Dielectric and Viscoelastic Properties of Some Meta-Tetramethyl Xylene Diisocyanate-Based Polyurethanes as a Function of Sample Composition

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SYNOPSIS

A series of linear segmented polyurethanes were synthesized, based on soft segments of polycaprolactone having an average number molecular weight of 2100, or hydroxy–terminated polybutadiene having an approximate molecular weight of 2800. Hard segments were made of meta–tetramethyl xylene diisocyanate and diethyl toluene diamine. The dynamic Young's modulus and loss tangent, relative permittivity, and dielectric loss, were found to be significantly affected by soft segment polarity and hard segment content. These results are discussed in terms of polymer morphology, such as degree of phase separation and soft segment phase state.

INTRODUCTION

It is generally agreed that the unique mechanical properties of polyurethanes, as compared to other types of elastomers, are the result of a predominantly two-phase morphology.[1-4] Thermoplastic polyurethanes are considered to be linear segmented block copolymers, made up of alternating hard and soft block segments. The soft segment is normally a low molecular weight polyester or polyether chain. The hard segment is composed of diisocyanate molecules condensed with a low molecular weight diol or diamine. The properties of these materials are largely governed by the phase separation of the hard and soft segments, which typically results in the formation of hard segment domains dispersed in a rubbery matrix.[1] Compositional variables and processing conditions are known to affect the degree of phase segregation, hard segment domain organization, and subsequent polyurethane properties.[2-6] Depending on the relative thermodynamic incompatibility of the hard and soft segments, a demixing process will occur during polymerization and post-cure annealing. This process will lead to at least two main phases; ordered domains of hard segments, and amorphous domains, mainly composed of soft segments.[7] In addition, other microphases with intermediate structures may exist.[8]

The effects of polyurethane composition on structure and resultant properties have been the subject of a number of investigations. These studies have largely centered on model compounds or polyurethanes based on aromatic diisocyanates, such as diphenyl methane diisocyanate (MDI)[9-14] or toluene diisocyanate (TDI),[13-16] motivated, at least in part, by the commercial importance of these materials. The two phase structure of these polyurethanes has been demonstrated by a variety of techniques including: small and wide angle X-ray scattering,[8,17-20] differential scanning calorimetry,[20-23] infrared spectroscopy,[24-26] microscopy,[27,28] and dielectric spectroscopy.[29,30]

Interest has also been shown in aliphatic isocyanates. These have been considered for use in cases where high hysteretic heat buildup has been a problem, or the discoloration due to light exposure, experienced by aromatic diisocyanate-based materials, is not desirable. One of the most commonly employed diisocyanates has been a commercially available mixture of the isomers of bis-(4–isocyanatocyclohexyl) methane.[31,32]

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In recent years, a new class of diisocyanate molecules, in which the isocyanate groups are bonded to aliphatic carbons, has become available.[33-38] These are structural isomers of tetramethyl xylene diisocyanate (TMXDI), which exist in meta and para forms. The para form of this isocyanate has been found to form polyurethanes that possess good mechanical properties and are less sensitive to the percentage of curative used in their formation, particularly with the aromatic diamine, diethyl toulene diamine (DETDA).[34] This insensitivity is believed to be due to the fact that these sterically hindered isocyanates are less reactive and, as a consequence, do not readily form the allophanate or biuret linkages found with conventional aromatic diisocyanates.[2] The fact that these urethanes do not readily crosslink makes them ideal candidates as model compounds for a basic study of compositional effects on properties. Since TMXDI exists in meta and para isomeric forms, it is also possible to study the effect of this structural isomerism on the properties of the resultant polyurethanes.

In contrast to the aromatic diisocyanate urethanes, there have been fewer systematic investigations of the effect of composition on the properties of polyurethanes, based on these aliphatic diisocyanates.[33-38] These investigations have focused primarily upon the para isomer. Since it is not clear whether the para isomer will become commercially available, emphasis is placed on the effects of composition on the dynamic mechanical and dielectric properties of polyurethanes, based upon the meta isomer of TMXDI, in the work described here. Some samples based upon the para isomer have also been included for comparison. DETDA was used as a chain extender in all samples.

There are a number of compositional variables that can be altered in the formation of a polyure-thane. The study described here focused on the effects of singly changing one of several compositional variables, while the remainder were held constant. The objectives were to gain an understanding of the relationship between polyurethane composition and temperature–frequency dependent viscoelasticity and dielectric behavior, and to elucidate the role of phase segregation and hydrogen bonding in the properties of these model segmented polyurethanes. The purpose of this article is to examine the viscoelastic and dielectric relaxation mechanisms and microphase structures in m-TMXDI based polyurethanes as a function of soft block polarity, isocyanate content, and cure stoichiometry.

EXPERIMENTAL

Polyurethane prepolymers were synthesized by reacting an excess of diisocyanate with a polyol, as described previously.[34,38] Prepolymers were made with differing amounts of excess isocyanate (4.3–6.3%) in order to obtain polyurethanes with varying hard segment contents. Polycaprolactone (Union Carbide Tone 240, with an average number molecular weight of 2100, hereafter referred to as PCL), or hydroxy-terminated polybutadiene (HTPBD, ARCO R45M with a molecular weight of approximately 2800), were used as the polyol soft segments. These prepolymers were cured into polyurethane elastomers by reaction with the liquid diamine, diethyl toluene diamine (DETDA). This curative is a mixture of 2,4 and 2,6 isomers, and has been previously reported to be satisfactory for this class of isocyanate.[34] The isocyanate/amine molar ratio was varied from 0.9 to 1.1. Symmetric alcohol curatives, such as 1,4 butanediol, did not cure satisfactorily with prepolymers made from the m-TMXDI. The

Table I The Glass Transition Temperatures of m–TMXDI-Based Polyurethanes

Hard Segment Content (%)	Soft Block Component	Curative Level (NCO/DETDA, %)	Glass Transition Temperature (°C)
28	PCL	100	−51.3
33	PCL	110	−51.4
33	PCL	100	−51.8
33	PCL	90	−51.6
40	PCL	100	−51.2
34	HTPBD	110	−74.9
34	HTPBD	100	−74.2
34	HTPBD	90	−74.5

polyurethane was cured at 70°C for 18 h and post-cured at ambient conditions for at least two weeks. Since only amine curatives were used, the final products were actually polyurethaneureas.

The Young's modulus and loss tangent were measured as a function of temperature at 10 Hz, using a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA). A temperature ramp of 4°C/min was used. Samples were run using the dual cantilever mode.

Conductive silver paint was spray-coated onto masked areas of nominal 5.08 cm diameter samples of polyurethanes. The approximate thickness of most samples was 2.5 mm. Micrometer calipers were used to determine exact sample thicknesses and diameters. A General Radio 1690A dielectric holder, General Radio 1689M RLC Digibridge, with a IEEE 4888 interface, and a Zenith 248 computer were used to measure the capacitance and dissipation of the dielectric holder with and without the sample. Measurements were made at discrete frequencies in the range from 10^2–10^5 Hz. Permittivity and loss values were then calculated at each frequency of measurement. Temperature control was provided by a Thermotron Model S1, with a temperature stability of ± 0.1°C. A platinum RTD in the body of the dielectric holder was used for temperature measurements. The approximate temperature range used was from -50 to 90°C. The upper limit was determined by

the ability of the dielectric cell to withstand only moderate temperatures.

Differential scanning calorimetry (DSC) measurements were made using a Perkin–Elmer DSC-4 and Model 3600 Data Station. A scan rate of 20°C/min was normally used.

FTIR spectra of polyurethanes were obtained on a Digilab FTS 40 using a Spectra Tech ATR attachment. Samples were run using as-cast polyurethanes, with a resolution of 4 cm^{-1}. Comparison spectra of polycaprolactone diol, polybutadiene diol, and diethyl toulene diamine were run as liquid films on salt plates.

RESULTS

DSC

DSC scans were run on each of the polyurethanes included in this study. No endothermic peaks were observed, indicating the absence of crystallinity in both the hard and soft segment phases of these polyurethanes. A low temperature glass transition was observed in each of these materials, attributable to the glass transition of the PCL or HTPBD soft segment. The midpoint was taken as the glass transition temperature (cf. Table I). Neither the amount of curative nor the isocyanate content had a signif-
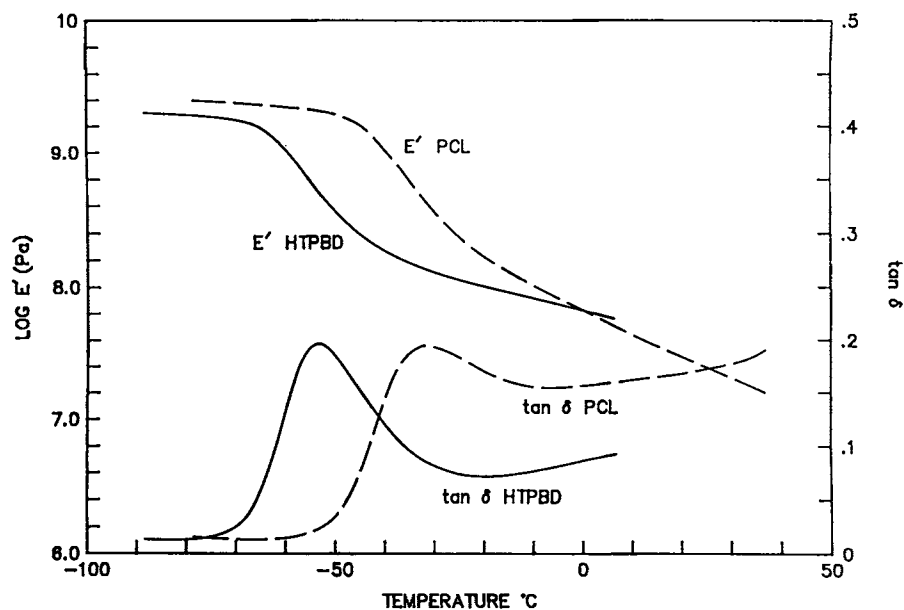

Figure 1 Plot of storage Young's moduli and loss tangents as a function of temperature at 10 Hz for PCL and HTPBD-based polyurethanes with 5.7% available isocyanate content (ANCO) in prepolymer and unit cure stoichiometry.

icant effect on this glass transition temperature, indicative of a predominantly two phase morphology in these materials. A distinct, hard segment melting peak was not observed in these materials, indicating that the hard segment domains are not highly ordered. Instead, they merely appeared to exhibit plastic flow and to decompose as the temperature was increased.

Dynamic Mechanical Spectra

The differences in the Young's moduli and loss tangents of as-cast polyurethanes, containing the polar polycaprolactone soft block and the nonpolar hydroxy-terminated polybutadiene at the same prepolymer isocyanate content and cure stoichiometry of unity, are shown in Figure 1. The polar polycaprolactone material gives more hard segment–soft segment interaction, as evidenced by the broadening in the loss tangent above the glass transition and the steeper slope of the modulus curve as a function of temperature. In addition, the peak of the loss tangent curve is shifted upward relative to pure polycaprolactone. This can be compared with polyurethanes prepared from the p-TMXDI isomer (Fig. 2), in which the hard blocks show less phase mixing. The dynamic mechanical spectra of these materials also did not show well-resolved hard segment transitions when measured at higher temperatures than those shown in Figures 1 and 2. The loss tangent tended to increase over a broad range, with the materials eventually softening and exhibiting plastic flow.

It was found that the dynamic mechanical properties at a fixed isocyanate content were relatively insensitive to cure stoichiometry (cf. Fig. 3). Normallly, biuret formation will be influenced by both the reaction stoichiometry and the cure temperature, as well as by the reaction exotherm. In the present instance, a low cure temperature was deliberately used to avoid this influence. The modulus scarcely varied with stoichiometry, while the loss tangent was seen to increase slightly in the rubbery region with increasing DETDA in the cure. This result is consistent with the insensitivity of the glass transition temperature to cure stoichiometry.

A more drastic effect was seen when varying the hard segment content of the polyurethane by increasing the isocyanate content. This effect is shown in Figure 4. The modulus increases and the loss tangent decreases and broadens as the hard segment content is increased.

FTIR Spectra

Assignment of FTIR vibrational frequencies was done by comparison of polyurethane spectra and spectra of diols and DETDA, and tables of charac-
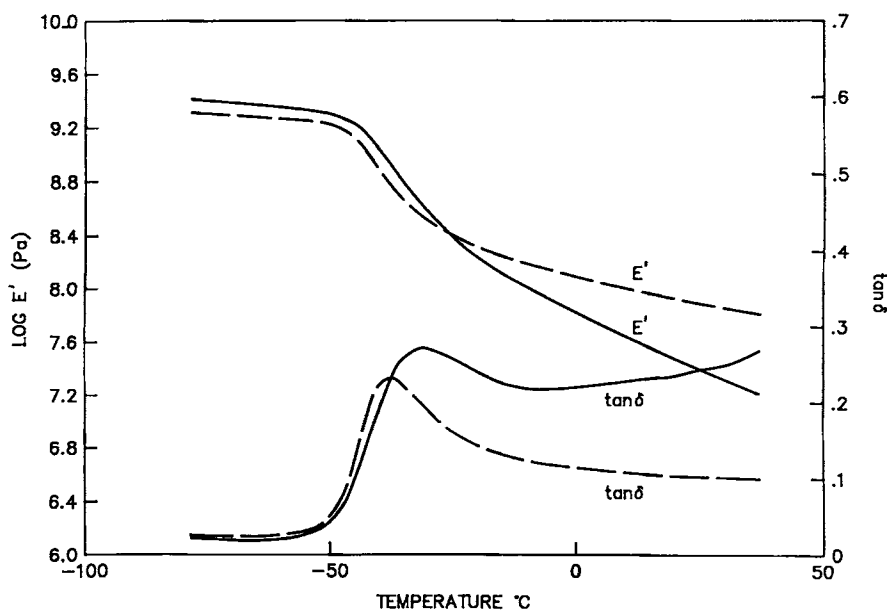

Figure 2 Plot of storage Young's moduli and loss tangents as a function of temperature at 10 Hz for PCL-based polyurethanes with para- (dashed line) and meta- (solid line) TMXDI at equal hard segment contents.
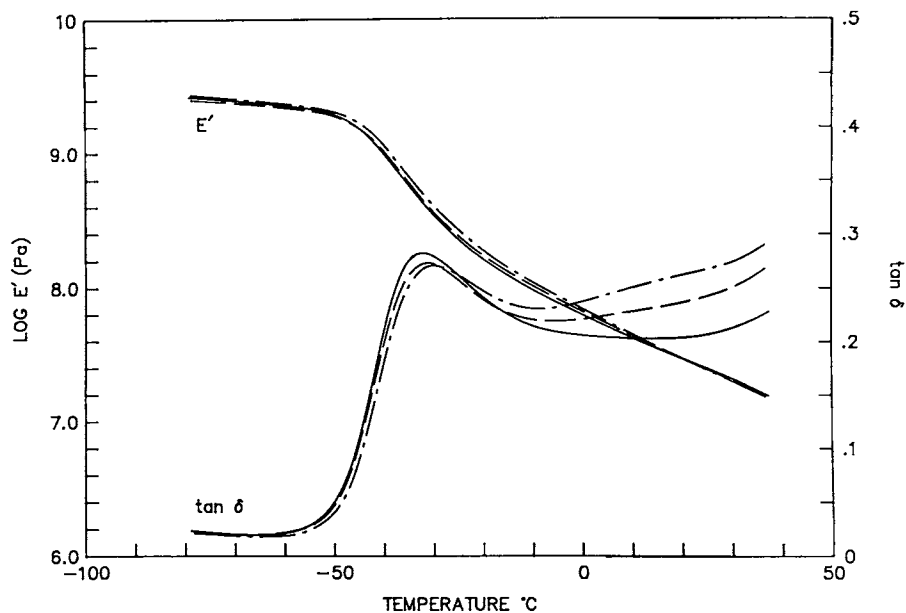
Figure 3   Plot of storage Young's moduli and loss tangents as a function of temperature at 10 Hz for PCL-based polyurethanes with 5.7% ANCO of *m*-TMXDI in prepolymer and varying cure stoichiometry: (double dashed line) NCO/NH$_2$ = 0.9; (dashed line) NCO/NH$_2$ = 1.0; (solid line) NCO/NH$_2$ = 1.1.

teristic vibrational frequencies (39–42). Representative IR spectra of the PCL and HTPBD polyurethanes are shown in Figure 5.

Interpretation of the IR spectra is not a simple matter, and is not without some ambiguities. The comparison of relative band intensities between
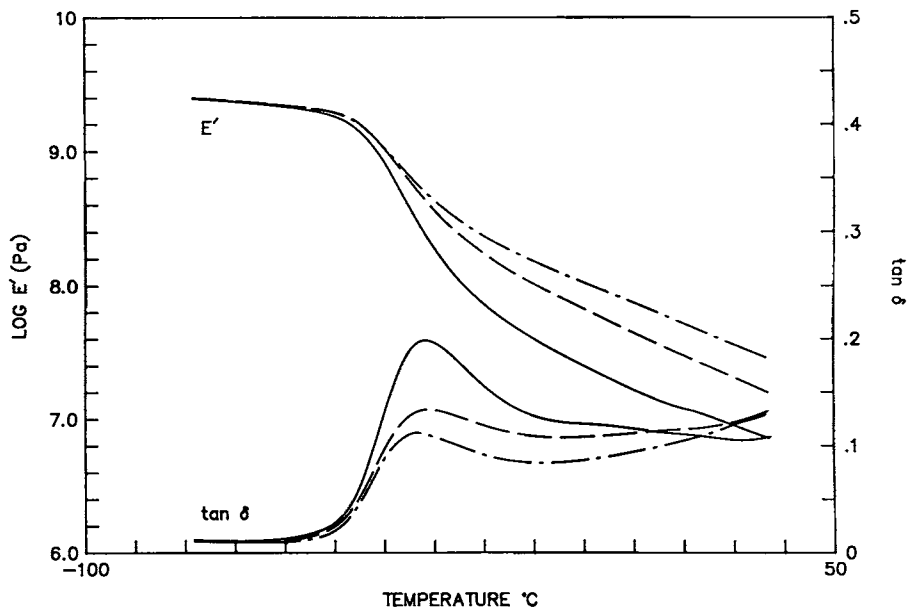

Figure 4   Plot of storage Young's moduli and loss tangents as a function of temperature at 10 Hz for PCL-based polyurethanes with differing available isocyanate content (ANCO) in prepolymer and cure stoichiometry of unity: (double dashed line) 6.3% ANCO; (dashed line) 5.7% ANCO; (solid line) 4.3% ANCO.
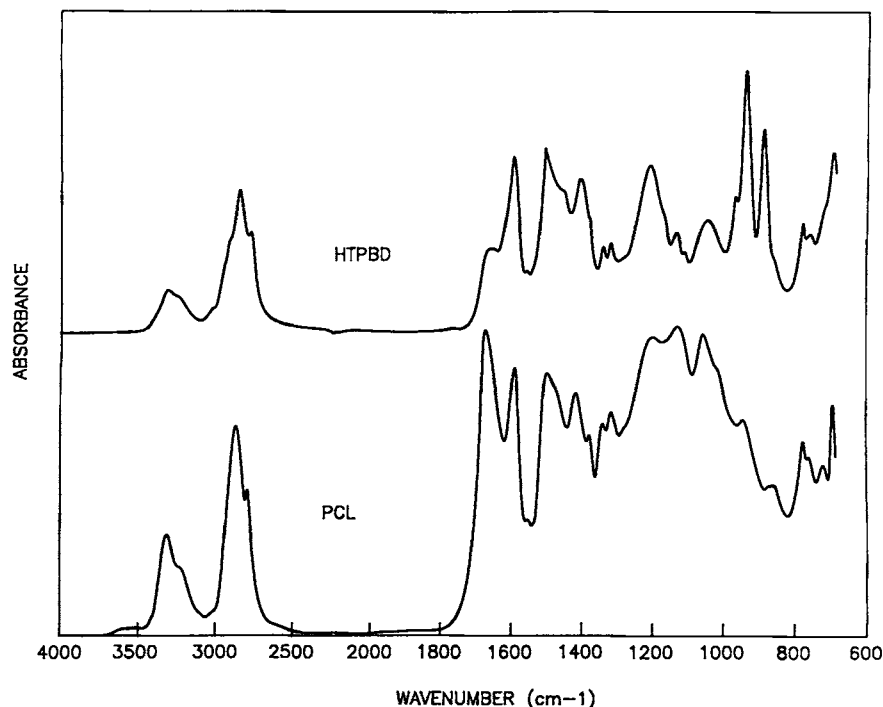
Figure 5   Infrared spectra of polycaprolactone and hydroxy-terminated polybutadiene polyurethanes with 5.7% ANCO of m-TMXDI in prepolymer and cure stoichiometry of unity.

samples is also hindered by the fact that the ATR technique causes distortion of band shapes and intensities, with spectra being influenced by the amount of contact with the internal reflectance element. Additionally, the ATR accessory used did not permit an easy examination of the N–H and carbonyl stretch regions, as a function of temperature. Both the PCL and HTPBD polyurethanes exhibit a doublet in the region near 3500 cm^{-1}, associated with the N–H stretch. The frequencies are 3355 and 3279 vs. 3355 and 3277 cm^{-1}, respectively, in the solid polyurethanes. The N–H stretch doublet, due to symmetric and asymmetric stretches in primary amines, normally occurs at higher frequencies. In liquid DETDA, these occur at 3459 and 3376 cm^{-1}. The N–H stretch doublet occurs at almost the same frequencies and with the same relative intensities in both the PCL and the HTPBD based polyurethanes. There will actually be two different types of amide structures found in these materials. The first is associated with the urethane group formed when the diisocyanate is initially reacted with the soft block diol to form the isocyanate-terminated prepolymer. The second is formed when the prepolymer is chain extended with the diamine. These multiple bands in solid amide structures are often described

in terms of cis and trans dimers, due to hydrogen bonding.[41] In the polyurethanes, the higher wavenumber stretch is assigned to N–H groups that are hydrogen bonding to the carbonyl groups in the urea moieties. The lower wavenumber stretch is assigned to an N–H stretch that is associated with the urethane moiety.[39-42]

The behavior of the two classes of polyurethanes is different in the carbonyl stretch region. A broad, intense carbonyl stretch, with a maximum at 1730 cm^{-1}, is observed in the solid PCL-based urethane, while a strong carbonyl absorption is observed at 1723 cm^{-1} in the unreacted polycaprolactone diol. The carbonyl stretching frequency in solid polyurethanes normally lies in the 1740–1690 cm^{-1} region, while the stretching frequency of ureas can range from approximately 1720 to 1620 cm^{-1}. A strong new absorption is found at 1640 cm^{-1}. This is characteristic of the Amide I band, associated with the carbonyl group of the urea. A new band, associated with an amide type deformation, occurs at 1545 cm^{-1}. Other characteristic frequencies of the PCL polyurethane moiety are summarized in Table II.

The spectrum of the HTPBD polyurethane shows a broad band at 1708 cm^{-1}, with a shoulder at 1730 cm^{-1}. The higher wavenumber band is assigned to

Table II   Characteristic IR Vibrational Assignments of PCL and HTPBD Polyurethanes at 5.7% NCO and NCO/NH$_2$ = 1

PCL ν, cm^{-1}	PCL Assignment	HTPBD ν, cm^{-1}	HTPBD Assignment
3354	N–H stretch (bonded), urea	3354	N–H stretch (bonded), urea
3278	N–H stretch (bonded), urethane	3277	N–H stretch (bonded), urethane
2939	C–H$_2$ asymmetric stretch	3074	Vinyl C–H$_2$ asymmetric stretch
2866	C–H$_2$ symmetric stretch	2972	Vinyl C–H$_2$ symmetric stretch
1727	C—O stretch, lactone group	2915	C–H$_2$ asymmetric stretch
1640	Amide I	2842	C–H$_2$ symmetric stretch
1602	C–C stretch (phenyl ring)	1730, 1708	C—O stretch
1545	N–H bend	1640	C—C stretch?
1521	C–N stretch + N–H bend	1604	C–C stretch (phenyl ring)
1383	C–H$_2$ wag	1545	N–H bend
1235	C–N stretch + N–H bend	1521	C–N stretch + N–H bend
1158	1, 3 substituted aromatic stretch	1384	C–H$_2$ wag
1085	C–O–C stretch	1241	C–N stretch + N–H bend
876	1, 3 substituted aromatic bend	1167	1, 3 substituted aromatic stretch
795	Out of plane (C—O)–O bend	1073	C–O–C stretch
		878	1, 3 substituted aromatic bend
		794	Out of plane (C—O)–O bend

the carbonyl group of the urea moiety, consistent with the earlier N–H stretch assignments. This band is not well resolved, and possibly represents different degrees of hydrogen bonding in hard segment domains of varying sizes. The dynamic mechanical and calorimetric measurements indicate that the HTPBD material is phase segregated, so that any hydrogen bonding will occur in the hard segments. The shoulder at 1708 cm^{-1} represents a urethane carbonyl stretch in the HTPBD polyurethanes. Although a strong band is present at 1640 cm^{-1}, the IR spectrum of the polybutadiene diol also shows a strong absorption at this wavenumber due to C—C stretching. Table II summarizes the other characteristic frequencies.

Dielectric Spectra

The dielectric spectra of these materials were found to be relatively complex. Figures 6 and 7 show the permittivity and loss, respectively, as functions of frequency at 297°K for a polycaprolactone and a hydroxy-terminated polybutadiene polyurethane of the same isocyanate content (5.7% in the prepolymer) and theoretical cure stoichiometry of unity. The relative permittivity and loss are seen to be high for the polycaprolactone polyurethane, corresponding to its much more polar nature. Figure 8 shows the loss for the PCL material, plotted as a function of temperature at a fixed frequency of 535 Hz. A primary transition is observed at low temperatures (250°K and below) that is due to the parallel component of the dipole moment of the soft block[43] in the PCL-based material. The rise on the high temperature end of the observed dielectric spectrum is attributable to the hard segment, and indicates phase mixing with behavior that is characteristic of Maxwell–Wagner–Sillars (MWS) interfacial polarization effects. It is not possible to go to higher temperatures, where the hard block transition should occur, with the present experimental arrangement. Additional evidence for the existence of MWS effects in the present case is seen in Figure 9, where the loss is plotted at a fixed frequency of 100 kHz for three different cure stoichiometries. Only the transition attributed to the soft block is observed. Similar behavior was reported by North et al.[44] in a series of polypropylene glycol polyurethanes.

The HTPBD-based polyurethane shows evidence of a weak transition at room temperature (Fig. 8), although this may not be apparent from the scale used. This appears to be a cooperative type of relaxation, due to the segmental motion of the nonpolar soft block segments with thermally activated rotational reorientation of dipoles due to the hard blocks. A separate hard block transition was not observed over the temperature range measured.

DISCUSSION

The morphology and resultant properties of the as-cast polyurethanes were significantly affected by the polarity of the soft segment material. More diffuse
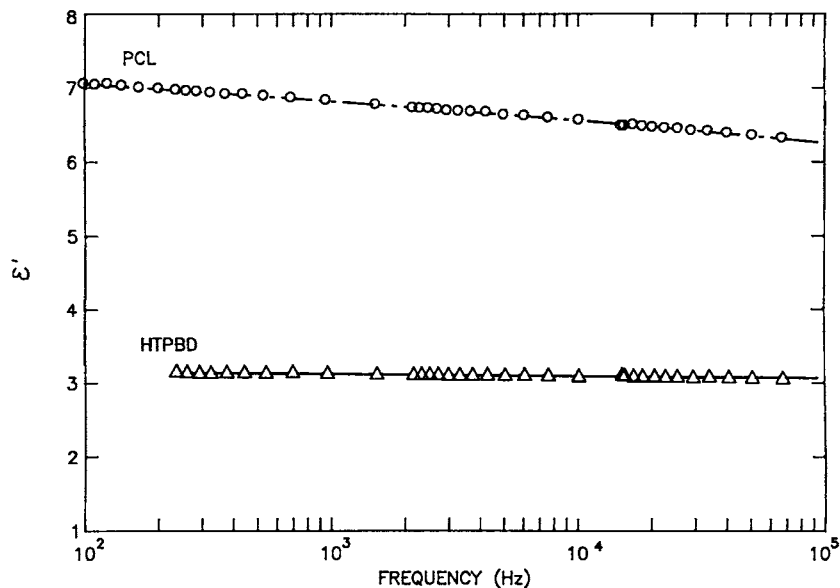
Figure 6 Plot of dielectric permittivity as a function of frequency at 297K for polycaprolactone and hydroxy-terminated polybutadiene polyurethanes with 5.7% ANCO of m–TMXDI in prepolymer and cure stoichiometry of unity.

phase boundaries appear to be present in polyurethanes using polycaprolactone as the soft block material, as compared to the hydroxy-terminated polybutadiene. Interpretation of the dynamic mechanical properties and dielectric behavior in terms of idealized structures and highly ordered domains in the polyurethanes is obscured, to a certain degree, by

the fact that the structural isomers of DETDA will probably differ in their degrees of reactivity, particularly in regard to the second amine group.

The meta isomer of TMXDI would also not be expected to form hard segments that can pack in as ordered a fashion as those formed from the para isomer,[36,37] due to steric considerations. In addition
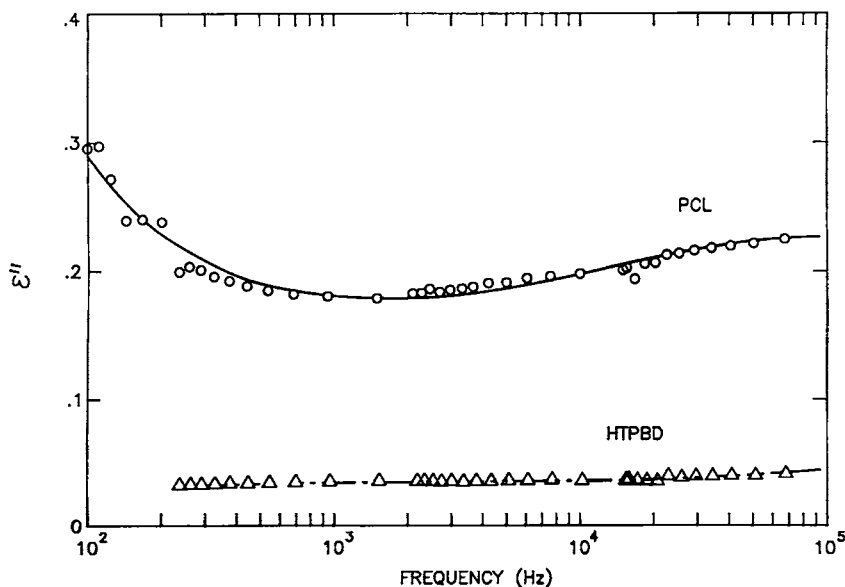

Figure 7 Plot of dielectric loss as a function of frequency at 297 K for polycaprolactone and hydroxy-terminated polybutadiene polyurethanes with 5.7% ANCO of m–TMXDI in prepolymer and cure stoichiometry of unity.
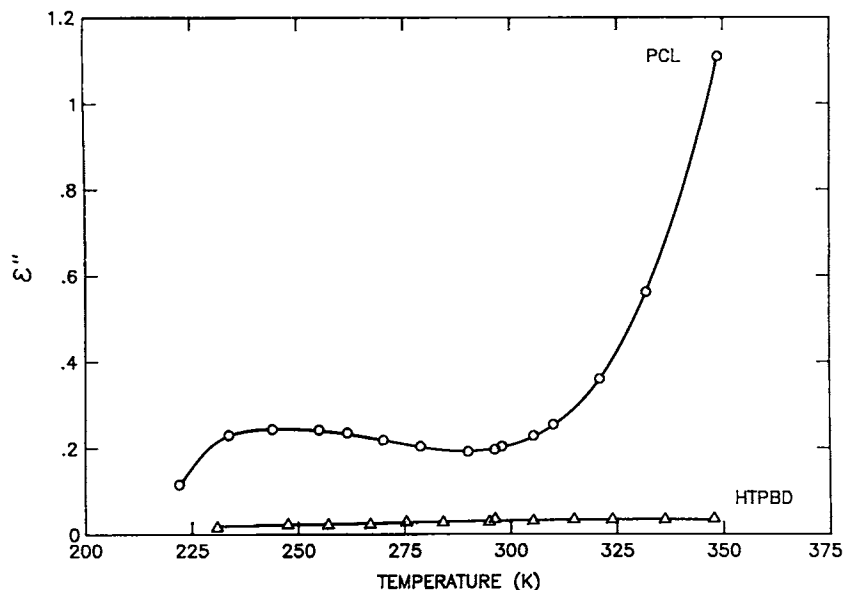
Figure 8   Plot of dielectric loss as a function of temperature at 535 Hz for polycaprolactone and hydroxy-terminated polybutadiene polyurethanes with 5.7% ANCO of m-TMXDI in prepolymer and cure stoichiometry of unity.

to the dynamic mechanical spectra discussed earlier, additional evidence for this can be seen when comparing the dielectric loss spectra as a function of temperature of PCL-based materials at low and high frequencies. These are shown in Figures 10 and 11. The polyurethane, based upon the para isomer of

TMXDI, does not show the pronounced low frequency rise found with the meta isomer. Additionally, the peak in the loss maximum at high frequency, associated with the parallel component of the soft segment dipole, occurs at a lower temperature. The lack of the prominent MWS effect and
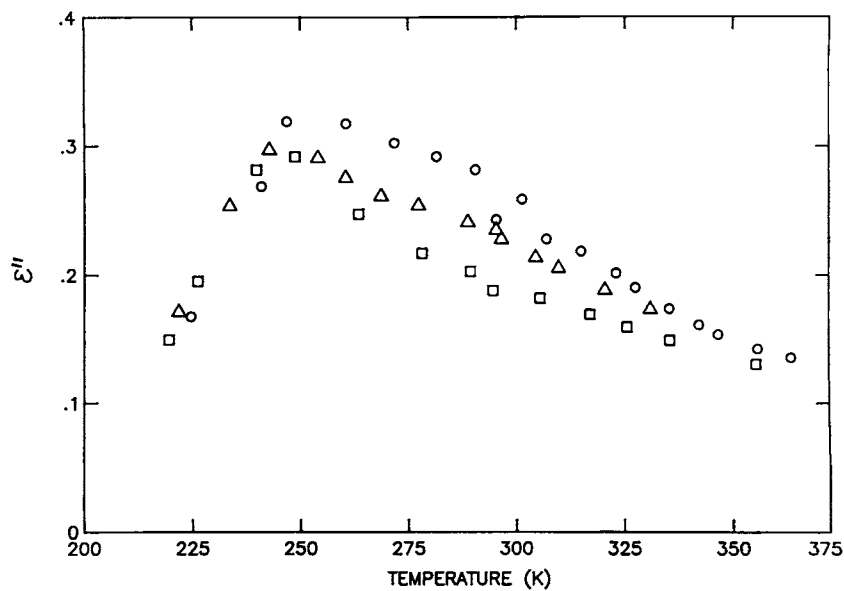

Figure 9   Plot of dielectric loss as a function of temperature at 100 kHz for polycaprolactone polyurethanes with 5.7% ANCO of m-TMXDI in prepolymer and varying cure stoichiometries: (circles) $NCO/NH_2 = 0.9$; (triangles) $NCO/NH_2 = 1.0$; (squares) $NCO/NH_2 = 1.1$.
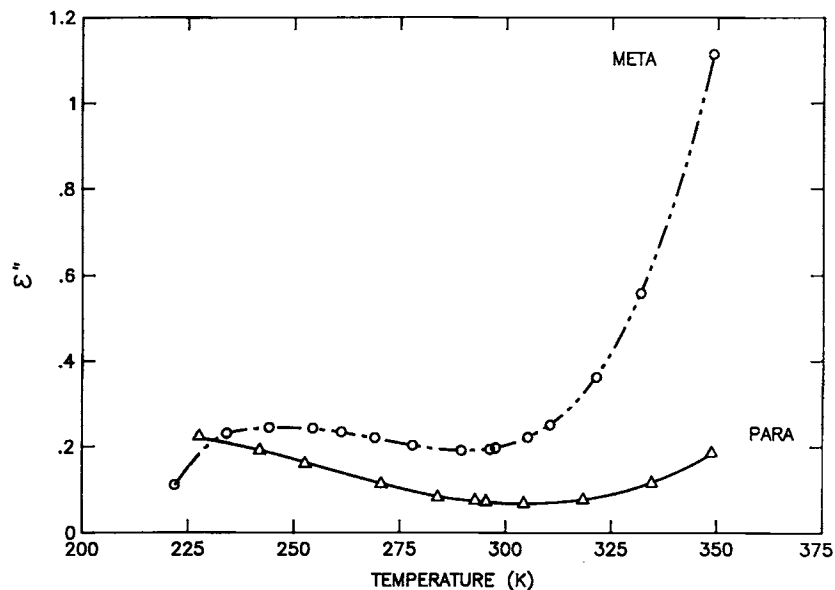
Figure 10   Plot of dielectric loss as a function of temperature at 535 Hz for polycaprolactone polyurethanes with 5.7% ANCO of m-TMXDI or p-TMXDI in prepolymer and cure stoichiometry of unity.

the lower soft-block transition temperature indicate that the hard segment domains are more ordered in the PCL polyurethanes formed with the para isomer of TMXDI.

Formation of domain structure in block copolymers, such as polyurethanes, is normally a time-dependent phenomenon that is significantly affected

by thermal history.[15,45,46] The results discussed above were obtained from as-cast samples. In order to evaluate the effects of thermal treatments, DSC, DMTA, and dielectric measurements were performed on samples annealed for 24 h at 145°C. The PCL-based polyurethane with the 4.3% isocyanate content, corresponding to a hard segment content
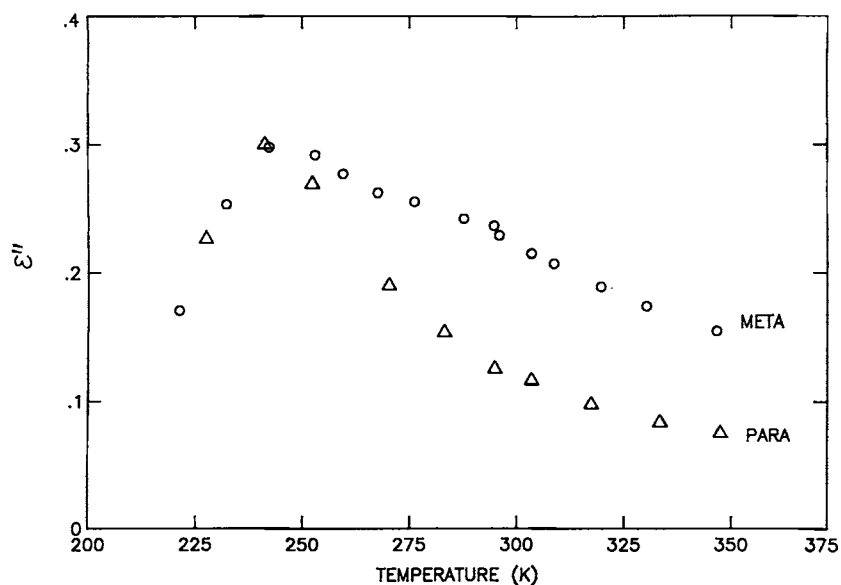

Figure 11   Plot of dielectric loss as a function of temperature at 100 kHz for polycaprolactone polyurethanes with 5.7% ANCO of m-TMXDI or p-TMXDI in prepolymer and cure stoichiometry of unity.
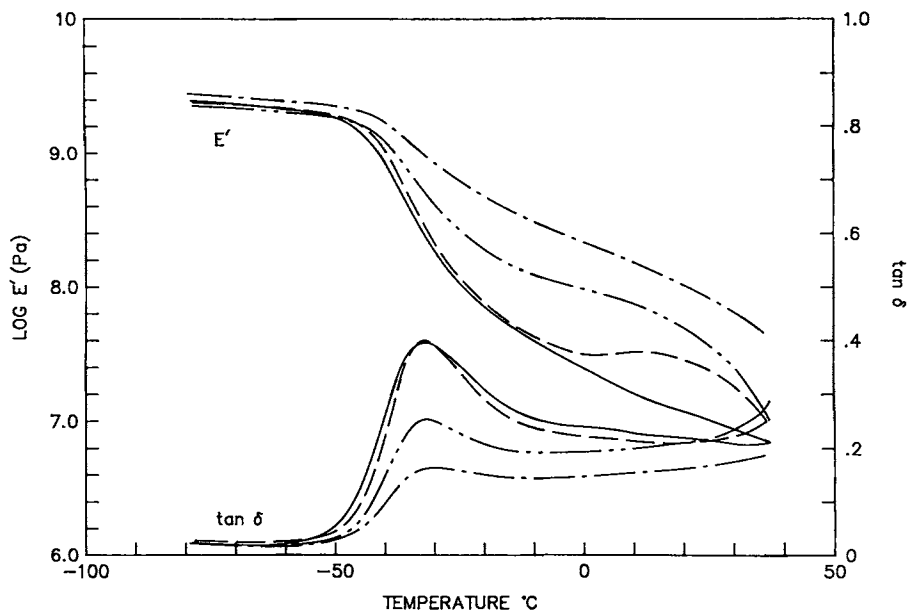
Figure 12   Plot of storage Young's moduli and loss tangents as a function of temperature at 10 Hz after various thermal treatments for PCL polyurethane with 4.3% ANCO in prepolymer and unit cure stoichiometry: (——) unannealed sample; (- -) annealed 24 h at 145°C and scanned from −80°C to 40°C on DMTA; (- - -) second DMTA cycle of annealed sample; (- · · -) third DMTA cycle of annealed sample.

of 28%, was sensitive to thermal treatment. This is shown in Figure 12. The behavior of the 28% hard segment content material is also time dependent. The annealing behavior was also mirrored in the dielectric spectra (not shown). Higher hard segment contents did not show as much sensitivity, yielding only moderate changes after annealing. The behavior was then stable (Fig. 13).
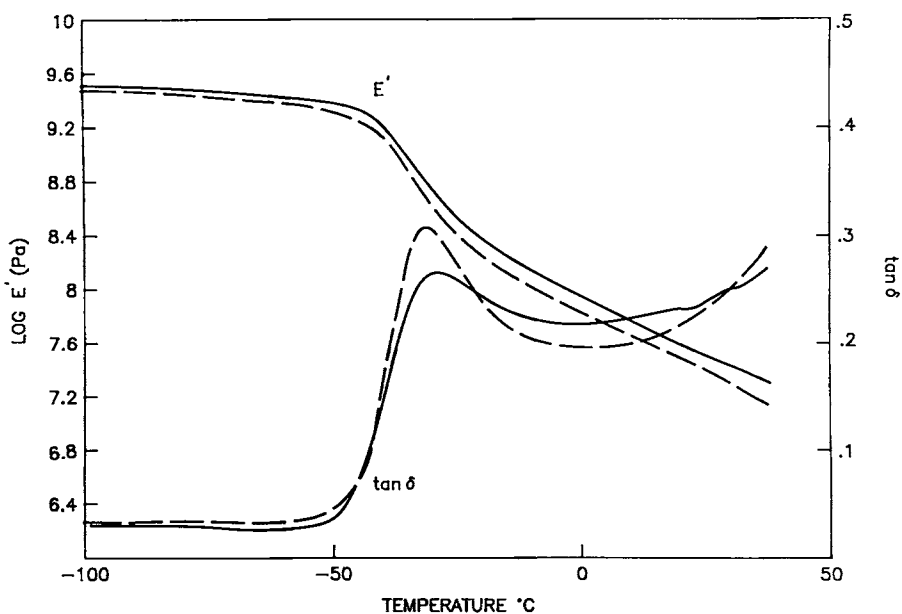

Figure 13   Plot of storage Young's moduli and loss tangents as a function of temperature at 10 Hz after thermal treatment at 145 deg C for 24 hrs for PCL polyurethane with 5.7% ANCO in prepolymer and unit cure stoichiometry.
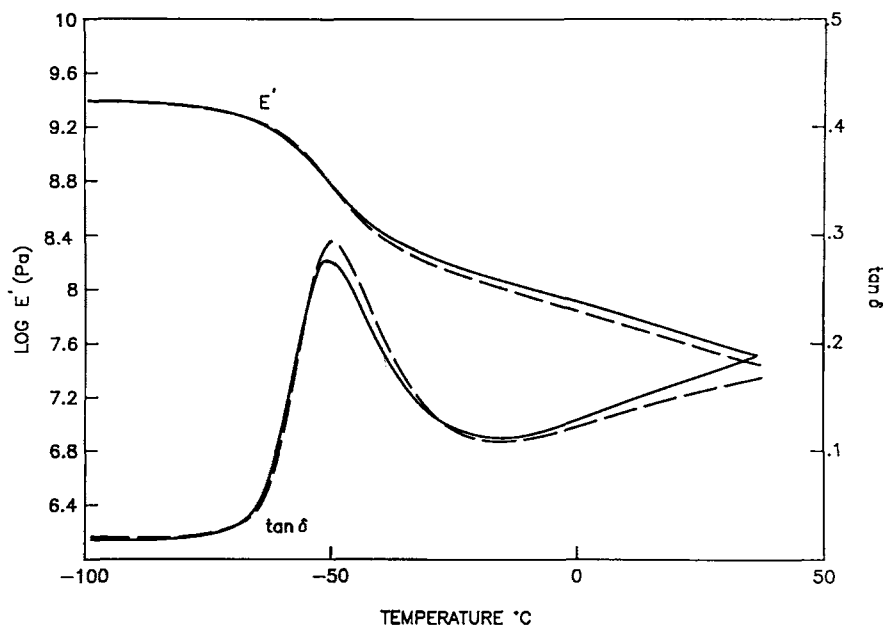
Figure 14 Plot of storage Young's moduli and loss tangents as a function of temperature at 10 Hz after thermal treatment at 145°C for 24 h for HTPBD polyurethane with 5.7% ANCO in prepolymer and unit cure stoichiometry.

The materials, based upon HTPBD as a soft block, showed only minor changes due to thermal treatment. The DMTA scans are shown in Figure 14, and exhibit less demixing than the corresponding PCL polyurethanes. This is a consequence of the fact that the as-cast materials already exhibit extensive phase segregation, and annealing appears to have a relatively minor effect on the hard segment ordering. Similar behavior has been reported in TDI-based polyurethanes with this soft block material.[15]
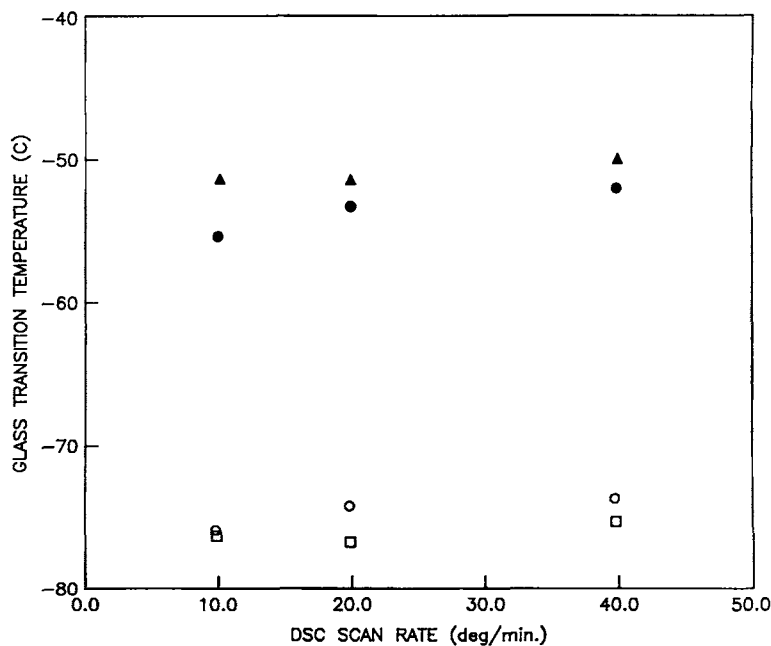

Figure 15 Plot of soft block transition temperatures after thermal treatment as a function of DSC scan rate for PCL and HTPBD polyurethanes with 5.7% ANCO in prepolymer and unit cure stoichiometry.

The trends shown in the dynamic mechanical spectra indicate that demixing occurs after a period of annealing. It is not clear from the present results whether this demixing is caused by an increase in the size of the hard segment domains, or an increase in the ordering of the hard segment domains. It is probable that both are involved to a certain extent. The trends shown in the dynamic mechanical spectra were mirrored in the DSC scans, which were dependent upon the heating rate used. The changes in soft segment T_gs are summarized in Figure 15.

SUMMARY

A series of linear, segmented polyurethanes, based upon the meta isomer of TMXDI and DETDA chain extender, have been prepared and characterized by calorimetry, FTIR, dynamic mechanical spectroscopy, and dielectric spectroscopy. These indicated that the morphology and resultant properties of the polyurethanes were significantly affected by the polarity of the soft segment material. Extensive phase mixing was present in polyurethanes using polycaprolactone as the soft block material. The FTIR measurements are interpreted to indicate that both hard segment–soft segment and hard segment–hard segment hydrogen bonding are present in the polycaprolactone-based urethanes. In contrast, the hydroxy-terminated polybutadiene materials appear to give primarily hard segment–hard segment hydrogen bonding.

The results obtained in the present study show that properties of polyurethanes, based upon the meta isomer of TMXDI, are relatively unaffected by cure stoichiometry. Available isocyanate content in the prepolymer is more of a controlling factor. The effect that the reaction stoichiometry has on the number average molecular weights or polydispersity in these materials, and the way in which these affect the measured dynamic mechanical and dielectric properties, are not clear. Experiments utilizing gel permeation chromatography and light scattering detection are currently underway to attempt to determine absolute molecular weights.

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