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1982

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Reprinted from RUBBER CHEMISTRY AND TECHNOLOGY,
Vol. 55, No. 5, November-December 1982

Printed in U. S. A.

THERMAL TRANSITION AND RELAXATION BEHAVIOR OF POLYBUTADIENE POLYURETHANES BASED ON 2,6-TOLUENE DIISOCYANATE*

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INTRODUCTION

An extensive study of segmented polyurethanes based on polybutadiene (PBD) soft segments and hard segments comprised of 2,4-toluene diisocyanate (2,4-TDI) and butanediol (BDL) has previously been reported¹. This class of materials is of interest as a model system because there is no possibility of hydrogen bonding between the hard and soft segment units. This is in contrast to the more familiar polyester or polyether urethanes. The results of the study on these polymers indicated the presence of an exceptionally high degree of phase segregation as evidenced by the low and compositionally independent soft segment glass transition temperature, T_{gs} . It was also found that their thermal, dynamic mechanical, and stress-strain behaviors are insensitive to thermal history as are the T_g 's of both the hard and soft segments. These results were interpreted to mean that there is little, if any, change in the composition of the soft segment phase on heating. This behavior may be contrasted with most polyester and polyether urethanes which undergo extensive phase mixing upon heating as indicated by increase in the T_{gs} ^{2,3}. This difference in behavior is largely attributed to the absence of urethane hydrogen bonding to the soft segment phase in these PBD-containing polyurethanes.

The present study is concerned with PBD-polyurethanes based on 2,6-toluene diisocyanate (2,6-TDI) and BDL hard segments. In contrast to the completely amorphous system described above, the symmetrical structure of the 2,6-TDI isomer results in crystalline hard segment domains⁴. Although a high degree of phase segregation is also expected (since crystallization of hard segments serves as an added driving force), the nature of the hard segment domain structure is strongly dependent on thermal history. This has been shown in segmented polyurethanes comprising crystalline hard segments as well as in other semicrystalline polymers^{5,6}. For example, in diphenylmethane diisocyanate (MDI) based polyurethanes^{5,7}, three characteristic hard segment transitions have been observed: a transition at 80°C which is attributed to the disruption of domains with limited short range order, a transition between 130 and 150° assigned to long range ordering, and a transition above 200° which is due to the melting of microcrystalline domains. Annealing studies have shown that the lower temperature transition can be shifted continuously upward to merge with the higher temperature transi-

*Presented at a meeting of the Rubber Division, American Chemical Society, Philadelphia, May 4-7, 1982

tion, with the final state of order depending on the annealing history and sample composition.

While polyurethanes based on 2,6-TDI/BDL hard segments have been the subject of a few recent studies^{4,8}, a detailed analysis of the melting and crystallization behavior of the hard segment domains in these polymers is lacking. The following therefore describes experiments aimed to better understand the morphology and annealing behavior of these materials as well as to examine the effects of compositional variables on transition behavior and other related polyurethane properties. The absence of polar and hydrogen bonding interactions between the hard and soft segment phase removes a complicating factor which has obscured the results of previous studies.

EXPERIMENTAL

MATERIALS

The synthesis was carried out by a two step method involving end capping the hydroxy terminated polybutadiene (HTPBD) with the diisocyanate followed by reaction with the chain extender. The details of this procedure have been described previously¹. The 2,6-TDI (Aldrich Chemical, 99%) was vacuum distilled, and a middle 60% was isolated for the synthesis. The HTPBD (Japanese Synthetic Rubber Co.) and the BDL (Aldrich) were used as received. The molar ratio of TDI to HTPBD was varied in three equal steps from 4 to 1 to 6 to 1 at a fixed NCO/OH ratio of approximately 1.05. The three samples were designated by the hard segment content in weight percent ranging from 30 to 50 (*i.e.*, JSR-50). All samples used for the study were compression molded into 25 mil thick films by using a pressure of 3 MPa.

MEASUREMENTS

Differential scanning calorimetry (DSC) was carried out by using a Perkin-Elmer DSC-2, purged with helium and chilled with liquid nitrogen for the low temperature runs (170–250°C). Runs were conducted on polymer samples of about 15 mg mass at a heating rate of 20°C/min. The higher temperature scans were conducted from 250–500°C by using dry ice and acetone to control the heating rate. Cyclohexane, indium, and tin were used as thermal standards. Heat capacity measurements at the glass transition were calibrated with a sapphire standard. Each glass transition temperature (T_g) was taken to be the midpoint of the step in heat capacity. The temperature of maximum excursion from the baseline of the melting endotherm was taken to be the melting point (T_m). Cooling and heating rate studies were performed on the three samples by using the temperature programming capability of the DSC. Samples were cooled and heated at rates of 2.5, 5, 10, 20, 40, 80, 160, and 320°C/min and DSC scans taken immediately.

Dynamic mechanical measurements were carried out on a Vibron Dynamic Viscoelastometer, Model DDV-II (Toyo Measuring Instruments Co.). The temperature range was from –150 to 220°C and the frequencies employed were 3.5, 11, and 110 Hz. Samples were heated at 1–2°C/min under dry nitrogen. Apparent activation energies were determined for major relaxations from the Arrhenius dependence of frequency on inverse temperature. Least square lines were fitted to plots of log (frequency) *vs.* T^{-1} and the activation energies to the 95% confidence limit determined from the slopes.

RESULTS

THERMAL MEASUREMENTS

The major DSC transitions observed for the three polyurethanes of varying hard segment content and the two pure segment homopolymers, HTPBD and TDI/BDL, are summarized in Table I. A soft segment glass transition, T_{gs} occurs at -54°C in these polyurethanes, only 8° higher than the T_g of the pure HTPBD and independent of hard segment content. Also listed in Table I are the heat capacity changes, ΔC_p , accompanying this transition which decrease with increasing hard segment content. For a two phase model, the weight fraction x_1 of a given amorphous phase is given by:

$$x_1 = \Delta C_{p1} / \Delta C_{p1}^0$$

where ΔC_{p1} is the observed heat capacity change at T_{gs} for the polymer and ΔC_{p1}^0 is the heat capacity change at T_{gs} for 100% soft segment phase. A plot of $\Delta C_p / \Delta C_p^0$ for the soft segment *versus* weight fraction of hard segment is given in Figure 1. It can be seen that the soft segment weight fraction is indeed given by the above equation, thus indicating ideal two-phase behavior.

Above ambient temperatures, each thermogram shows a hard segment glass transition, T_{gH} , at about 62°C . On further heating, a melting endotherm occurs between 140 – 150°C (T_{m1}) followed by a clear exotherm (T_c) between 145 – 155°C , and then a final melting process of increased area between 190 – 210°C (T_{m2}). Increasing the heating rate shows that only the first melting peak is characteristic of the initial crystal distribution. All later structure is caused by recrystallization, which is nearly removed on heating at $160^{\circ}/\text{min}$. The precise nature of this recrystallization will be discussed later.

Unlike T_{gs} and T_{gH} , the positions of the two melting endotherms vary systematically with hard segment content. T_{m1} and T_{m2} occur 10 and 20° higher in JSR-50 as compared to JSR-31. The enthalpies of fusion normalized to the weight fraction hard segment, ΔH_m , are nearly the same for all compositions with the exception that ΔH_m corresponding to T_{m2} is some 50% lower for JSR-31 as compared to JSR-42 and JSR-50. As indicated in Table I, these values are significantly higher for the higher temperature melting peak.

TIME-DEPENDENCE OF TRANSITIONS

Heating the polyurethanes to 220°C and cooling produced no change in either the temperature or shape of the T_{gs} transition. This behavior is similar to that

TABLE I
TRANSITIONS IN HTPBD-POLYURETHANES

Sample	Lower transition			T_{gH}	Upper transitions			ΔH_m , J/g
	T_{gs} , $^{\circ}\text{C}$	ΔC_p^a	$\Delta C_p / \Delta C_p^0^b$		T_{m1}	ΔH_m , J/g	T_{m2} , $^{\circ}\text{C}$	
JSR-31	-54	.071	64.3	64	142	2.00	192(197) ^c	5.48(9.24)
JSR-42	-54	.065	58.9	60	144	3.28	199(203)	14.88(18.52)
JSR-50	-53	.054	48.9	63	148	4.68	208(211)	22.52(25.68)
HTPBD	-63	.110						
TDI/BD							(220)	(55.12)

^a ΔC_p in $\text{cal g}^{-1} \text{K}^{-1}$.

^b ΔC_p of polymer normalized to that of prepolymer.

^c Values in (), samples annealed 8 h at 160°C .

FIG. 1.—Observed heat capacity change at T_g for HTPBD-2,6-TDI polyurethanes of varying hard segment content, (open circles); normalized heat capacity change compared to ideal two-phase behavior, (closed circles).

observed earlier in the polyurethanes with 2,4-TDI hard segments¹ and indicates that there is little, if any, change in the composition of the soft segment phase as a result of heating.

Representative DSC curves for the hard segment transitions are shown in Figure 2 for JSR-42. Each curve shows the DSC trace as a function of time after quenching at 320°/min to room temperature. Following the initial scan, the excess enthalpy peak occurring at T_{gh} is replaced by the characteristic step change in the specific heat which then increases in temperature and magnitude before recovering its original appearance within 20 days. This time-dependent behavior is most probably due to a densification of the amorphous phase within the hard segment domains⁹ and not due to the reordering phenomena commonly observed in other semicrystalline segmented polyurethanes^{5,10}. This will become more evident in the annealing studies to be discussed.

As shown in Figure 2, the endotherm, T_{m1} , is absent in the short time repeat scans. However, the crystallization exotherm, T_c , and T_{m2} reappear immediately after quenching and are shifted some 10° to higher temperatures. Cooling at slower rates (160–2.5°/min) resulted in similar behavior; the position of T_{m2} is essentially unchanged though its area decreases with decreasing cooling rate. A longer storage period (ca. 24 h) results in decreases in the areas of both peaks. Within 20 days, however, most of the original thermal behavior is restored, including the T_{m1} endotherm which now appears 10° higher than the control. It should be mentioned that this endotherm reappears much sooner (<4 h) on annealing at temperatures 10–15° lower than the transition. Similar time dependent

FIG. 2.—DSC scans for JSR-42 taken at different times following quenching. (Arrow designates the position of the hard segment T_g .)

behavior was observed in JSR-50, though in JSR-31, the T_{m1} peak is still evident immediately after quenching.

ANNEALING STUDY

In Figures 3–5, the effects of annealing on the melting behavior of these materials at constant DSC scanning rate ($20^\circ\text{C}/\text{min}$) is reported. Each series of curves shows the DSC trace for samples annealed 4 h (with the exception of the bottom trace, where the samples were annealed 8 h) at the designated temperatures. It is at once apparent that the dependence on annealing temperature, T_a , is not simple but is controlled by the compositional variables.

In JSR-50 (Figure 3), annealing at temperatures $T_a < 130^\circ\text{C}$ results in increases in the area and position of T_{m1} and corresponding decreases in the area associated with T_{m2} . At higher annealing temperatures ($T_a > 150^\circ\text{C}$), the lower endotherm (T_{m1}) as well as the exotherm disappear and only the high temperature endotherm (T_{m2}) is observed. At longer annealing times (8 h), the onset of melting

FIG. 3.—Effect of annealing on the melting behavior of JSR-50.

of T_{m2} (taken as the temperature of initial departure from the baseline) increases by about 30° and the peak becomes more intense. The maximum in T_{m2} , however, is essentially unaffected by these annealing conditions. It should also be mentioned that this melting peak occurs 10° lower than that of the pure hard segment analog annealed under the same conditions.

A different series of curves is obtained for polyurethanes of 42 and 31 wt. % hard segment (Figures 4 and 5). In JSR-42, low annealing temperatures ($T_a < 110^\circ\text{C}$) result in 10° shifts of T_{m1} , T_c , and T_{m2} to higher temperatures. At intermediate annealing temperatures ($100^\circ < T_a < 140^\circ\text{C}$) only a double endotherm of low intensity appears, intermediate in position between the original endotherms, T_{m1} and T_{m2} . At the highest annealing temperature and time (160°C , 8 h), again a double endotherm is observed but now appears some 40° higher than the previous endotherm and only 3° higher than T_{m2} in the control.

FIG. 4.—Effect of annealing on the melting behavior of JSR-42.

FIG. 5.—Effect of annealing on the melting behavior of JSR-31.

Unlike JSR-50 and JSR-42, the T_{m1} endotherm in the lowest urethane sample is still apparent after prolonged annealing (8 h at 160°C) and occurs at the same temperature as in the control (though its area has decreased appreciably). The T_{m2} endotherm, however, increases by 5° and becomes narrower (see Figure 5). Further annealing resulted in negligible change in the thermal transition behavior of these samples.

It should be mentioned that, unlike the melting endotherms, the position of T_{gH} was essentially unchanged by these annealing conditions. Its intensity however, decreases with annealing, until it is no longer discernible after the most prolonged and high temperature annealing conditions. This behavior may be contrasted to that of the typical MDI-based polyurethanes⁵ where annealing shifts the lower transition (*ca.* 80°C) up to merge with the next higher transition (*ca.* 130°C). Apparently, the degree of crystallinity in the hard segments of the 2,6-TDI polyurethanes can be greatly increased by annealing.

A final point to note lies in the enthalpies of fusion, ΔH_m , of the T_{m2} endotherm in samples annealed at the highest temperature (see Table I). As in the unannealed materials, these values increase approximately linearly with hard segment content, with the corresponding values being slightly higher. Since ΔH_m stems from those hard segments which form highly ordered crystalline domains, the fraction w_c of crystalline hard segments relative to that of the fully annealed TDI/BDL homopolymer may be obtained:

$$w_c = \Delta H_m / w_H \cdot \Delta H_m^0$$

where ΔH_m and ΔH_m^0 are the enthalpies of fusion of the polymer and homopolymer, respectively, and w_H is the weight fraction of hard segment. The values obtained are .93, .83, and .54 for JSR-50, JSR-42, and JSR-31, respectively.

DYNAMIC MECHANICAL MEASUREMENTS

The dynamic mechanical response of these materials at 11 Hz is shown in Figures 6 and 7 and summarized in Table II. As in the corresponding 2,4-TDI

FIG. 6.—Temperature dependence of the storage and loss modulus for HTPBD-2,6-TDI-BDL polyurethanes.

FIG. 7.—Temperature dependence of the loss tangent for HTPBD-2,6-TDI-BDL polyurethanes.

polyurethanes, the relaxation behavior clearly illustrates the two-phase nature of these PBD-urethanes. A low temperature relaxation maximum, α_s , at -54°C with an activation energy of about 140 kJ/mole is apparent for each sample, independent of hard segment concentration. These results are in good agreement with the DSC soft segment glass transition temperatures reported earlier. Consistent with findings for other phase-segregated systems, the magnitude of α_s decreases with increasing hard segment content, while the magnitude of the storage modulus above this relaxation increases.

Above ambient temperatures, a relaxation associated with the hard segments, α_H occurs at about 45°C for all samples followed by a high temperature δ relaxation. The latter process is associated with the melting of hard segment crystallites. Unlike α_s and α_H , the temperature of the δ relaxation shows a strong dependence on hard segment concentration as does T_{m2} by DSC measurements; both increase

TABLE II
DYNAMIC MECHANICAL RELAXATIONS IN HTPBD-POLYURETHANES

Sample	Relaxation ^a	Temperature, °C	Activation Energy, kJ/mole	Magnitude tan δ
JSR-31	α_s	$-54 (-55)^b$	150 ± 40	.460 (.350)
	α_H	42 (42)	—	
	δ	152 (173)	—	
JSR-42	α_s	$-55 (-54)$	140 ± 20	.375 (.320)
	α_H	45 (45)	270 ± 50	
	δ	170 (185)	—	
JSR-50	α_s	$-54 (-54)$	140 ± 20	.345 (.240)
	α_H	40, 82 (105)	—	
	δ	185 (215)	—	

^a α_s determined from E''_{max} , α_H from $(\tan \delta)_{max}$, δ from $\log (E')$, softening temp; all at 11 Hz.

^b Values in bracket annealed at 155°C for 8 h.

with increasing hard segment content. This effect can be assigned to an increase in the hard segment block length as the hard segment content is increased.

The effects of thermal history on the dynamic mechanical properties was also investigated. For JSR-42 retested immediately after the first experiment (to 200°C) and one month later, the position, shape, and activation energy of the α_s relaxation is essentially unchanged. However, in contrast to the previous study based on 2,4-TDI/BDL, the storage modulus decreased by about 40% over the temperature interval 25–170°C, while the magnitude of the α_H dispersion increases and broadens. These effects can be attributed to the disruption of the original crystal structure, as also evident in DSC studies. After one month, however, the recovery is very nearly complete. The δ relaxation appears unaffected by heating to 200°C.

The effects of annealing on the relaxation behavior of all three materials are summarized in Table II (values in parentheses) and also shown in Figures 6 and 7 for JSR-50. As in the DSC study, samples were annealed 8 h at 160°C.

Consistent with DSC results, the position of the α_s relaxation is unaffected by the annealing process, though the magnitude of this loss peak decreases as does the broad loss peak (20–200°C) associated with the α_H relaxation. In addition, the level of the storage modulus above α_s is shown to increase as much as 70% over a temperature interval of 0–150°C while the temperature of the δ relaxation is shifted 20° to higher temperatures. The observed changes are most pronounced in JSR-50, the sample with the higher hard segment content. These effects can be attributed to an increase in the size and stability of the crystalline domains following annealing; this will be discussed below.

DISCUSSION

The quantitative analysis of the melting and crystallization behavior by DSC in these 2,6-TDI polyurethanes suggests that the hard segments form crystalline domains whose sizes and therefore melting temperatures are dependent on such factors as heating rate, annealing temperature, and hard segment length. Two melting endotherms (T_{m1} and T_{m2}) are observed at low heating rates while only T_{m1} persists at higher scanning rates (>80°C/min). Moreover, both endotherms appear at low annealing temperatures. At higher temperatures ($T_a > 140^\circ\text{C}$), a single endotherm (T_{m2}) can be obtained, the position and area of which increases with increasing annealing temperature. These results are interpreted to mean that, at low heating rates or annealing temperatures, the original crystal distribution, corresponding to T_{m1} , can reorganize to increase its stability and consequently crystals can melt at higher temperatures (T_{m2}) with higher ΔH_m values. At higher scanning rates, the relatively slow recrystallization process is impeded. It is also concluded that crystalline domains formed at the higher annealing temperatures ($T_a > 140^\circ\text{C}$) are not the result of reorganization during the scan in the DSC, but rather a new crystal distribution formed at T_a (hence, no T_{m1}). As indicated in Table I, the degree of crystallinity, as measured by ΔH_m , is nearly the same for the reorganized structure (T_{m2}) whether formed during scanning at 20°/min or high annealing temperatures and the crystallinity is appreciably higher than the original crystal distribution, T_{m1} .

The precise nature of the reorganization described above depends on hard segment composition. It will be recalled that the positions and areas of T_{m1} and T_{m2} in the control and annealed samples vary systematically with hard segment content, with T_{m2} occurring some 20° higher in JSR-50 as compared to JSR-31 and the enthalpy of fusion, ΔH_m , increasing from 1.37 to 5.63 cal/g. A similar increase in the δ relaxation temperature with hard segment content is also ob-

served by rheovibron measurements. These effects can be assigned to an increase in the hard segment block length as the hard segment content is increased. The longer hard segments can then form better organized and more stable domains, which melt at higher temperatures. Employing the number average hard segment length at 99% conversion and a μ value of 3 from Peebles theoretical data¹¹, the equation given by Flory¹² can be used to obtain the melting temperature for the infinite chain:

$$1/T_m = \frac{2R}{n\Delta H_n} + \frac{1}{T_m^\infty}$$

A plot of the inverse of T_{m2} against the inverse of the hard segment length, n , is shown in Figure 8 for both control and fully annealed samples. The two sets of data were both found to fit a straight line with an identical value of T_m^∞ of 220°C, in good agreement with the experimentally determined T_{m2} of the TDI/BDL homopolymer. The depression of the melting points of the polymers (in respect of the melting point of the infinite chain) can be accounted for by the presence of crystal defects or surface effects which are presumably more abundant in the shorter hard segment materials. From the slope of the line, the heat of fusion per repeat unit, ΔH_n , was calculated as 158 J/g in the control samples and 180 J/g in the annealed samples. The slight increase (ca. 10%) in ΔH_n of the annealed samples reflects an increase in the perfection and order of the crystalline domains as compared to those formed during scanning in the DSC. As in the controls, the extent of this perfection or reorganization is also governed by the hard segment length. Under the most severe annealing conditions, JSR-50 exhibits a single sharp melting peak (T_{m2}) while JSR-41 shows a double melting peak of enhanced breadth about 10° lower. In JSR-31, there is still evidence of a T_{m1} endotherm under these same conditions. These shorter sequences giving rise to T_{m1} presumably cannot co-crystallize with longer segments. Only crystals selectively built up of longer hard segments out of the total length distribution will contribute to higher melting behavior. These longer segments consequently yield a more ordered and well developed domain structure on annealing. Using the ΔH_m values at T_{m2} , it was shown that the fraction of hard segments which form crystalline

FIG. 8.—Reciprocal of average hard segment length vs. $1/T_m$ for HTPBD-2,6-TDI-BDL polyurethanes.

domains, w_c , relative to the pure homopolymer increases with increasing hard segment content. Whether this is due to an increase in the degree of crystallinity or a consequence of an increase in size of the crystalline domains cannot be answered unequivocally until further studies (*i.e.*, SAXS) are made. In any event, w_c was found to be surprisingly high in JSR-50, nearly approaching that of the TDI/BDL homopolymer. These results must be attributed to the high degree of phase separation occurring in the materials, which facilitate reorganization and perfection of the hard segments.

CONCLUSIONS

As in the corresponding polyurethanes based on 2,4-TDI/BDL hard segments, these materials consisting of crystalline hard segment domains are well phase-separated as evidenced by the low and composition-insensitive glass transition temperature, T_{gs} . Furthermore, thermal treatment was found to have negligible effect on T_{gs} both by dynamic mechanical and DSC measurements. These results have previously been attributed to the high degree of incompatibility and absence of hydrogen bonding between the hard and soft segments, the latter of which promotes phase mixing in polyester and polyether polyurethanes^{2,13}. However, in contrast to the completely amorphous system whose hard segment glass transition temperature increases systematically with urethane content, all 2,6-TDI polyurethanes exhibit a T_{gH} at about 62°C. On further heating, melting occurs (T_{m1}) followed by recrystallization and then a final melting process (T_{m2}). It appears that a distribution of hard segment domains of varying size and stability is responsible for the observed behavior with T_{m1} arising from the smaller and less stable domains. At higher temperatures, the longer sequences reorganize to give rise to higher melting endotherms (T_{m2}). Annealing is shown to improve the perfection of this crystalline order, the details of which also depend on the hard segment length.

SUMMARY

The thermal transition and relaxation behavior of a series of segmented polyurethanes based on 2,6-toluene diisocyanate-butanediol hard segments and polybutadiene soft segments have been studied *via* differential scanning calorimetry and rheovibron measurements. Both techniques show a constant low temperature transition at -54°C corresponding to the T_g of the soft butadiene phase and a hard segment transition at about 62°C, both of which are independent of hard segment content. At higher temperatures, a melting endotherm, T_{m1} , appears between 140 to 150°C followed by recrystallization and then a final melting process, T_{m2} , between 190 and 210°C. The positions of the melting peaks and the corresponding heats of fusion, ΔH_m , show a strong dependence on hard segment content, annealing temperature and, to a lesser degree, on heating rate. The data indicate that crystals of varying stability are formed at different annealing temperatures. Moreover, only those segments involved in the initial crystal distribution (T_{m1}) which are long enough will give rise to the higher melting crystals, the size and perfection of which are governed by the hard segment length.

ACKNOWLEDGMENTS

We are grateful to the Army Materials and Mechanics Research Center, Watertown, MA, for the support of this research under contract DAAG 46 79 C 0004. We are also grateful to Mr. B. Bengston for preparing the polyurethane samples.

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