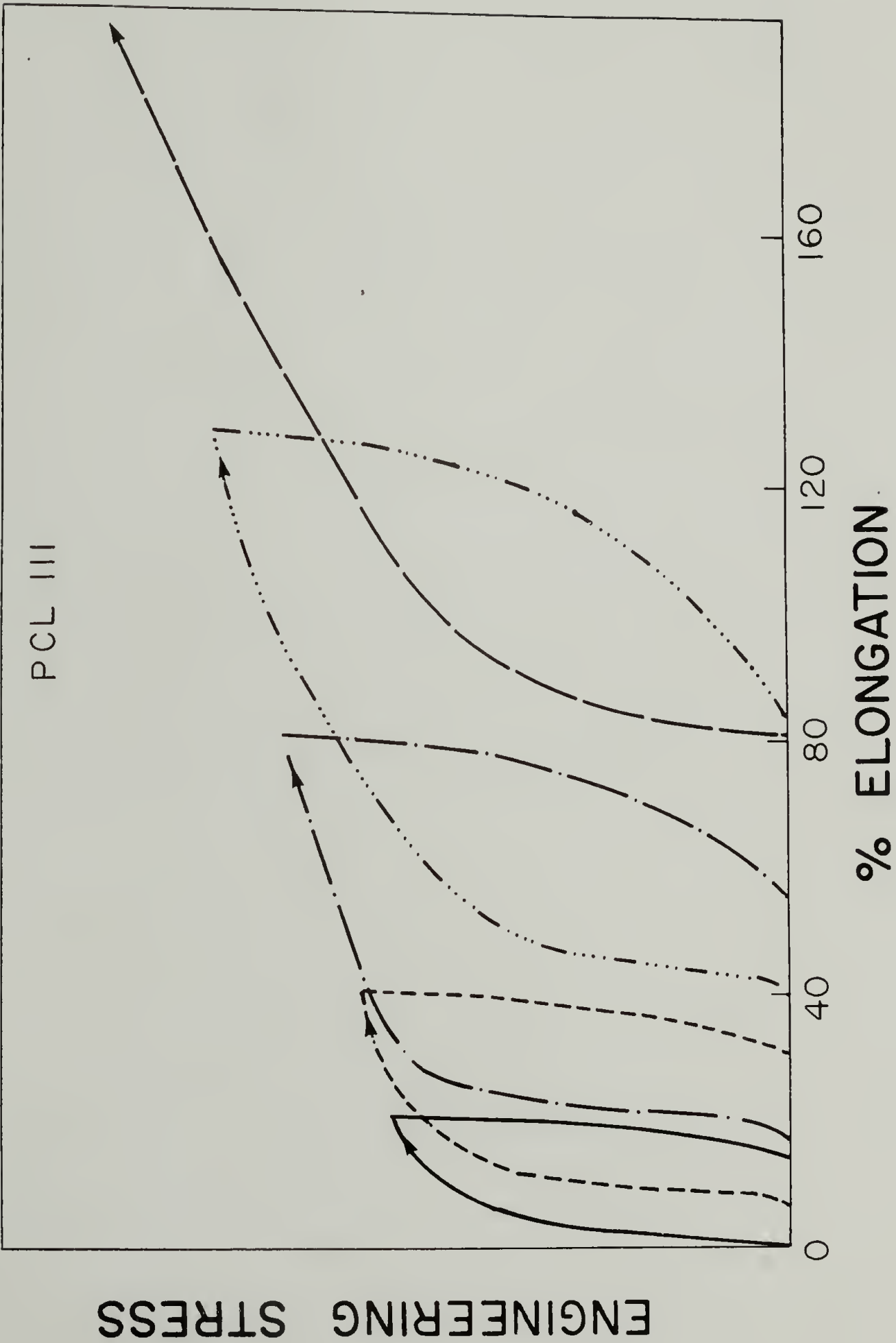


Figure 3-13 Cyclic stress-strain curve for PCL-111.



morphological transformation may be responsible for the low recovery.

CONCLUSIONS

Extensive segmental mixing occurs in these polyurethanes. The T_g data from quenched samples shows a reasonably close agreement to values calculated by the Fox equation for compatible systems.

PCL polyurethanes crystallize when the materials contain less than 45% hard segment. The crystalline portion has WAXS d spacings identical to those from the soft segment oligomer. Therefore, pure crystalline PCL domains occur along with the amorphous domains made up of mixed hard and soft segments.

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C H A P T E R I V
STRUCTURE-PROPERTY RELATIONSHIPS IN TETRAMETHYLENE
GLYCOL POLYURETHANES

INTRODUCTION

Polytetramethylene glycol (TMG) is often used as a soft segment for polyurethanes¹⁻⁵ as well as for segmented polyester elastomers such as Hytrel.⁶ This soft segment is also used in commercial polyurethanes such as Lycra^R and Estanes^R.⁷

An extensive study of TMG/TDI/BDO polyurethanes has been carried out by Schneider et al.¹⁻⁴ and the dynamic mechanical behavior of these materials has also been examined.⁸ The glass transition temperature of 2,4-TDI polymers with 1,000 molecular weight TMG displayed a strong dependence on hard segment content. This was attributed to extensive phase mixing in these amorphous materials. Increasing the molecular weight of the TMG to 2,000 induced phase segregation in these polyurethanes as evidenced by a T_g independent of hard segment content. The polyurethanes from 1,000 molecular weight TMG and the symmetrical 2,6-TDI isomer displayed a T_g independent of hard segment content. An endotherm associated with the melting of the crystalline 2,6-TDI/BDO hard segments also occurred at higher temperature. A degree of soft segment crystallinity developed in 2,000 molecular weight TMG polyurethane with this crystalline hard segment. Dynamic mechanical studies on these materials generally supported these results.⁸ The transitions were very broad, characteristic of a significant degree of

phase mixing and poor phase organization. No pure component phases were thought to exist in these polyurethanes of 2,000 molecular weight TMG and 2,4-TDI/BDO hard segments containing less than 43% hard segments. As these materials were prepared in bulk using an excess of diisocyanate and low hard segment content, it was decided to use a solution polymerization to prepare strictly linear polyurethanes and examine materials of higher hard segment content.

EXPERIMENTAL

Polytetramethylene glycol (TMG) Lot #2705 were obtained from Polysciences. The 2,4-TDI used was obtained from Sigma. All experimental methods were similar to those presented earlier except that the polyurethane was precipitated into a hexane layer above water. A vapor phase osmometry (VPO) measurement was performed on one sample by use of a Knauer vapor phase osmometer and a benzil calibration.

RESULTS AND DISCUSSION

Polymer Characterization

The copolymers synthesized for this study are listed in Table 4-1 with the same categories and definitions as with the other series. The accuracy of the values for molecular weight should be equivalent to that of the other series. The GPC data for the soft segment oligomer ($M_n = 2,000$) agrees within the same limits as the other series with the value determined by end group analysis (1850) as in the other series. Values of the molecular weight distributions are again around 2. A comparison

Table 4-1
Characterization of TMG Polyurethanes

Sample	Wt. Fraction Hard Segment	M_n	\overline{DP}_n	Properties
TMG-25	0.24	20,300	8	soft tacky
TMG-35	0.31	43,500	15	clear, soft, very tacky
TMG-45	0.39	15,700	5	clear, soft, tacky rubber
TMG-72	0.49	53,700	14	clear, tough rubbery
TMG-106	0.60	10,500	2	clear, tough, flexible
TMG-108	0.60	45,200	9	clear tough flexible
TMG-228	0.76	18,700	2	clear, stiff
TMG-275	0.80	27,600	3	clear, stiff

of the \bar{M}_n determined from GPC and an absolute method (VPO) for TMG-106 indicates that GPC data should be reasonably accurate. TMG-106 was chosen for this study as it contains 60% hard segments and has a \bar{M}_n in the applicable range for VPO (less than 20,000). The value of \bar{M}_n determined by VPO was $11,300 \pm 10\%$ which is in excellent agreement with the GPC \bar{M}_n of 10,500. These results can be used to justify the validity of the GPC results for all three series, as the the hard segments are the same and the soft segment GPC behaviors are similar. The proximity of the \bar{M}_n determined by GPC to the accepted value for the oligomers is very similar in all three series; 2400 vs. 2200 for JSR, 2200 vs. 2060 for PCL, and 2000 vs. 1850 for TMG. Values of molecular weight give \overline{DP}_m 's above the generally accepted minimum for high polymer polyurethane mechanical properties for most of these samples; that is, the average number of hard segments per chain is above 3 - 6.¹⁰

As with the other series, the amount of allophonate formation should be zero, in contrast to the work of Schneider et al.¹⁻⁴ and Senich,⁸ where an excess of isocyanate was used along with high reaction temperatures.

DSC

TMG 200 is a highly crystalline material with a very slight T_g at -83°C and a melting temperature (T_m) at 38°C . Quenched scans reveal a lowered T_m of 23°C . Camberlin reports that TMG of roughly equivalent molecular weight could be rendered completely amorphous by quenching samples of less than 5 mg resulting in a T_g of -93°C .¹¹ As this was

unable to be duplicated on our DSC, Camberlin's value of -93°C will be assumed as the true soft segment T_g . The highly crystalline nature of the TMG oligomer increases T_g by providing crystalline crosslinks to the amorphous portion and thereby limiting chain mobility. A polymer formed by linking TMG with 2,4-TDI was also examined. The original scan gave a small T_g at -73°C with a crystalline melting peak at 23°C . Quenched scans showed a T_g at -78°C and a recrystallization peak at -38°C that is 90% of the area of the crystalline melting peak. One would expect the T_g of this material to be significantly higher than the oligomer's since the molecular weight is higher by a factor of 6 and a constituent of higher T_g , TDI, is incorporated in the chain.

These data and others are presented in Table 4-2, and several DSC traces are included in Figure 4-1. Thermal transition data (DSC and DMTA) are plotted vs. hard segment content in Figure 4-2. As with the data of Fu¹² for the same system with monodisperse hard segment, a small amount of soft segment crystallinity is observed for well-aged materials containing less than 32% hard segment content. These samples also have soft segment T_g 's significantly higher than the remainder of the series. The T_g of TMG-35 is in good agreement with the value calculated from the Fox equation for compatible systems. Elevated T_g is generally taken as evidence of a higher degree of phase mixing and therefore, limited domain formation. This is a possible explanation for the poor mechanical properties of these materials that are to be discussed later.

At 49% hard segment, a hard segment T_g becomes readily apparent as shown by curve for TMG 72 in Figure 4-1. The hard segment T_g 's are

Table 4-2
Thermal Analysis Data for TMG Polyurethanes

	T _g		T _m	ΔH_m	$\Delta C_p / \Delta C_p^N$	
	Initial	Quenched			Initial	Quenched
TMG-2000	-85	-81	38	28.16		
TMG-10	-73	-78	33	24.81		
TMG-25	-72	-69	28	---		
TMG-35	-58	-58	40	3.13	0.95	0.95
TMG-45	-69	-67			0.86	0.91
TMG-72	-72, a	-69, 49			0.56	0.75
TMG-106	-78, 43	-78, 59				
TMG-108	-79, 42	-79, 61				
TMG-228		74				
TMG-275	-76, a	-82, 85				

^aTransition difficult to quantify.

Figure 4-1 DSC traces for TMG-35, TMG-72 and TMG-275.

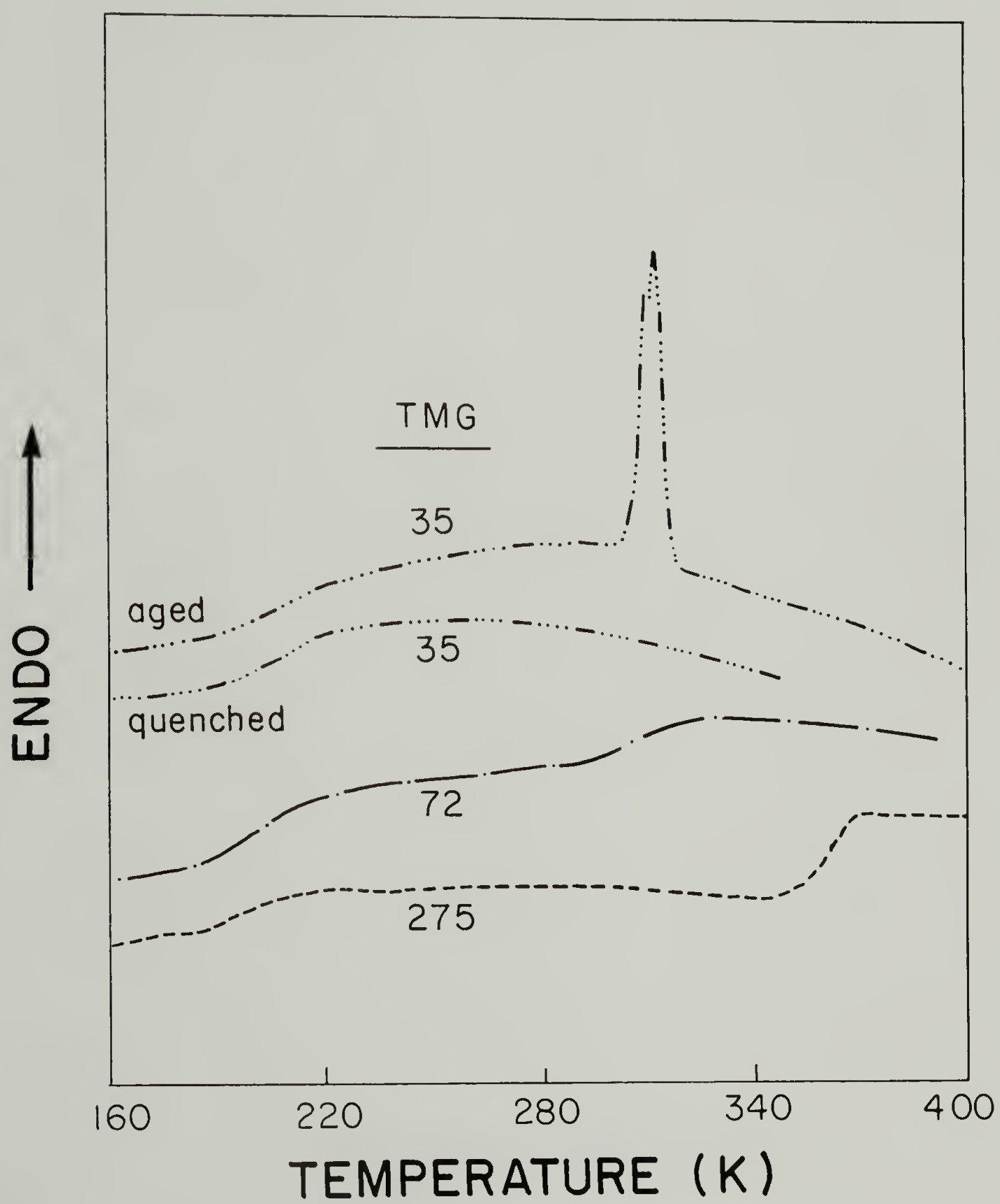
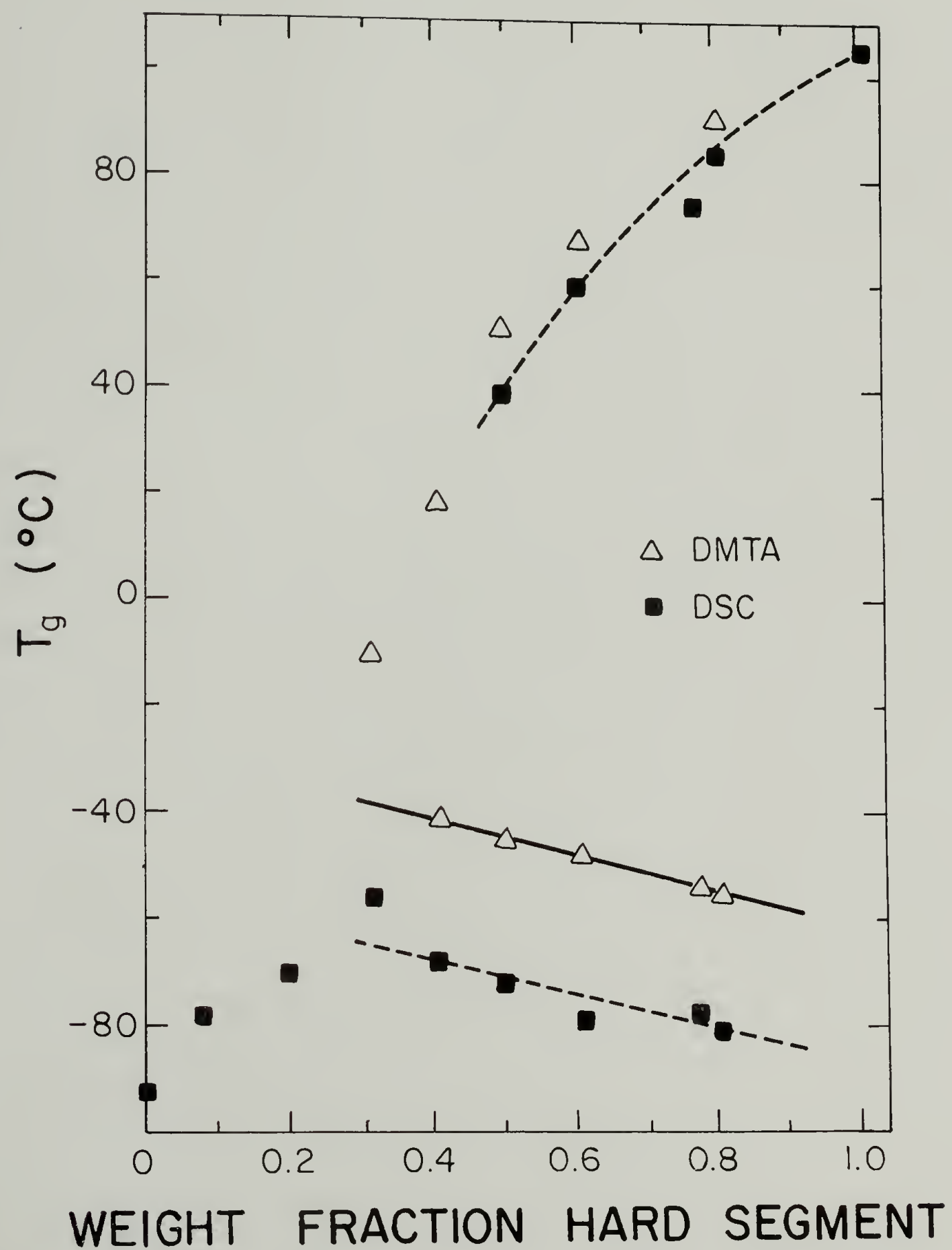


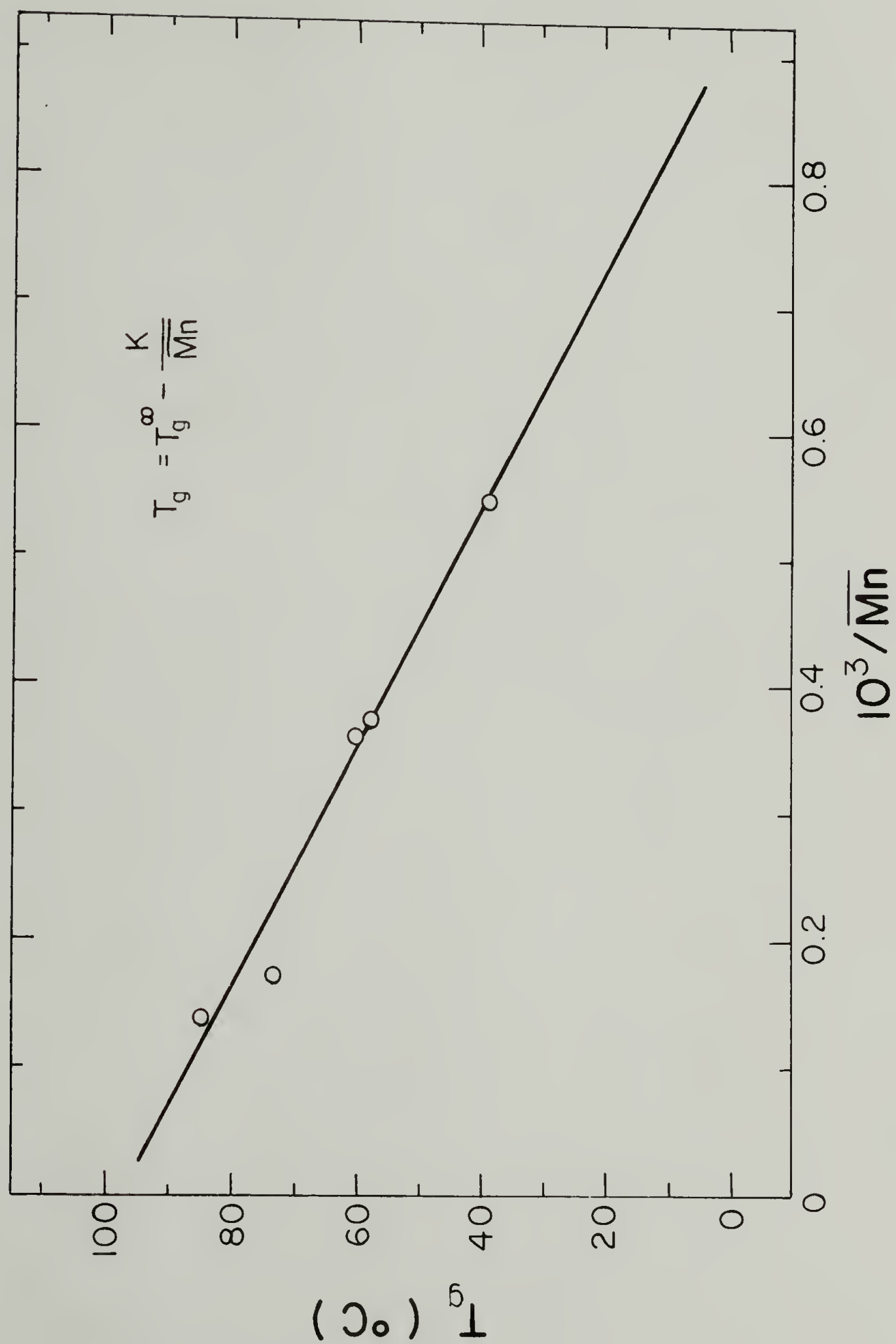
Figure 4-2 Tg as a function of hard segment content for TMG polyurethanes.



plotted vs. inverse molecular weight in Figure 4-3. As can be seen, the T_g values fall on a Fox-Flory relationship as did the JSR samples. The K value in this case is 105,000 with a T_g^∞ of 98°C . The value for T_g^∞ is reasonably close to the hard segment homopolymer T_g of 105°C . However, the slope (value of K) is twice as steep as the one for the JSR materials. This suggests that the chain ends of the hard segments coupled to TMG molecules add more free volume to the hard segment domains than do those coupled to polybutadienes. A possible explanation for this behavior could arise from the differences in the interfacial thicknesses of these materials. JSR polyurethanes have very sharp domain boundaries¹³ while the domain boundaries of TMG/TDI polyurethanes are known to have a moderate thickness.⁹ This interfacial volume could be the source of the extra free volume, as more of the hard segment chains can exist in regions of ready relaxation. As the hard segment length increases, the hard segment domains would be expected to become better organized and the interfacial thickness might decrease. The behavior would then approach that of the JSR polyurethanes.

The soft segment thermal behavior shows a systematic decrease of T_g with increasing hard segment content/length. This is indicative of an increasing amount of phase segregation, as might be expected due to the decrease in the entropy change on mixing as the molecular weights (lengths) increase. It appears that the interaction parameter, χ_{AB} , defined previously, lies in a transition region for these components. That is, χ_{AB} equals a value such that the entropic effects of molecular weight on phase segregation become highly significant. Along these

Figure 4-3 Fox-Flory relationship for the hard segment T_g of TMG polyurethanes.



lines, comparison of the soft segment T_g of samples of above and below 40% hard segments indicates a critical molecular weight for phase separation of about 1000. Fu¹² noted a profound change in mechanical properties around this composition and it is well known that polyurethane mechanical properties are highly dependent on sample morphology.

The change in soft segment ΔC_p also indicates significant changes in this region. The values obtained for three samples bracketing this transition region are included in Table 4-2. Following the pattern explained earlier for the JSR series, it is apparent that different morphologies are present. Contrary to the negligible effect of time on the JSR behavior, these materials exhibit a time dependence of this behavior. Camberlin et al. explain this as a kinetic effect on the phase separation process.¹¹ From the ΔC_p value for quenched TMG-72, one can infer that the hard and soft segments do not completely mix at the conditions used (150°C for 10 minutes). One would not expect the hard segment and JSR to mix at any temperature, hence the time independent nature of $\Delta C_p / \Delta C_p^N$ for the JSR materials. But there is an opportunity for specific interactions between the polyether soft segment and the urethane hard segments by hydrogen bonding, and this should enhance phase mixing. The effect of aging, i.e. the decrease of $\Delta C_p / \Delta C_p^N$, is most probably a result of the increased value of ΔG_m caused by the lowered temperature. Camberlin reported that for MDI hard segment BDO systems, there is an equilibrium time for phase segregation that is a function of the soft segment viscosity. The driving force for this

behavior might be the time dependent crystallinity of the hard segment. More detailed experiments of ΔC_p vs. room temperature annealing time on Fu's JSR/TDI samples have been carried out in our labs and no effect of time is found on $\Delta C_p / \Delta C_p^N$.¹⁴

DMTA

The dynamic mechanical properties for this series are presented in Figures 4-4 through 4-8 and listed in Table 4-3. Combining $\tan \delta$ and loss modulus data proves the existence of two phases, as the loss modulus peak indicates the soft segment T_g at the expected temperatures, and the hard segment T_g is similarly evidenced by a strong $\tan \delta$ peak. The upper $\tan \delta$ transition increases in strength and temperature with increasing hard segment content/length. As the hard segment content increases, the width of the peak narrows as well. This can be considered as evidence for more highly defined hard segment domains.⁸

A marked transition in soft segment relaxation behavior occurs at about 40% hard segment content. The $\tan \delta$ peak is replaced by a step rise at a much lower temperature. The position of this step transition and its corresponding $\log E''$ peak are essentially independent of hard segment content. Fu noted a marked change in mechanical properties around this composition, and this change in properties can be related to this change in morphology. The dynamic mechanical behavior of TMG-45, 39% hard segments (Figure 4-8), is intermediate between the behaviors of TMG-35 and TMG-72. Both the $\tan \delta$ step rise, characteristic of higher hard segment content, and the $\tan \delta$ peak, as for TMG-35, are present.

Figure 4-4 Temperature dependence of E' and E'' for aged TMG polyurethanes.

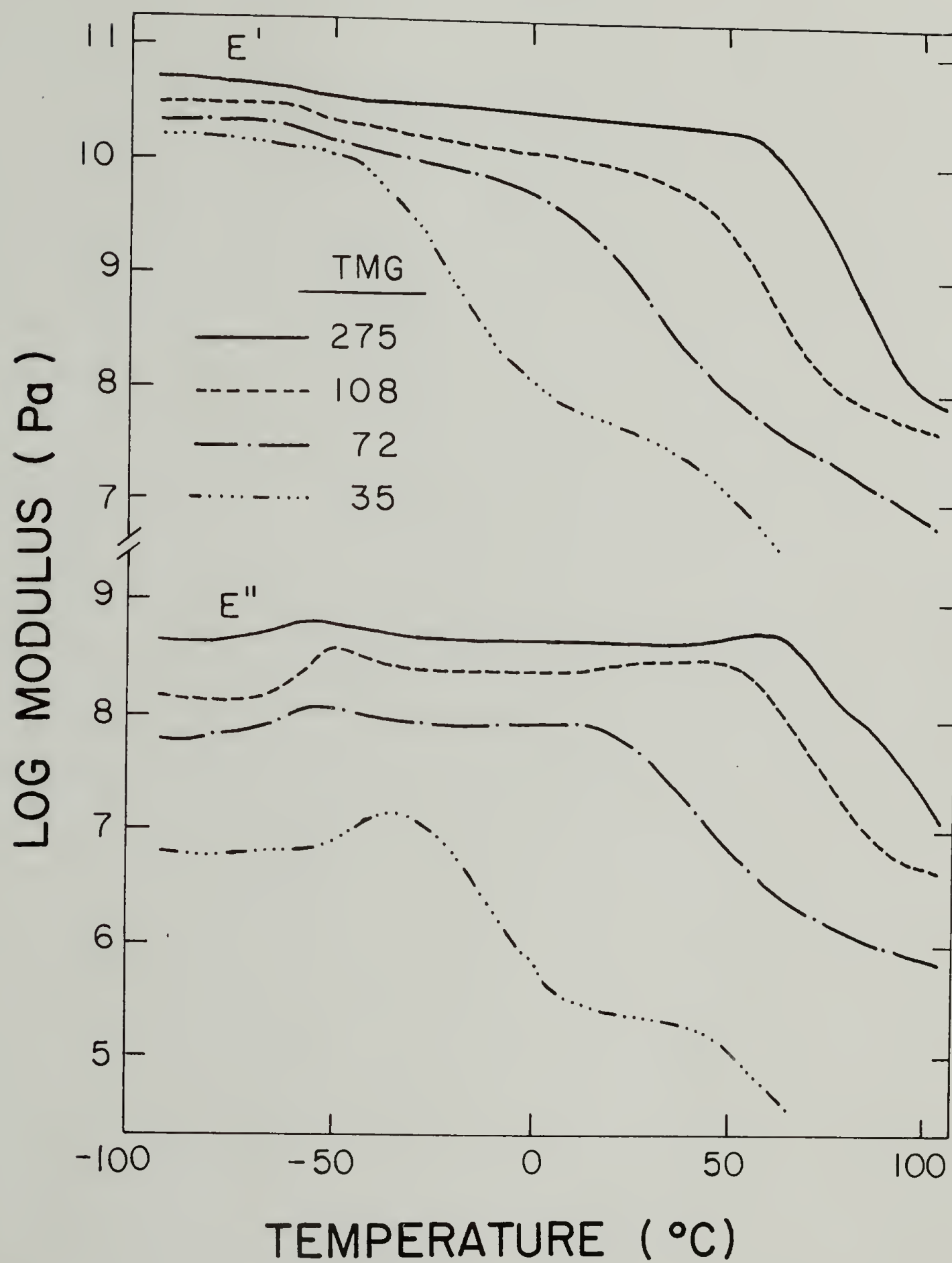


Figure 4-5 Temperature dependence of $\tan \delta$ for aged TMG
polyurethanes.

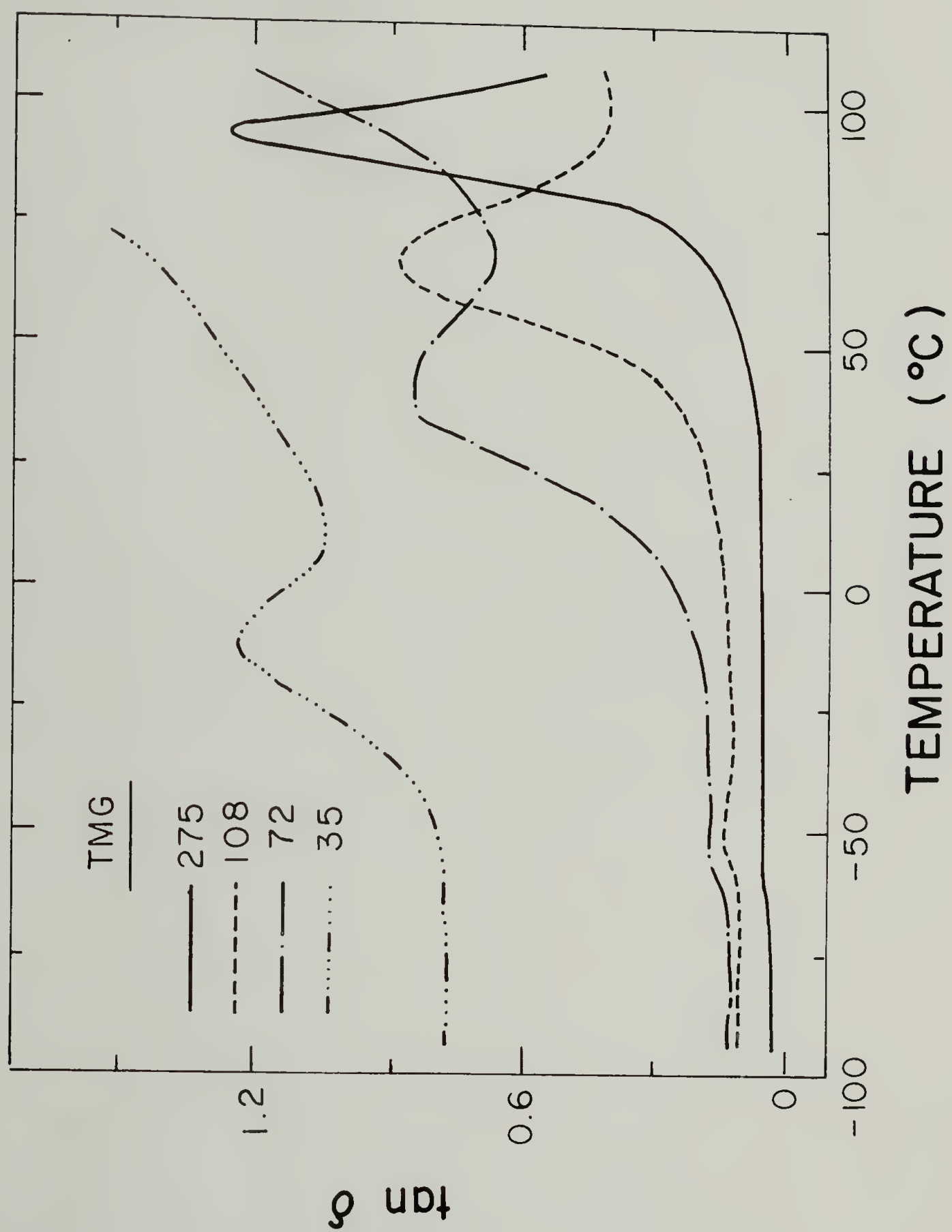


Figure 4-6 Temperature dependence of E' and E'' for quenched TMG polyurethanes.

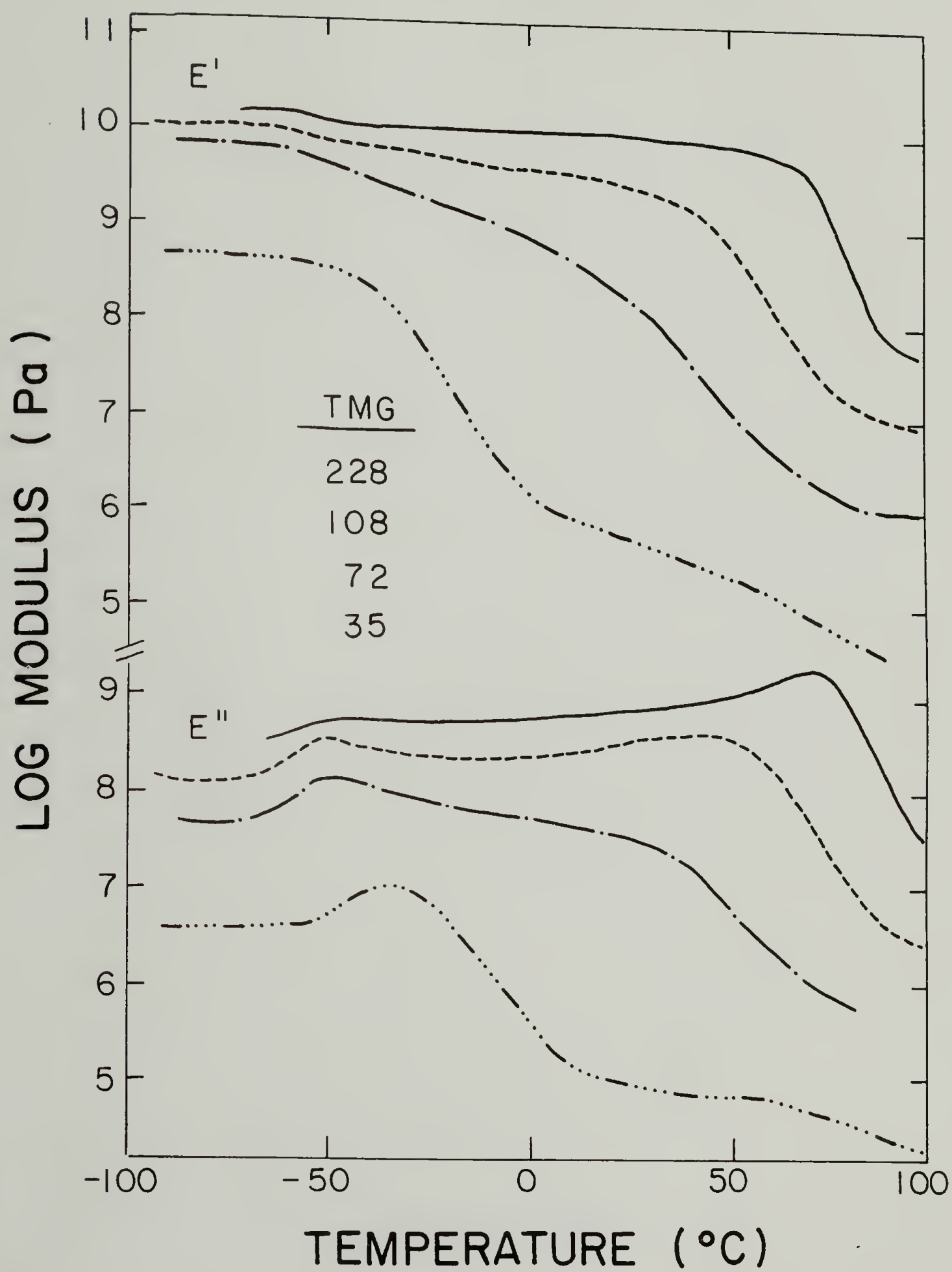


Figure 4-7 Temperature dependence of $\tan \delta$ for quenched TMG
polyurethanes.

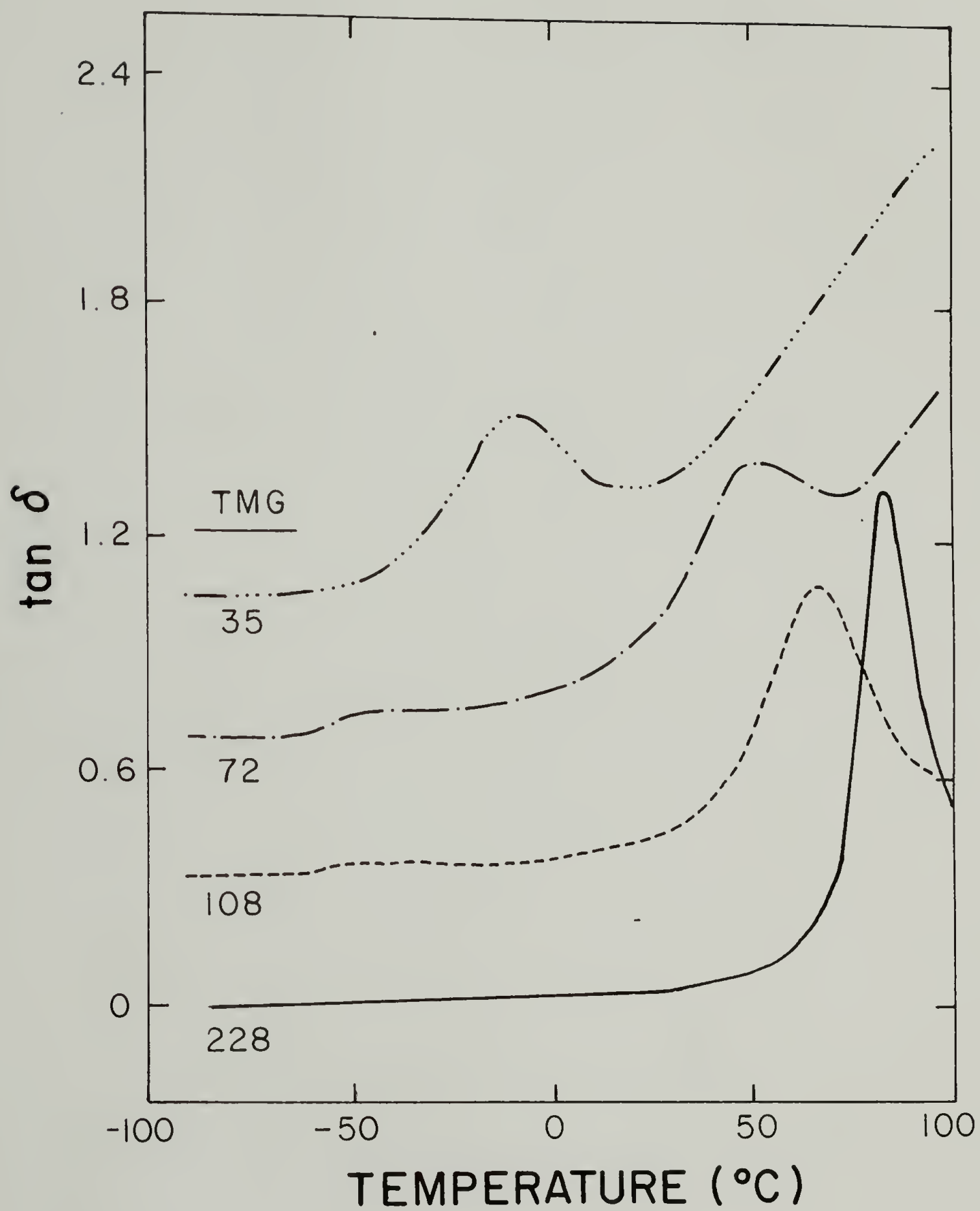


Figure 4-8 Comparison of dynamic mechanical behavior of aged and TMG-45.

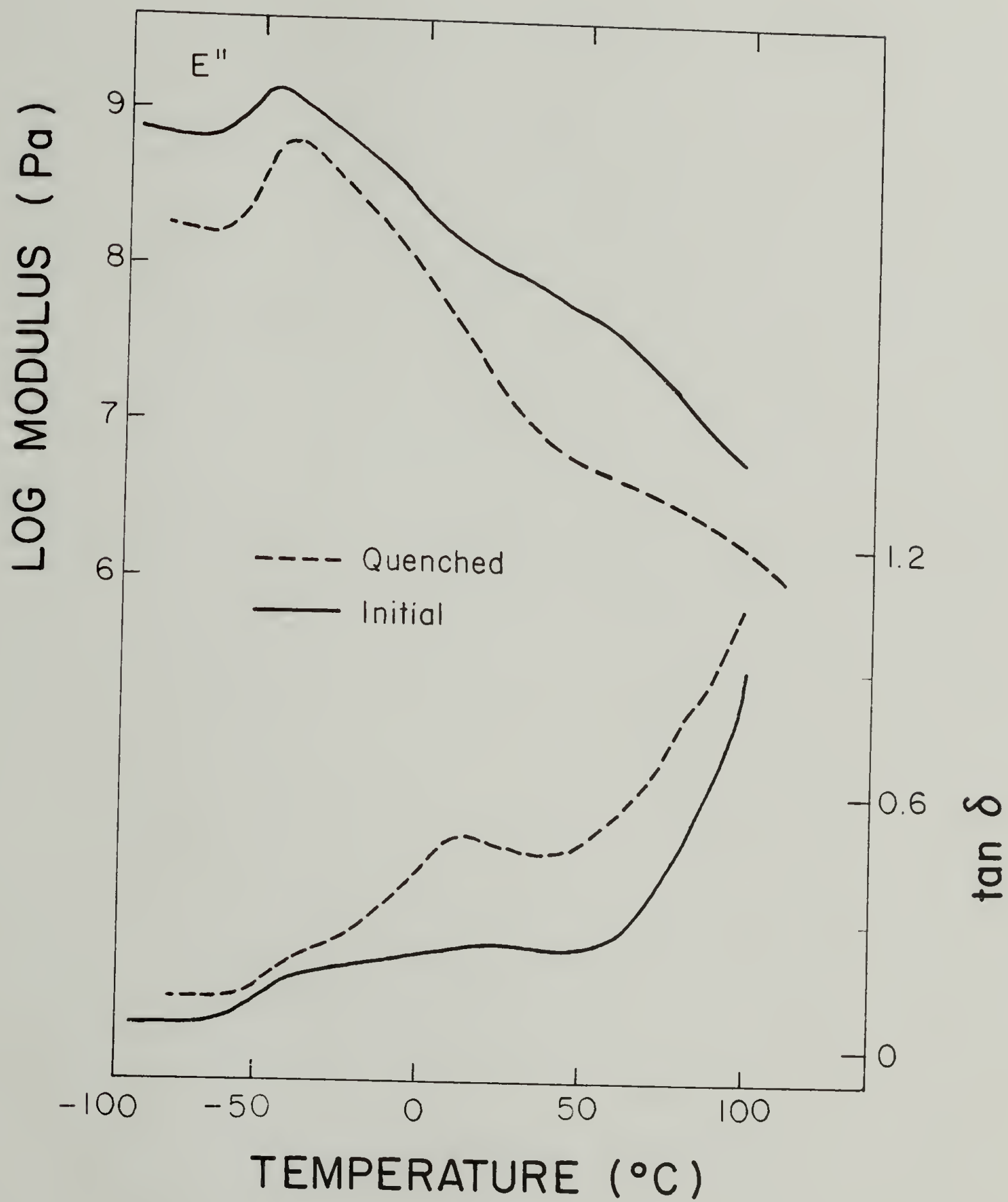


Table 4-3

DMTA Data for TMG Polyurethanes

Sample	tan δ ($^{\circ}\text{C}$)		log E'' ($^{\circ}\text{C}$)	
	Initial	Quenched	Initial	Quenched
TMG-35	-13	-8	-40	-35
TMG-45	-41 ^a , 18 ^b	-35 ^a , 12	-37, -10 ^c	-36, -5 ^c
TMG-72	-55 ^a , 41	-45 ^a , 52	-53, 20 ^c	-50, 30 ^c
TMG-108	-48 ^a , 68	-47 ^a , 68	-50, 48	-50, 45
TMG-228	-58 ^a , 87	-53 ^a , 88	-50, 60	-55, 73
TMG-275	-55 ^a , 92		-59, 74	

^aStep rise in tan δ ; ^bWeak, broad peak; ^cShoulder.

The lower transition is corroborated by DSC results but no DSC data exist for the upper transition. This is probably a result of the fact that the fraction of the sample that would be expected to undergo this glass transition (or the mechanical relaxation indicated here) is too small to be observed by DSC. In well aged samples, the $\tan \delta$ peak is very broad, characteristic of relaxations of poorly defined domains.⁸ Upon quenching from 100°C, the transitions move closer together, indicative of increased phase or segmental mixing. The $\tan \delta$ peak also becomes greater and more pronounced; perhaps this is indicative of a greater percentage of mixed (interfacial) material. TMG-45 was the only sample of this series to display a significant effect of thermal history on the dynamic mechanical properties of these polyurethanes.

DMTA results for Fu's monodisperse hard segment TMG polyurethanes are quite different. Only single relaxations are found, indicative of single phase behavior, up to 48% hard segment. The presence of longer hard segment lengths in polydisperse hard segment polyurethanes at similar compositions probably allows for better hard segment domain formation and, hence, two phase behavior.

Mechanical Properties

The tensile properties of TMG polyurethanes depend greatly on hard segment content as the morphology varies with composition. The stress strain curves for the series are displayed in Figure 4-9, and data for the various quantities are listed in Table 4-4. As in the JSR series and other polyurethanes, the initial modulus and ultimate strength

Figure 4-9 Stress-strain behavior of TMG polyurethanes.

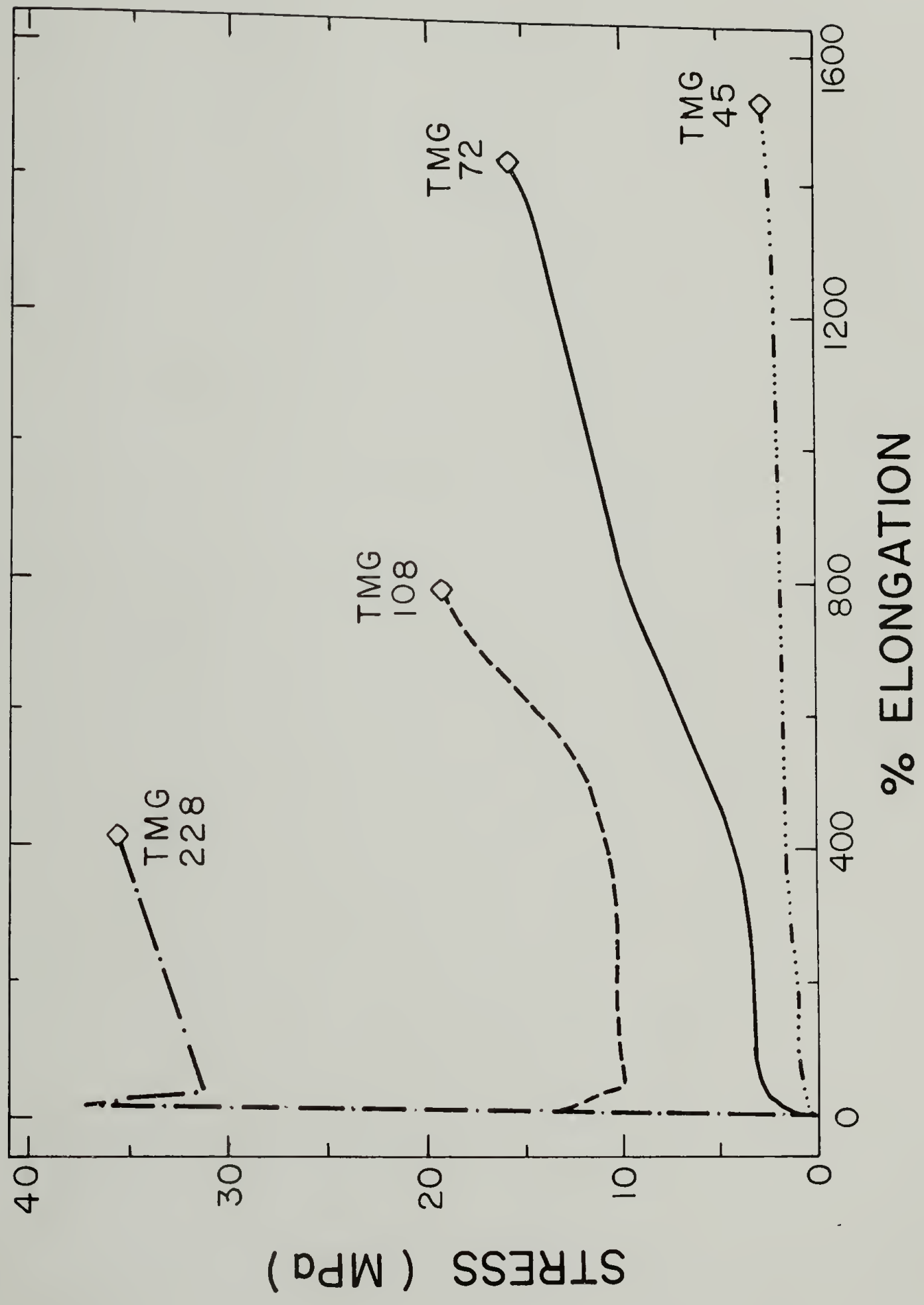


Table 4-4
Mechanical Properties of TMG Polyurethanes

Sample	Weight Fraction Hard Segment	\bar{M}_n	σ_B (MPa)	ϵ_B (%)	Modulus, (MPa)	σ_{yield} (MPa)
TMG-35	0.31	43,500	Too soft to test			
TMG-45	0.39	15,700	2.7	1,500	10	—
TMG-72	0.49	53,700	16.0	1,400	45	—
TMG-106	0.60	10,500	10.7	900	130	7
TMG-108	0.60	45,200	20.0	800	210	12
TMG-228	0.76	18,700	36.2	410	800	37

increase with increasing hard segment content while ultimate elongation decreases. Tensile properties are generally improved by a higher degree of phase segregation, as the discrete domains act as reinforcing filler that is strongly adsorbed by the elastomeric matrix. These tensile data support the sharp change in mechanical properties found by Fu at or about 40 - 45% hard segment content. A material of 31% hard segments, TMG-35, behaves as a polymer well above its T_g by irreversibly deforming in a flow-like manner at room temperature. TMG-45 (39% hard segments) is a very soft, weak rubber. TMG-72 (49% hard segments) has highly bicontinuous behavior as in JSR-87 and JSR-104. TMG-108 (60% hard segments) is highly extensible, yields, and has moderate strength. TMG-228 behaves very similarly to the equivalent hard segment content JSR material by necking and stress whitening at essentially the identical stress and strain.

In general the TMG series exhibits higher strengths and elongations than the JSR series at higher hard segment content. This could be because the glycol is a stronger and more highly extensible soft segment than JSR, given the high 1,2 addition content in the latter. The opportunity for interphase hydrogen bonding may also strengthen the material. The low mechanical properties evidenced by the lower hard segment content polymers are probably due to the lower extent of phase segregation.

The effect of molecular weight on these materials can be quite pronounced. A comparison of TMG-106 and TMG-108 from Table 4-4 shows that for equivalent compositions an increase in molecular weight from

10,000 to 45,000 (\overline{DP}_m from 2 to 9) doubles the strength and yield stress, and increases the modulus significantly while leaving the ultimate elongation essentially unchanged.

Hysteresis under cyclic loading conditions is a severe deficiency in many polyurethane applications due to heat build up. The extent of hysteresis is related to the interconnectedness of the hard segment domains.¹⁵ Breakage of interconnecting hard segment domains through mechanical deformation and heat setting leads to the destruction of properties.¹⁶ Therefore, hysteresis measurements can be expected to detect differences in morphology.

The hysteresis behaviors of samples in this series is presented in Figures 4-10 through 4-12. All samples show strain softening (often called the Mullins effect) and three distinct types of behavior occur. The change in hysteresis between TMG-45 and TMG-72 can be thought of as equivalent to the transition in the JSR series, i.e. a transition from separate hard segment domains to interconnected ones. TMG-108 yields and has a uniformly high value of hysteresis. This is indicative of more highly continuous hard domains.

Comparisons of the mechanical data of F_u ¹² for TMG polyurethanes with monodisperse hard segments show qualitatively similar behavior. Elongations at break and the general curve shapes are comparable. However, the materials with polydisperse hard segments have much higher tensile strengths. This might be a result of the formation of more well-defined hard segment domains in the latter caused by the presence of longer hard segments, favoring increased phase segregation. This

Figure 4-10 Hysteresis as a function of elongation for TMG
polyurethanes.

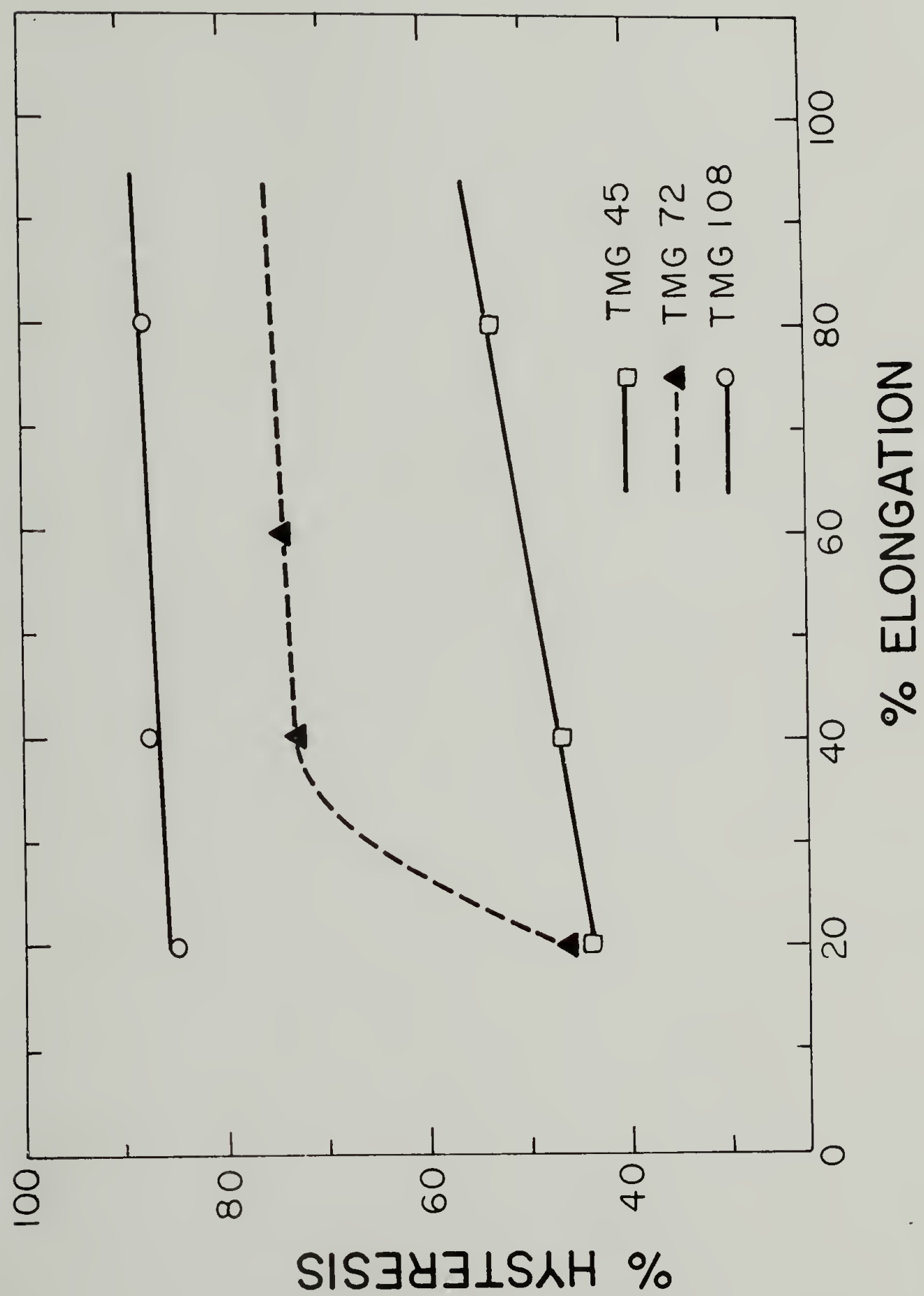


Figure 4-11 Cyclic stress-strain curves for TMG-72 and TMG-108.

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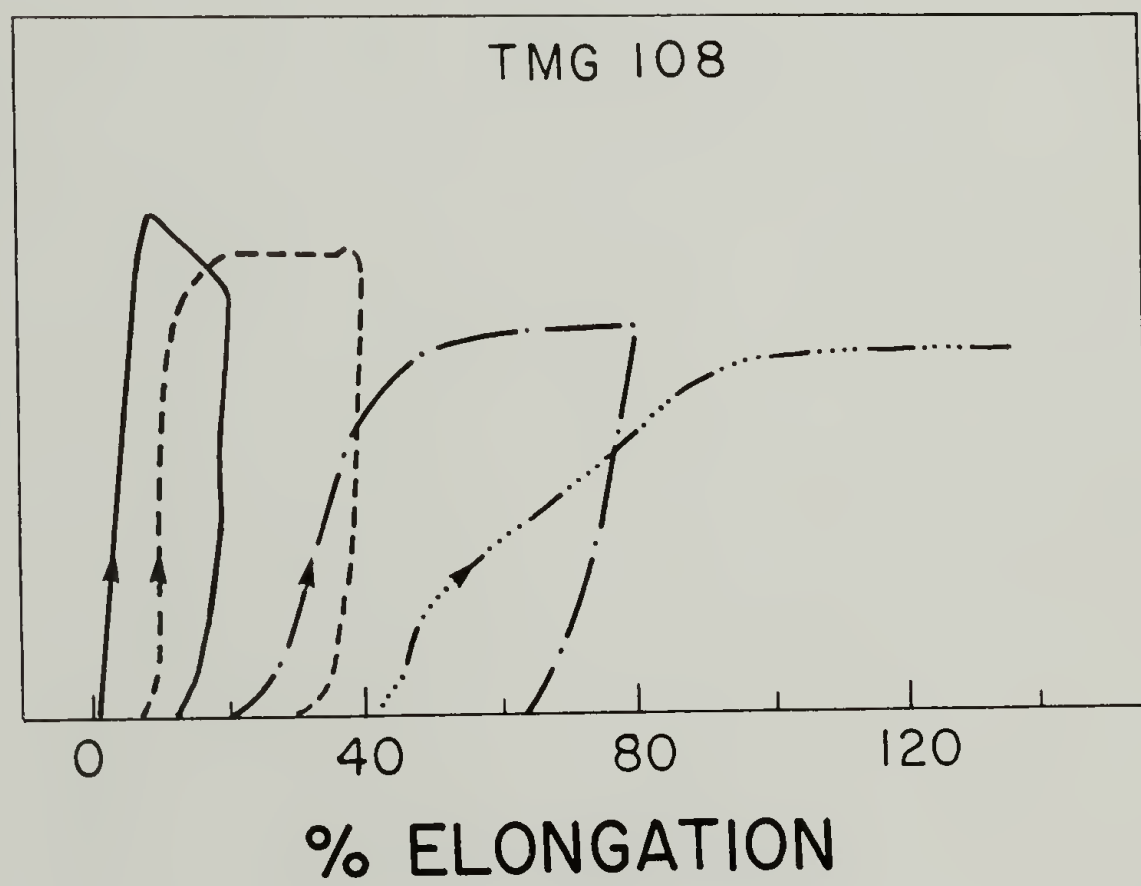
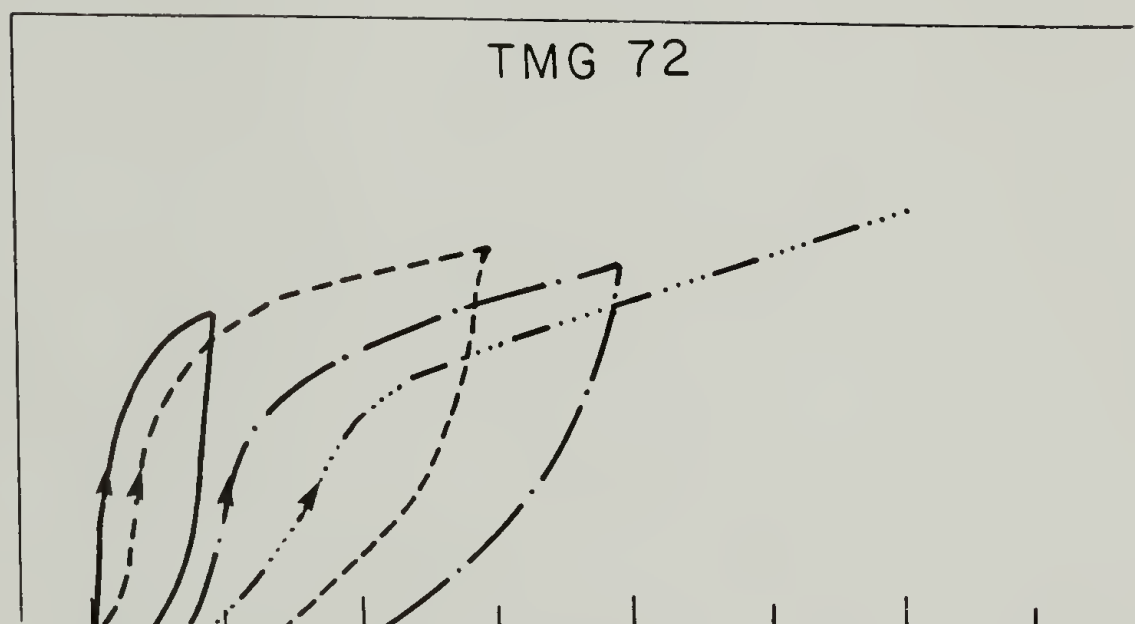
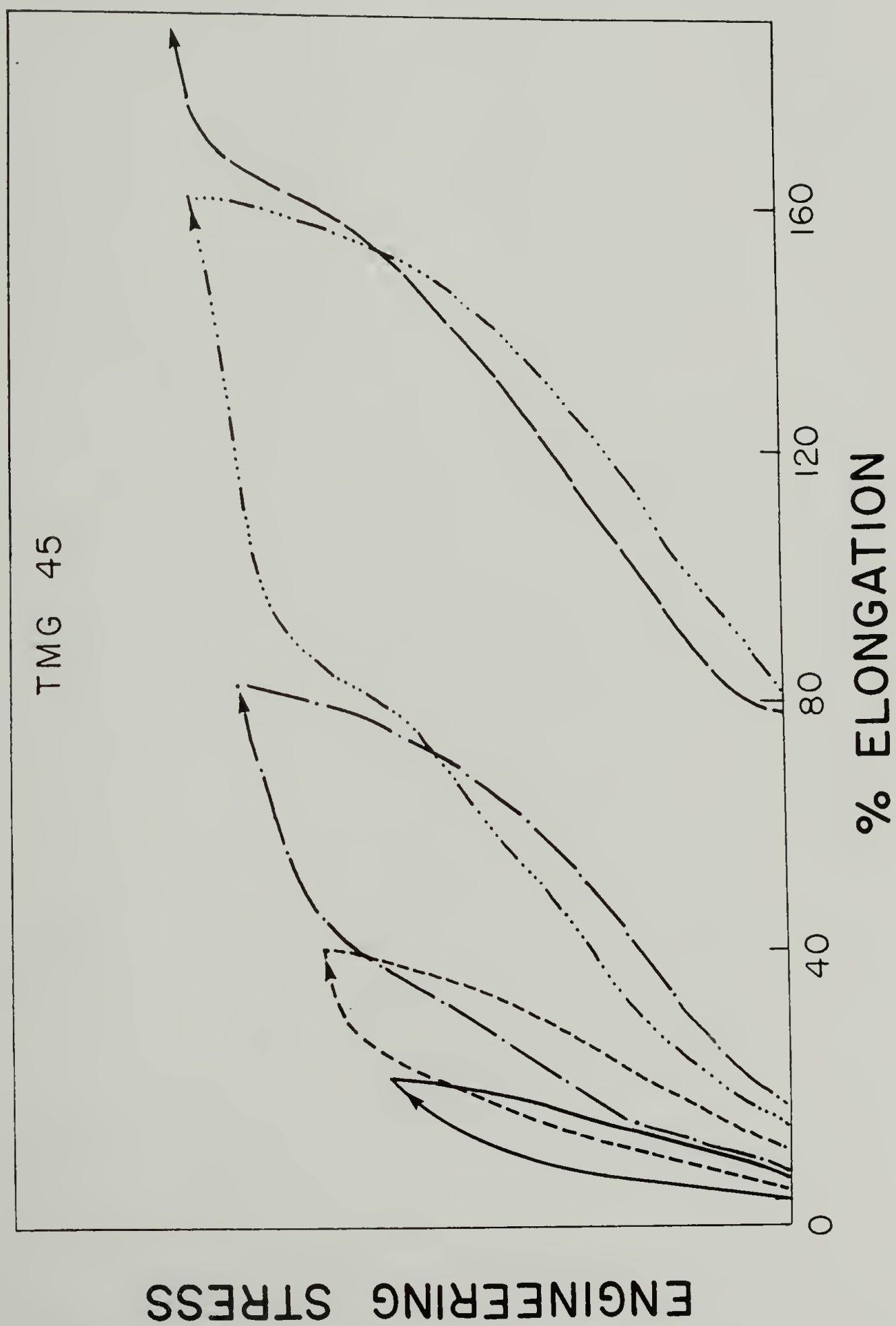


Figure 4-12 Cyclic stress-strain curve for TMG-45.



differential in strength does not result from differences in polyurethane molecular weights as they are comparable in both studies.

CONCLUSIONS

The GPC data for the copolymer studied in this thesis are fairly accurate measures of \bar{M}_n as VPO data agree with the GPC results for one member of this TMG series.

For the TMG series, an increasing degree of phase segregation with hard segment length is indicated by the decrease in soft segment T_g as the hard segment length increases. This is a manifestation of the chemical nature of the constituents where the interaction parameter, χ_{AB} , is such that the entropic effects of sequence length become highly significant as far as phase segregation is concerned.

Morphological transitions occur with increasing hard segment content. A range of mechanical properties results from this phenomenon. Polyurethanes of this chemical composition show improved mechanical properties for polydisperse hard segment materials over monodisperse hard segment materials.

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C H A P T E R V

SUMMARY AND SUGGESTIONS FOR FURTHER RESEARCH

This chapter presents a summary and comparison of the three polyurethane series studied. Some suggestions and considerations for future efforts in this area of research will also be presented.

The most significant accomplishment of this work is the synthesis and study of a true segmented copolyurethane incorporating polybutadiene soft segments. The solution polymerization method used (in all three series) overcomes the problems encountered with a bulk polymerization as discussed in Chapter II. These polyurethanes are completely phase segregated as evidenced by a soft segment T_g independent of hard segment content and very close to the value for the free oligomer. Morphology and consequently, mechanical properties of compression molded samples are determined solely by the relative fractions of hard and soft segments.

At the other extreme, that of a compatible block copolymer, is the series of polyurethanes that have polycaprolactone (PCL) incorporated as the soft segments. A solution polymerization method was used to extend the compositional range studied in the literature for this system. Contrary to the earlier study,¹ and consistent with the results of Fu,² for a chemically identical system with monodisperse hard segments, soft segment crystallization occurs. Crystallization takes place in samples containing less than 45% hard segments (by weight). As expected for copolymers, the rate and extent of crystallization are decreased with

increasing hard segment content. The mechanical properties of these polyurethanes are directed by the presence of crystallinity or the T_g of amorphous samples. Strong evidence of the expected strain induced crystallization is found.

An extended compositional range of polyurethanes with polytetramethylene oxide (TMG) soft segments has also been studied. These polyurethanes show a critical hard segment composition or molecular weight above which phase segregation occurs. The degree of phase segregation increases with increasing hard segment content/ \bar{M}_n as evidenced by a decreasing value of the soft segment T_g . A range of mechanical behaviors (morphologies) qualitatively similar to those of the polybutadiene polyurethanes was found to occur.

The major limitation of this work lies in the values of molecular weight for these polyurethanes. These materials showed a considerable variation in \bar{M}_n from sample to sample. While the molecular weights are above the minima generally accepted as necessary for the absence of molecular weight effects on mechanical properties,³ recent investigations indicate that the mechanical properties may vary significantly with molecular weight above this standard.⁴ Therefore, the variation in molecular weight may invalidate a significant portion of the comparisons made between different samples.

With the preceeding caveat in mind, general comparisons of the mechanical properties of these polyurethanes will be made. The mechanical properties are summarized as a function of increasing hard segment content in Table 5-1. As in most polyurethane systems, the

Table 5-1
Comparisons of Mechanical Properties

Sample	Weight Fraction Hard Segment	\bar{M}_n	Modulus (MPa)	σ_B (MPa)	ϵ_B (%)	σ_{yield} (MPa)
JSR-33	0.27	23,000	10	10.3	620	--
PCL-35	0.29	32,000	130	7.3	900	--
TMG-35	0.31	43,500	---	<0.4	>2,500	--
JSR-45	0.34	41,000	10	7.5	1,120	--
PCL-50	0.36	30,000	110	11.0	1,140	6.3
TMG-45	0.39	15,700	10	2.7	1,500	--
JSR-58	0.41	24,000	15	7.3	450	--
TMG-72	0.49	53,700	45	16.0	1,400	--
JSR-87	0.51	35,000	84	12.4	260	--
JSR-104	0.55	30,000	175	18.6	250	--
PCL-111	0.56	26,200	20	23.8	1,100	--
TMG-108	0.60	45,000	210	20.0	800	12
JSR-253	0.76	18,500	450	38.6	150	38
TMG-228	0.76	18,700	800	36.2	410	37

general trend in each phase segregated series is that modulus and tensile strength increase and elongation at break decreases with increasing hard segment content. This is a result of the increasing amount of reinforcing filler provided by the hard segment domains. The initial modulus increases dramatically when the hard segments form a continuous phase at around 50% hard segment. Samples with this bicontinuous morphology are TMG-72 (49% hard segment), JSR-87 (51%), JSR-104 (55%) and TMG-108 (60%). The modulus increases proportionally with increasing hard segment content (degree of connectivity) in this region. These TMG samples have superior ultimate properties vis a vis corresponding JSR materials due to the greater extensibility of the TMG soft segments.

Phase segregated systems of low hard segment content display similar low moduli, characteristic of rubbery matrices. The ultimate properties of TMG-45 are quite different from those of corresponding JSR samples. The tensile strength of TMG-45 is much lower due to poorer phase segregation. Elongation at break is much greater due to this lack of phase segregation and the aforementioned increased extensibility of the TMG soft segments.

JSR and TMG samples of 76% hard segment have nearly identical ultimate and yield stress values. Both also neck and stress whiten, characteristic of rubber toughened plastics. The TMG has a higher ultimate elongation for reasons explained earlier. This material also has a modulus nearly twice that of the JSR material. The reason for this is most likely a difference in the degree of the continuity of the hard segment phase caused by the different soft segments.

SUGGESTIONS FOR FURTHER RESEARCH

A study of the hard segment length and length distribution produced by this synthetic method would assist in the understanding of the final morphology of these materials. Selective cleavage of the soft segments leaving the hard segments unchanged, would produce hard segment residues suitable for analysis by GPC as to \bar{M}_n and polydispersity. Ozonation of the polybutadiene soft segments would satisfy these requirements and the monodisperse hard segments of Fu^2 are available as molecular weight standards. It would be useful to compare these results with the theoretical calculations in the literature to verify if this synthetic method produces well defined polyurethanes.

Another interesting line of research would be to use this synthetic method to study polyurethanes with different hard and soft segments. The symmetrical 2,6-TDI isomer could be used to produce crystallizable hard segments and most likely improved mechanical properties. Preliminary attempts at this have been made but reaction solubility problems have resulted in only low molecular weight materials. The use of different solvent systems should correct this. New amorphous soft segments would include polypropylene oxide (PPO) and polydimethyl siloxane (PDMS). Exactly difunctional monodisperse PDMS is available from a method developed in labs at University of Massachusetts.⁵ It would provide a soft segment with a lower solubility parameter ($\delta = 8.5 \text{ (cal/cm}^3)^{1/2}$) and better oxidative stability than polybutadiene. The effect of the molecular weight dispersity of the soft segment on polyurethane properties could also be ascertained. PPO has a solubility

parameter ($\delta = 9.0$) midway between those of PCL and TMG and the study of these polyurethanes would assist in the determination of $(\chi)_{cr}$ for phase segregation in polyurethanes. The use of different PPO molecular weights should also vary the degree of phase segregation, with higher molecular weights producing more highly phase segregated materials.

A better understanding of the thermodynamics of phase segregation could be obtained by analysis of blends of hard and soft segment oligomers of varying molecular weights and dispersities. Techniques suitable for this are DSC and dynamic mechanical analysis using supported specimens, i.e. torsional braid analysis and dynamic spring analysis.

Morphological studies using techniques such as small angle x-ray scattering and electron microscopy should be extended to the TMG and PCL series. Significant information would be gathered to compliment the results presented in this thesis. Further morphological information could be supplied by the analysis of the dielectric properties of these materials. Specific information concerning the nature of the domain interface might be obtained from the study of any interfacial polarization that occurs.

The nature of the morphology at large scale deformations would also be of interest in the understanding of these materials. The extent of phase segregation or the occurrence of strain induced crystallization could be determined by DSC of samples stretched to different extension ratios. An examination of stretched samples using wide angle x-ray diffraction would supply a more complete study of the strain induced crystallization.

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