DAMPING PROPERTIES OF ALIPHATIC POLYURETHANES FROM 4,4'-DICYCLOHEXYLMETHANE DIISOCYANATE

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Abstract

Polyurethanes cover a wide range of damping properties depending in large part on their two-phase morphology. Hard segment crystallinity was proposed to be the dominant factor in determining these properties. The evidence for this conjecture came from a comparison of a system in which hard segment crystallinity was present with a system where crystallinity was inhibited by using a different chain extender. To verify our assumption, in this work crystallinity was inhibited not by changing the chain extender but by changing the diisocyanate from the aromatic 4,4'-diphenylmethane diisocyanate or MDI to the cycloaliphatic 4,4'-dicyclohexylmethane diisocyanate or $H_{12}MDI$. Prepolymers of poly(tetramethylene ether glycol) (PTMG) of four different molecular weights (650, 1000, 2000, 2900) with $H_{12}MDI$ were synthesized and chain extended with 1,4 butanediol. Measurements of the dynamic mechanical properties of these materials verified the assumption that hard segment crystallinity is the dominant factor in determining the damping characteristics of polyurethanes. All non-crystalline hard segment systems have very similar properties regardless of the diisocyanate type or the chain extender type.

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INTRODUCTION

Polyurethanes are widely used in many damping applications, but the large number of possible chemical compositions makes it difficult to know which one to choose for a particular application without a tedious trial and error evaluation program. For this reason, it is desirable to be able to determine general rules governing the behavior of these materials, which allows one to predict which materials will be useful for a given application. For some applications, a high, narrow loss factor is required while for others a low, broad loss factor is needed.

It was suggested in our earlier work[1] that the presence of hard segment crystallinity has a dominant effect in determining damping properties. It was found that polyurethanes with hard segment crystallinity have higher rubbery modulus and lower, broader loss factors than those lacking crystallinity. In that work, crystallinity occurred when a chain extender without pendant groups was used while the substitution of a chain extender with pendant groups inhibited crystallinity. It was proposed that the difference between the two cases was a result of the presence or absence of hard segment crystallinity and should be independent of the chain extender if some other way could be found to control crystallinity.

The chain extender without pendant groups used previously was 1,4-butanediol or BDO. Due to the simple, regular structure of this material, all the polymers made using it were found to develop hard segment crystallinity. By contrast, a chain extender with pendant methyl groups, 2,2-dimethyl-1,3-propanediol or DMPD, hinders hard segment orientation and inhibits crystallinity[1].

The present work was undertaken in an attempt to verify the importance of crystallinity by examining a system similar to the previous one but one in which crystallinity is controlled not by the chain extender but by the diisocyanate. If our assumption is correct, the same chain extender that gave rise to high rubbery modulus and low, broad loss factor will have low modulus and high, narrow loss factor if crystallinity can be inhibited.

The diisocyanate used earlier with both of the above chain extenders was 4,4'-diphenylmethane diisocyanate (MDI). In the present work, a cycloaliphatic diisocyanate, $H_{12}MDI$, will be substituted. $H_{12}MDI$ is a cycloaliphatic diisocyanate composed of a mixture of the three geometric isomers: trans-trans, trans-cis, cis-cis. While the MDI based polyurethanes can form a well defined crystalline hard segment as we have previously seen, hard segment crystallinity is inhibited in $H_{12}MDI$ based polymers due to the presence of these three isomers. Our supposition is that the same qualitative properties will be obtained by varying the diisocyanate portion rather than the chain extender portion provided that hard segment crystallization can be inhibited (i.e. morphology is more important than chemistry).

The remainder of this paper will discuss the synthesis of the polyurethanes, the thermal analysis to determine transition temperatures, the dynamic mechanical analysis to determine damping characteristics, and the conclusions reached. It will be verified that the presence or absence of hard segment crystallinity is the dominant factor in determining the qualitative form of the dynamic mechanical properties, independent of the specific diisocyanate or chain extender.

SYNTHESIS

All the polymers synthesized were based on the same polyglycol used previously, poly(tetramethylene ether) glycol or PTMG (DuPont Terathane). Nominal molecular weights of PTMG were 650, 1000, 2000, and 2900. In the earlier study, an aromatic diisocyanate was used, 4,4'-diphenylmethane diisocyanate or MDI (Dow Isonate 2125M). In the present work a cycloaliphatic diisocyanate, 4,4'-dicyclohexylmethane diisocyanate or H_{12}MDI (Mobay Desmodur W), was used. This material is about 65 percent cis-trans, 30 percent trans-trans, and 5 percent cis-cis isomer. The three isomers are illustrated in Figure 1.
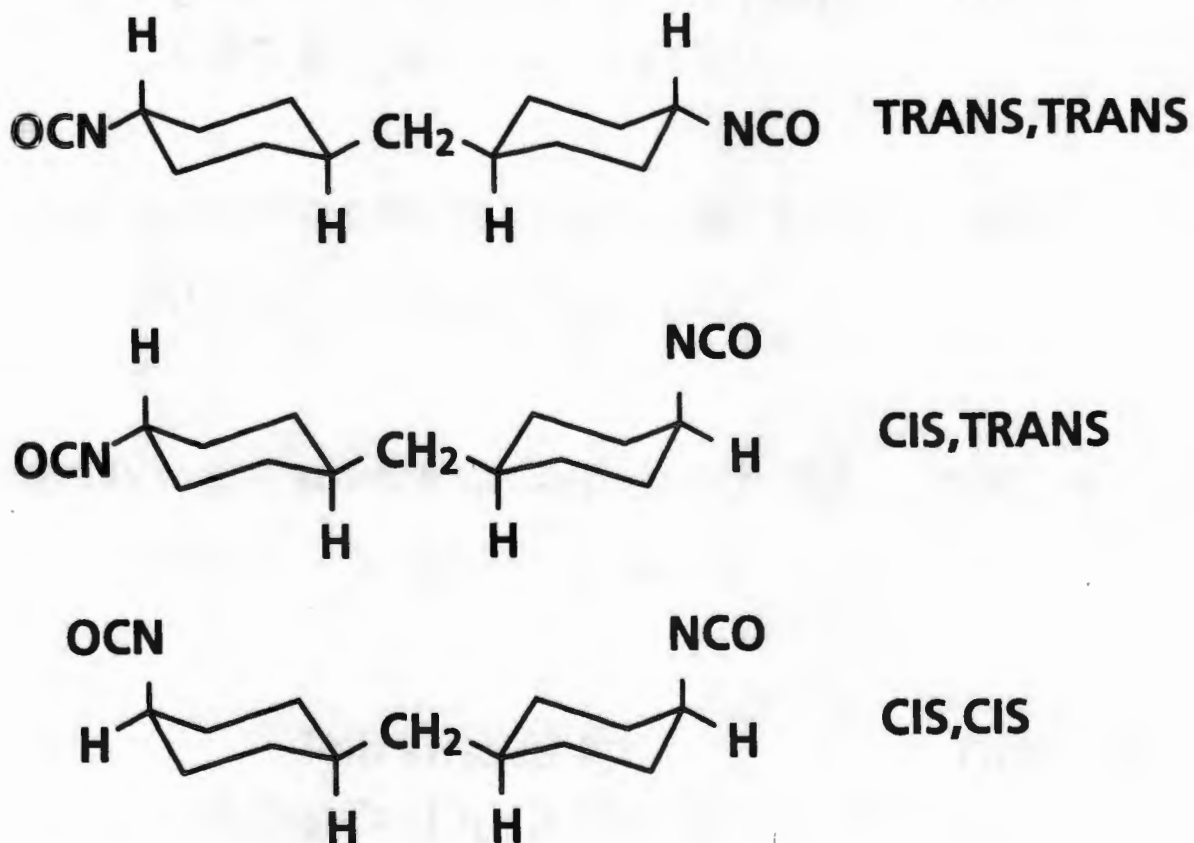

Figure 1. Isomers of H_{12}MDI

All of the above polyglycols were reacted with H_{12}MDI under nitrogen using 1 mole of PTMG and 3 moles of H_{12}MDI to form prepolymers. The reaction temperature was kept between 75 and 80°C for at least two hours after the addition of polyglycol was complete. A small amount of dibutyl tin dilaurate (Air Products DABCO T-12) catalyst was used to speed up the reaction between the polyglycol and the diisocyanate. This mixture was then degassed and stored under nitrogen until further use.

The PTMG/H_{12}MDI prepolymer was chain extended with BDO. Figure 2 shows the structures of PTMG, MDI, H_{12}MDI, BDO, and DMPD. The prepolymer was heated to 80°C and degassed then chain extended with BDO. The BDO was added and mixed under vacuum at high speed using a laboratory mechanical mixer for about three minutes. The polymer was poured into a pre-heated Teflon coated mold at 100°C. The isocyanate index was 1.05, which ensures that there is 5 percent excess diisocyanate for crosslinking during the cure. All of the samples were cured at 100°C for 16 hours. Then the samples were equilibrated at room temperature and 50 percent RH for a minimum of two weeks before dynamic mechanical analysis.
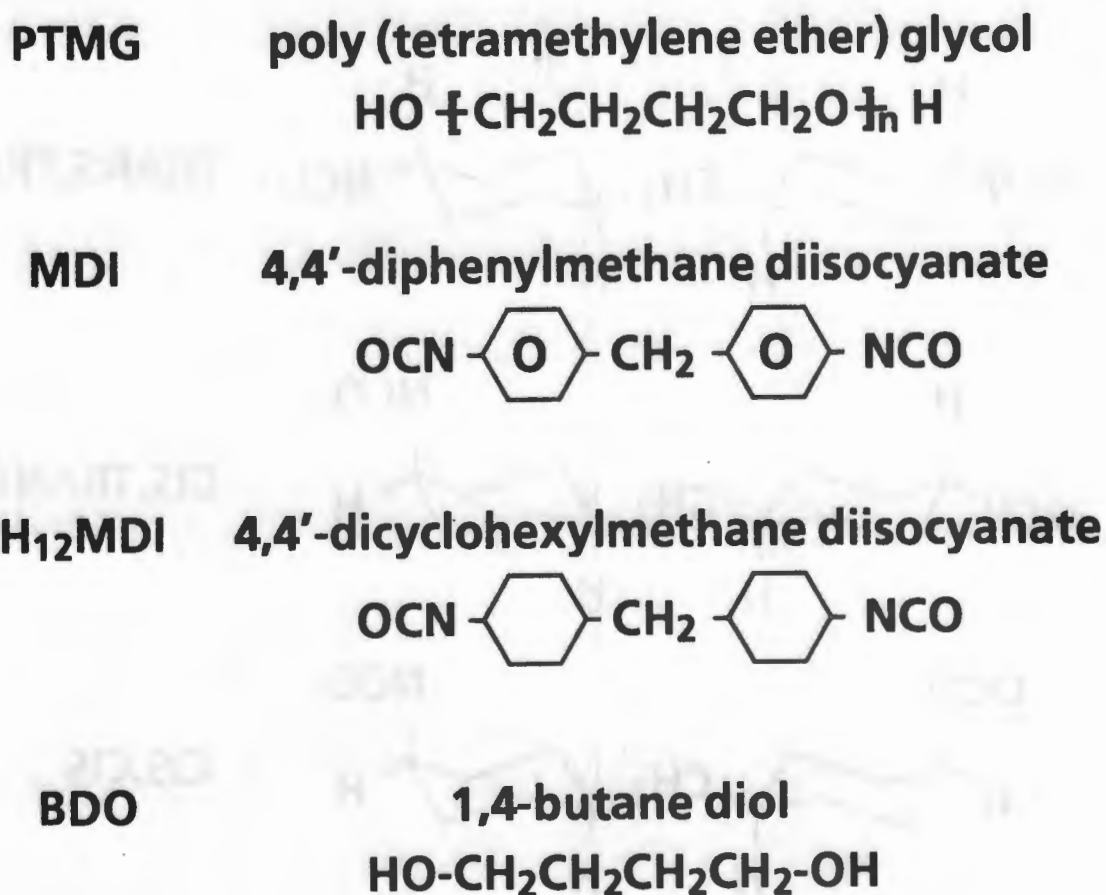
PTMG   **poly (tetramethylene ether) glycol**

$$HO \left[CH_2CH_2CH_2CH_2O \right]_n H$$

MDI   **4,4′-diphenylmethane diisocyanate**

OCN —⟨O⟩— CH₂ —⟨O⟩— NCO

H₁₂MDI   **4,4′-dicyclohexylmethane diisocyanate**

OCN —⟨ ⟩— CH₂ —⟨ ⟩— NCO

BDO   **1,4-butane diol**

$$HO-CH_2CH_2CH_2CH_2-OH$$

Figure 2. Chemical Structures of Components

THERMAL ANALYSIS

A DuPont 9900 Thermal Analyzer was used in conjunction with a 910 DSC (differential scanning calorimeter) module to obtain thermograms. Samples (15-20 mg) were cut from the test bars used for the dynamic mechanical measurements and placed in aluminum test pans for analysis. Measurements were carried out in a argon atmosphere at a scanning rate of 10°C/min. Two runs were made on each sample, each from -170 to 250°C.

Thermograms were analyzed to determine the glass transition temperature in the soft segment, $T_g(ss)$, the melting temperature in the hard segment, $T_m(hs)$, and the melting temperature in the soft segment, $T_m(ss)$, if any. In addition, the heat of fusion was determined whenever crystallinity was present.

DYNAMIC MECHANICAL ANALYSIS

Dynamic mechanical properties were obtained using the resonance apparatus previously described[1]. In this apparatus, Figure 3, modulus and loss factor were obtained over a frequency range of about two decades for temperatures from -60 to 70°C. All data will be presented at a reference temperature of 25°C.
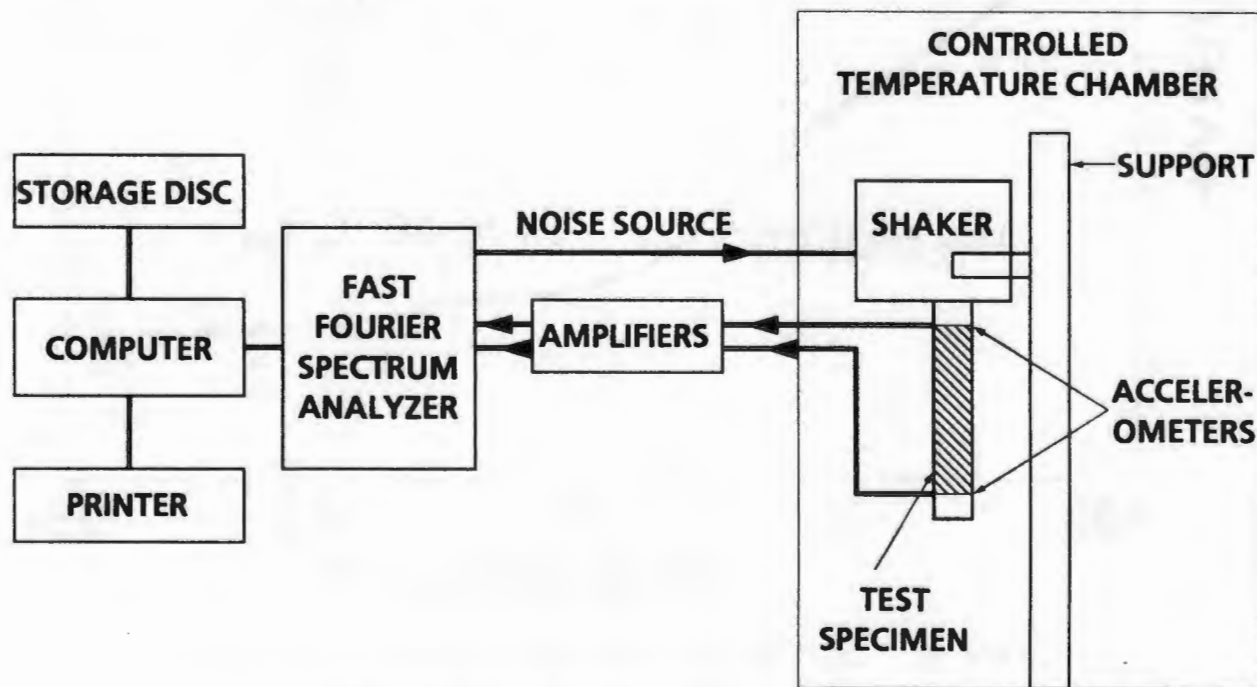

Figure 3. Resonance Apparatus

Measurements were made at 5 degree temperature intervals and the sample was equilibrated for twenty minutes at each interval before measurement. This data was shifted, using the time-temperature superposition principle to form master curves of

modulus and loss factor as a function of frequency over a very wide frequency range at a reference temperature of 25°C. Measurements and data analysis were carried out in the same fashion as the earlier work[1].

RESULTS AND DISCUSSION

Transition temperatures were determined from DSC thermograms. A typical example of the results obtained is shown in Figure 4, where we have compared the data for PTMG 1000/H_{12}MDI/BDO with that PTMG 1000/MDI/BDO. As can be seen, there is a well developed melting peak for the MDI based polymer, indicating that hard segment crystallinity was present, but no crystallinity is seen in the H_{12}MDI based polymer.

MDI/BDO

$T_g = -48\ ^{\circ}C, T_m = 157\ ^{\circ}C$

H_{12} **MDI/BDO**
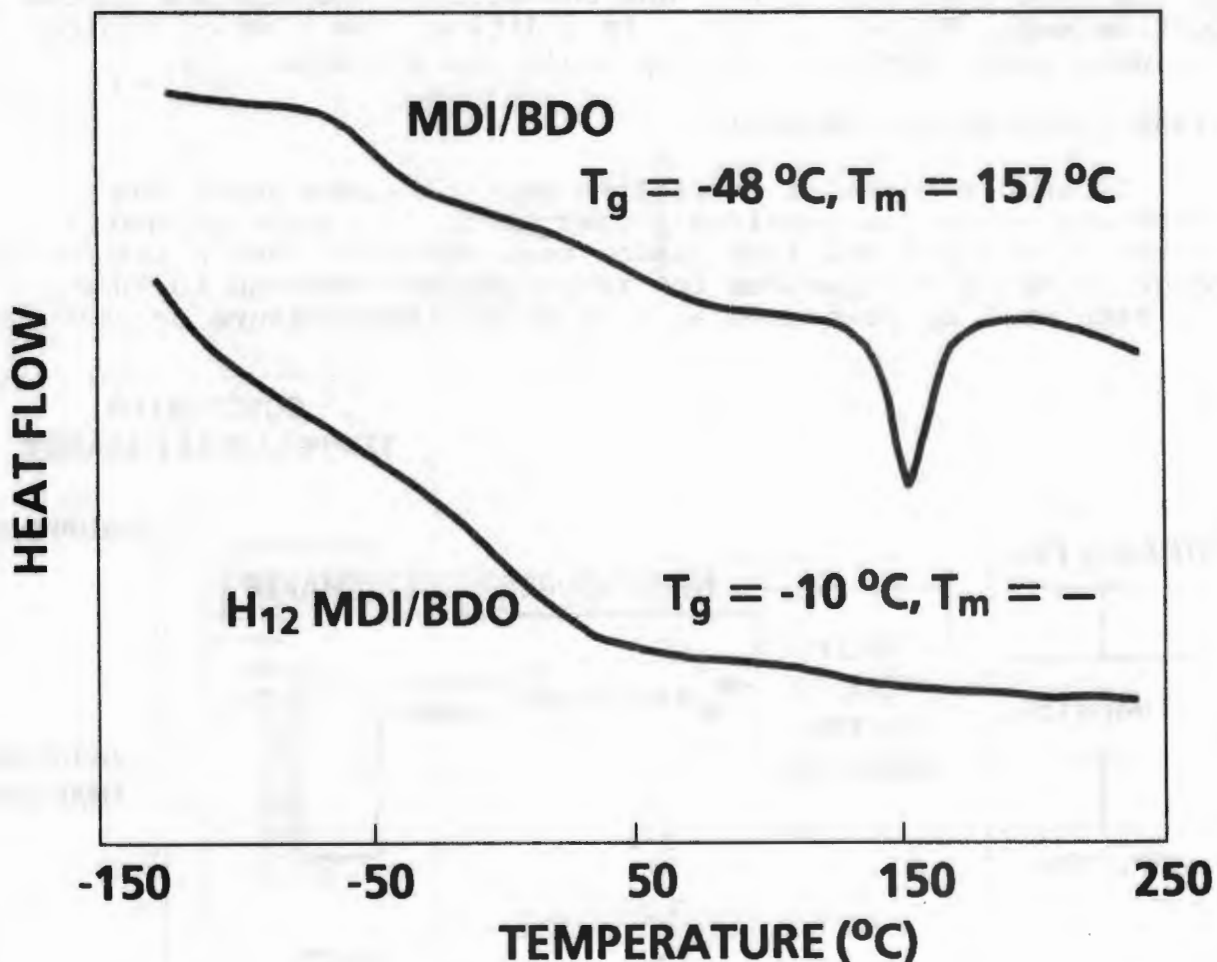
$T_g = -10\ ^{\circ}C, T_m = -$

Figure 4. DSC Thermograms of PTMG 1000 Polymers

Thermograms for the other molecular weights were analyzed in a similar manner, and the transition temperatures obtained are listed in Table 1. Densities of the H_{12}MDI polymers and the analogous MDI based polymers are also listed in Table 1.

Table 1. Transition Temperatures and Densities for
PTMG 650-2900/H₁₂MDI/BDO and PTMG 650-2900/MDI/BDO

	T_g(ss) °C	T_m(hs) °C	T_m(ss) °C	Density g/cm³
PTMG 650/H₁₂MDI/BDO	13	152	--	1.096
PTMG 1000/H₁₂MDI/BDO	-10	--	--	1.075
PTMG 2000/H₁₂MDI/BDO	-68	--	--	1.040
PTMG 2900/H₁₂MDI/BDO	-71	--	18	1.027
PTMG 650/MDI/BDO	-24	160	--	1.174
PTMG 1000/MDI/BDO	-48	157	--	1.139
PTMG 2000/MDI/BDO	-66	184,197	2	1.080
PTMG 2900/MDI/BDO	-71	191,198	10	1.056

ss - soft segment   hs - hard segment

In comparing the results for the two systems, the glass
transition temperature for the PTMG 2900/H₁₂MDI/BDO polymer is
identical to that for the analogous MDI based polymer and the
value for PTMG 2000/H₁₂MDI/BDO polymer is nearly the same
as the analogous MDI based polymer. For the lower molecular
weight PTMG, however, the H₁₂MDI based polymers have
significantly higher glass transition temperatures than the
analogous MDI based polymers. For PTMG molecular weight of 1000,
the T_g for H₁₂MDI based polymer is 38 degrees higher than the MDI
based polymer. while T_g for PTMG 650/H₁₂MDI/BDO polymer is 37
degrees higher than the analogous MDI based polymer. Since, for
these systems, the lower the PTMG molecular weight the higher the
hard segment concentration, it follows that the cycloaliphatic
diisocyanate has the most effect in those polymers with the
higher hard segment concentration. This increase in T_g is
presumably a result of phase mixing of the hard segment into the
soft segment.

We notice that hard segment crystallinity has been inhibited
in the H₁₂MDI polymers with the exception of the lowest molecular
weight, where there is a small amount of hard segment
crystallinity. The heat of fusion for the 650 MW polymer is 7
J/g compared with 20 J/g for the analogous value for an MDI
system[2]. Thus we expect the slightly crystalline PTMG
650/H₁₂MDI/BDO polymer to behave similar to the non-crystalline
PTMG 650/MDI/DMPD polymer, though with a slightly higher rubbery
modulus and lower, broader loss factor. This behavior is, in
fact observed[1]. The non-crystalline PTMG 1000/H₁₂MDI/BDO polymer
should be very close in behavior to the non-crystalline PTMG
1000/MDI/DMPD polymer, and this is also found experimentally[1].

Finally, we observe that soft segment crystallinity occurs
for the PTMG 2900 polymers which we have seen before. When the

soft segment gets long enough, soft segment crystallinity occurs regardless of the hard segment. Based on our previous experience, there is likely some soft segment crystallinity in the PTMG 2000 polymers that does not appear in the DSC at a scanning rate of 10°C/min but which does appear when sufficient time for annealing is allowed, as in the dynamic mechanical measurements where the sample is equilibrated at each temperature interval. The step-wise isothermal dynamic mechanical measurements are made in steps of five degrees with an equilibration time of 20 min after each step. The equivalent heating rate is then 0.25°C/min.

Density values determined by water displacement (ASTM Method D 792) are also listed in Table 1. It can be seen that, for both systems, the polymer density decreases as the molecular weight of the PTMG increases. Since the higher the PTMG molecular weight, the higher the soft segment concentration, the decrease in density is a soft segment concentration effect. For any given PTMG molecular weight, the density of the MDI polymer is about 5 percent higher than the analogous $H_{12}MDI$ polymer, due to the hard segment crystallinity in the MDI based polymers.

Dynamic mechanical modulus results for PTMG 650/H_{12}MDI/BDO and PTMG 1000/H_{12}MDI/BDO are shown in Figure 5.
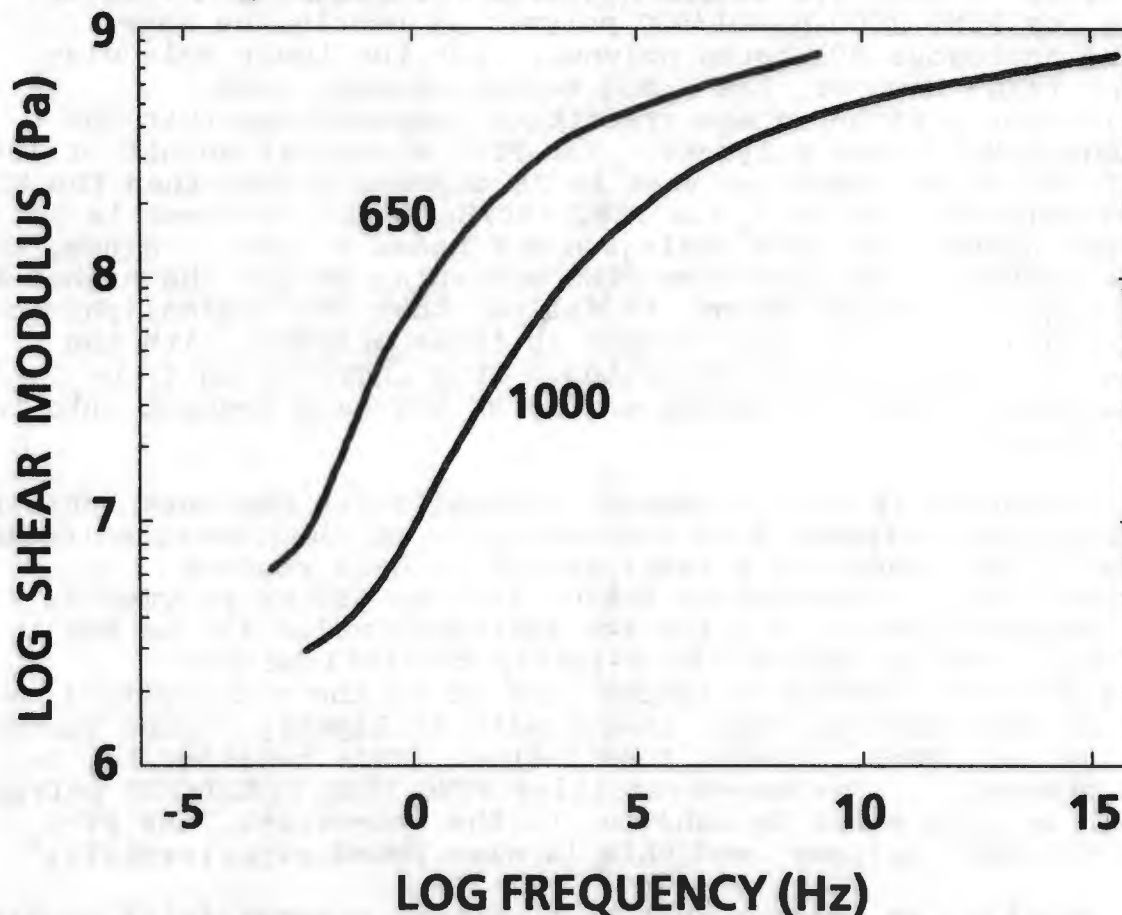

Figure 5. Shear Modulus for PTMG 650 and 1000/H_{12}MDI/BDO

The PTMG 2000 polymer was not thermorheologically simple so that master curves could not be generated. This behavior is probably due to a small amount of soft segment crystallinity which occurs during the slow heating cycle of the dynamic mechanical testing but which is not seen in the more rapid scanning used in the DSC. For the PTMG 2900 polymer, definite soft segment crystallinity was present even in the DSC thermogram and again the data could not be shifted.

Looking more closely at the modulus results (Figure 5), the glassy modulus of both polymers is about 1 GPa, typical for polyurethanes regardless of chemical composition. The rubbery modulus, however, shows much more variation with the chemistry and morphology of the particular system. Both molecular weights tend asymptotically to a rubbery modulus of about 2 MPa, the same as the PTMG/MDI/DMPD systems. In fact, the PTMG/H_{12}MDI/BDO data is very close to the PTMG/MDI/DMPD system. In contrast, both these polymers are qualitatively different than the PTMG/MDI/BDO system where the rubbery modulus tended to about 20 MPa, as can be seen in Figure 6, where a comparison is made for the three PTMG 1000 polymers.
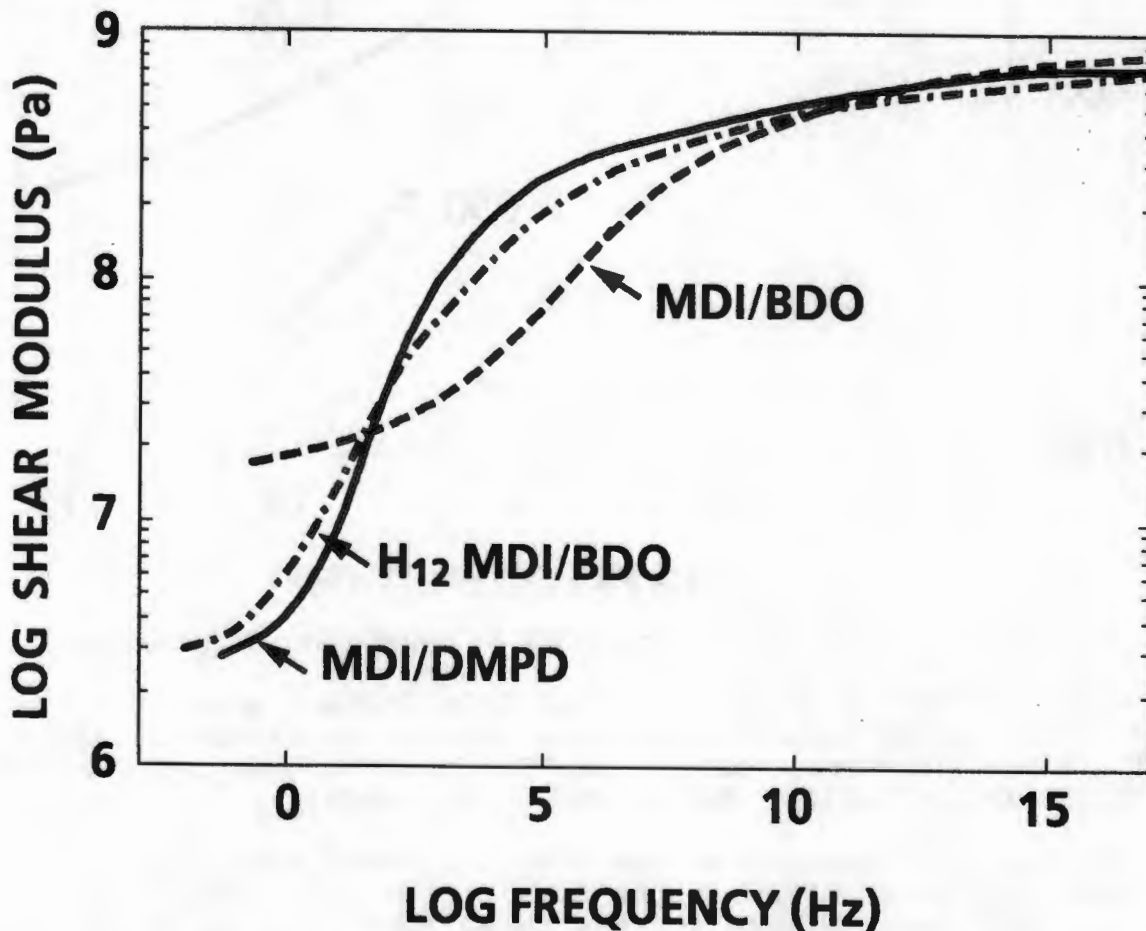

Figure 6.   Shear Modulus for PTMG 1000/MDI/BDO,
            PTMG 1000/MDI/DMPD, and PTMG 1000/H_{12}MDI/BDO

Note that the two polymers with very similar modulus values
(MDI/DMPD and H_{12}MDI) have rather different chemistry. What they
have in common is that they have no hard segment crystallinity.
The polymer without hard segment crystallinity (MDI/BDO) has very
different modulus values.   These observations are in agreement
with our supposition that hard segment crystallinity dominates
the dynamic mechanical properties not chain extender or
diisocyanate type.

The loss factor data for the two H_{12}MDI polymers is shown in
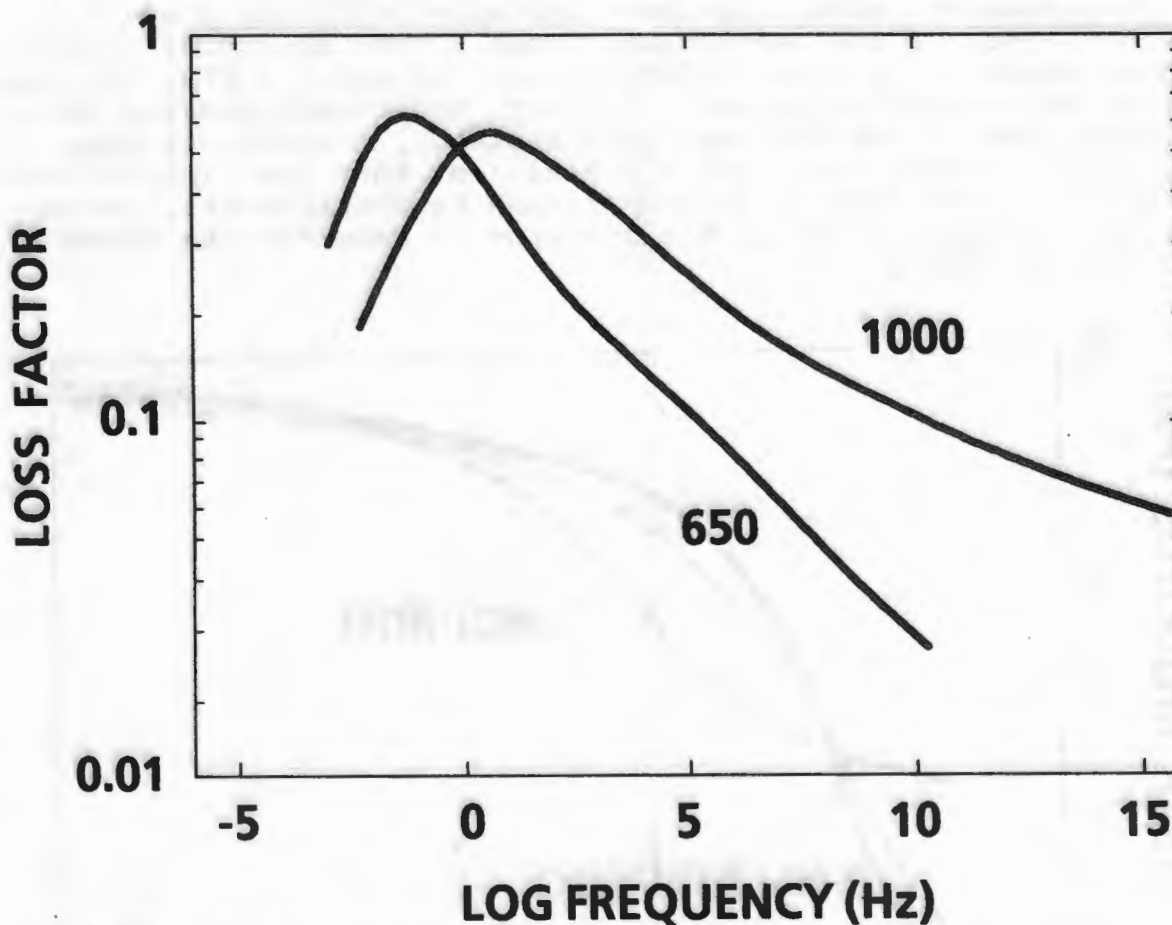Figure 7.

Figure 7.   Loss Factor for PTMG 650 and 1000/H_{12}MDI/BDO

Both polymers have a relatively high loss factor, about 0.8, and
the maximum values occur about three decades of frequency apart.
The T_g values for these polymers differ by 23°C, and a difference
of 7°C/decade is typical for polymers in general.

Further confirmation of the effect of hard segment
crystallinity is observed in the loss factor data, Figure 8,
where a comparison is made for the three PTMG 1000 polymers. The
PTMG/H_{12}MDI/BDO data is very close to the PTMG/MDI/DMPD, both
having a peak loss factor of about 0.8, but these polymers are
qualitatively different than the PTMG/MDI/BDO, with a peak loss

factor of about 0.3. Once again, morphology is more important than chain extender or diisocyanate type.
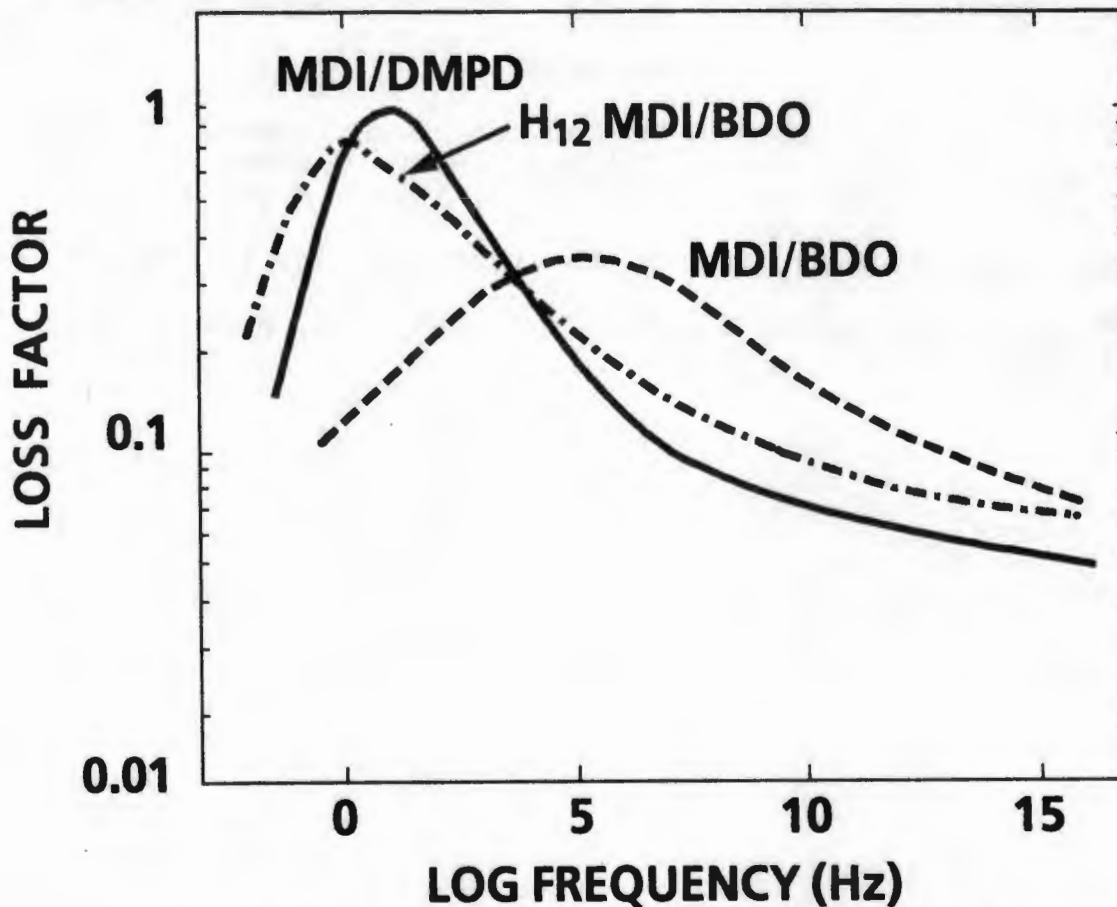

Figure 8.   Loss Factor for PTMG 1000/MDI/BDO, PTMG 1000/MDI/DMPD, PTMG 1000/H$_{12}$MDI/BDO

CONCLUSIONS

Thermal and dynamic mechanical measurements were made on a series of polyurethanes based on cycloaliphatic diisocyanate and the results obtained compared to similar data on the aromatic analog. The results confirm our hypothesis that the presence or absence of hard segment crystallinity is the dominant factor in determining the qualitative form of the dynamic mechanical properties, independent of the specific diisocyanate or chain extender. The following specific conclusions were reached:

- Hard segment crystallinity is the dominant factor in determining the dynamic mechanical properties of polyurethanes

- Regardless of the chain extender or diisocyanate, high loss is obtained if crystallinity is avoided

- Regardless of the chain extender or diisocyanate, low rubbery modulus is obtained if crystallinity is avoided

ACKNOWLEDGEMENT

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