We expect on physical grounds that the structure factor for interior melting should reduce to that for a once broken rod, eq 12, when $n_B \rightarrow 0$. From eq 43 we see that this is indeed true. Calculation of the diffusion coefficient for interior melting involves more labor since the integral in eq 39 is difficult to evaluate analytically for this case. One can, however, perform the double sum analytically and evaluate the remaining integral over $\mathbf{q}_0$ numerically.

In Figure 3 the structure factor for interior melting is plotted against $Z = \mathbf{q}an$ for several values of the melting parameter $\sigma = (n_B/n)$ with $n_A = n_C = (n/2)(1 - \sigma)$. The figure has been constructed for the regime where Z is of order unity but $u = (n\mathbf{q}^2a^2/6) = Z^2/6n^2 \ll 1$ so that the structure facture depends only on Z. Physically this condition states that the wavelength of light is large compared with all possible coil lengths but comparable to possible rod lengths. The curve $\sigma = 0$ corresponds to the once-broken rod case.

Concluding Remarks

We have presented a simple method for determining the properties of partially melted macromolecules when these properties depend upon some function of the distance between pairs of segments of the polymer. We find that in partially melted conformations the macromolecule exhibits significantly different behavior than in the extreme circumstances of no melting or complete melting. Quantitative results are displayed for the light-scattering structure factor and the translational diffusion coefficient for a number of cases.

The analysis may be extended in a number of ways, *e.g.*, to heterogeneous chains, to polydisperse systems, or to other hydrodynamic or equilibrium properties. Experimentalists should note that the proper interpretation of measurements in the melting region must take into account the variation of partially melted chains as discussed here. A particular measurement will require an appropriate average over the different conformations represented in the system during the process of melting.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Thermal Transition Behavior of Polyurethanes Based on Toluene Diisocyanate

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ABSTRACT: The thermal transition behavior of two series of polyurethane block copolymers, one based on 2,4-toluene diisocyanate, the other on 2,6-toluene diisocyanate, was studied to determine the influence of an asymmetric diisocyanate structure, such as that represented by 2,4-toluene diisocyanate, on domain organization and polyurethane properties. The 2,4-TDI polyurethanes were transparent and amorphous, and the properties varied progressively with urethane concentration; the 2,6-TDI polyurethanes were opaque, semicrystalline, and hard but tough. In the 2,4-TDI samples the glass transition T_g was a strong function of urethane concentration. Similar behavior was shown by an intermediate temperature transition T_2. A higher temperature transition T_3 was detected only in the samples of highest urethane content and then only on the initial heating. In the 2,6-TDI samples T_g was generally independent of urethane concentration. No T_2 transition was observed. The T_3 transition was repeatable and increased with urethane concentration. It is suggested that the T_2 transition which occurs in the 2,4-TDI polyurethanes is indicative of weak domain structure and that the increase in T_g with urethane concentration is due to extensive hard segment mixing with the soft segment phase. The absence of a T_2 transition in 2,6-TDI is taken to indicate that all domain structure which occurs is highly ordered and, therefore, that hard segment–soft segment mixing is minimal. This is in keeping with the strong T_3 transition and observed crystallinity and could account for the invariance of T_g with urethane concentration.

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 diisocyanate 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. The polyurethanes based on diphenyl methyl diisocyanate (MDI) have been the subject of intensive investigation by a variety of techniques. Three characteristic endothermic transitions have been detected by differential scanning calorimetry and penetrometer techniques:[1-3] a transition at 80° which is attributed to the disruption of domains with limited short-range order; a transition at 130 to 150° which represents the dissociation of domain structure with improved short-range order; and a transition above 200° which is due to the melting of crystalline structure in samples with sufficiently long hard segments. Annealing studies[2] have shown that the lower sitions can be shifted continuously upward to merge with

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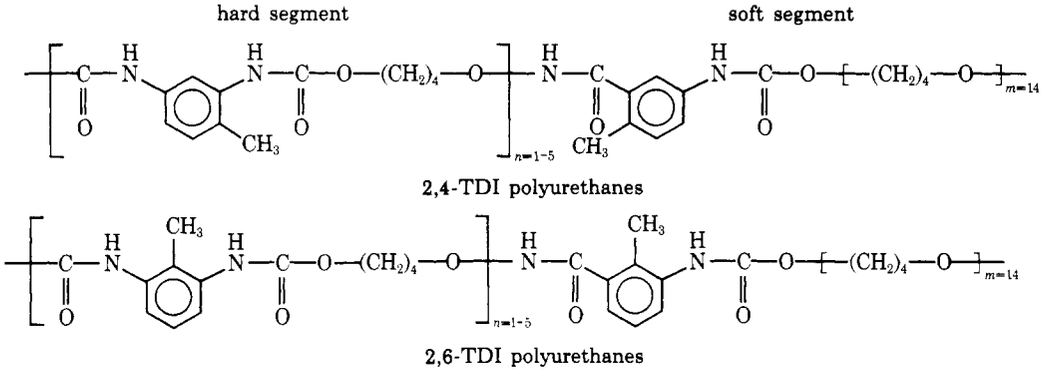
Chart I



the higher transition, the final state of order depending on the annealing history and sample composition. Apparently the potential for hydrogen bonding contributed by the urethane group plays only a secondary role in determining the transition behavior and polymer properties.

Additional information bearing on domain organization has been obtained from infrared studies[4] which in polyether containing polyurethanes allow a direct estimate of the distribution of the hydrogen bonded NH group between interurethane hydrogen bonding and hydrogen bonding to the ether oxygen of the soft segment. The first type represents hard segment–hard segment bonding whereas the second represents the degree of hard segment mixing with the soft segment phase. It is expected that the samples with superior domain organization will exhibit less hard segment–soft segment mixing. Small angle X-ray scattering has been used to confirm the presence of domain structure[3,5,6] inferred from other measurements but, thus far, has been generally limited to relative intensity measurements and qualitative interpretation.

Very little consideration has been given to similar studies of polyurethanes based on other aromatic diisocyanates. However, polyurethanes with piperazine in the hard segment[7] have received special attention as a model system because of the absence of the usual urethane proton and the availability of research quantities of samples with a narrow distribution of hard and soft segment lengths. The domains in these polyurethanes are predominantly microcrystalline in nature and a spherulitic superstructure is formed which incorporates the soft as well as the hard segments.[8] Nonetheless, an amorphous hard segment transition occurs at 80° and responds to annealing in a manner similar to the MDI polyurethanes.[9] Some limited examination has also been made of polyurethanes based on 1,5-naphthalene diisocyanate.[6]

A common feature of all the work referred to is that the studies have dealt with polyurethanes based on symmetrical diisocyanates. The present study of polyurethanes based on toluene diisocyanate (TDI) was undertaken to determine the effect of an unsymmetrical aromatic diisocyanate structure on polyurethane properties and to extend present concepts of the relation between polyurethane structure and properties. Two series of samples were prepared, the first based on 2,4-TDI where 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. The second series was based on 2,6-TDI where this problem is absent. The chain structure is represented in Chart I. A comparison of analogous polymers from the two series should clarify the effect of inversion in the 2,4-TDI orientation on domain structure, microphase segregation, and polyurethane properties. Detailed studies of the thermal transition behavior, structural organization, and properties should also be of practical interest in view of the large scale commercial utilization of TDI in castable and millable polyurethanes as a mixture of isomers (20:80 2,6-TDI–2,4-TDI) and more recently as pure 2,4-TDI.

Experimental Section

Synthesis. The 2,4-TDI (Aldrich Chemical, 97%) and 2,6-TDI (Kipers Laboratory, 99%) were vacuum distilled and a middle 60% was isolated for the synthesis. Anhydrous 1,4-butanediol (General Aniline and Film) and poly(tetramethylene oxide) (Quaker Oats, 1000 mol wt) were used as received. The polymerization was based on the two-step procedure outlined by Pigott and coworkers[10] where prepolymer was first made by end-capping poly(tetramethylene oxide) with diisocyanate and butanediol was added in the second step.

Sample Characterization. Film samples 15-mil thick were prepared by compression molding at 160 or at 180° with a pressure of 100 bar, as well as by casting from 5–10% DMF solution. The films were cast on Teflon-coated aluminum foil which had been applied to a glass plate and were dried in a vacuum oven at 50°. The fact that the polyurethanes are soluble (up to 10%) indicates the absence of any appreciable amount of chemical cross-linking. Bulk samples of the as-polymerized material employed for DSC runs were frozen in liquid nitrogen, then ground in a small Wiley mill.

The number average molecular weight of the polymers was estimated by vapor phase osmometry (Perkin Elmer-Coleman Model 115) on a 2% polymer solution in dimethylformamide. Differential scanning calorimetry was carried out with a Perkin-Elmer DSC II. Normal scanning speed was 20°C/min and the sample weight was approximately 10 mg. The thermomechanical analysis (TMA) was conducted with a Perkin-Elmer TMS-1 equipped with the UU-1 temperature programmer. This instrument provides a trace of the displacement of a weighted probe as a function of a programmed increase in the sample temperature. The transition is detected by the probe penetration which accompanies the softening of the sample at the transition point. A normal scanning speed of 20°C/min and probe weights of 5–30 g were employed.

X-Ray Diffraction. X-Ray diffraction patterns were recorded using a Warhus camera and radiation from a graphite monochromated Norelco copper fine-focus tube operated at 50 kV and 30 mA. Wide angle diffraction patterns were obtained on samples exposed for 45 hr with a sample-to-film distance of 5.43 cm; low angle diffraction patterns were exposed for 96 hr using a sample-to-film distance of 29 cm. In both cases three thicknesses of a 15-mil film compression molded at 180° were used.

Results

General Characteristics. The composition, number average molecular weight, and some properties of the polymers are listed in Table I. Despite the somewhat low molecular weight of certain of these polymers, the transition temperatures related to the soft and hard segment units will depend primarily on the length of these segments and will be unaffected by the overall molecular weight. A scheme for sample designation has been adopted which specifies the TDI isomer followed by an integer indicating the number of moles of diisocyanate per mole of polyether. The

Table I
Polyurethane Sample Composition and Properties

Sample no.	Wt % of urethane[a]	TDI–BD–PTMO	$M_n \times 10^{-3}$	Properties
2,4-TDI-2	31	2.10 : 1 : 1	16	Soft tacky rubber
2,4-TDI-3	42	3.15 : 2 : 1	14	Tough, live rubber
2,4-TDI-4	49	4.20 : 3 : 1	13	Elastic, not snappy
2,4-TDI-5	55	5.25 : 4 : 1	25	Flexible, but boardy
2,4-TDI-6	60	6.30 : 5 : 1	14	Almost plastic
2,6-TDI-2	31	2.10 : 1 : 1		Transparent, waxy
2,6-TDI-3	42	3.15 : 2 : 1	13	Opaque, hard and tough; thin sections are elastic
2,6-TDI-4	49	4.20 : 3 : 1	14	
2,4-TDI-5	55	5.25 : 4 : 1	7	
2,6-TDI-6	60	6.30 : 5 : 1	13	

[a] Calculated as weight percentage of TDI and BD per total polymer weight.

composition is specified more precisely in columns 2 and 3. Major differences in the properties of the 2,4-TDI and 2,6-TDI polyurethanes were at once evident. All of the 2,4-TDI samples were transparent and, as noted in column 5, these samples exhibited a progressive change in properties with composition from soft and tacky to rubbery and finally plastic with increasing urethane concentration. All of the 2,6-TDI samples except the first were opaque, white materials which were hard but tough and proved to be elastic in thin sections. The sample of lowest urethane composition, 2,6-TDI-2, was translucent and was not used in further studies since it could not be molded into a coherent film.

Thermal Transition Behavior. The initial examination of the thermal transition behavior was made on films molded at 160° using DSC. This method has been the mainstay for characterizing the thermal transition behavior and the annealing effects in MDI-based polyurethanes.[1-3] However, with these compression molded films of the TDI polyurethanes only a broad and relatively undifferentiated increase in heat capacity was observed in the expected glass transition region. No transition could be detected for either type of polyurethane in the intermediate temperature range up to 120° where the lower temperature transitions associated with the disruption of domain structure in MDI are observed. In the 2,6-TDI polyurethanes there was some evidence of a melting process which occurred at temperatures above 130°. This melting transition was not examined in detail by DSC for these samples molded at 160°. Somewhat different DSC behavior was observed in samples having other than 160° compression molding history as will be discussed later.

Measurements were then carried out by TMA which fortunately gave clearly defined low temperature and high temperature transitions with the same films. Examples of the penetrometer traces obtained with 2,4-TDI and 2,6-TDI polyurethane films of intermediate urethane composition are shown in Figure 1. The transitions will be designated T_1, T_2, and T_3 in order of increasing temperature to correspond with prior notation.[1]

In view of the heavy dependence on results obtained by TMA, the reliability of observations made by this technique requires some comment. Penetration can sometimes be observed at temperatures which have no relation to a glass or melting transition temperature determined by other methods. A notable case in point are the penetrometer results once taken as evidence of a glass transition at −65° for nylon 6 and 66.[12,13] In this case, a small degree of penetration was observed at the lower temperature and softening and massive penetration at 50° was believed due to another process. The weight given to the assignment of −65° as the glass transition was due to the observation of crystallization in nylon at temperatures below 0°. In general, correlation with some other method is required in order to identify penetration with a transition. Prior results from a study of MDI based polyurethanes showed good accord between DSC and TMA in mapping hard segment domain related transitions in the range of 80 to 150°.[1] The TMA values were uniformly 20° lower than the DSC results at the T_2 transition in these samples but were in closer agreement at T_3. No comparison was available for a test of the reliability of TMA results in the glass transition region. However, results presented in a later section of this paper show that TMA results are in good agreement with values of the glass transition temperature determined by DSC. Therefore, the evidence indicates that TMA results can provide a reliable assessment of the transition behavior in these polyurethanes.

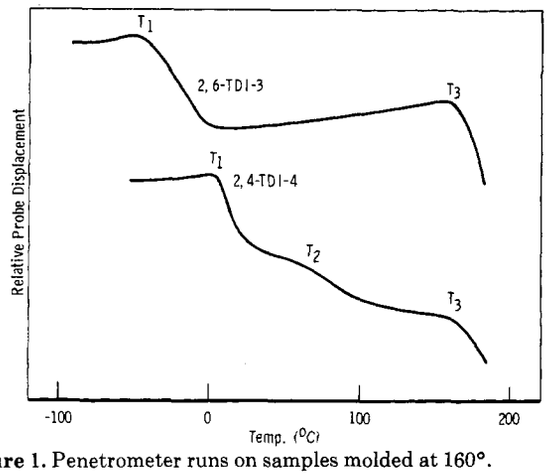


Figure 1. Penetrometer runs on samples molded at 160°.

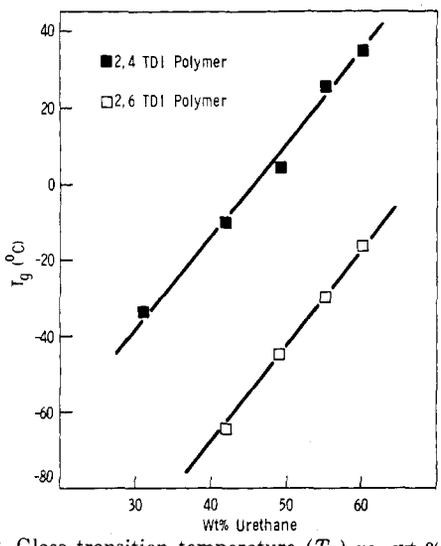


Figure 2. Glass transition temperature (T_g) *vs.* wt % urethane. Samples molded at 160°.

Figure 2 compares values for T_1 determined as a function of composition for the 2,4-TDI and 2,6-TDI polyurethanes. Each data point for the 2,4-TDI samples is the average of two and sometimes three independent determinations which generally agreed within three or four degrees. However, the results for the 2,6-TDI samples sometimes varied by 10° or more, and it was necessary to repeat the determination five or six times to define the average value shown in Figure 1. In both series of samples T_1 increases

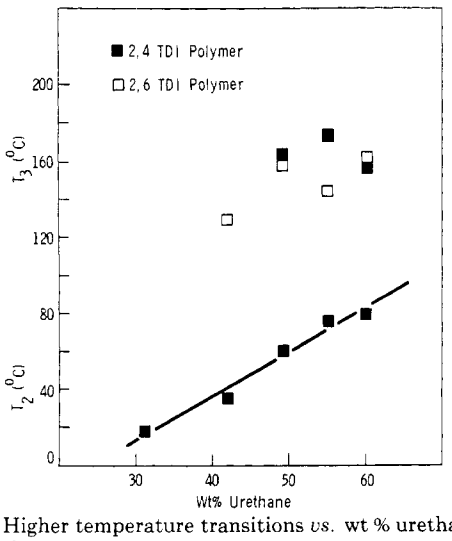


Figure 3. Higher temperature transitions *vs.* wt % urethane. Samples molded at 160°.

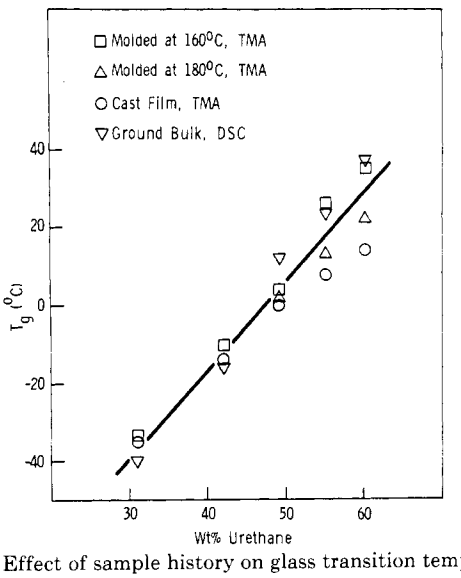


Figure 4. Effect of sample history on glass transition temperature (T_g), 2,4-TDI polyurethanes.

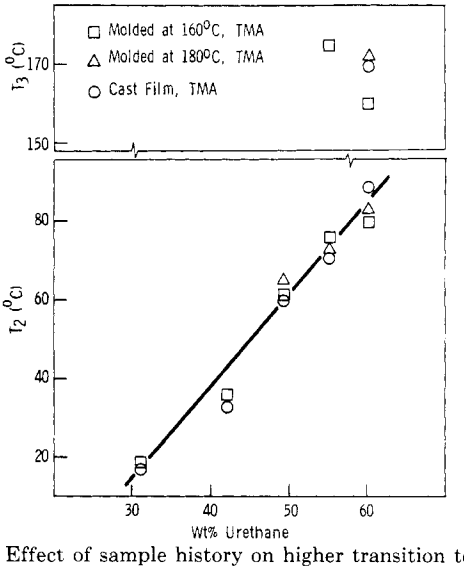


Figure 5. Effect of sample history on higher transition temperatures (T_2, T_3), 2,4-TDI polyurethanes.

strongly as a function of composition but values for 2,6-TDI samples are uniformly lower by 50°. By comparison with corresponding MDI polyurethanes, T_1 can be identified as the glass transition temperature of the polyether soft segment and, henceforth, will be referred to as T_g.

The transition behavior obtained at higher temperature is shown in Figure 3. In 2,4-TDI samples a transition T_2 is observed, which, like T_g, increases with increasing urethane concentration. There is no evidence for a corresponding transition in this intermediate temperature range in any of the 2,6-TDI samples. Above 150° a third transition is observed in three of the 2,4-TDI polyurethanes with highest urethane concentration, but this transition disappears after the first heating. All of the 2,6-TDI polyurethanes display a repeatable transition in the range of 120 to 160°.

It was noted that the 2,6-TDI samples, which were initially flat squares, were curled after heating. This suggested the presence of residual stress due to the molding conditions which, it was suspected, might be responsible for the variability of the T_g results commented on above. As a consequence the effect of molding history was examined by comparing the results obtained on samples which were compression molded at 160° with samples molded above T_3 at 180° and with solution cast films. In addition, it was discovered that clearly analyzable glass transitions could be determined on ground samples of the as-polymerized 2,4-TDI and 2,6-TDI materials.

Before proceeding with a discussion of these results we summarize some additional observations of transition behavior indicative of unstable states which, like the transitions above 150° in the 2,4-TDI polyurethanes noted above, were evident only in the initial heating. Higher temperature endotherms of various types were found by DSC in the ground bulk samples. In 2,4-TDI-6 an endotherm at *ca.* 200° was noted but could not be reproduced after the first scan. In three of the 2,6-TDI polyurethanes of highest urethane content, endothermic transitions at about 80° were observed in the first scan. A transition at 80° was also detected by TMA in two solution cast 2,6-TDI samples of intermediate urethane content but only in the first run. In an attempt to determine whether annealing would result in an improvement of hard segment order, indicated by an upward movement of the T_2 transition, a molded sample of 2,4-TDI-6 was annealed in the DSC overnight at 80°. The annealing was without effect. In keeping with the behavior noted earlier it was not possible to detect a transition at 80° or at any higher temperature by DSC. The TMA analysis was also unchanged. A transition was again observed at 80° accompanied by extensive penetration. This experiment suggests that, unlike the MDI-based polyurethanes, it is not possible to improve the hard segment organization in 2,4-TDI polyurethanes by annealing.

The results obtained by the several different methods of sample preparation are compared in Figures 4 and 5 for the 2,4-TDI samples and in Figures 6 and 7 for the 2,6-TDI samples. For the 2,4-TDI samples there is overall agreement in the behavior obtained although some consistent influence of sample history is evident in the glass transition results. It appears that lower T_g values are generally obtained with the cast films than with 180° compression molded films and the highest T_g values result from the bulk samples and 160° molded films. By contrast, the 2,6-TDI samples exhibit a marked change in T_g behavior compared to the films molded at 160°. It is now found with all the other types of samples indicated in Figure 6 that T_g is essentially independent of urethane concentration. This behavior contrasts strongly with the original behavior and

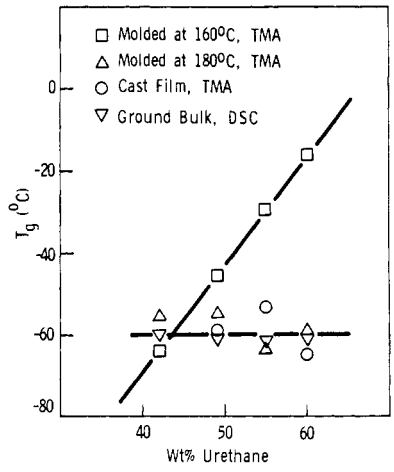


Figure 6. Effect of sample history on glass transition temperature (T_g), 2,6-TDI polyurethanes.

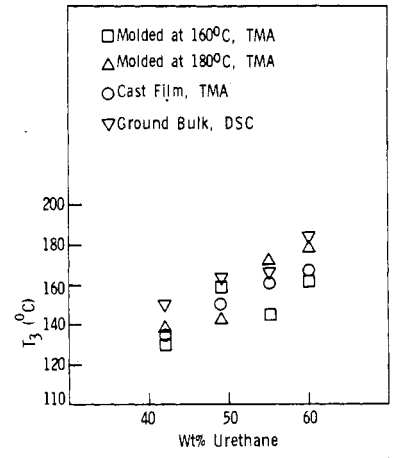


Figure 7. Effect of sample history on higher transition temperature (T_3), 2,6-TDI polyurethanes.

with the steep dependence of T_g on urethane concentration in the 2,4-TDI samples. Figure 7 shows that no repeatable T_2 transition is observed in any of the 2,6-TDI samples while T_3 now shows an increase in transition temperature with increasing urethane concentration. The DSC scans showed a repeatable endothermic peak at T_3 indicative of crystalline melting in the 2,6-TDI polyurethanes. These samples readily supercooled and crystallized during the heating cycle. On further heating, melting occurred followed by recrystallization at a higher temperature and then a final melting process. The DSC values appearing in Figure 7 correspond to the temperature of the second melting peak.

X-Ray Diffraction Results. 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 crystalline diffraction. Sample 2,6-TDI-6 showed fiye reflections; a strong line with a spacing at 4.62 Å, a line of medium intensity at 3.93 Å, two weak lines with spacings of 3.44 and 5.22 Å, and a very weak line at 10.79 Å. A similar pattern occurred in 2,6-TDI-5 and 2,6-TDI-4. The line widths appeared to be typical of the reflections which we have observed for crystalline MDI-based polyurethanes and additional detail undoubtedly could be developed, particularly at higher angles, with longer exposures. None of the spacings correspond to those expected for poly(tetramethylene oxide)[14] indicating that the diffraction is due to hard segment crystallinity, in agreement with the thermal transition behavior. In the low angle region only 2,4-TDI-6 showed strong scattering. The intensity from 2,4-TDI-5 was much weaker and diffuse low angle scattering from the remaining three samples was just discernible. No low angle photographs were recorded for the 2,6-TDI samples.

Discussion and Conclusions

The fundamental difference between the 2,4-TDI and 2,6-TDI polyurethanes resides in the asymmetry of 2,4-TDI and the interference with domain organization resulting from expected variations in head-to-tail orientation of the TDI unit in the hard segment. This is at once evident in the fact that the 2,6-TDI samples show crystalline X-ray diffraction whereas the corresponding 2,4-TDI samples are amorphous. It is to be expected that the observations on the thermal transition behavior and properties can be explained in terms of the differences in domain organization so clearly indicated by these results.

Borrowing from the general concepts developed with MDI-based polyurethanes[2] it appears reasonable to interpret the thermal transitions above T_g in terms of domain structure with increasing perfection of short-range order as the transition temperature increases. The transition temperature T_2 observed in 2,4-TDI samples accordingly represents domain structure with limited short-range order. Apparently the domain structure improves in stability and organization with increasing hard segment length as indicated by the monotonic increase in T_2 with increasing urethane concentration.

Perhaps it is a coincidence that the values for 2,4-TDI-5 and -6 fall within the range for the lower transition temperature, 80°, which is characteristic of domains with limited short-range order in MDI polyurethanes. No stable intermediate transitions of any kind are found in the 2,6-TDI samples although, as previously noted, transitions at about 80° were detected in several solution cast films but only on the first heating. Apparently all the domain structure in these 2,6-TDI samples is microcrystalline in nature and gives rise to a single repeatable high-temperature transition. This behavior is unusual since even the crystalline piperazine-based polyurethanes display a stable 80° transition which responds to annealing in a manner analogous to that observed with the MDI polyurethanes.[9,11]

It will be recalled that MDI polyurethanes exhibit in addition to the 80° transition a second characteristic amorphous transition at 130–150° and in specially annealed samples a range of intermediate transition temperatures.[2] The 2,4-TDI- and 2,6-TDI–butanediol copolymers and MDI–butanediol copolymers, which are analogs of the hard segment in the respective polyurethanes, have similar glass transition temperatures (101,[15] 107,[15] 109°[16]). From the similarity of the hard segment glass transitions it might be expected that transitions above 80° would also appear in the TDI samples. The absence of a TDI polyurethane transition at 130–150°, in particular, is undoubtedly due to the fact that in the MDI polyurethanes this represents the dissociation temperature of an intermediate or paracrystalline state of order which cannot be achieved in the 2,4-TDI samples.

The question of whether any intermediate states of order can occur in the TDI samples cannot be answered unequivocally. Although the possibility of shifting the transition temperatures by annealing has not been thoroughly explored, the results in Figure 3, which indicate that sample history has little effect on the upper transition temperatures, as well as the single annealing experiment on 2,4-TDI-6, suggest that a continuous range of domain order analogous to MDI polyurethanes does not occur. Perhaps,

this difference between the TDI and MDI types of polyurethane arises from the fact that in the 2,4-TDI samples hard segment crystallization cannot occur due to immutable chain defects, whereas the defects in the MDI polyurethane domain organization can be removed by annealing. In the 2,6-TDI polyurethanes the absence of any stable T_2 transition suggests that noncrystalline domain structure converts readily and directly to the crystalline state. The apparent absence of a range of stable intermediate states of order as observed in MDI polyurethanes might be due to the symmetry and smaller size of the 2,6-TDI unit.

We continue with some further comments bearing on the T_2 transition in the 2,4-TDI polyurethanes. We believe that the steep increase of T_2 with urethane concentration is due not only to the increasing hard segment length, but also to an accompanying increase in the concentration of sequences of 2,4-TDI units with the same orientation within the hard segment. The appearance of transitions in three of the 2,4-TDI polyurethanes above 150° in the absence of any evidence of crystallinity is unexpected. It will be recalled that these transitions were evident only in the initial scans. That structures giving rise to such a high-temperature transition can be formed at all requires that long sequences of identically oriented TDI units are present. This, like the change in T_2 with composition, suggests that the hard segment is not completely random and indicates the need for calculations of the statistical distribution of 2,4-TDI orientations in the hard segment. These calculations are in progress.[17]

The weakness of the SAXS in all the 2,4-TDI samples excepting 2,4-TDI-6 is further evidence that domain organization is poor. It should not be concluded, however, that the absence of strong scattering indicates that there is no domain structure. It has been noted in a study of MDI polyurethanes[5] that SAXS is less sensitive to the presence of domain structure than the thermomechanical behavior. The intensity of SAXS is dependent not only on the volume fraction of the two phases but also on the difference in electron density[18] and, therefore, is influenced both by the extent of hard segment mixing with the soft segment and the degree of order in hard segment domains.

One of the most striking differences between the 2,4-TDI and 2,6-TDI series of polyurethanes is the strong dependence of T_g on urethane concentration in the first series and the invariance of T_g in the second series of polyurethanes. This characteristic behavior must be a consequence of differences in domain organization which have already been discussed. In keeping with these observations it is expected that there would be extensive hard–soft segment mixing in the 2,4-TDI samples but that relatively complete phase separation would occur in the 2,6-TDI polyurethanes. If this interpretation is correct then the variation in T_g with urethane concentration initially observed in the 2,6-TDI samples indicates that molding at 160° produces substantial phase mixing whereas all the other methods of sample preparation result in relatively complete phase segregation. This example and certain others cited earlier indicate the manner in which sample history can affect the structural organization and polymer properties.

The additional property differences of the two series of polyurethanes can be explained on the basis of the foregoing considerations. The opacity and hardness of the 2,6-TDI samples is due to the ease with which the hard segments crystallizes. It is expected that morphological examination will reveal the presence of large scale spherulitic texture similar to that observed in MDI and piperazine polyurethanes.[8] The transparency of the 2,4-TDI samples is the result of more limited phase segregation, poorer domain organization, and the absence of crystallinity. The progressive change in the properties of the 2,4-TDI samples with composition appears to be due primarily to the increase in soft segment T_g with urethane concentration which, in itself, is the result of hard segment–soft segment interactions promoted by the disruption of domain organization. A more detailed and quantitative explanation of this behavior requires the determination of the extent of hard segment–soft segment mixing from the infrared spectra. These measurements have been carried out[19] and will be reported in detail in a later paper.

Acknowledgment. The authors wish to express their appreciation to Stanley Wentworth for guiding the synthesis of the samples.

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