

Structure-property relationships of polyurethanes based on toluene di-isocyanate

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Eight series of polymers containing 2, 4 toluene di-isocyanate (2, 4 TDI) or 2, 6 TDI, butanediol and 1000 or 2000 molecular weight polyether or polyester soft segment were prepared, and their thermal transitions and structures studied by differential scanning calorimeter, thermo-mechanical analysis, infra-red spectroscopy and X-ray methods in order to obtain the effect of compositional variables on transition behaviour, the extent of phase segregation, and polymer properties. Results indicate that polyester soft segment contributes to greater phase mixing than the polyether, even competing with crystallization of 2, 6 TDI hard segment. This implies that hydrogen bonding of urethane NH to polyester is stronger than to polyether. In weakly phase-segregated samples, hydrogen bonding in the mixed phase raises the T_g beyond the value predicted from the copolymer equation and i.r. estimates of the degree of phase mixing. The additional increase in T_g can be accounted for by treating hydrogen bonding as cross-links. The results also indicate the effectiveness of increased polyether soft segment molecular weight in promoting phase segregation while less pronounced molecular weight effects occur with polyester soft segment. Thermal behaviour of hydrogen bonding suggests that the cause of hydrogen bond dissociation bears little relation to the state of structural organization.

1. Introduction

The thermoplastic polyurethanes are linear segmented copolymers which consist of alternating soft and hard segment units. The soft segment is commonly a low molecular weight polyether or polyester whereas the hard segment generally consists of an aromatic di-isocyanate condensed with a low molecular weight diol. It is now generally accepted that the properties of these materials are primarily due to the phase segregation of soft and hard segments, leading to the formation of hard segment domains which are dispersed in the rubbery matrix. There are a wide variety of compositional variables which can affect the degree of phase segregation and hard segment organization and, accordingly, the sample properties. In

this paper we report the results obtained on an extensive series of polyurethanes based on 2, 4 toluene di-isocyanate (2, 4 TDI) and 2, 6 toluene di-isocyanate (2, 6 TDI). In 2, 4 TDI polymers, the asymmetric placement of the isocyanate residues with respect to the methyl group can result in some head-to-tail isomerization in the hard segment. In 2, 6 TDI polymers, this problem is absent since the molecule is symmetrical. Other compositional variables examined included polyether versus polyester soft segment, the molecular weight of the soft segment and the length of hard segment. Extensive physico-chemical techniques such as thermal analysis, wide- and small-angle X-ray studies and i.r. spectroscopic analysis have been employed to provide detailed inform-

ation on the thermal transition behaviour, structural organization, and properties.

2. Experimental

Preparation of the polymers was carried out by the two-step method described previously [1]. 2, 4 TDI (Aldrich Chemical, 97%) and 2, 6 TDI (Kipers Laboratory, 89%) were vacuum distilled. Anhydrous 1, 4-butanediol (GAF), polytetramethylene oxide (Quaker Oats) and polybutylene adipate (Hooker Chemical) were used as received. The molar ratio of TDI, butanediol and polyether (PTMO) or polyester (PBA) was varied in five equal steps from 2:1:1 to 6:5:1 with 5% molar excess of di-isocyanate. In sample designation, the integer following the TDI isomer indicates the number of moles of di-isocyanate per mole of polyether or polyester. Fig. 1 represents the chain structure of the polymers. All the samples used for the study of thermal transition were compression moulded into 15 mil* thick films with a pressure of 100 bar at 180°C. Differential scanning calorimetry was carried out at heating rate of 10°C min⁻¹ with a sample weight of approximately 10 mg using the Perkin-Elmer DSC II. Thermo-mechanical analyses (TMA) was conducted with the Perkin-Elmer TMS-1 equipped with the UU-1 temperature programmer at a load of 5 to 10 g and a heating rate of 20°C min⁻¹. The infra-red analyses were carried out on films (~1 μm) cast on sodium chloride plates from 2% solution in dimethyl formamide. The films were dried in a vacuum oven at 50°C and scanned on a Beckman-12 infra-red spectrophotometer. The temperature dependence of i.r. was determined using a variable temperature unit (Wilks model # 19) connected to the temperature controller (Wilks model # 37).

For wide-angle X-ray diffraction studies, a Warhus camera was used, while for small-angle X-ray studies a Kratky camera equipped with automatic step scanning, counting and printing devices was employed. Radiation was supplied by a graphite monochromated Norelco copper fine-focus tube operated at 50 kV and 30 mA.

3. Results and discussion

3.1. Polyurethanes with polyether soft segment

3.1.1. PTMO-1000 polymers

The two series of polymers in this category are designated as 2, 4 TDI-PTMO 1000 and 2, 6 TDI-PTMO 1000. Major differences in the properties of the 2, 4 TDI and 2, 6 TDI polyurethanes were evident as indicated in the top portion of Table I.

Wide angle X-ray patterns of the 2, 4 TDI samples displayed only a broad amorphous ring and gave no indication of crystallinity. The three 2, 6 TDI samples of highest urethane content exhibited five crystalline reflections. None of the spacings corresponded to the lines expected for poly(tetramethylene oxide) indicating that the diffraction was due to hard segment crystallinity. In view of the amorphous nature of 2, 4 TDI samples, the small-angle X-ray scattering was carried out to characterize the structure of amorphous hard segment domains. The angular dependence of intensity obtained at room temperature is shown in Fig. 2. It is clear that the three polymers with longer hard segment exhibit the type of angular dependence which implies the presence of domain structure. It is also to be noted that total area under the curve is strongly dependent on the urethane content. Since the integrated scattering intensity is proportional to the product of three

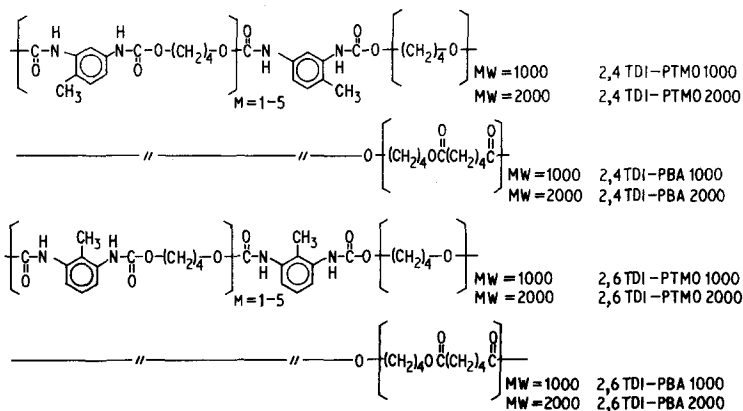


Figure 1 Diagram representing the chain structure of the polymers.

* 1 mil = 0.001 in.

TABLE I Properties and thermal transitions of TDI based polyurethanes

Sample	Urethane (wt %)	2, 4 TDI polymers			2, 6 TDI polymers				
		Properties	T_g (°C)	T_2 (°C)	T_m (°C)	Properties	T_g (°C)	T_2 (°C)	T_m (°C)
PTMO									
1000									
2	31	clear, soft sticky rubber	-36	18	-	clear, waxy	-	-	-
3	42	tough, live rubber	-14	33	-		-60	-	135
4	50	elastic, not snappy	1	60	-	opaque, hard	-60	-	155
5	56	flexible, but boardy	14	70	-	and tough	-63	-	160
6	61	almost plastic	23	80	(160)*		-61	-	165
PTMO									
2000									
2	19	clear snappy rubber	-67	-	-	clear, weak rubber	-	-	-
3	27	clear soft rubber	-65	50	-	translucent rubber	-73	61	-
4	33	translucent	-69	45	-	opaque, slightly	-74	71	171
5	39	rubbery	-72	40	-	rubbery, moderately	-74	72	210
6	44	moderately tough	-70	60	-	tough	-77	-	166-210
PBA									
1030									
2	31	translucent, rubbery	-13	39	-	translucent	-20	70	103
3	42	clear, weak rubber	1	50	-	high modulus rubber	-23	70	184
4	50	clear, slightly elastic	14	63	-	opaque,	-22	60	193
5	56	clear, somewhat stiff	25	75	-	slightly elastic	-14	141	181
6	61	clear, rigid	36	78	-	tough	-14	138	195
PBA									
2000									
2	19	opaque, moderately stiff	-40	-	-	translucent rubber	-	-	-
3	27	stretches, draws	-31	12	-	translucent, slightly	-51	85	167
4	33	opaque, somewhat flexible	-23	20	-	elastic, moderately tough	-51	67	177
5	39		-15	45	-	opaque, stiff, tough	-49	67	194
6	44		-6	64	-		-50	67	195

*Transition appears in the initial heating but not in the second run.

terms representing the electron density difference and the weight fractions of the dispersed and the continuous phase, the results imply that the extent of phase segregation increases with increasing urethane content, perhaps accompanied by some

improving domain organization. No attempt was made to carry out a quantitative analysis of the data along the lines suggested by Bonart [2-4].

Thermal analyses were carried out using both DSC and TMA to probe the details of the poly-

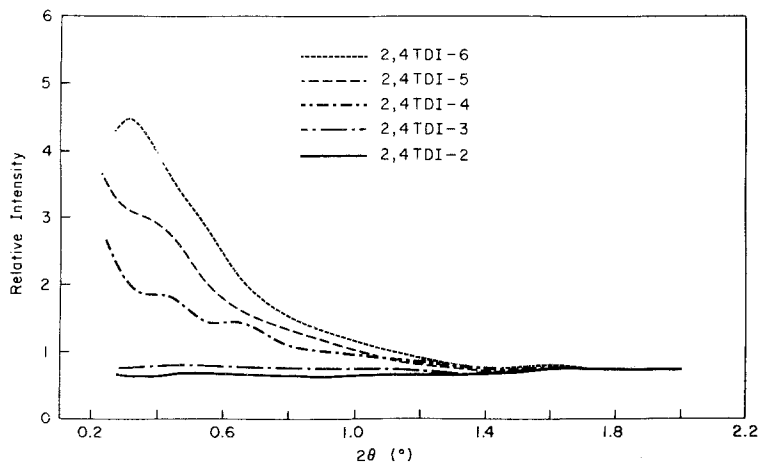


Figure 2 Angular dependence of small-angle X-ray scattering intensity in 2, 4 TDI polyurethanes.

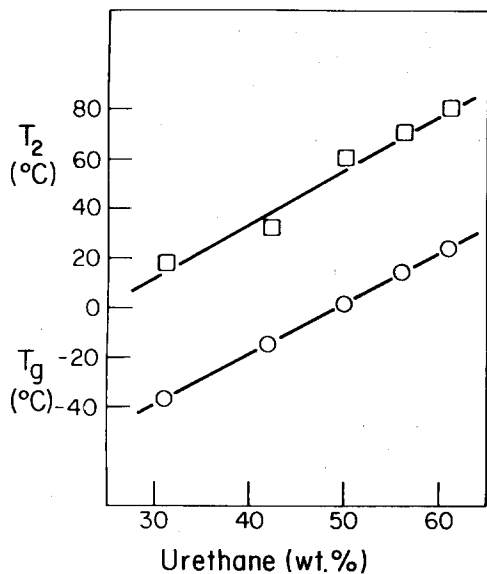


Figure 3 Glass transition temperature (T_g) and intermediate transition temperature (T_2) as a function of urethane content in 2,4 TDI-PTMO 1000.

urethane transition and their relation to the structure. In the 2,4 TDI samples, the glass transition temperature, T_g , of the soft segment phase was found to be a strong function of urethane content, as shown in Fig. 3 and the data of Table I.

T_g varies from -36°C to 23°C with increasing urethane concentration. This corresponds to an elevation from the T_g value of the free soft segment (-85°C), in the range of 49 to 108°C . The increase in T_g explains the progressive change observed in properties of 2,4 TDI polymers. Similar behaviour was shown for an intermediate temperature transition T_2 observed by TMA analysis. The T_2 transition in 2,4 TDI polymers ranges from 18 to 80°C , as shown in Fig. 3. This transition is interpreted as the glass transition temperature of the amorphous hard segment domains whose structure improves with increasing hard segment length, which is proportional to the urethane content. A higher temperature transition T_3 was detected only in the samples of highest urethane content, and then only on the initial heating. This T_3 transition is believed to result from some allophonate or biuret bonding which arises from the small excess of diisocyanate in the polymerization recipe.

In semicrystalline 2,6 TDI polymers, as listed in Table I, the glass transition temperature of the soft segment phase was generally independent of

urethane concentration and the elevation of T_g above that of the free soft segment is 25°C , which is much smaller than the value for 2,4 TDI polymers. No T_2 transition was observed with 2,6 TDI polymers. Instead, the TMA scans revealed repeatable T_3 transitions in the range of 130 to 170°C , as shown in Fig. 4. The DSC scans showed an endothermic peak at T_3 indicative of crystalline melting. Both the increase in T_3 and the change in melting peak appearance indicated improvement in crystalline order with increasing urethane content.

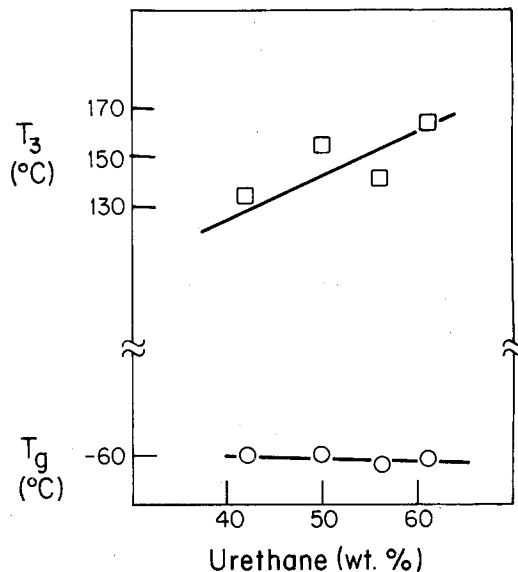
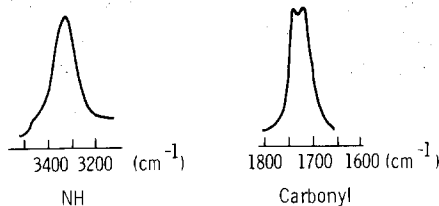


Figure 4 Glass transition temperature (T_g) and melting temperature (T_3) as a function of urethane content in 2,6 TDI-PTMO 1000.

2,4 TDI-PTMO 1000



2,6 TDI-PTMO 1000

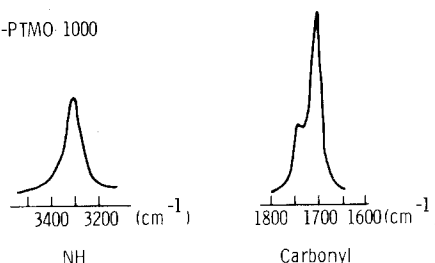


Figure 5 I.r. spectra in the NH and carbonyl regions.

A more detailed understanding of the relation between composition, transition behaviour and properties requires a quantitative measure of the extent of phase mixing. The analysis of absolute small-angle X-ray scattering provides an approach for estimating the extent of phase segregation. However, this method depends on a knowledge of the electron density of the dispersed and matrix phases, which in turn depends upon the degree of hard segment–soft segment mixing in these phases. In view of this difficulty, preference was given to the approach which relies on a quantitative analysis of the infra-red spectra.

The infra-red analysis depends on the resolution of the urethane NH and the carbonyl band into the bonded and non-bonded components. If the only proton acceptors are the carbonyl group of the urethane hard segment, and the oxygen of the polyether soft segment, then, the fraction of bonded carbonyl can be taken as a measure of the extent of phase segregation. In turn, the fraction of NH groups bonded to ether, determined by difference, indicates the degree of hard segment–soft segment mixing. Fig. 5 illustrates the i.r. spectra in the regions of NH stretching and carbonyl stretching. It is well known that a band near 3300 cm^{-1} is caused by the H-bonded NH groups while the free NH group appears near 3460 cm^{-1} . MacKnight and Yang have reported an integrated extinction coefficient $E_f = 3.44 \times 10^3\text{ l mol}^{-1}\text{ cm}^{-1}$ for the free NH group and $E_b = 1.19 \times 10^4\text{ l mol}^{-1}\text{ cm}^{-1}$ for the H-bonded NH groups from measurements of a model compound [4]. Based on these extinction coefficients, the fraction of H-bonded NH groups was calculated by the curve resolving technique [5]. The results indicate that for both 2, 4 TDI and 2, 6 TDI polymers 95% of

all NH groups are hydrogen bonded in the solid state at room temperature. The carbonyl region shows splitting of the absorption band into two peaks at 1740 and 1720 cm^{-1} for 2, 4 TDI polymers and at 1740 and 1700 cm^{-1} for 2, 6 TDI polymers. Studies on model compounds of *n*-butyldiurethane of 2, 4 TDI and 2, 6 TDI in solution indicated that a band at 1740 cm^{-1} is due to free carbonyl and that at 1720 or 1700 cm^{-1} is a result of hydrogen bonded carbonyl for 2, 4 TDI and 2, 6 TDI, respectively.

The fraction of bonded carbonyl calculated is listed in the third column of Table II by assuming same extinction coefficients for both bonded and free carbonyl bands. These results indicate that approximately 46 to 60% of the urethane carbonyl groups of 2, 4 TDI polyurethane samples and 80% for 2, 6 TDI samples are bonded to the urethane NH group. The remainder of NH groups are necessarily bonded with other proton acceptors

It has been commonly assumed that the only other proton acceptor is ether oxygen of the soft segment. However, the i.r. spectra on copolymers which contained only the appropriate diisocyanate (2, 4 TDI, 2, 6 TDI and MDI) and butanediol indicated that while NH is almost completely hydrogen bonded, a significant fraction (10 to 30%) of the carbonyl groups remain in the free state. The only additional proton acceptor in these copolymers is the urethane alkoxy oxygen. If the alkoxy oxygen is also involved in hydrogen bonding in the segmented polyurethanes, then the fraction of hydrogen bonded carbonyl underestimates the degree of hard–hard segment bonding and the values calculated from the difference provide, at best, an estimate of the maximum amount of intermixing of hard with soft segment.

TABLE II Elevation of T_g (K) based on the copolymer equation, 2, 4 TDI- and 2, 6 TDI-PTMO 1000 samples

Samples	Urethane* (wt %)	T_g (obs) (K)	H-bonded carbonyl (%)	W_2^\dagger	T_g (calc) (K)
2, 4 TDI-2	31	237	46	0.20	209
3	42	259	50	0.25	215
4	50	274	60	0.29	220
5	56	287	60	0.34	227
6	61	296	66	0.36	230
2, 6 TDI-3	42	213	78	0.13	202
4	50	213	78	0.16	207
5	56	210	80	0.20	209
6	61	212	80	0.20	214

*Calculated as TDI plus BD.

†Weight fraction of hard segment units (TDI-BD) in mixed soft segment phase, from i.r. results.

Since the glass transition behaviour in 2, 4 TDI polymers is believed to be the result of extensive mixing of hard and soft segment regions, it appeared useful to inquire to what degree the i.r. evidence on hard segment-soft segment interaction could be used to explain the glass transition behaviour. One approach is to treat the infra-red data in a simple form of the copolymer equation and then account for any remaining differences between the predicted and observed T_g values.

T_g values were calculated using the following relation;

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}}$$

where W_1 and W_2 are the weight fraction of the soft segment and hard segment in the mixed soft segment phase estimated from i.r. data, $T_{g_1} = 188$ K for PTMO, $T_{g_2} = 380$ K for 2, 4 TDI-butanediol hard segment, and $T_{g_2} = 374$ K for the 2, 6 TDI butanediol analogue. The calculated values are listed in the last column of Table II. It is evident that the observed values of T_g for the 2, 4 TDI samples are substantially higher than the calculated values and the difference ΔT_g increases progressively with the increasing urethane content. Even if the T_g values are calculated assuming complete mixing, using the hard segment concentration which corresponds to the sample composition, the results are 15 to 25% lower than the observed T_g values. On the other hand for the 2, 6 TDI samples there is rather good agreement between the observed and calculated results.

For 2, 4 TDI polymers, the additional contribution to the increase in T_g , above that predicted by the copolymer equation, can be attributed to hydrogen bonding between hard and soft segment which acts as an effective cross-link. The following empirical equation was employed to fit the experimental results,

$$\Delta T_g = 820X_c/(4.6 - X_c)$$

where X_c , the fraction of ether groups which are hydrogen bonded, is equal to the effective degree of cross-linking. The equation has the same form as the relation between T_g and the degree of cross-linking proposed by DiBenedetto and DiMarzio [6, 7].

TABLE III Additional contribution to the increase in T_g , 2, 4 TDI-PTMO 1000 samples

Samples	ΔT_g (obs) (K)	Free carbonyl (%)	X_c^*	ΔT_g^\dagger (calc) (K)
2, 4 TDI-2	28	54	0.17	32
3	44	46	0.22	44
4	54	40	0.26	49
5	60	40	0.32	61
6	66	34	0.33	63

*Fraction of hydrogen bonded ether groups, equal to the effective degree of cross-linking.

$\dagger \Delta T_g = 820 X_c / (4.6 - X_c)$.

The calculated T_g values based on the modified equation are listed in Table III. A comparison between ΔT_g calculated and ΔT_g observed shows that, in combination with the copolymer equation, the observed values of T_g can now be predicted within 5° C from the infra-red data.

Some insight concerning the effect of hydrogen bonding on the higher thermal transitions has been obtained by analysing the temperature dependence of the infra-red spectra in the NH and carbonyl regions using simple procedures for resolving hydrogen bonded and non-bonded components of the two absorption bands [8]. In the 2, 6 TDI polymers, the change in the NH band and in the carbonyl band as a function of temperature indicates that extensive disruption of hydrogen bonding occurs within the hard segment domains. This behaviour is clarified when the fraction of bonded NH and carbonyl is plotted as a function of temperature, as shown in Fig. 6. A common onset temperature for the dissociation of hydrogen bonding appears in both the NH and carbonyl results. The onset temperature occurs at about 65° C for all 2, 6 TDI samples and the dissociation energy ΔH is about 4 kcal mol⁻¹, independent of urethane content. These results indicate that the dissociation of hydrogen bonding can occur well below the melting point (130 to 170° C). Perhaps the onset temperature represents the glass transition temperature of amorphous hard segment regions not otherwise detectable by thermal analytical methods (see also results on 2, 6 TDI-PTMO 200 samples), but the fact that dissociation of inter-urethane hydrogen bonding occurs to levels of 50% or more at temperatures which are still well below the melting point, indicates that extensive disruption of hydrogen bonding can occur within the crystalline structure.

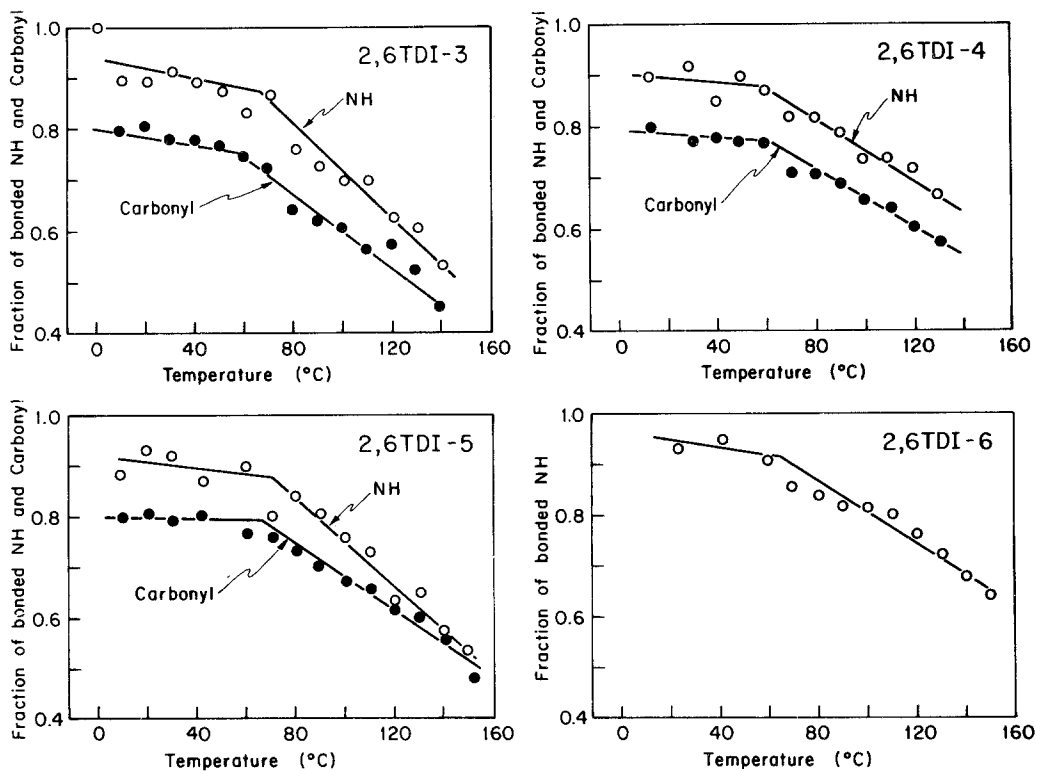


Figure 6 Fraction of bonded NH groups and carbonyl in 2, 6 TDI-PTMO 1000 polymers as a function of temperature.

For 2, 4 TDI polymers, the onset temperature for dissociation of hydrogen bonded NH, as shown in Fig. 7, is variable and occurs at 40 to 60°C, which is close to the glass transition temperature observed by thermo-mechanical analysis for amorphous hard segment domain structure. Surprisingly, there is little change in the carbonyl region up to the highest temperature studied (150°C), implying that the dissociation of NH is due almost entirely to the disruption of urethane-to-ether bonding.

A surprising observation is the relative stability of the inter-urethane bonding in 2, 4 TDI samples by comparison with the behaviour in the 2, 6 TDI samples. This could reflect the greater stability of hydrogen bonding at the 4 position in the 2, 4 TDI ring due to smaller steric hindrance than the 2 or 6 position in the 2, 6 TDI ring.

It should be noted that several of the observations presented here are similar to results reported by Seymour and Cooper for MDI segmented polyurethanes [9]. They demonstrated that the onset temperature for hydrogen bond dissociation was insensitive to annealing pro-

cedures which resulted in improvement in the hard segment organization, as evidenced by the higher domain transition temperatures. Overall, the results obtained here and in the important work of Seymour and Cooper indicate that onset of hydrogen bond dissociation bears little relation to the state of structural organization.

3.1.2. PTMO-2000 polymers

Increasing the molecular weight of the polyether soft segment from 1000 to 2000 produces a drastic improvement in phase segregation in 2, 4 TDI polymers [10]. As listed in Table I, the soft segment T_g and the glass transition of amorphous domains for these samples are generally independent of urethane content. This contrasts with the behaviour of the 2, 4 TDI-PTMO 1000 samples where the soft segment T_g and glass transition of domains exhibited a steep dependence on urethane content. As a result, 2, 4 TDI-PTMO 2000 polymers provide good low-temperature flexibility in addition to moderate toughness as rubbers. Results from the analysis of the infra-red spectra in several of the 2, 4 TDI-PTMO 2000 samples

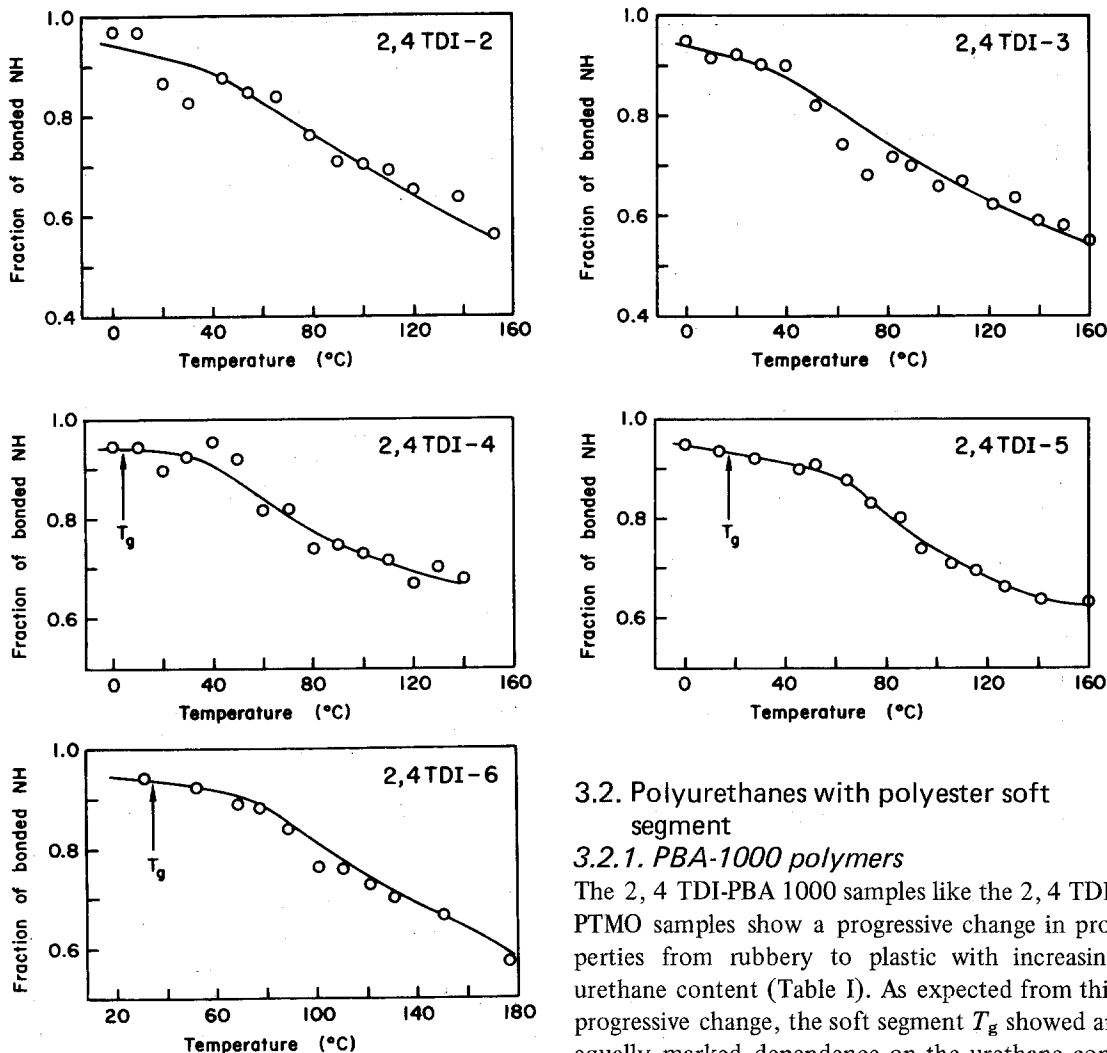


Figure 7 Fraction of bonded NH groups in 2, 4 PTMO 1000 polymers as a function of temperature.

indicate that these samples fall intermediate between the 2, 4 TDI-PTMO 1000 and 2, 6 PTMO 1000 samples in terms of the extent of phase segregation as measured by W_2 .

In 2, 6 TDI-PTMO 2000, soft segment T_g is even lower than in 2, 4 TDI-PTMO 2000 samples and appears to decrease somewhat with increasing urethane content as listed in Table I. A hard segment T_g is observed both in DSC and TMA scans on these samples but was absent from the 2, 6 TDI-PTMO 1000 samples. This indicates some improvement in phase segregation due to the increased soft segment molecular weight with the result that hard segment species which might otherwise be mixed with the soft segment phase now contribute to glassy hard segment regions.

3.2. Polyurethanes with polyester soft segment

3.2.1. PBA-1000 polymers

The 2, 4 TDI-PBA 1000 samples like the 2, 4 TDI-PTMO samples show a progressive change in properties from rubbery to plastic with increasing urethane content (Table I). As expected from this progressive change, the soft segment T_g showed an equally marked dependence on the urethane content.

As indicated in Table I, 2, 6 TDI-PBA 1000 samples show increasing toughness compared to 2, 4 TDI-PBA 1000 samples. The several DSC scans in Fig. 8 show a clearly-defined soft segment glass transition which shifts by about 30 °C between the first run and the third run, after heating above the melting point of hard segment crystallites. This suggests that the original conditions of compression moulding have considerably enhanced phase segregation, probably as a result of increasing the degree of hard segment crystallization by the application of pressure during the moulding and cooling cycles. The results summarized in Table I show that the initial values of T_g are only slightly dependent on composition, but those determined after melting exhibit a marked dependence on urethane content. There is some evidence of a hard segment glass

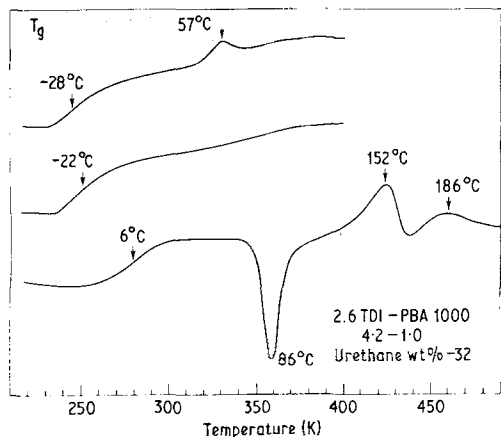


Figure 8 DSC scans of 2, 6 TDI-PBA 1000 polymer.

transition in the first but not in the second melting run, which again is consistent with greater phase segregation in the original compression moulded sample. There are also various transitions associated with the crystalline hard segment structure.

3.2.2. PBA-2000 samples

The DSC scan of 2, 4 TDI-PBA 2000 samples show a clearly-defined soft segment transition as well as the melting of soft segment polyester crystallinity. Results listed in Table I indicate that the soft segment and hard segment T_g are again dependent on urethane content. Both types of behaviour suggest that the two-fold increase in polyester molecular weight has not produced a significant improvement in the degree of phase segregation.

The behaviour of the 2, 6 TDI-PBA 2000 samples are completely analogous to the 2, 6 TDI-PTMO 2000 samples with the appearance of the soft segment T_g , crystallization and melting temperatures. The data are listed in Table I.

3.3. Comparison of transition behaviour

The glass transition temperatures plotted as a function of urethane content are shown for the various 2, 4 TDI samples in Fig. 9 and for the various 2, 6 TDI samples in Fig. 10. The ordinate represents the increase in the soft segment T_g above the values for the free soft segment, and is plotted in this fashion to compensate for differences in T_g for PBA and PTMO.

Fig. 9 for the 2, 4 TDI samples shows that the elevation of T_g for PBA 2000 as well as PBA 1000 falls close to the curve for PTMO 1000 samples, indicating that the degree of phase mixing in both series of polyester samples is comparable to that in the PTMO 1000 samples. The dramatic change in the T_g behaviour of the PTMO 2000 samples brought about by the two-fold increase in soft segment molecular weight is emphasized by the contrast with the other samples.

Fig. 10 for the 2, 6 TDI samples reveals that extensive phase mixing occurs in the PBA 1000 samples despite the driving force for phase segregation provided by hard segment crystallization. Even the 2, 6 TDI-PBA 2000 samples show an elevation, $\Delta T_g = 20^\circ\text{C}$, suggesting that some phase mixing occurs despite the apparent insensi-

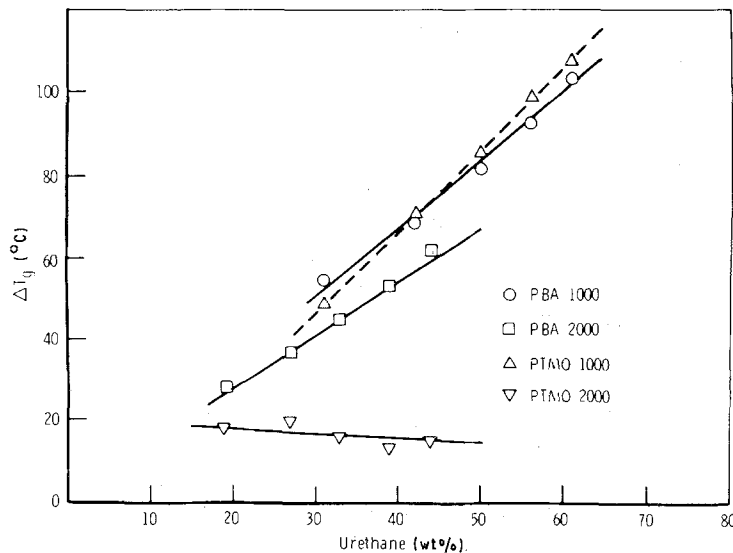


Figure 9 ΔT_g values for 2, 4 TDI polyurethanes.

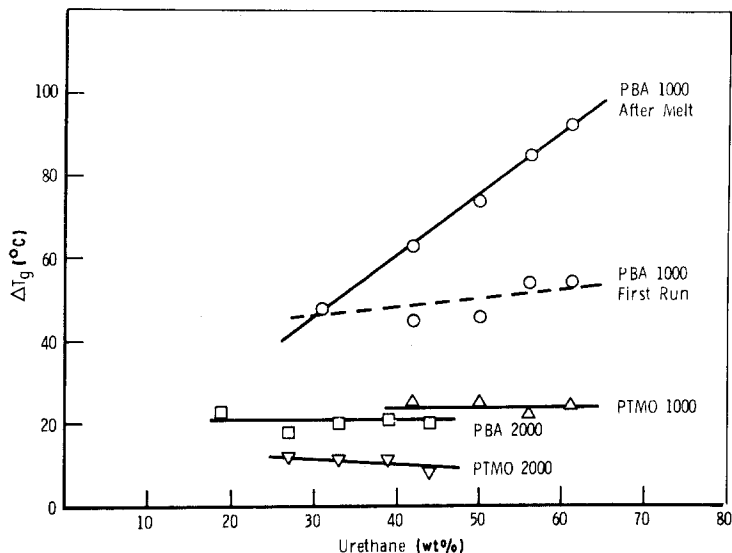


Figure 10 ΔT_g values for 2, 6 TDI polyurethanes.

tivity of T_g to urethane content. With the 2, 6 TDI-PTMO 2000 samples the increase in T_g is limited to a value of about 10°C . This result indicates that the effect of anchoring the ends of the soft segment by attachment to the urethane hard segment is only responsible for a small increase in T_g .

4. Conclusions

All of the 2, 4 TDI polyurethanes have amorphous domain structures with hard segment glass transitions below 100°C , while all of the 2, 6 TDI polymers exhibit semicrystalline hard segment structures with melting temperatures in the range of 130 to 200°C . Apparently structural regularity is a requirement for the occurrence of short-range order in hard segment domains and the interurethane hydrogen bonding is not sufficient in itself to stabilize the hard segment domains or to assure extensive phase segregation. Other conditions can also contribute to phase incompatibility such as the increase in the soft segment molecular weight, as demonstrated by the results presented here, or by the use of a less polar soft segment, exemplified by the hydroxy terminated polybutadienes which are now available.

When one compares the effects of polyether and polyester soft segment, it becomes obvious that the PBA soft segment generally introduces greater phase mixing than the PTMO soft segment, thereby raising T_g of the soft segment. PBA soft segment even competes with segregation and crystallization of the 2, 6 TDI-butenediol hard segment. This result suggests that the hydrogen

bonding to ester is stronger than to ether. It is clear that where the low temperature properties of polyurethanes are important, the choice of polyether soft segment and use of a 2000 rather than a 1000 molecular weight soft segment is preferred.

It seems reasonable to expect that hydrogen bonding between hard and soft segment units will make a specific contribution to the increase in soft segment T_g beyond the additive effect of mixing described by the copolymer equation. However, the contribution of such specific interactions appears to be important only when the extent of phase mixing is substantial, as in 2, 4 TDI-PTMO 1000. For 2, 4 TDI-PTMO 2000 and 2, 6 TDI-PTMO 1000 polyurethanes, where the mixing is limited, one can account for T_g quite well, although not exactly, by applying the copolymer equation to the infra-red results. There is also some direct evidence that hydrogen bonding interaction can interfere with soft segment crystallization. This is indicated by the fact that soft segment crystallization does not occur in the 2, 4 TDI-PTMO 2000 samples, whereas with the slight improvement in phase segregation which occurs in the 2, 6 TDI-PTMO 2000 samples, as indicated by the further reduction in T_g , the soft segment crystallizes freely. A similar comparison holds for the PBA 2000 samples. Extensive experimental evidence of both 2, 6 TDI and MDI segmented polyurethane samples shows that hydrogen bond dissociation can occur within an ordered domain structure at temperatures well below the domain transition temperature and with little regard for

improvement in the degree of order. Thus, the thermal behaviour of hydrogen bonding appears to be virtually independent of the structural organization in such materials.

Finally, the glass transition temperature deserves recognition as a sensitive index of phase mixing, perhaps almost as useful as infra-red analysis and small-angle X-ray scattering, which are also not free of ambiguity. The copolymer equation will continue to serve as a useful approximation for estimating the extent of phase segregation in strongly phase separated systems. In weakly phase separated systems, the empirical relation developed here for the 2, 4 TDI-PTMO 1000 samples in combination with the copolymer equation could serve as a useful approximation for relating T_g to the extent of phase segregation.

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