Thermal and Dynamic Mechanical Properties of Polyurethaneureas

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Synopsis

Measurements were made of the thermal and dynamic mechanical properties of 22 polyurethaneureas of varying diol molecular weight, type of aromatic chain extender, diol molecular weight distribution, and chain extender stoichiometry. The dynamic mechanical data, obtained as a function of temperature and frequency (in the kHz region), were used to construct master curves of shear modulus and loss factor over a wide range of reduced frequencies. Based on these master curves, interpreted in conjunction with the thermal analysis results, it was found that: Soft segment crystallization occurs at the higher diol molecular weights, dynamic mechanical properties are well correlated with the soft segment glass transition, diol molecular weight influences dynamic mechanical properties by affecting the degree of phase separation and hence glass transition temperature, and neither diol molecular weight distribution nor chain extender stoichiometry have a significant effect, in the ranges studied, on transition temperatures or dynamic mechanical properties.

INTRODUCTION

Certain polyurethanes exhibit unique dynamic mechanical properties, primarily as a result of their two-phase morphology.[1] These materials are alternating block copolymers made up of hard segments of aromatic groups from the diisocyanate/chain extender and soft segments of aliphatic chains from the diol. The hard and soft segments are chemically incompatible and microphase separation of the hard segments into domains dispersed in a matrix of soft segments can occur in varying degrees. Polyurethanes may then exhibit two separate glass transitions, in the hard and soft segment domains, respectively. In addition, crystallization may occur in one or both of the phases.[2] Since dynamic mechanical properties change significantly in the vicinity of each of these transitions, it is important to know their location. For this reason, differential scanning calorimetry (DSC) is a useful adjunct to dynamic mechanical measurements.

Thermal analysis is also valuable in the interpretation of dynamic mechanical results since the degree of phase separation is at least qualitatively related to the transition temperatures, e.g., as the degree of phase separation decreases, the T_g of the soft phase increases. This behavior is the result of two effects. Hard segments solubilized into the soft segment amorphous domains act to raise the soft segment T_g in a manner similar to that predicted for compatible blends or random copolymers. In addition, the hard domains act as a reinforcing filler which can also provide a small increase in the rubbery phase T_g. For these reasons, the soft segment T_g is a sensitive index of phase

separation and quantitative relations have been proposed.[3] The melting temperature (T_m) of both the hard and soft segments, if they are of sufficient length and regularity to crystallize, are also affected by phase mixing. In general, phase mixing will lower a given microdomain's T_m.

A number of structural variables are known to influence phase separation and hence dynamic mechanical properties. Using a diamine chain extender introduces urea linkages into the hard segment, resulting in a polyurethaneurea. There is considerably more phase separation in a urethaneurea than in the analogous urethane.[4] The increased phase separation is attributed to a three dimensional interurea hydrogen bonding network. Another important structural variable is the diol molecular weight. All other things being equal, the higher the diol MW, the greater the degree of phase separation.[4] Other important structural variables are the type of diol (ether or ester), the type of isocyanate, and the stoichiometry used.

In addition to the above structural variables, the degree of phase separation can also show considerable dependence on temperature and time. Phase separation is favored at low temperature where the enthalpic factors dominate the entropic factors, but the separation in quenched samples may only develop slowly, over a period of days. Thus thermal and mechanical data may be misleading unless the thermal history of the specimen has been given.[5] Finally, the method of fabrication, whether the sample is compression-molded or solution-cast, or whether a thin film or a bulk specimen is used, can have a significant effect on the extent of phase separation and on the morphology of the separated phase.[3]

Because of the wide variety of applications for these polymers, it is of practical interest to characterize their dynamic mechanical behavior with master curves of modulus and loss factor over a wide range of reduced frequencies using time–temperature superposition of the data. This type of characterization is also the most complete description of dynamic mechanical properties. Little information of this type is available for block polyurethanes, but in a preliminary investigation of this type, it was pointed out that superposition of the data is complicated by the semicrystalline morphology.[1] A more complete analysis was done for dielectric measurements in polyurethanes,[6] where similar conclusions were reached. Most dynamic mechanical data in the literature for polyurethanes was obtained at only one frequency so that master curves cannot be generated. There are some measurements available in the frequency range from 1 to 100 Hz as a function of temperature, but the data was not shifted to form master curves.[2,7] Other measurements have been made at 1.5 MHz of sound speed using polymer systems nearly identical to some of those studied here, but master curves were not obtained.[8]

In the work presented in this paper, dynamic mechanical measurements were made over a range of frequencies in the kHz region as a function of temperature. This data was used to construct master curves of shear modulus and loss factor over a wide range of reduced frequencies. These measurements were carried out for a series of polyurethaneureas as a function of the following structural variables: diol molecular weight, type of diamine chain extender, diol molecular weight distribution, and chain extender stoichiometry. In order to interpret the master curves in terms of phase separation, DSC

measurements were run in conjunction with the dynamic mechanical measurements.

EXPERIMENTAL

Synthesis

All the polymers studied were based on poly(tetramethylene ether glycol) (PTMG). With the exception of those with nonstandard molecular weight distribution, all of the diols used were commercial products (Terathane series from E. I. DuPont de Nemours and Co.). Four nominal molecular weights of PTMG were used without modification: 650, 1000, 2000, and 2900. The molecular weights determined from the hydroxyl number using acetic anhydride titration (ASTM E222) are listed in Table I. Gel permeation chromatography was used to determine the ratio of weight average molecular weight to number average molecular weight. This ratio is a measure of the width of the molecular weight distribution and will be referred to as the MWD. The values are also given in Table I. In addition to the above commercial diols, having the standard MWD, some special diols were prepared with both narrower and broader distributions about the nominal values of 1000 and 2000. These diols are prepared using a catalytic process which is difficult to control and as a consequence, the number average molecular weights obtained are not precisely the same.

All of the above diols were reacted with 2,4-toluene diisocyanate (TDI) (Mondur TDS from Mobay Chemical Co.) using 1 mol of diol and 2 mol of TDI to form prepolymers. The polyol was added to TDI at 45–50°C, producing an exotherm with a maximum of 80°C. The mixture was held at 75°C for 1–2 h, then 200–300 ppm benzoyl chloride was added as a stabilizer, and the mixture was degassed, cooled, and sealed under nitrogen. The percent free isocynate (NCO) was determined the following day using a modification of ASTM method D1638. In this procedure, the prepolymer is dissolved in toluene and reacted with an excess of $0.1N$ di-n-butylamine in toluene. The solution is diluted with isopropyl alcohol and the excess di-n-butylamine is backtitrated with $0.1N$ hydrochloric acid. The difference between the amount

TABLE I
Prepolymer Characteristics[a]

Designation	PTMG MW (g/mol)	PTMG MWD	NCO (%)
PTMG 650/TDI	682	1.53	7.8
PTMG 1000/TDI	1015	1.54	6.0
PTMG 2000/TDI	2047	1.59	3.2
PTMG 2900/TDI	2899	2.04	2.5
PTMG 2000B/TDI	2000	1.87	3.6
PTMG 2041N/TDI	2041	1.34	3.5
PTMG 1035B/TDI	1035	2.16	6.0
PTMG 1259N/TDI	1259	1.34	5.1
PTMG 932N/TDI	932	1.33	6.3

[a] B = broad molecular weight distribution; N = narrow molecular weight distribution.

PTMG   poly (tetramethylene ether) glycol

$$HO-[(CH_2)_4O]_n-H$$

TDI   2, 4-toluene diisocyanate

MBOCA   4, 4'-methylene-bis-orthochloroaniline

TMAB   trimethyleneglycol-di-p-aminobenzoate

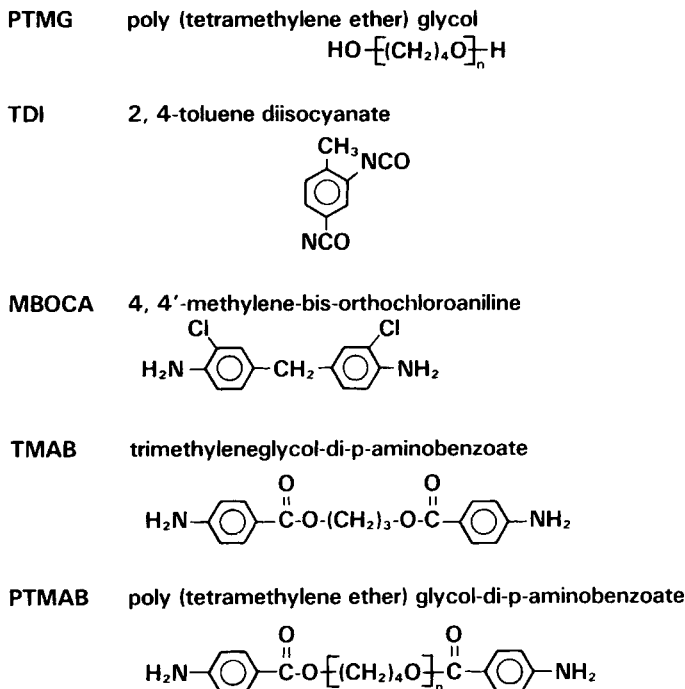**PTMAB**   poly (tetramethylene ether) glycol-di-p-aminobenzoate

Fig. 1.   Chemical structures.

of HCl required to titrate the sample and a blank determination done under the same conditions is then a result of the free NCO.

Three aromatic diamines were used as chain extenders: 4,4'-methylene-bis-orthochloroaniline (MBOCA), trimethyleneglycol-di-p-aminobenzoate (TMAB) (Polacure 740 M from Polaroid Corp.), and polytetramethyleneglycol-di-p-aminobenzoate (PTMAB) (Polamine 1000 from Polaroid Corp., with a tetramethylene glycol molecular weight of 1238). The chemical structures of all components are shown in Figure 1. The standard composition was 95% chain extender stoichiometry, but, in one case, PTMG 650/TDI/TMAB, the following stoichiometries were prepared: 90, 95, 100, 105, and 110%. Specimens with dimensions $0.635 \times 0.635 \times 20$ cm were cast in silicone molds and cured as follows: MBOCA systems, 100°C/3 h; TMAB systems, 100°C/5 h; PTMAB systems, 100°C/6 h. Samples were stored at ambient conditions for a period of at least 1 month before testing, to allow the specimens to reach equilibrium.

A listing of all the polymers synthesized, along with their hard segment weight concentration, room temperature density, and durometer hardness, on both the A and D-2 scales, is given in Table II. Hard segment concentration is listed primarily for comparison purposes with other papers that characterize samples in terms of this parameter. The basic definition of this quantity is the molecular weight of the hard segment divided by the molecular weight of the entire repeat unit. Usually, the hard segment is taken to be the chain extender/isocyanate moiety but in the case of PTMAB a modification must be made. This chain extender contains a considerable amount (about 1000 g/mol) of aliphatic ether identical to the soft segment diol. Because of this,

TABLE II
Polymer Characteristics

Designation	Hard segment (wt %)	Density (g/cm³)	Hardness	
			A	D − 2
1. PTMG 650/TDI/MBOCA	48.8	1.161	100	58
2. PTMG 1000/TDI/MBOCA	38.0	1.130	97	43
3. PTMG 2000/TDI/MBOCA	23.9	1.067	86	28
4. PTMG 2900/TDI/MBOCA	17.3	1.051	78	21
5. PTMG 650/TDI/TMAB	50.6	1.164	99	44
6. PTMG 1000/TDI/TMAB	40.0	1.113	98	43
7. PTMG 2000/TDI/TMAB	24.6	1.061	78	22
8. PTMG 2900/TDI/TMAB	18.3	1.048	79	20
9. PTMG 650/TDI/PTMAB	24.6	1.090	59	14
10. PTMG 1000/TDI/PTMAB	21.5	1.075	74	18
11. PTMG 2000/TDI/PTMAB	15.8	1.047	59	9
12. PTMG 2900/TDI/PTMAB	12.7	1.037	55	7
13. PTMG 2000B/TDI/TMAB	24.4	1.072	80	23
14. PTMG 2041N/TDI/TMAB	24.1	1.066	74	21
15. PTMG 1035B/TDI/TMAB	38.4	1.124	84	29
16. PTMG 1259N/TDI/TMAB	33.9	1.107	85	32
17. PTMG 932N/TDI/TMAB	40.9	1.129	76	24
18. PTMG 650/TDI/90TMAB	49.9	1.160	100	50
19. PTMG 650/TDI/95TMAB	50.6	1.161	100 +	52
20. PTMG 650/TDI/100TMAB	51.2	1.163	100 +	50
21. PTMG 650/TDI/105TMAB	51.7	1.166	100 +	50
22. PTMG 650/TDI/110TMAB	52.3	1.168	100 +	50

polymers are softer with PTMAB than TMAB, and it is therefore reasonable to include the aliphatic portion of the chain extender as part of the soft segment rather than part of the hard segment. This has been done in Table II.

Density is listed not only because it is used in the dynamic mechanical data analysis, but also because this is an important fundamental parameter characterizing polymers. Within each group, the lower the hard segment weight percent, the lower the density. For a simple two-component model (hard segment and soft segment), the measured density should be a linear function of hard segment volume fraction. Hard segment volume fractions were calculated from the hard segment weight fractions in Table II using the reported[9] soft segment density of 0.982 g/cm³. For each of the three hard segments, good linear fits were found. From these fits, hard segment densities were found to be: 1.46 g/cm³ for the MBOCA based hard segment, 1.39 g/cm³ for TMAB, and 1.63 g/cm³ for PTMAB.

Finally, hardness is listed because this value is often quoted in practical work, but the values show considerable variation for each specimen and are considered to be qualitative measures only. Hardness is a measure of low frequency modulus and should be at least qualitatively related to the dynamic mechanical measurements presented here.

Thermal Analysis Technique

A DuPont 9900 computer/thermal analyzer was used in conjunction with a 910 DSC module to obtain thermograms. Samples (10–15 mg) were cut from

the test bars and placed in aluminum test pans for analysis. For the first run, the cell was cooled from room temperature to −170°C in about 5 min and then heated to 250°C at a programmed rate of 10°C/min in an argon atmosphere. A second run was made immediately after by cooling at a rate of 40°C/min and then rerunning using the same conditions in order to determine the effect of thermal history on transition temperatures.

The data was analyzed using the available 9900 computer software. Both the heat flow and temperature scales were expanded in the transition region to improve on data definition. For some of the systems considered here, the glass transition occurred over a wide temperature range, as a result of phase mixing. In order to determine a single number for T_g, the following procedure was used. Tangents to the pretransition and post-transition portions of the heat flow curve were drawn by the computer using two operator-selected points. A third line was drawn through the transition portion of the heat flow curve connecting the two tangents. The temperatures at the two junction points were recorded as well as the midpoint of the transition line. It was this latter temperature that was used as the glass transition temperature of the sample.

In the case of exothermic crystallization or endothermic melting point peaks, a baseline was drawn across the pre and post portions of the heat flow curve. A tangent was then drawn through the onset of the crystallization or melting curve to intersect the baseline. This point was recorded as the temperature at which crystallization or melting began. The peak temperature was also determined automatically and was used in this work to define the transition point.

Dynamic Mechanical Analysis Technique

The apparatus used[10] is based on producing resonance in a bar specimen as shown schematically in Figure 2. An electromagnetic shaker is used to drive the test specimen at one end while the other end is allowed to move freely. Miniature accelerometers are adhesively bonded on each end to measure the driving point acceleration and the acceleration of the free end. The output signals from the accelerometers are analyzed by a dual channel Fast Fourier Transform spectrum analyzer. The analyzer digitizes and displays the measured signals as the amplitude of the acceleration ratio and phase difference of
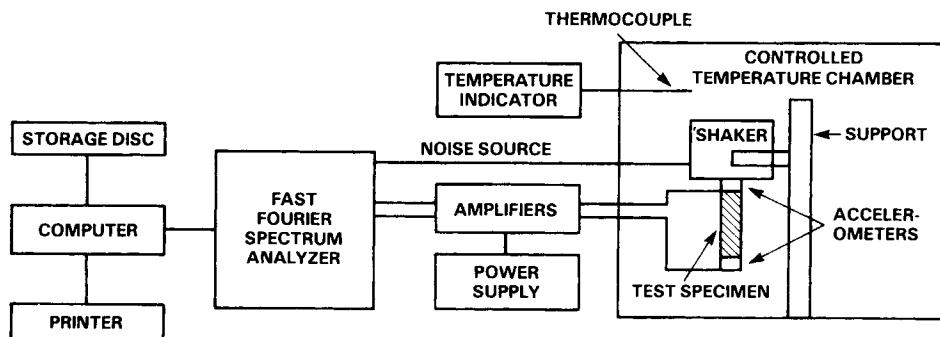
Fig. 2. Resonance apparatus.

the two accelerometers and also provides a noise source to drive the shaker. The data are always sampled and rms averaged at least 8 times, for low noise data, and up to 128 times, for noisy data. A minicomputer is used to collect and store the data from the analyzer for later calculations. Typical length of the test specimens is about 10–15 cm with square lateral dimensions of 0.635 × 0.635 cm. The output of the spectrum analyzer shows that at certain frequencies the amplitude of the acceleration ratio goes through local resonant peaks. At −60°C, it was found for these polyurethaneureas that the resonant peaks appeared between 2000 and 22,000 Hz, while at the highest temperature used of 70°C, they appeared between 100 and 4000 Hz. From the peak amplitude and frequency, the Young's modulus and loss factor can be determined as functions of frequency and temperature. By assuming a Poisson's ratio of 0.5, Young's moduli were converted to shear moduli.

Modulus and loss factor data are processed into a reduced frequency plot in the following manner. After selecting a reference temperature, the modulus and loss factor data for other temperatures are shifted along the frequency axis until they partially overlap each other, while leaving the reference temperature data unshifted. The final result is a constant temperature plot or master curve over a wider range of frequency than actually measured. Melting and crystallization were found to occur in the polyurethaneureas synthesized from PTMG 2000 and PTMG 2900. At these transition points, the modulus and loss factor data, when shifted, do not lead to superposition.

Since crystallization and melting were found to depend on the thermal cycle used in the dynamic mechanical measurements, a routine testing procedure was used that standardized these effects. The specimen was cooled from room temperature to the minimum temperature available in the test chamber used, −60°C, in 1 h and held for at least 12 h. Measurements were then made as the temperature was raised, typically in 5°C intervals, with a minimum of 20 min allowed to elapse between each measurement in order to reach thermal equilibrium. The upper temperature limit was set by the maximum use temperature of the shaker, 70°C. Measurements were made from −60°C to room temperature during the course of 1 day, the specimen was then held overnight at room temperature, and finally measurements were made from room temperature to 70°C on the following day.

To determine the reproducibility of the resonance apparatus, several specimens were remeasured. It was concluded that the modulus can be determined within 3% and the loss factor within 5%.

RESULTS AND DISCUSSION

Thermal Analysis

The DSC results from the four molecular weight PTMG/TDI prepolymers chain extended with MBOCA are shown in Figures 3 and 4. Transition temperatures were determined from expanded versions of these figures and the results are given in Table III. (Recall that the glass transition can occur over a 100°C range, but only the midpoints are listed.) The data presented in all DSC traces shown are unexpanded so that all four MW polymers could be presented on the same figure. The PTMG 2900/TDI/MBOCA polymer shows
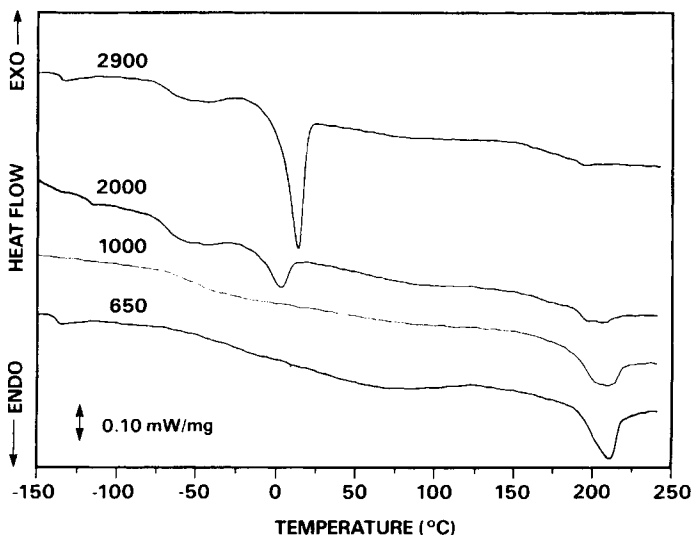
Fig. 3. DSC curves for PTMG/TDI/MBOCA, first run.

a soft segment T_g at $-70°C$, which approaches the glass transition tempera-
ture of pure PTMG, $-85°C.$[4] The broad exotherm at $-20°C$ is due to soft
segment crystallization which is followed by a sharp melting of the soft
segment at $13°C$. This value is to be compared with pure PTMG, which melts
at $45°C.$[9,11] The weight fraction of soft segment crystallinity is estimated to
be 0.13, based on the area under the DSC curve (27 J/g) and the reported[9]
heat of fusion of pure PTMG, 206 J/g. There is an endotherm at about $200°C$,
which is tentatively identified as the hard segment melting temperature. The
PTMG 2000/TDI/MBOCA polymer exhibits very similar behavior with a T_g
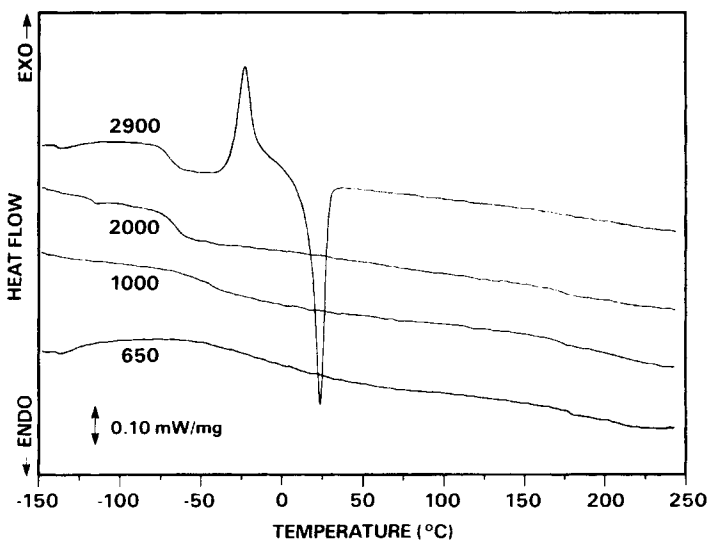
Fig. 4. DSC curves for PTMG/TDI/MBOCA, second run.

TABLE III
Transition Temperatures[a]

| Designation | Soft segment | | Hard segment |
	T_g	T_m	T_m
1. PTMG 650/TDI/MBOCA	$-3\,(-7)$	—	210
2. PTMG 1000/TDI/MBOCA	$-52\,(-47)$	—	205
3. PTMG 2000/TDI/MBOCA	$-69\,(-69)$	3	200
4. PTMG 2900/TDI/MBOCA	$-70\,(-73)$	13 (22)	—
5. PTMG 650/TDI/TMAB	$21\,(-5)$	—	—
6. PTMG 1000/TDI/TMAB	$-36\,(-51)$	—	—
7. PTMG 2000/TDI/TMAB	$-69\,(-69)$	6 (20)	—
8. PTMG 2900/TDI/TMAB	$-73\,(-74)$	10 (22)	—
9. PTMG 650/TDI/PTMAB	$-43\,(-46)$	—	—
10. PTMG 1000/TDI/PTMAB	$-51\,(-56)$	—	—
11. PTMG 2000/TDI/PTMAB	$-63\,(-65)$	9 (20)	—
12. PTMG 2900/TDI/PTMAB	$-69\,(-71)$	16 (22)	—
13. PTMG 2000B/TDI/TMAB	$-71\,(-69)$	10 (22)	—
14. PTMG 2047S/TDI/TMAB	$-69\,(-69)$	6 (20)	—
15. PTMG 2041N/TDI/TMAB	$-64\,(-67)$	—	—
16. PTMG 1015S/TDI/TMAB	$-36\,(-51)$	—	—
17. PTMG 1035B/TDI/TMAB	$-15\,(-54)$	—	—
18. PTMG 1259N/TDI/TMAB	$-45\,(-52)$	—	—
19. PTMG 932N/TDI/TMAB	$-19\,(-30)$	—	—

[a]All temperatures are in °C. Values in parenthesis are for the second run. B = broad molecular weight distribution (MWD); S = standard MWD, and N = narrow MWD. Samples 6 and 16 are the same sample.

at -69°C and melting at 3°C, both attributable to the soft segment and indicative of a highly phase separated system. In this case, the weight fraction of soft segment crystallinity is 0.03. (It should be remembered that this value is calculated on the basis of the total polymer weight, not just the soft segment weight.) Once again, there is hard segment melting at about 200°C. The PTMG 1000/TDI/MBOCA polymer shows a change in behavior due to copolymer effects and the onset of phase mixing. T_g for this system is now -52°C, which is an increase of 33°C from the T_g of pure PTMG. Hard segment melting is more prominent and occurs at 205°C. Phase mixing has increased still further in the PTMG 650/TDI/MBOCA polymer as evidenced by a broad soft segment T_g at -3°C. The transition covers a region from about -65 to 60°C and is the result of increased phase mixing due to greater compatibility of the hard segments with the lower molecular weight PTMG 650 than with the higher molecular weight PTMG 2000 and PTMG 2900. T_m for the hard segment is 212°C.

The decrease of T_g with increasing PTMG molecular weight is the opposite of what is observed in homopolymers. Further, the variation of T_g with composition cannot be represented by the copolymer equation (which expresses the reciprocal measured T_g as the weighted sum of the reciprocal T_g's of the components). In attempting to use the copolymer equation, taking the measured T_g and the reported soft segment T_g (-85°C) as known, the calculated hard segment T_g is found not to be a constant. This lack of agreement with the copolymer equation is observed in all three chain extender

series. This result shows clearly that these materials cannot be considered as simple copolymers. Their behavior is complicated by the other effects that we refer to collectively as phase separation.

The second DSC run for this system shows a number of interesting differences in the thermograms. The T_g of the PTMG 2900/TDI/MBOCA shows essentially no change in T_g from the first run but there is a considerable sharpening in the crystallization exotherm at $-27°C$ followed by melting at $22°C$. This behavior is explained by the fact the crystallization process is time dependent, and, since most of the soft segment is amorphous at the start of the second run, we see a large increase in the area under the crystallization exotherm peak (from 27 to 33 J/g). The melting temperature of the soft segment also increases due to the formation of larger and more perfect crystals during the crystallization process of the second run. T_g of the PTMG 2000/TDI/MBOCA shows no increase from the first run and complete loss of the soft segment melting peak. Evidently, there is insufficient time for nucleation to occur. The PTMG 1000 and PTMG 650/TDI/MBOCA polymers show changes in their T_g's of 5 and $-4°C$, respectively, and both systems fail to show a reappearance of hard segment melting during the second run.

The TMAB-cured prepolymers have transition properties similar to MBOCA, and the results are shown in Figures 5 and 6. The PTMG 2900/TDI/TMAB polymer shows a soft segment T_g at $-73°C$, a crystallization exotherm at $-35°C$, and melting at $10°C$. The PTMG 2000/TDI/TMAB polymer has a T_g at $-69°C$ and melting of the soft segment at $6°C$. Phase mixing is more apparent in the PTMG 1000/TDI/TMAB polymer as evidenced by an increase in soft segment T_g to $-36°C$. This trend continues in the PTMG 650/TDI/TMAB polymer, where the T_g rises to a value of $21°C$ and occurs over the temperature range from 0 to $50°C$.
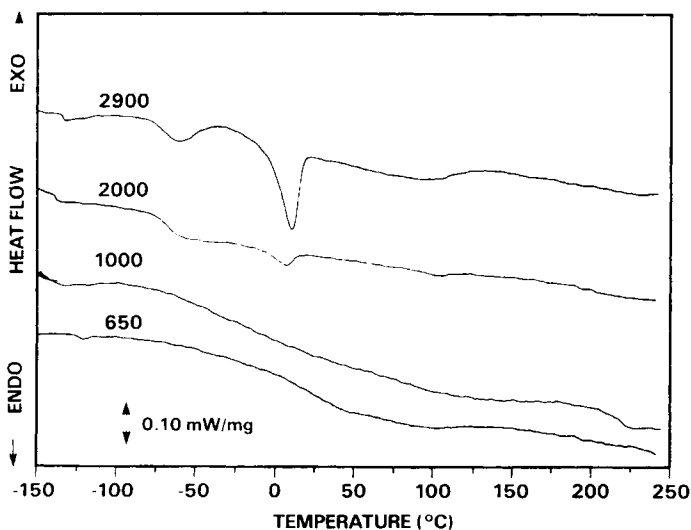
Fig. 5.   DSC curves for PTMG/TDI/TMAB, first run.
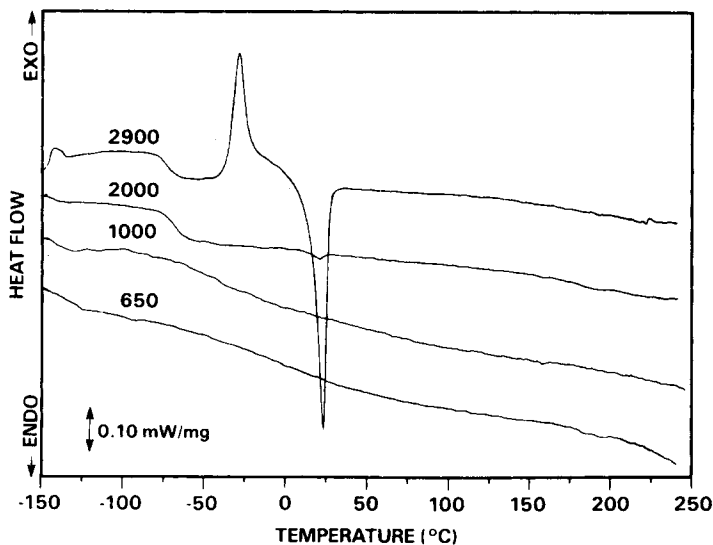
Fig. 6.   DSC curves for PTMG/TDI/TMAB, second run.

The second DSC run on these TMAB samples introduces some significant differences. The T_g of the soft segment in PTMG 2900/TDI/TMAB and PTMG 2000/TDI/TMAB remain unchanged. The crystallization exotherm for the PTMG 2900/TDI/TMAB appears as a sharp peak at $-30°C$, which is similar to the MBOCA cured polymer. Melting of the soft segment increases from 10°C in the first run to 22°C for PTMG 2900/TDI/TMAB and from 6 to 20°C for PTMG 2000/TDI/TMAB. For PTMG 1000/TDI/TMAB, T_g for the second run decreases from the first run value $(-36°C)$ to $-51°C$. In the case of PTMG 650/TDI/TMAB a large decrease also occurs in T_g during the second run (from 21 to $-5°C$). This may be due in part to the difficulty in accurately determining the T_g of this system because it is very broad in nature. The hard segment melting shown by PTMG 1000/TDI/TMAB and PTMG 650/TDI/TMAB during the first run does not reappear during the second run because the rate at which crystallization occurs is too slow.

PTMAB is structurally similar to TMAB except that the glycol used in its preparation has a higher molecular weight (about 1000), which serves to make the backbone more flexible. Results from the DSC for the series PTMG/TDI/PTMAB are shown in Figures 7 and 8. T_g for PTMG 2900/TDI/PTMAB is $-69°C$ and continues to increase $(-63, -51, -43°C)$ as the molecular weight of the PTMG decreases from 2000 to 650. It should be noted that the glass transition temperature of the PTMG 650/TDI/PTMAB polymer never gets as high as the same systems cured with MBOCA or TMAB. This is due to the fact that the PTMAB contains more soft segment than the equivalent systems cured with either MBOCA or TMAB which causes a correspondingly lower T_g. Soft segment melting appears at 9 and 16°C for the PTMG 2000 and PTMG 2900 polymers, respectively.

During the course of the second DSC run on these systems, the T_g's of each polymer remains the same or decreases slightly. Thus, for PTMG 2900, PTMG 2000, PTMG 1000, and PTMG 650 the T_g's were $-71, -65, -56$, and $-46°C$, respectively. A large crystallization peak appears in the PTMG 2900 system as
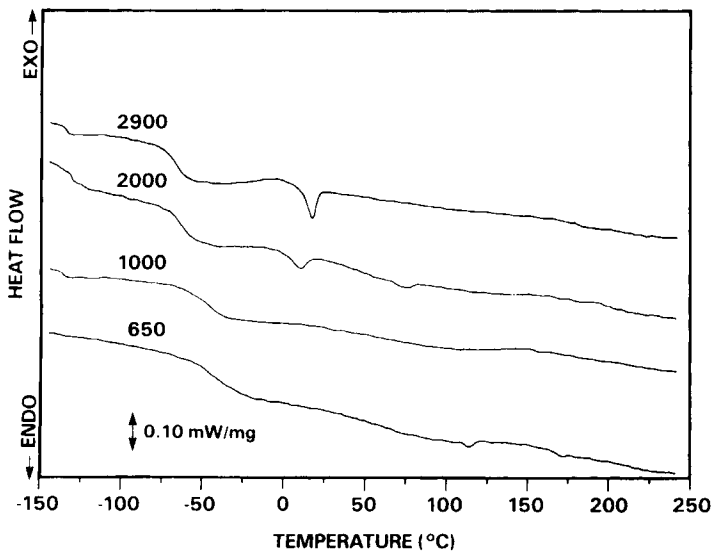
Fig. 7. DSC curves for PTMG/TDI/PTMAB, first run.

previously seen for the MBOCA and TMAB systems. Melting occurs at 22°C for PTMG 2900 and at 20°C for PTMG 2000.

In addition to studying the effect of PTMG molecular weight on transition properties, we also were interested in determining the effect of diol molecular weight distribution (MWD) on T_g and T_m. To determine this effect, standard (S), narrow (N), and broad (B) MWDs were available for the nominal 1000 and 2000 MW diols. Values of MWD for these systems are given in Table I. The results for the PTMG 2000/TDI/TMAB series are shown in Figures 9 and 10. It should be noted that because the MW variation in this series is
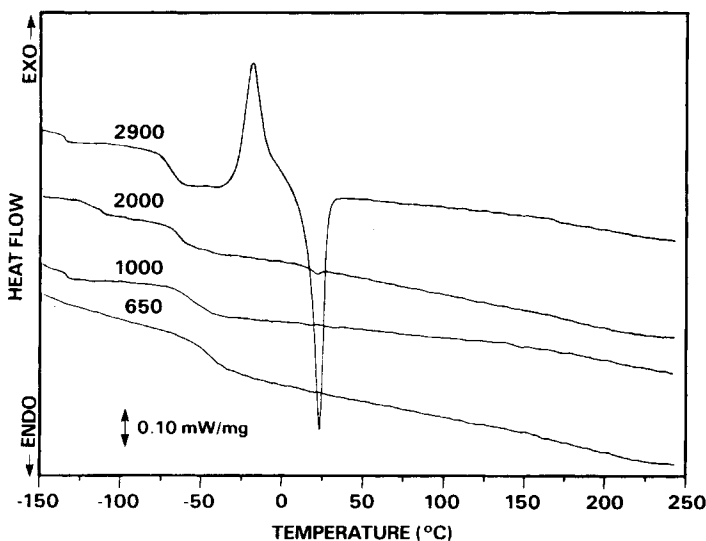
Fig. 8. DSC curves for PTMG/TDI/PTMAB, second run.
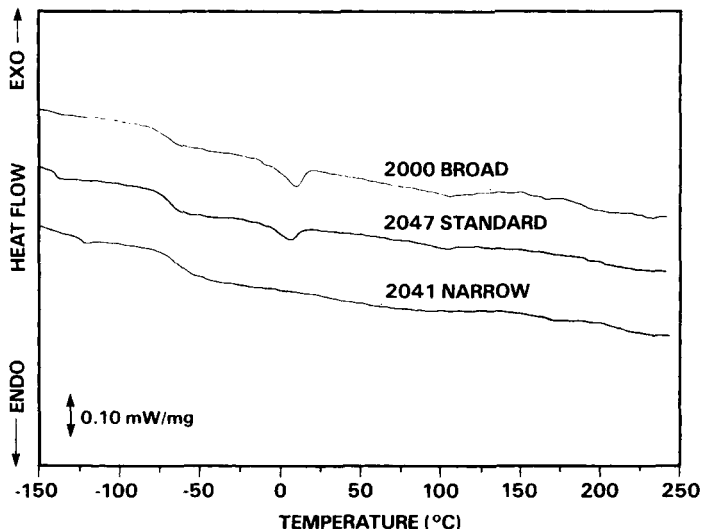
Fig. 9.   DSC curves for PTMG 2000/TDI/TMAB MWD, first run.

quite small, it is possible to separately study the influence of MWD on transition properties. The first DSC run shows the soft segment T_g's at -71, -69, and $-64°C$ for PTMG 2000B, PTMG 2047S, and PTMG 2041N, respectively. The fact that the T_g's for these polymers are very close and independent of MWD shows that in this MW range the phases are already well separated and any change in MWD does not increase phase separation or raise T_g. The melting of PTMG 2000B at 10°C and PTMG 2047S at 6°C is due to the presence of higher MW species which do not appear in PTMG 2041N. The second DSC run in this series shows essentially no change in the T_g's (-69, -69, and $-67°C$, respectively). The melting of the soft segments
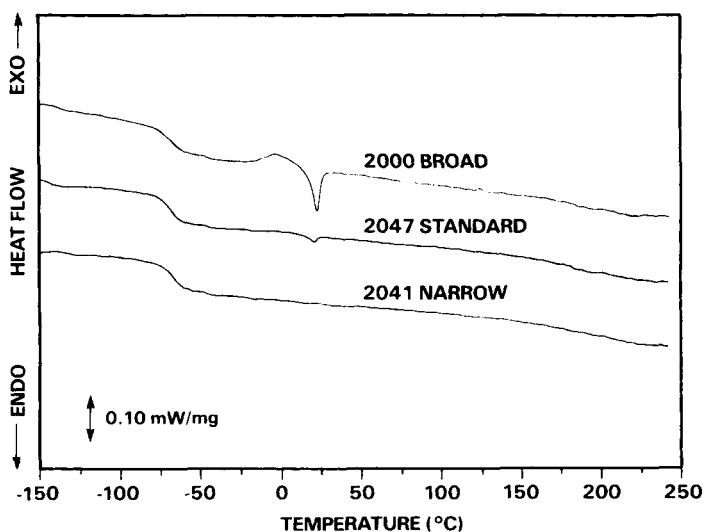
Fig. 10.   DSC curves for PTMG 2000/TDI/TMAB MWD, second run.
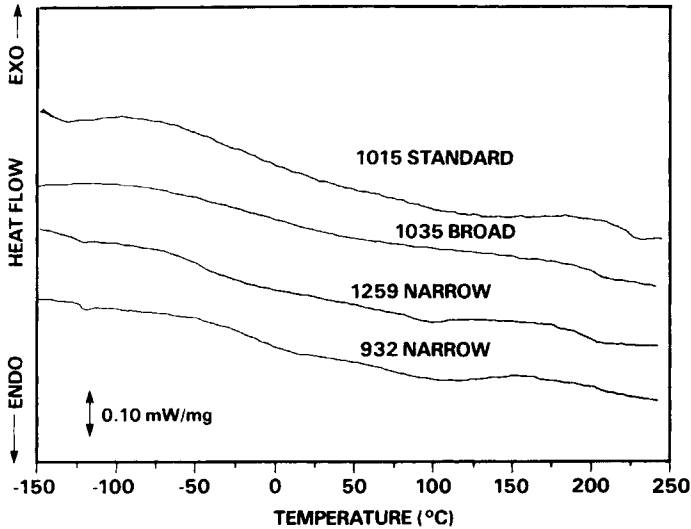
Fig. 11.   DSC curves for PTMG 1000/TDI/TMAB MWD, first run.

in PTMG 2000B and PTMG 2047S at 22 and 20°C are the result of an increase in crystalline perfection during programmed heating. These results are in general agreement with other studies of MWD.[12,13]

In the PTMG 1000 series of MWD polymers (Figs. 11 and 12), control over molecular weight of the PTMG in the prepolymer was not as good as in the 2000 MW series. As a result of variability in both MW and MWD and the fact that this is the region where phase separation becomes an important factor, only limited conclusions are possible. Additional work with other more closely controlled MW and MWD systems is necessary in this series, but this may be difficult to obtain in practice. The PTMG 1015S and PTMG 1035B are the two systems that agree most closely in MW and therefore can be compared as
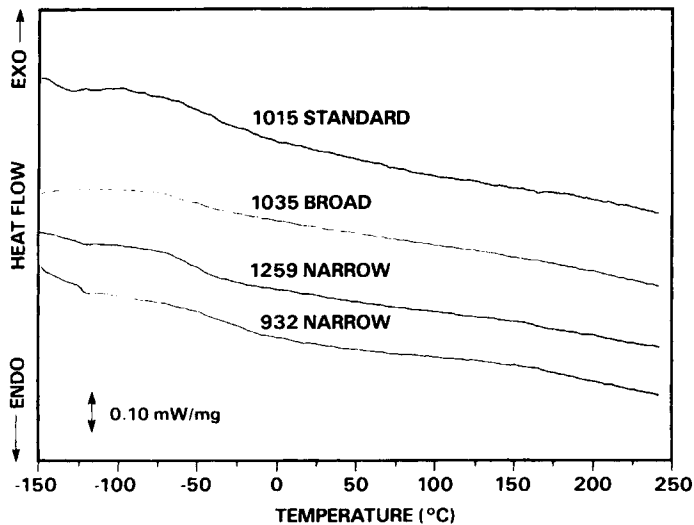
Fig. 12.   DSC curves for PTMG 1000/TDI/TMAB MWD, second run.

to the effect of MWD on T_g. The results show that the T_g's are quite different (-36 and $-15°C$, respectively). One possible explanation for this large difference is that since PTMG 1035B has a broader MWD than PTMG 1015S more low MW PTMG species are available for phase mixing with the hard segments which causes an increase in the resulting T_g, as noted before.[14] When these systems are rerun after having been heated to 250°C, the resulting T_g's are $-51°C$ for PTMG 1015S and $-54°C$ for PTMG 1035B. This suggests that some phase mixing occurred during cure at 100°C, but, when the system is heated above the T_m of the hard segment and then cooled, phase separation occurs and both systems have more nearly the same T_g's.

Two narrow MWD polymers which had slightly different MWs were also studied. PTMG 1259N had a T_g at $-45°C$ while PTMG 932N has its T_g at $-19°C$. It appears that somewhere in this range of MWs a critical value is reached where a large increase in phase separation occurs. This is the reason that T_g's for these systems differ significantly when only a modest MW difference occurs and the MWD is identical. During the second run on these systems, phase separation occurs by the same mechanism previously described, which causes both T_g's to decrease (-52 and $-30°C$). It should be noted that the higher MW systems PTMG 1259N, PTMG 1035B, and PTMG 1015S have the lowest T_g values (-52, -54, and $-51°C$, respectively) while the lowest MW (PTMG 932N), which is the most phase mixed system, has the highest T_g ($-30°C$).

Chain extender stoichiometry was studied to determine whether or not crosslinking in the hard segment had any noticeable effect on phase mixing and T_g of the soft segment. A low MW system (PTMG 650/TDI/TMAB) was selected in order to have a high hard segment content in the polymer. TMAB extender equivalent weight percentages of 90, 95, 100, 105, and 110% were used. All other variables were rigorously controlled so that the effect of crosslinking on transition properties could be isolated. The results showed no influence of stoichiometry on soft segment T_g. Values for T_g of 5, 4, 2, 1 and 0°C were obtained for chain extender contents of 90, 95, 100, 105, and 110%, respectively, during the first DSC run. The T_g values during the second DSC run were 0, -5, -6, -6, and $-6°C$, respectively.

Dynamic Mechanical Analysis

Typical shear modulus data obtained with the resonance apparatus is shown in Figure 13. By shifting this data along the log frequency axis, the master curve in Figure 14 is obtained. Data are shown over a wide range of frequencies, most of which are outside the experimental range. It is important to keep in mind that Figure 14 represents extrapolated values based on the principle of time–temperature superposition. For this reason, plots of this type are often presented in an equivalent form as a function of reduced radian frequency, $\log \omega a_T$, where $\omega = 2\pi f$ and a_T is the shift factor. For ease in displaying the results, a log frequency display will be used. The loss factor is analyzed in the same manner.

During the course of the measurements, it was found that some of the systems crystallized below room temperature. The effect of this crystallization on dynamic mechanical properties can be illustrated with measurements on PTMG 2000/TDI/PTMAB. Recall that the standard test procedure is to
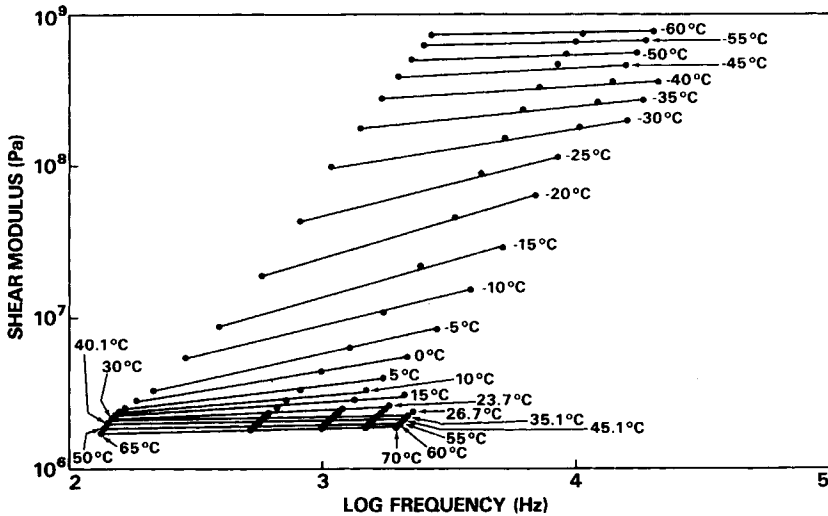
Fig. 13.   Shear modulus vs. frequency for PTMG 1000/TDI/PTMAB at various temperatures.

start by cooling the specimen from room temperature to −60°C in 1 h. This specimen will be referred to as "rapid cooled." In this case, relatively little crystallization occurs. Measurements were then made as the temperature was raised. Another specimen was cooled to −30°C (the soft segment crystallization temperature determined by DSC) and held at that temperature until the modulus no longer increased (4 days). This specimen contains the maximum amount of soft segment crystallinity and is referred to as "annealed." The specimen was cooled to −60°C and measurements were then made as before (Fig. 15). The modulus is as much as 20 times higher in the annealed specimen than in the rapid cooled specimen. Obviously, the thermal history is critical. All of the results to be given in this paper will be for rapid cooled specimens.
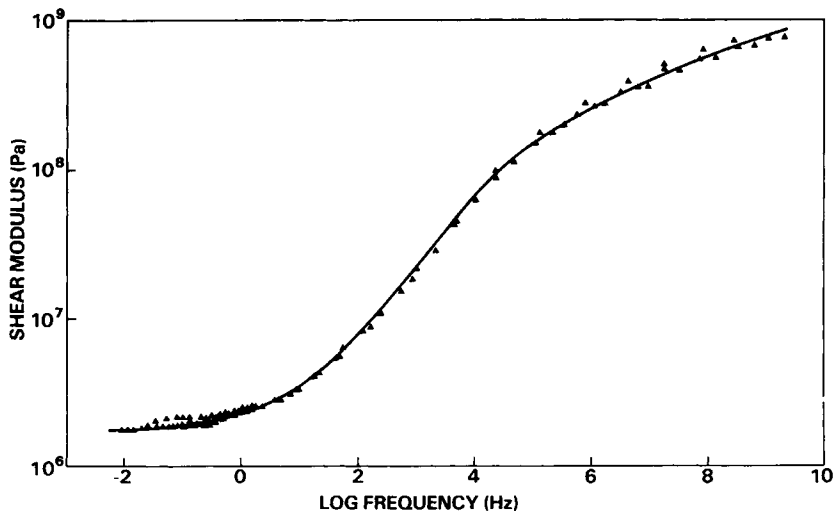
Fig. 14.   Shear modulus vs. shifted frequency at T_{ref} = −20°C for PTMG 1000/TDI/PTMAB.
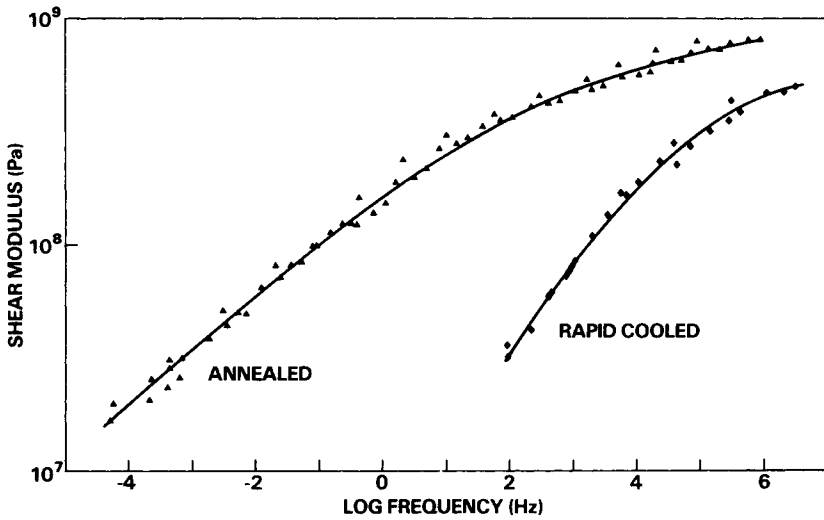
Fig. 15.   Shear modulus vs. shifted frequency at $T_{ref} = -45°C$ for PTMG 2000/TDI/PTMAB, annealed and rapid cooled.

Shear modulus vs. shifted frequency at a reference temperature of 25°C for PTMG/TDI/MBOCA of various PTMG molecular weights is shown in Figure 16. Only limited data for the PTMG 2000 and PTMG 2900 polymers is available since soft segment crystallization occurred as the testing temperature was lowered (i.e., for higher shifted frequencies on Fig. 16). Only data from the noncrystalline region will be presented in this paper. For the PTMG 1000, a major relaxation is evident, changing from a relaxed (low frequency/high temperature value) of about 5×10^7 Pa to an unrelaxed value of 10^9 Pa, a change of a factor of 20. The relaxation is centered at about 10^6 Hz
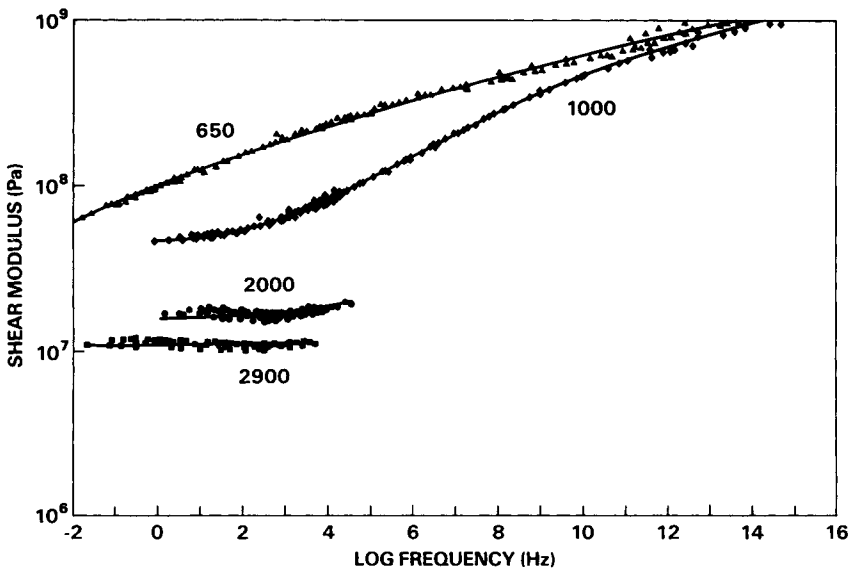
Fig. 16.   Shear modulus vs. shifted frequency at $T_{ref} = 25°C$ for PTMG/TDI/MBOCA of various molecular weights.
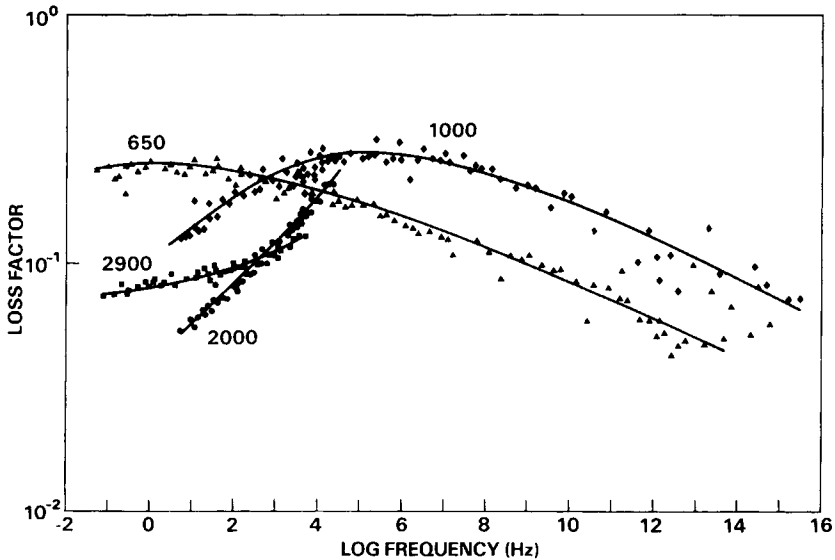
Fig. 17.   Loss factor vs. shifted frequency at $T_{ref} = 25°C$ for PTMG/TDI/MBOCA of various molecular weights.

and is quite broad, covering many decades. Similar behavior is shown by the PTMG 650, which shows an even broader relaxation centered at lower frequency. Based on the hardness of the two polymers, the PTMG 650 is expected to have the higher limiting relaxed modulus, but there is insufficient data to determine the value. Loss factor results for these systems are shown in Figure 17. It is seen that the PTMG 1000 peak occurs at about 10^6 Hz while the PTMG 650 peak occurs at about 10^0 Hz. Thus the relaxation peak moves to higher frequency (equivalent to lower temperature) as the MW increases. In the temperature range of our measurements, the only molecular transition expected to produce a dynamic mechanical relaxation is the soft segment glass transition. The above results are qualitatively consistent with this interpretation since it was shown above that T_g decreases as diol MW increases. Further, since each decade of frequency is approximately equivalent to a T_g shift of $7°C$,[15] the six decade difference in relaxation peak frequency for the PTMG 650 and PTMG 1000 would imply a T_g difference of $42°C$, in excellent agreement with the measured DSC value of $\Delta T_g = 49°C$. (Always comparing with the DSC first run.) We also note that the modulus in the relaxed region becomes lower as the diol MW increases. This results from a lower hard segment concentration.

Results for the TMAB series are shown in Figures 18 and 19. As before, little data can be obtained on PTMG 2900 before crystallization occurs. In this case however, PTMG 2000 does not crystallize, presumably because the crystallization kinetics are too slow. The system can crystallize to some extent, as shown in the DSC measurements, but was not detected in the resonance test. All the polymers seem to be approaching the same unrelaxed (glassy) modulus, about 10^9 Pa, which is the same as the MBOCA series. The relaxed (rubbery) moduli values, however, are lower than those found with MBOCA, even though the hard segment weight percents are about the same. The higher rubbery modulus in the MBOCA series is a result of hard segment
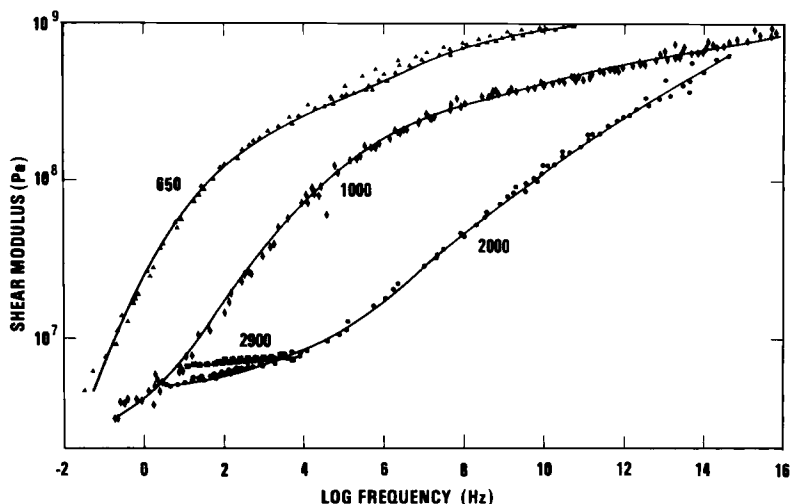
Fig. 18. Shear modulus vs. shifted frequency at T_{ref} = 25°C for PTMG/TDI/TMAB of various molecular weights.

crystallinity. For the same reason, the relaxation region in the MBOCA series is broader than in the TMAB series. The relaxation peaks for PTMG 1000 and PTMG 2000 occur at 10^1 and 10^7 Hz, respectively, which would imply a difference of 42°C in their T_g values. The peak for PTMG 650 cannot be determined from the data but is probably more than three decades lower than PTMG 1000. These expectations are borne out by the DSC measurements that show that ΔT_g = 33°C for PTMG 1000 and PTMG 2000 and ΔT_g = 57°C for PTMG 650 and PTMG 1000.

Results for the PTMAB series are significantly different than MBOCA or TMAB. As shown in Figure 20, the entire transition region is well defined for PTMG 650 and PTMG 1000, and moves to lower frequency (higher temperature) as the molecular weight decreases. While the glassy modulus is about the
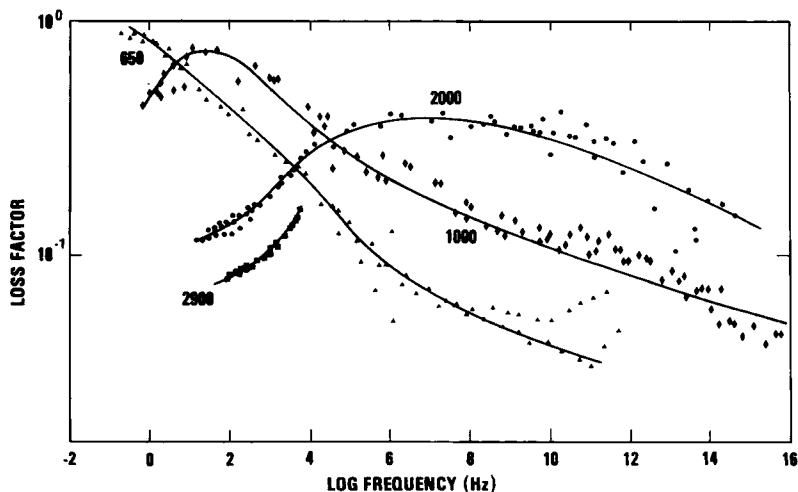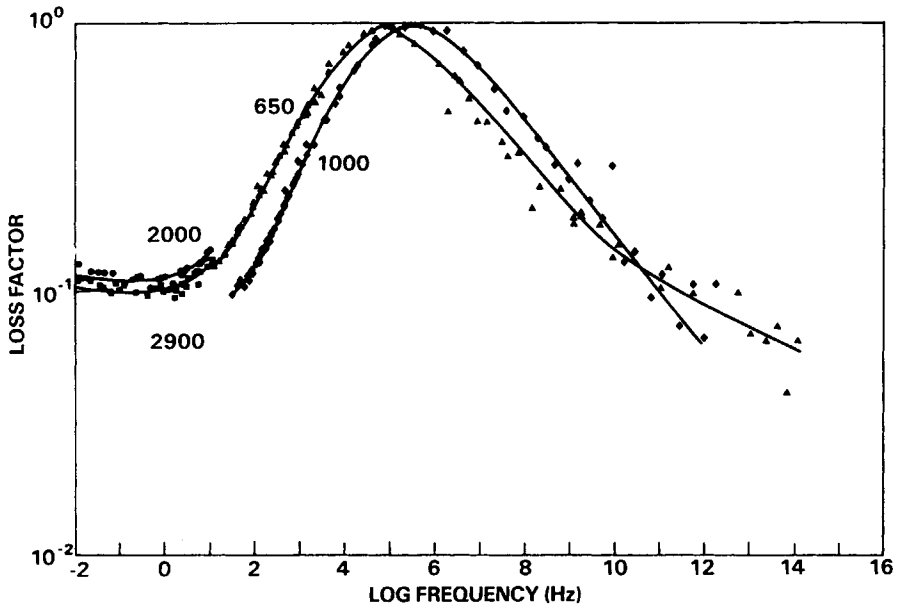

Fig. 19. Loss factor vs. shifted frequency at T_{ref} = 25°C for PTMG/TDI/TMAB of various molecular weights.
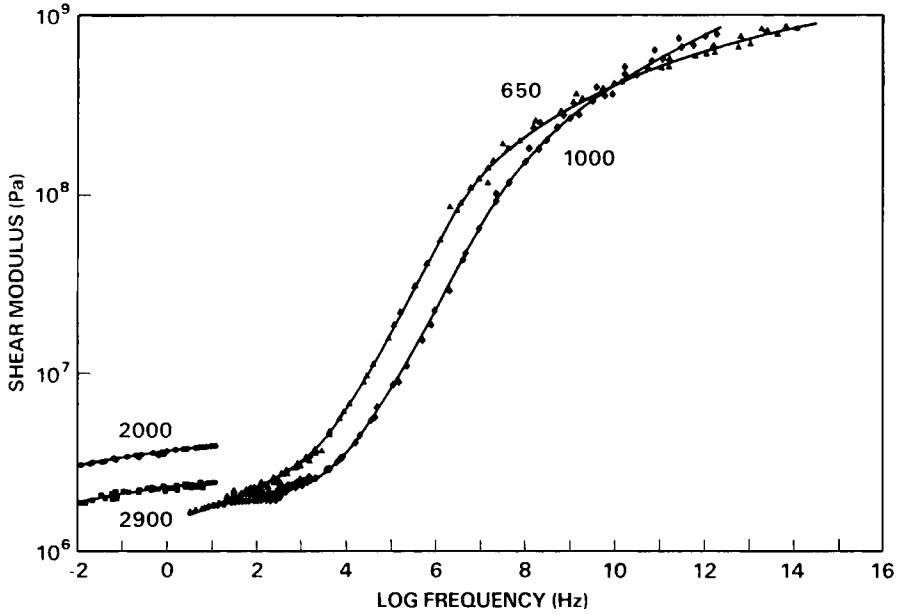
Fig. 20. Shear modulus vs. shifted frequency at T_{ref} = 25°C for PTMG/TDI/PTMAB of various molecular weights.

same as before, 10^9 Pa, the rubbery value is much lower, 10^6 Pa, so that the glassy and rubbery moduli differ by a factor of 1000. The transition also occurs over a narrower range of frequency than for the other two chain extenders. This is presumably a reflection of the fact that these polymers are closer to exhibiting homopolymer behavior than the more phase separated

Fig. 21. Loss factor vs. shifted frequency at T_{ref} = 25°C for PTMG/TDI/PTMAB of various molecular weights.
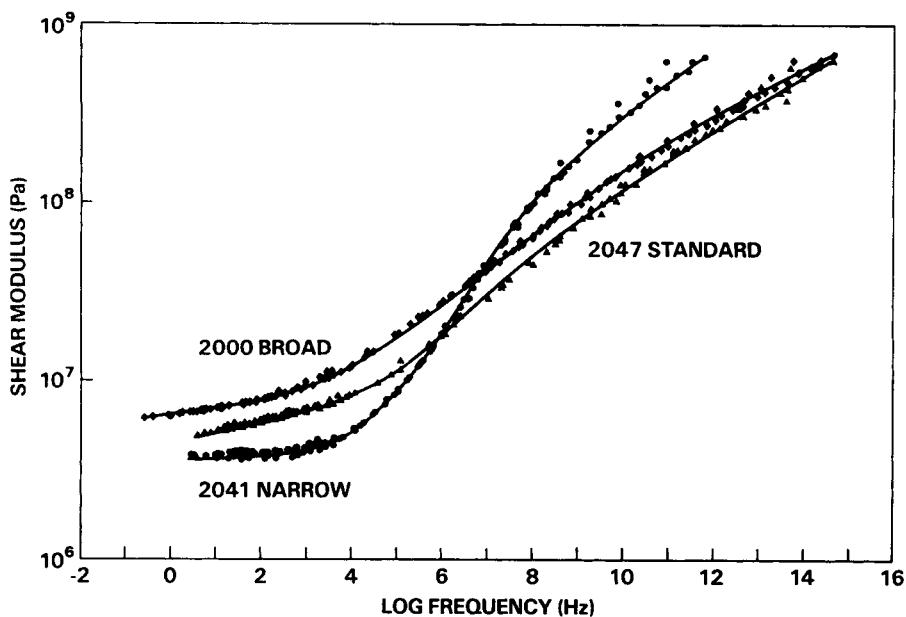
Fig. 22.   Shear modulus vs. shifted frequency at T_{ref} = 25°C for PTMG 2000/TDI/TMAB of various MWDs.

polymers. As shown in Figure 21, the magnitude of the loss factor is high and the peaks for PTMG 650 and PTMG 1000 occur at 10^5 and 10^6 Hz, respectively. We thus expect a 7°C difference in T_g, compared with ΔT_g = 8°C from the DSC measurements, so that the position of the modulus transition is greater and the width narrower as a result of the increased soft segment concentration.
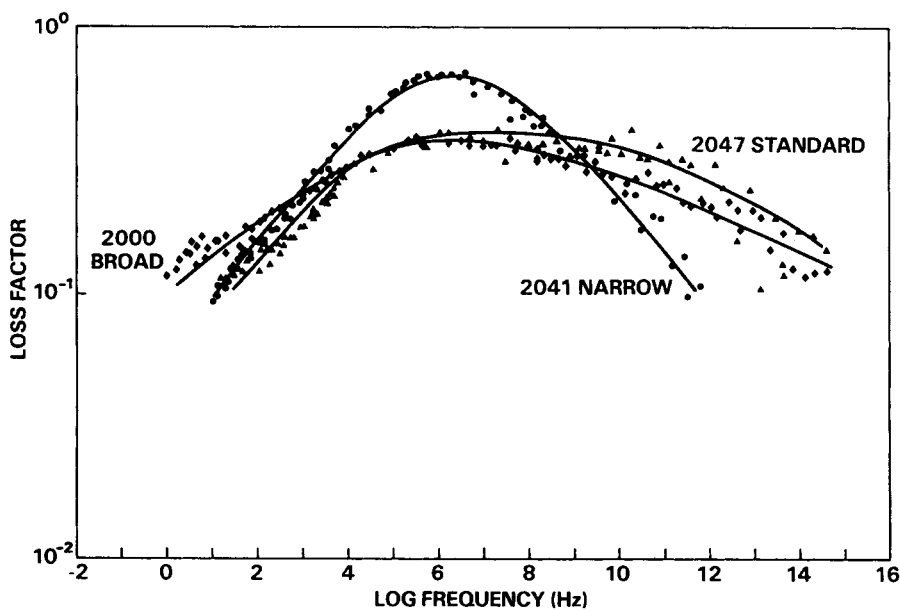
Fig. 23.   Loss factor vs. shifted frequency at T_{ref} = 25°C for PTMG 2000/TDI/TMAB of various MWDs.
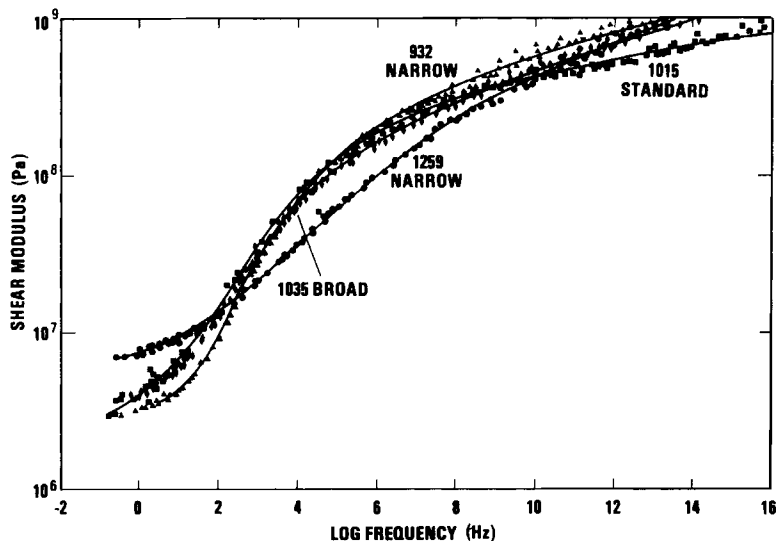
Fig. 24. Shear modulus vs. shifted frequency at $T_{ref} = 25°C$ for PTMG 1000/TDI/TMAB of various MWDs.

The effect of soft segment MWD was studied in the PTMG/TDI/TMAB series for nominal MW of 1000 and 2000. Results for the 2000 MW are shown in Figures 22 and 23. (MWD values are listed in Table I.) As expected, the narrow MWD polymer has a transition occurring over a narrower frequency and the broad MWD occurs over a broader range than the standard MWD. As usual, the narrower transition has the higher loss factor. In other respects, the three polymers are very similar. Results for the PTMG 1000 are shown in Figures 24 and 25. Unfortunately, not only does the MWD vary for these
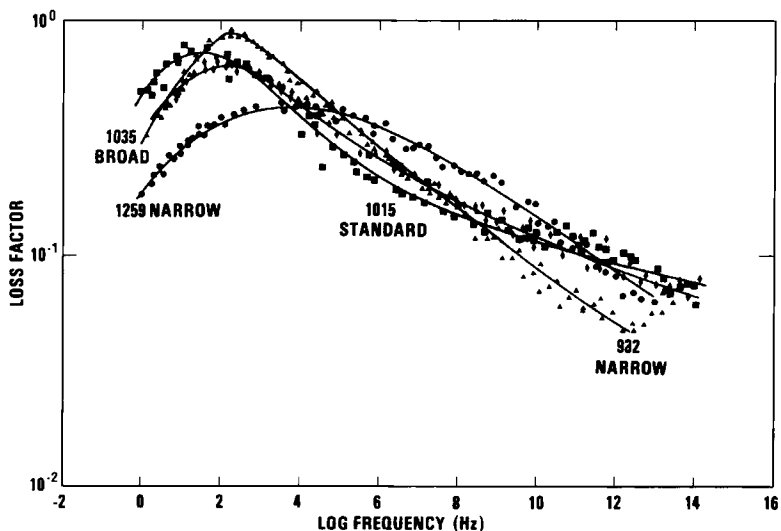

Fig. 25. Loss factor vs. shifted frequency at $T_{ref} = 25°C$ for PTMG 1000/TDI/TMAB of various MWDs.

systems but also the MW itself so that our conclusions are somewhat tentative. The PTMG 932N has a narrow transition as expected, though the rubbery modulus value is higher than expected. Overall, MWD does not have a major impact on dynamic mechanical properties in either the PTMG 1000 or PTMG 2000 series.

The final structural variable studied was chain extender stoichiometry. The PTMG 650/TDI/TMAB system was chosen for this study and chain extender stoichiometries of 90, 95, 100, 105, and 110% were considered. Specimens 5 and 19, Table II, then had identical theoretical structures and were found to have nearly identical dynamic mechanical properties. Very little effect on either shear modulus or loss factor was found. All the stoichiometry specimens had properties close to the PTMG 650 values shown in Figures 18 and 19. These results are in agreement with the DSC findings that stoichiometry has little effect in the PTMG 650 system. This insensitivity may result because this system has poor phase separation to begin with. There may be a more significant effect at higher PTMG molecular weights.

CONCLUSIONS

Measurements were made of the thermal and dynamic mechanical properties of 22 TDI/polyurethaneureas of varying diol molecular weight, type of aromatic diamine chain extender, diol molecular weight distribution, and chain extender stoichiometry. Based on these measurements, a number of conclusions were reached:

—time-dependent soft segment crystallization occurs in PTMG 2000 and PTMG 2900 polymers, with T_m between 3 and 22°C;

—hard segment crystallization can occur in PTMG 650 and PTMG 1000 polymers, with T_m about 200°C;

—dynamic mechanical properties are well correlated with the soft segment glass transition;

—increasing diol MW enhances phase separation, which lowers T_g, which in turn shifts dynamic mechanical properties;

—MBOCA, TMAB, and PTMAB have very similar transition temperatures (except for PTMG 650) and similar glassy moduli but successively lower rubbery moduli and higher loss factors;

—diol MWD does not have a significant effect on transition temperatures or dynamic mechanical properties;

—chain extender stoichiometry does not have a significant effect on transition temperatures or dynamic mechanical properties.

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