Thermal Analysis of Polyurethane Block Polymers

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ABSTRACT: An analysis of data from differential scanning calorimetry and infrared spectroscopy for a series of polyurethane block polymers is presented. It is found that the DSC endotherms observed result from short- and long-range ordering of the hard segments, rather than from hydrogen-bond dissociation as previously thought. Hydrogen-bond disruption as studied by infrared spectroscopy is influenced primarily by the glass transition temperature of the hard segments. Differences in domain morphology of these materials, which are sensitive to sample thermal history, are not revealed by changes in the extent or thermal stability of the hydrogen bonds. An explanation for the lack of correlation between hydrogen-bond effects and the DSC endotherms is presented.

Polyurethane block polymers are a family of elastomeric materials whose chains are composed of alternating low glass transition (soft) segments and more rigid, polar urethane (hard) segments which soften much above room temperature. The soft segments are generally polyethers or polyesters and the hard segments are formed from the extension of a diisocyanate (often aromatic) with a low molecular weight diol. The existence of microphase separation, caused by clustering of at least some of the hard and soft segments into separate domains, has been well established.[1-3] The typical polyurethane is extensively hydrogen bonded,[4] the donor being the NH group of the urethane linkage. The hydrogen-bond acceptor may be in either the hard urethane segment (the carbonyl of the urethane group) or the soft segment (an ester carbonyl or ether oxygen).

Various thermoanalytical techniques such as dta, DSC, thermomechanical analysis, and thermal expansion measurements have been employed in the study of morphology and intermolecular bonding in polyurethane block polymers. The well-known thermal lability of the hydrogen bond has led to the interpretation of thermoanalytical data primarily in terms of hydrogen-bond disruption. Specifically, a dta or DSC endotherm in the region of 80° has been ascribed to the dissociation of the urethane–soft segment hydrogen bonds, while an endotherm around 150-170° is related to the breakup of inter-urethane hydrogen bonds.[5-7] In addition, a higher temperature melting endotherm from microcrystalline hard segments is observed in materials having longer aromatic urethane segments. We have previously reported similar endotherms for both polyether and polyester urethanes.[8] It was found, however, that the behavior was strongly dependent on thermal history in a fashion not entirely consistent with previous interpretations. The endotherm ascribed to hard-soft segment interaction (hereafter referred to as "I") may be moved continuously upscale in temperature by annealing until it merges with the presumed inter-urethane hydrogen-bond dissociation endotherm ("II"). Severe annealing can lead to a material showing only a single microcrystalline peak ("III") in the DSC.[8] Materials of low diisocyanate content (and thus short hard segments) are incapable of crystallization and show only the merging of the I and II peaks under annealing.

The role of hydrogen bonds may be more directly studied by infrared spectroscopy, primarily in the NH vibration region. A previous publication[4] detailed the use of ir in hydrogen-bond studies of polyurethane block polymers, though it did not include temperature dependence. In other polymeric systems, infrared thermal analysis has been used to determine hydrogen-bond transitions and equilibrium constants.[9-12] In this paper we present a comparison of DSC and infrared results which clarify the role of hydrogen bonding in the thermal behavior of polyurethane block polymers. The implications of this analysis for the understanding of the importance of secondary bond interactions in other polymer systems is also briefly discussed.

Experimental Section

Materials. The primary materials used in this study were polyether (polytetramethylene oxide) and polyester (polybutylene adipate) urethanes having a hard segment formed from p,p'-diphenylmethane diisocyanate (MDI) chain extended with butanediol. Their chemical structure has been published previously.[13,14] These materials are referenced in this report by the soft segment type, ES (polyester) or ET(polyether), weight per cent diisocyanate and soft segment molecular weight in thousands by a code such as ES-38-1. For comparison, a polymer containing a polyether soft segment and piperazine–butanediol hard segment has also been studied. It is from a series of polymers prepared by Dr. L. L. Harrell, Jr. which have varying segment lengths and segment polydispersity,[15] and is designated 4B-1B. This polymer contains 22 wt % piperazine with broad size distributions in both segments.

Calorimetry. Differential scanning calorimeter data were obtained on a Du Pont 900 thermal analyzer with the DSC module. The heating rate was 10°/min and sample size was 15–20 mg. ES and ET series samples were cut from compression-molded sheets, while the 4B-1B sample was cast from a 10% methylene chloride solution. The cell was calibrated for quantitative measurements using Ga, In, and Sn standards.

Infrared. Infrared spectra were obtained on a Perkin-Elmer Model 180 infrared spectrophotometer utilizing a specially built environmental chamber for the temperature studies. Temperature control was within ±1°. Data for quantitative analysis were taken with manual slits at 0.7 mm, recorded in linear absorbance. Films for ir study were cast onto mercury surfaces where the sol-

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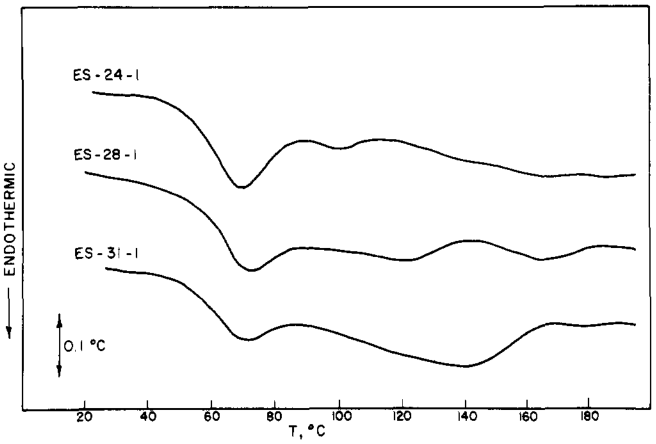

Figure 1. DSC curves for unannealed samples of varying diisocyanate content.

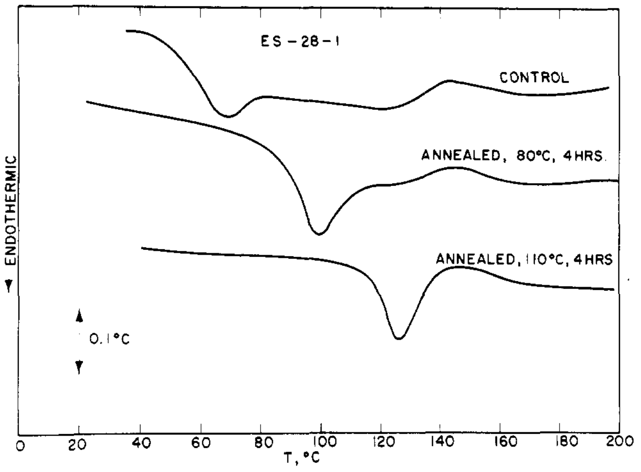

Figure 2. DSC curves for ES-28-1 as a function of thermal treatment.

vent was allowed to evaporate slowly over several days. The samples were then vacuum dried for 4 hr at 40° to remove residual solvent. Infrared spectra showed no absorption due to the solvents after this treatment. Solvent systems used were tetrahydrofuran, tetrahydrofuran-dimethylformamide mixtures, and pyridine. Base lines were drawn as in previous publications^{4,13} and absorption peak areas were measured with a planimeter. Peak areas and heights as a function of temperature or time have been normalized to the value at 25° or zero time.

Results and Discussion

DSC curves as a function of thermal history have previously been presented for ES-38-1 and ES-31-1.^{8} Briefly, three endotherms were found for ES-38-1: I, around 70°; II, a broad peak with a maximum at 160°; and III, a small peak at 185°. Annealing moves the I peak up scale until it merges with the original II region to form a single endotherm. The merging of endotherms I and II required annealing at 130° for completion. The III peak was unaffected by this thermal history. A discontinuous movement of the merged I and II endotherms into a single peak in the III region could be accomplished by annealing at 150°. This is accompanied by the appearance of a distinct ring in the wide-angle X-ray pattern which is not observed in the control or samples annealed at a lower temperature. ES-31-1 showed no III peak in the control and only the first process, the merging of peak I with peak II, occurred on annealing. The III peak is undoubtedly due to microcrystalline regions which cannot be formed in ES-31-1 due to the short hard segment length. The average hard segment in ES-38-1 consists of about three MDI units, while in ES-31-1 it is only 2.^{14}

Figure 1 compares DSC curves for unannealed control samples as a function of diisocyanate content (and thus average hard segment length). The I peak is common to all samples, while the II region is well defined only in ES-31-1. Figure 2 shows that the I peak may also be moved upscale by annealing in ES-28-1, a material without a well-developed II region. Similar peak movement is also observed in ES-24-1, though the maximum temperature attainable is lower. The polyether urethanes (ET series) show analogous behavior.

At this point it is evident that the appearance of the DSC endotherms is a function of hard segment length. ES-24-1, having the shortest average hard segments, exhibits only the I peak. ES-31-1 has the I and II peaks, while ES-38-1 shows all three endotherms. To further investigate this point, samples of longer segment length, at constant diisocyanate content, were studied. These are ES-38-2 and ES-38-5, in which the average lengths of both the hard and soft segments are about two times and five times those of ES-38-1. The composition of all three materials in terms of diisocyanate content is the same, however.

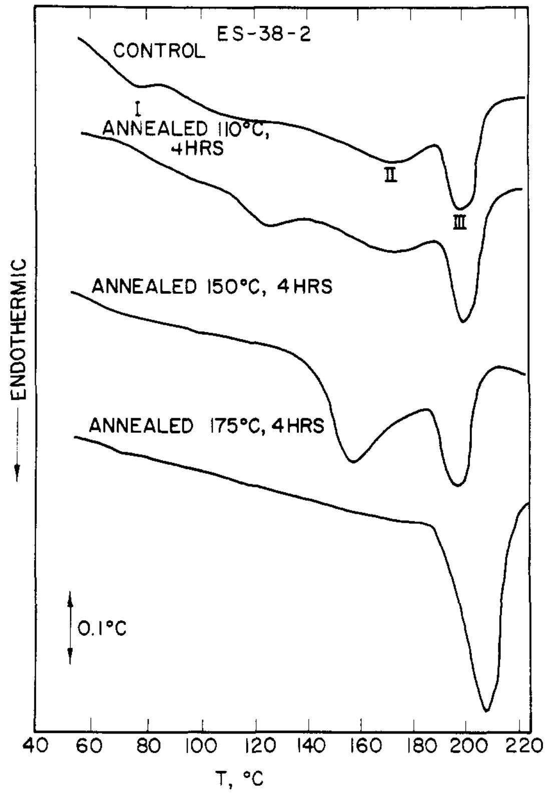

Figure 3. DSC curves for ES-38-2 as a function of thermal treatment.

Typical DSC curves for ES-38-2 are shown in Figure 3. As expected, the III region is more pronounced than in ES-38-1 due to the longer segment length and greater microcyrstallinity. Annealing moves the I peak up scale to merge with II, precisely as was reported for ES-38-1. The merged endotherm may then be transformed into the III region by further annealing, resulting in a DSC curve showing only a single high-temperature peak.

The III peak is the dominant feature of the DSC curves for ES-38-5 (Figure 4). There is also a small endotherm in the I region which again can be moved by annealing through the II region and eventually into the III peak. We have also studied the material ET-38-2, which resembles ES-38-5 in its general behavior.

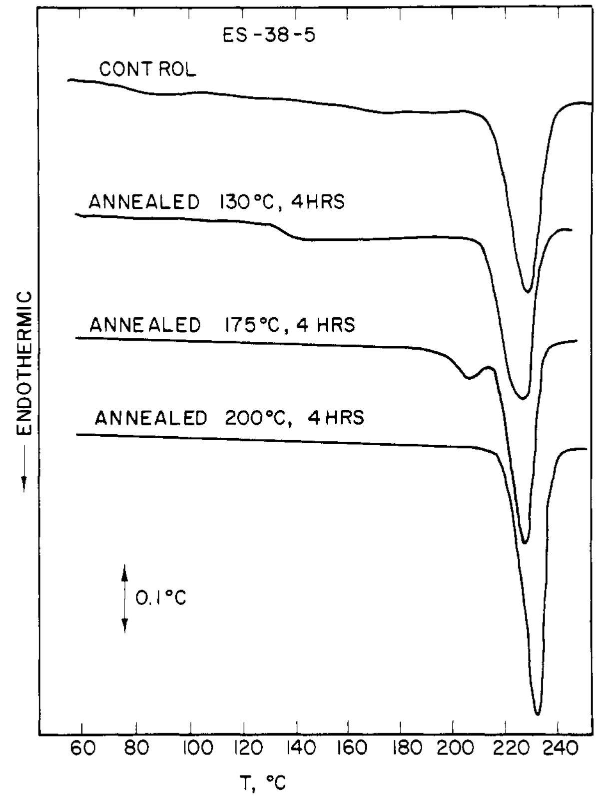

Figure 4. DSC curves for ES-38-5 as a function of thermal treatment.

Heats of transition for the III peak (ΔH_{III}) are listed in Table I for control and annealed ES-38-2, ET-38-2 and ES-38-5 samples. The greater degree of microcrystallinity in ES-38-5 is reflected in the higher enthalpy values. It is also interesting that the heat of transition increased significantly for the fully annealed specimens in all cases.

Table I
III Peak Heats of Transition

Material	Treatment	ΔH_{III}, cal/g
ES-38-2	Control	0.9
	Full anneal[a]	3.3
ET-38-2	Control	1.2
	Full anneal[a]	3.4
ES-38-5	Control	4.0
	Full anneal[a]	6.4

[a] Conditions of annealing: ES-38-2 shown on Figure 3, ES-38-5 shown on Figure 4, and ET-38-2 similar thermal history to ES-38-5.

These data cast doubt upon the interpretation of the I and II peaks in terms of hydrogen-bond dissociation for several reasons. First, it seems unlikely that the strength of the hydrogen bonds themselves should be affected by annealing, though this could be implied by the data. Second, the I peak is continuous with the II peak in the sense that the two regions may be combined into a single endotherm by annealing. Such a result would not be expected if the peaks represented distinct processes. Interpretation of these results in terms of hydrogen bonds would require the conclusion that there be no bond dissociation below the III temperature in a well-annealed sample, as there are no lower temperature peaks. Infrared evidence that this is not true is discussed below.

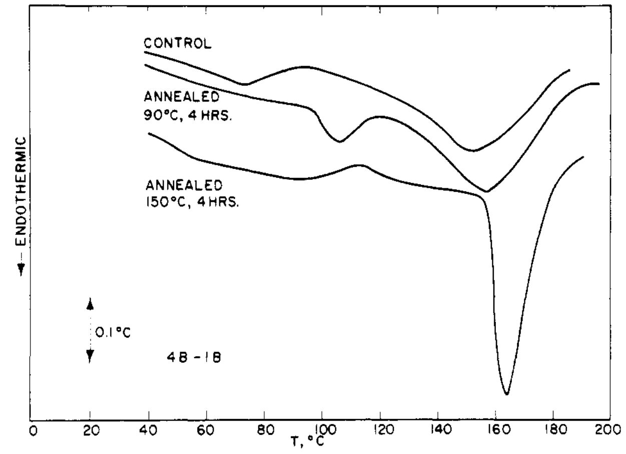

Figure 5. DSC curves for 4B-1B as a function of thermal treatment.

Finally, DSC curves for the piperazine based polyether urethane, sample 4B-1B, in Figure 5 confirm these conclusions. This material has approximately the same weight per cent hard segment and soft segment molecular weight as ES-38-1 or ET-38-1, yet possesses no capability for hydrogen bonding. The remarkable similarity of the DSC curves of Figure 5 to the curves for polymers which are extensively hydrogen bonded suggests that the relation of DSC endotherms to hydrogen-bond dissociation may be seriously questioned in the ES and ET series.

It is thus proposed that all three endotherms are morphological in origin. The III peak may be assigned to relatively well-ordered microcrystalline aromatic polyurethane segments, the amount and perfection of which are determined by the segment length and thermal history. The I and II endotherms represent disordering of hard segments with relatively short-range order that may be improved in a continuous manner by annealing. The appearance of two peaks and the broad temperature region over which they occur are partially the result of the wide distribution of hard segment lengths. Clusters of shorter hard segments, perhaps of only one MDI unit, give rise to the lower temperature endotherm, while the longer segments disorder at higher temperatures. In this regard it is interesting to note Bonart's assignment of a dta endotherm at 170° in similar polyurethanes to a paracrystalline ordering.[16]

This short-range order may be reorganized into microcrystalline regions if the hard segments are sufficiently long, though this transformation occurs in a discontinuous manner.[8] Improvement of short-range ordering is still possible in materials not capable of microcrystallization.

The transformation to microcrystalline order is the cause for the increase in ΔH_{III} on annealing seen in Table I. A quantitative relationship between the I, II, and III peak areas could not be obtained because of the difficulty in determining a suitable base line for the lower temperature peaks. It is reasonable to expect a lower heat of transition (on a mol basis) for the I and II peaks, so that the total area of all peaks at different annealing conditions would not be constant. This is qualitatively shown by ES-38-5 (Figure 4 and Table I) where the increase in III peak area (60%) cannot be accounted for by simply adding on the area of the I peak.

The remaining question concerns the thermal lability of the hydrogen bonds. This has been investigated by

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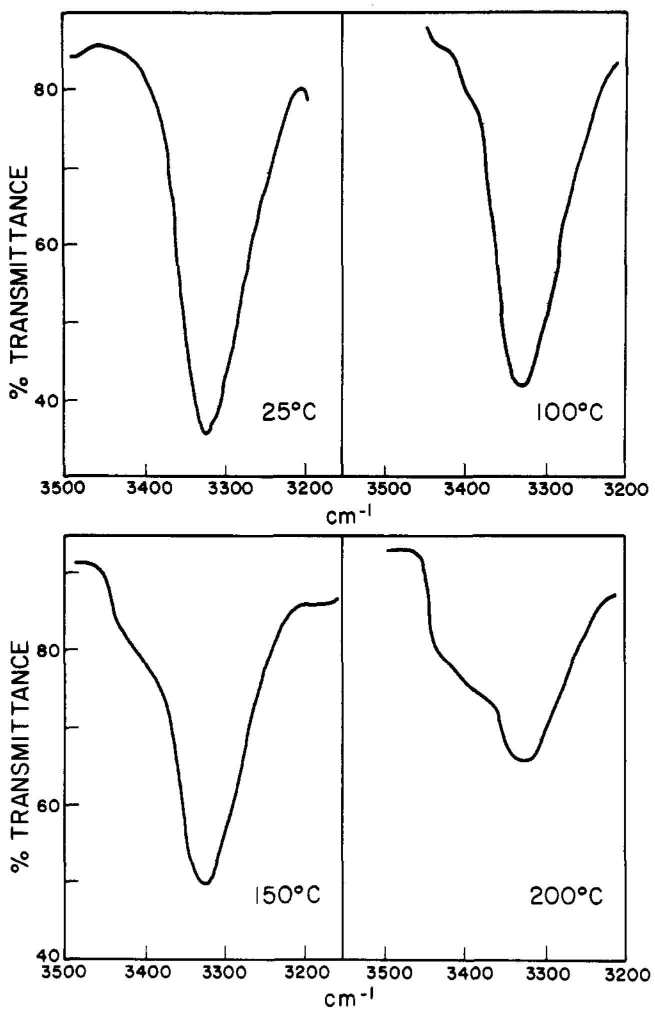

Figure 6. Effect of temperature on NH absorption region for ET-38-1.

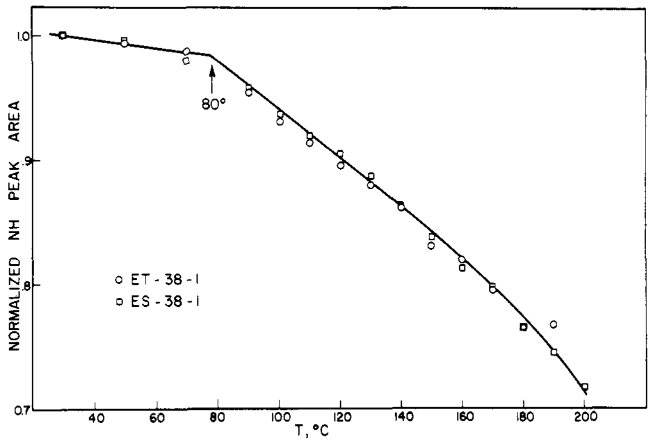

Figure 7. Integrated NH absorbance as a function of temperature for ES-38-1 and ET-38-1.

Table II
Infrared Transition Temperatures from Integrated NH Absorbance

Material	Transition Temp, °C
ES-24-1	75
ET-24-1	75
ES-28-1	80
ET-28-1	80
ES-31-1	80
ET-31-1	80
ES-35-1	80
ET-35-1	80
ES-38-1	80
ET-38-1	80
ET-38-1[a]	80
ES-38-2	90
ES-38-5	100
ET-38-2	90

[a] Annealed 4 hr at 80, 110, 130, 150°.

studying the temperature dependence of infrared absorption for the NH vibration. The NH region as a function of temperature for ET-38-1 is shown in Figure 6. At 25° virtually all of the NH groups are hydrogen bonded, giving a single peak at 3320 cm^{-1}.[4] As the temperature is raised, a high-frequency shoulder develops and the overall intensity diminishes. Nonbonded NH groups are known to absorb at a higher frequency and with much lower intensity, so that the latter effect can be used to monitor hydrogen-bond disruption. To quantitatively characterize this dissociation, the area of the total NH peak has been measured as a function of temperature. Because of the intensity decrease with bond disruption, the area should decrease as the number of free NH groups increases. This method was chosen as it was impossible to adequately resolve the free and bonded NH absorptions. Typical data analyzed in this way for ES-38-1 and ET-38-1 are shown in Figure 7. Similar curves were obtained for all materials studied. The onset of the decrease in absorption intensity is summarized in Table II for all materials studied. Slope discontinuities in absorbance-temperature curves have previously been used to detect transitions in several polymers, including those without specific secondary-bond interactions. A theoretical justification for this effect has been developed.[17]

The change in slope of the absorbance curves is attributed to the onset of hydrogen-bond dissociation which occurs at the glass transition temperature of the hard segments. The rigidity of the hard segments below their T_g should restrict hydrogen-bond disruption. As the temperature is raised and sufficient mobility is attained, secondary-bond dissociation can occur more readily, perhaps even according to the equilibrium law commonly applied to low molecular weight compounds and solutions. This concept is embodied in the theoretical treatment of Wolkenstein and Ptitsyn.[18]

The data of Table II show a slight increase in T_g with hard segment length, a result which would be expected regardless of the presence of hydrogen bonds. The values are reasonable in view of MacKnight's data on a pure MDI-butanediol copolymer for which he reported a T_g of 109°.[19] It must be emphasized that the infrared transition near 80° it not related to the DSC peak which appears at about the same temperature. The position of the DSC endotherm is very sensitive to thermal history, whereas the ir transition temperature is not (Table II).

A second interesting point with regard to the effect of annealing results from the study of the carbonyl region in

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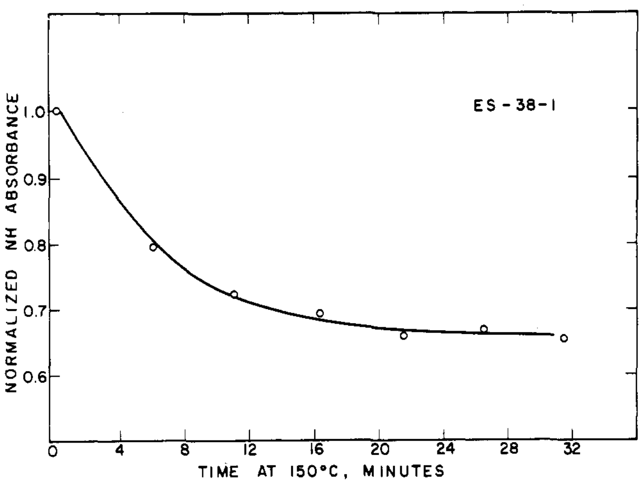

Figure 8. NH absorbance as a function of time for ES-38-1. Sample heated from room temperature to 150°.

the ET series. Previously the ratio of intensities of the free and hydrogen-bonded carbonyl peaks were used as a measure of the degree of microphase separation.[4] This may be done because the degree of carbonyl bonding in a polyether urethane is the same as the degree of hard-hard segment bonding, there being only urethane carbonyls. The relative amount of inter-urethane bonding will increase with the degree of microphase separation. It is found that this intensity ratio does not change with annealing, so that the morphological development observed in the DSC does not involve a change in the degree of phase separation.

The infrared analysis demonstrates that hydrogen-bond dissociation does occur, increasing steadily as the temperature is raised above the hard segment T_g. It is important to note, however, that there is still significant hydrogen bonding at 200° (Figure 6) and that the thermal behavior of the hydrogen bonds is insensitive to the morphological details. No annealing effects are seen in the ir data, whereas they dominate the DSC.

A final point concerns the insensitivity of the DSC experiment to the hydrogen bonds. Since hydrogen-bond dissociation is accompanied by an enthalpy change, one would expect to observe a response in a calorimetric experiment. There are two factors which prevent this. The first is shown in Figure 8, where the NH absorbance (measured as the height of the bonded NH peak) is plotted as a function of time for a thin-film sample of ES-38-1 quickly heated from room temperature to 150°. The time required to reach a constant value of absorbance at 150° (about 20 min) is greater than the time for an entire DSC scan to 200°. The DSC experiment thus does not allow sufficient time for maximum hydrogen-bond dissociation effects to occur.

It is also possible to calculate that even if the scan rate were sufficiently slow, the contribution of hydrogen-bond dissociation to the observed DSC curve would be very slight. Assuming a time scale slow enough to ensure the attainment of dissociation equilibrium at all temperatures, the expected DSC curve may be calculated using eq 5 derived in Appendix I. This equation allows prediction of the DSC curve for a given instrument if ΔH and ΔS are known. The results for reasonable ΔH and ΔS values are slowly varying curves which would contribute only a minor fraction to the observed thermal response. The results of two calculations for ES-38-1 are shown graphically in Figure 9. The lack of equilibrium conditions would further lessen the contribution of hydrogen-bond dissociation effects. It is thus not surprising that hydrogen bonding plays no observable role in the DSC.

Conclusions

The regions of endothermal activity observed in the DSC for polyurethane elastomers may all be ascribed to morphological effects. These effects can be broadly divided into loss of long- and short-range order. Different degrees of short-range order may exist simultaneously, due to the distribution in hard segment lengths. The short-range ordering may be continuously improved by annealing, manifest in the merging of the I and II regions of the control into a single endotherm. This process occurs without affecting any long-range order which may be present. Regions of short-range order can be made microcrystalline by severe annealing, but only if the average hard segment length is sufficiently great.

The thermal behavior of the hydrogen bonds is insensitive to the degree of ordering present and is affected primarily by the glass transition temperature of the hard segments. Above this temperature bond dissociation may be governed by an equilibrium law, as suggested in some theories[18] though we have no evidence for or against this.

The presence of hydrogen bonds serves to increase the overall cohesion of the materials, as these bonds are stronger and more directional than other intermolecular forces. They should not be regarded as "tie down" points, however, particularly at temperatures above the hard segment T_g, nor should they be expected to necessarily enhance mechanical properties. Such lack of enhancement has been noted by several workers,[9,20,21] primarily in long-time relaxation studies where the hydrogen-bond interchange rate is appreciably greater than the experimental time scale. The unusually good mechanical properties of segmented polyurethanes must be ascribed to the incompatibility of the segments resulting in phase separation, rather than to the presence of hydrogen bonds *per se*.

In addition, it is interesting to note that the dynamic mechanical spectra of these polyurethanes show few if any characteristics which need to be ascribed to hydrogen bonding.[14] It seems that chain mobility controls secondary-bond dissociation, rather than the opposite case. This suggests that at least in these systems the heterobonded solid-state concept,[22] which predicts that such secondary bonding would play a major role in transition behavior, does not apply.

Overall the presence and behavior of the hydrogen bonds has much less effect on the mechanical properties of these polyurethanes than has been generally thought. Interpretation of structure-property relationships should be placed more on a morphological basis. An exception to this, however, is the case of highly crystalline polyurethanes, where inter-chain alignments giving the greatest degree of hydrogen bonding are favored.[23]

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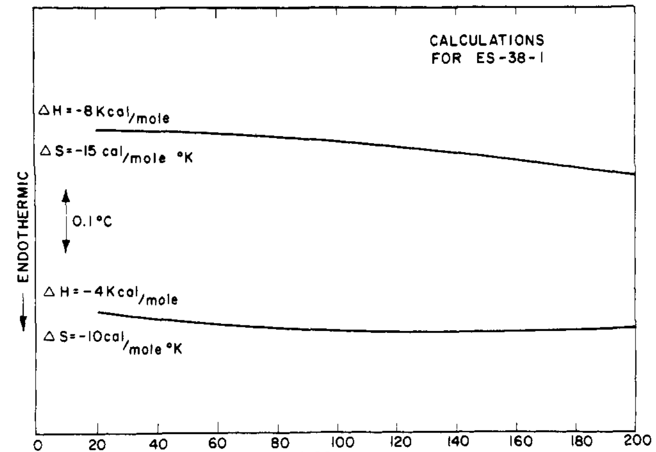

Figure 9. Calculated DSC curves for equilibrium-controlled dissociation of hydrogen bonds.

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Appendix I

Derivation of DSC Response for Equilibrium-Controlled Dissociation. For simplicity, only a single donor–acceptor reaction is considered:

$$\mathrm{D} + \mathrm{A} \rightleftharpoons \mathrm{D}\cdots\mathrm{A} \tag{1}$$

D is the donor, A the acceptor, and D····A the hydrogen-bonded complex. We may then write

$$K = [\mathrm{D_b}]/([\mathrm{D_f}][\mathrm{A_f}]) \tag{2}$$

where the subscripts b and f refer to bonded and free groups and the brackets to concentrations. K is the equilibrium constant, whose temperature dependence is given by

$$K = \exp(-\Delta H/RT + \Delta S/R) \tag{3}$$

where ΔH and ΔS are the enthalpy and entropy changes associated with hydrogen-bond formation.

To predict the DSC curve we need the temperature derivative of $[\mathrm{D_b}]$, which may be found by combining eq 2 and 3 and differentiating. The result is

$$\frac{\mathrm{d}[\mathrm{D_b}]}{\mathrm{d}T} = \frac{-\Delta H}{RT^2}\left[K^{-1} - \frac{c_1K^{-1} + K^{-2}}{(K^{-2} + 2c_1K^{-1} + c_2)^{1/2}}\right] \tag{4}$$

c_1 is the sum of the total acceptor and donor concentrations and c_2 their difference squared. The actual deflection on the DSC chart is the heat input rate, $\mathrm{d}Q/\mathrm{d}t$, given by

$$\mathrm{d}Q/\mathrm{d}t = (w/\rho Eb)(\Delta H)(\mathrm{d}[\mathrm{D_b}]/\mathrm{d}T)(\mathrm{d}T/\mathrm{d}t) \tag{5}$$

w is the sample weight, ρ the sample density, E the instrument calibration factor, b the ordinate scale factor and $\mathrm{d}T/\mathrm{d}t$ the heating rate.

A Study of Radiation-Induced Grafting by Differential Scanning Calorimetry

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ABSTRACT: The melting behavior of styrene-grafted low-density polyethylene film was studied by differential scanning calorimetry (DSC). Styrene was randomly grafted to the polyethylene film by γ radiation at a dose rate of 0.23 Mrad/hr. The apparent graft (total polystyrene content) in the samples ranged from 5 to 200%. Several DSC runs were made for each sample. Grafting was found to lower both the melting point and the heat of fusion during the first DSC determination. For subsequent DSC runs, the melting point depression remained constant while the heat of fusion increased to the original value and became independent of grafting. Accordingly, the heat of fusion determined in the second DSC run was used to calculate the apparent graft of the samples. The lowering of the heat of fusion observed in the first DSC run was explained by a graft-induced strain on the surface of the crystals, which was later relieved by melting and recrystallization. This explanation was substantiated by a correlation between the heat of fusion from the first DSC run and the degree of covalent grafting.

The grafting of side chains to a polymer backbone has a pronounced effect on its physical and mechanical properties. Although this technique has been widely used to modify polymer properties, there are relatively few studies which deal with the influence of the side chains on the melting of the grafted polymer.

This paper is concerned with the melting behavior of styrene-grafted low-density polyethylene film where the grafting is initiated by γ radiation. The objective is to quantitatively isolate the effect of covalent grafting on the melting of polyethylene which contains both grafted and microdispersed styrene homopolymer.[1] The melting point and the heat of fusion were determined by differential scanning calorimetry (DSC) and discussed in reference to previously studied copolymer systems.

The melting point depression has been utilized by previous workers for monitoring radiation damage in homopolymers.[2-5] However, the radiation dosages in all these studies were several orders of magnitudes higher than those used in the present work. These studies showed that

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