extent of polar alignment for moments nearly orthogonal to the backbone could lie in the range 4-10%. This range suggests that interchain dipolar coupling is an important phenomenon in these polymers. On this basis one may expect that localized ferroelectric ordering enhances cooperative behavior during the transition from poled solid to liquid crystal. The observed phenomena could be useful in the formation of polymeric solids with electrical or nonlinear optical properties.

Acknowledgment. This work was supported through a research grant from the 3M Co.

Appendix

$$\alpha = 4n_2^2/[n_1^2(\tan\theta)(1 - n_2^2/n_1^2 \sin^2\theta)^{1/2}(1 - n_2^2/n_1^2)]$$

$$\beta = [4n_2^2(1 - n_2^2/n_2^2 \sin^2\theta)]/[n_1^2(\tan\theta)(1 - n_2^2/n_1^2 \sin^2\theta)^{1/2}(1 - n_2^2/n_1^2 \sin^2\theta + n_2^4 \cot^2\theta/n_1^4)]$$

$$\gamma = 4n_2^2/[n_1^2 (\tan\theta)(1 - n_2^2/n_1^2 \sin^2\theta)^{1/2}(1 - n_2^2/n_1^2 \sin^2\theta + n_2^4 \cot^2\theta/n_1^4)]$$

Registry No. (*p*-Acetoxybenzoic acid)(ethylene glycol)(terephthalic acid) (terpolymer), 52237-98-6.

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Spectroscopic Analysis of Phase Separation Behavior of Model Polyurethanes

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ABSTRACT: Infrared spectra as a function of temperature have been obtained for model polyurethanes. Unique spectroscopic features in the N—H and C=O stretching regions have been found for rapidly cooled samples. The changes of these newly found features have been useful in the interpretation of the phase-separation behavior. A direct correlation between changing hydrogen bonding characteristics in soft and hard domains and macroscopic phase transformation as a function of temperature has been presented.

Introduction

Segmented polyurethanes are copolymers that consist of hard and soft segment units. Due to incompatibility between the two types of structural units, it is generally agreed that the polymers formed undergo microphase separation resulting in hard-segment-rich hard domains, soft-segment-rich soft matrix, and poorly characterized interphase. Since the glass-transition temperatures (T_g) of soft segments and hard segments are well below and higher than the usual service temperature, i.e., usually room temperature, respectively, polyurethanes are thermoplastic elastomers with a wide range of mechanical properties depending on the ratio of the two structural components.

Even though the phase-separated domain structure is not unique to polyurethane, it is geneally accepted that the strength and high elasticity of polyurethanes are due to the hard domains stabilized by the hydrogen bonding between hard segments.[1] The perfection and degree of phase separation have been found to be important to the properties of polymers and are dependent on molar composition, synthesis procedure, and thermal history.[2,3] Hydrogen bonding may form between the N—H and C=O groups in the hard domain. If polyether is part of the polymer, then hydrogen bonding between the N—H group of hard segment dispersed in the soft matrix and the C—O—C group of soft segment has also been suggested.[4-7] Because of its importance, hydrogen bonding properties of urethane functional groups have been extensively investigated. Spectroscopic techniques, mainly infrared, have complemented other characterization techniques to better understand the phase-separated structures of polyurethanes. Even though a considerable amount of information has been obtained, a direct interpretation of the spectroscopic data is still difficult. More recently, these difficulties have again been mentioned in the literature.[8-11]

It is well-known that polyurethane structures and properties change as a function of temperature and these changes have been followed by thermal analysis,[12-14] spectroscopy,[8,9,14-16] dynamic mechanical analysis,[1,18,19] wide-angle X-ray diffraction,[20,21] and small-angle X-ray scattering.[22] Several processes have been suggested to occur concurrently as a function of temperature. These structural changes are (1) weakening and disassociation of H bonding; (2) disordering of hard segment domain; (3) hard–soft segment mixing; and (4) thermal degradation, mainly occurring in urethane linkages.[23] Vibrational spectroscopy, more specifically, infrared technique, has demonstrated its particular usefulness in characterizing the hydrogen bonding characteristics in each domain. Some of the localized vibrations such as the N—H stretching vibration or C=O stretching vibration are strongly perturbed by the formation of hydrogen bonds. Both the frequency shifts and intensity changes are

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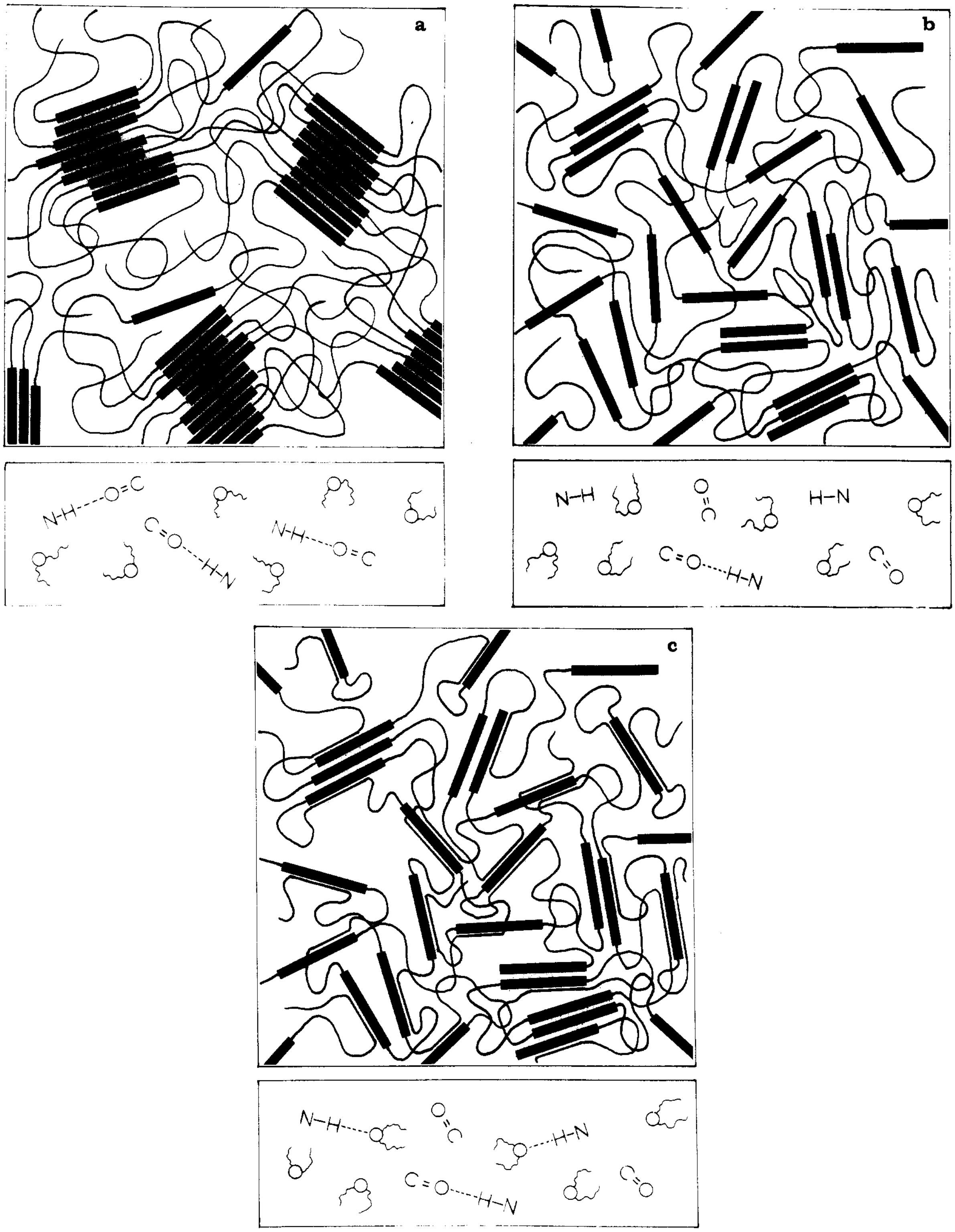

Figure 1. Schematic representations of polyurethane structures at various temperatures: (a) room-temperature phase-separated morphology; (b) most disassociated structures at high temperature; (c) dispersed phase "trapped" at extremely low temperature.

characteristic of the specificity or magnitude of the hydrogen bonds formed. The intensity of each type of hydrogen bonded vibration, if properly assigned, can potentially yield the degree of phase separation in the polyurethanes being studied.

Because of recent interest, and the ongoing controversy regarding the spectroscopic interpretation of domain structure, we feel additional studies are needed. In this paper, a direct correlation between changing hydrogen bonding characteristics in soft and hard domains and macroscopic phase transformation as a function of temperature will be presented. Schematic representations of phase-separated morphology at three different temperatures are given in Figure 1. Characteristic hydrogen bonded species are also included in each diagram. By increasing the temperature above the "melting" transition of the hard domain, homogeneous structure (Figure 1b) is obtained accompanied by the disassociation of most of the hard segment–hard segment hydrogen bonding. If it is rapidly cooled (quenched), almost all the high-temperature structure is "frozen" resulting in a significant number of interactions between the hard and soft segments as

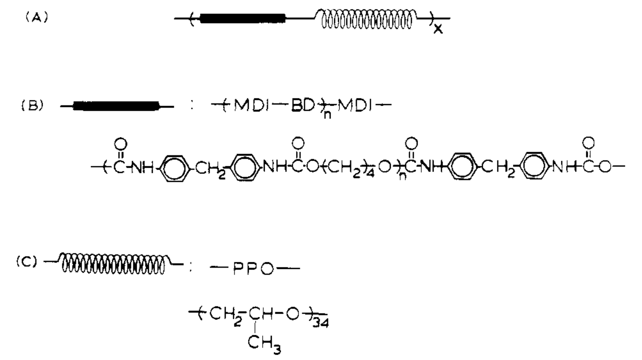

Figure 2. Schematic drawings of the model polyurethanes (n = 2 corresponds to B2): (a) polymer; (b) hard segment; (c) soft segment.

shown in Figure 1c. Quenching to lower temperature is then a good way to retain the degree of phase mixing at the elevated temperature. If the quenched temperature is much lower than the glass-transition temperature (T_g) of the soft segment, the slow rate of segmental separation at low temperature (depending on the segmental diffusion rate at the temperature) will prevent reformation of hard segment–hard segment hydrogen bonding. This low-temperature structure undergoes phase separation to become a room temperature structure when the temperature is raised. In this way direct correlation between microscopic evidence for hydrogen bonding characteristics in soft and hard domains and macroscopic phase transformation can be obtained. Of course, the definition of a homogeneous phase at high temperature is difficult to establish. We can only add that the samples to be studied are quenched from a temperature 20 °C above the melting temperature reported for the sample. The quenched samples studied are optically clear. Our experimental results and the interpretation of phase separation in two unique polyurethanes are reported here.

Experimental Section

The polyurethane samples used in our study have been described previously.[24] The distribution of the hard segment [1,1′-methylenebis(4-isocyanatobenzene)–butanediol (MDI-BD)] length is strictly monodisperse. The soft segment used is poly(propylene oxide) (PPO) (Voranol, molecular weight 2000). The preparation of the prepolymer and the monodisperse hard segments have been described earlier.[24] As done previously, the samples containing three or five MDI units have been designated as B2 or B4 polyurethanes and are shown schematically in Figure 2. The glass-transition temperature for the soft segment is -40 °C. For the phase-mixed system, the glass temperature depends on the degree of phase mixing and can be as high as 0 °C. It is difficult to establish the glass-transition temperature for the hard segment because of its disassociation. This value is in the range of 100 °C.

The spectroscopic experiment was carried out on an IBM Model 98 Fourier transform vacuum spectrometer. We found for this set of experiments involving a large temperature range, it was much easier to build a separate purge box in the sampling area to accommodate a specially designed infrared cell. The entire optical table is maintained under vacuum except for the sampling area. In this section, atmosphere absorptions were removed by boiled nitrogen gas. Since our major emphasis is to capture the temperature-induced structural changes, a considerable effort was expended to design a sample cell with good temperature control which can be used over a large temperature range. This cell is shown schematically in Figure 3. With this cell, when connected to a proportional controller, we found that a sample temperature from -100 to 200 °C can be comfortably reached. The temperature accuracy is within one degree of the set point.

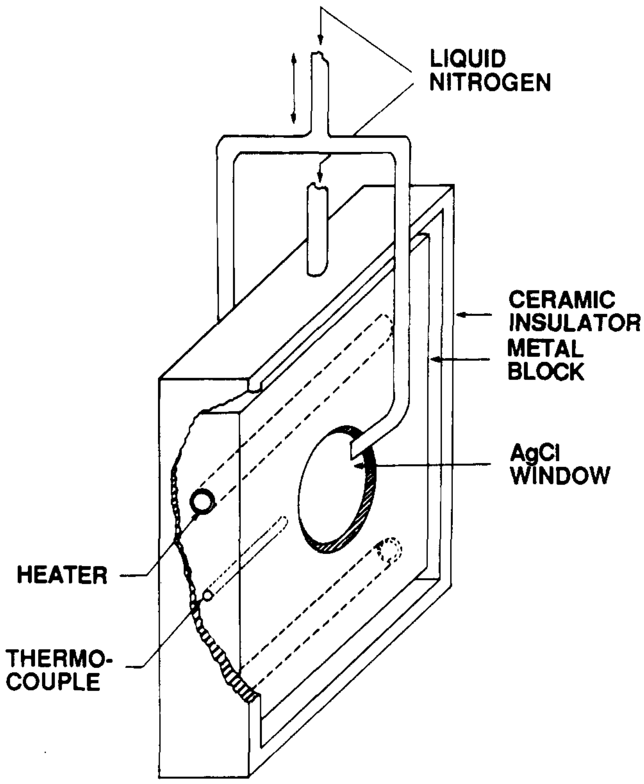

Figure 3. Variable-temperature cell used in our infrared experiments.

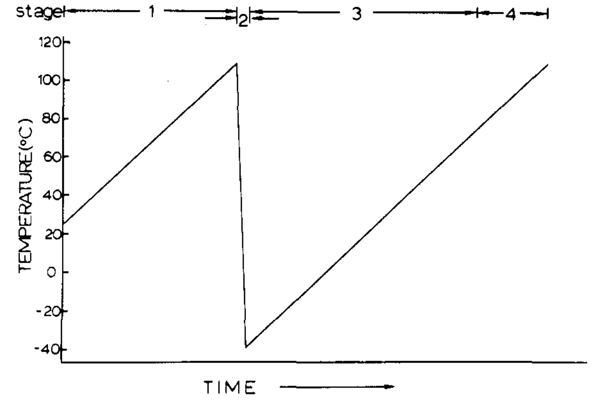

Figure 4. Temperature cycles of the polyurethanes studied.

For the quenching experiment, liquid nitrogen is blown directly from an opening on top of the cell as well as to the sample held between two AgCl windows (Figure 3). The temperature of the sample is always measured with the copper–constantan thermocouple held between the windows in the infrared beam path. It took less than 20 s to cool the sample from 185 to -70 °C. The low temperature was maintained by blowing boiled-off nitrogen gas from a separate liquid nitrogen reservoir. No water condensation was observed any time during the experiment. The background spectra at each temperature was recorded and stored for later use. We still found it was difficult to obtain a flat base line at temperatures below -45 °C. Since we found little or no change for the infrared spectra of polyurethanes below -45 °C, these data were not used in our analysis. At each measurement temperature, we let the sample equilibrate for 10 min before spectra were obtained. How temperature changes as a function of time is shown schematically in Figure 4. The infrared spectra obtained for the B2 model polyurethane for two temperatures are shown in Figures 5 and 6. The changes in the N—H stretching and C=O stretching vibrations as a function of temperature in the 3300- and 1700-cm^{-1} regions, respectively, are shown in Figures 7 and 8.

Results and Discussion

Infrared Spectroscopic Features Sensitive to Structural Changes. Infrared spectra of polyurethanes

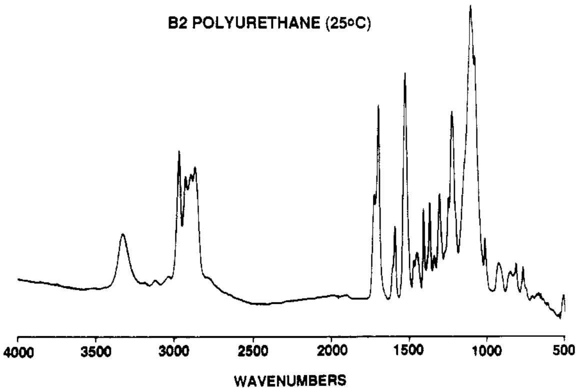

Figure 5. Infrared spectra obtained for B2 polyurethanes: 2-cm^{-1} resolution; 200 scans; room temperature.

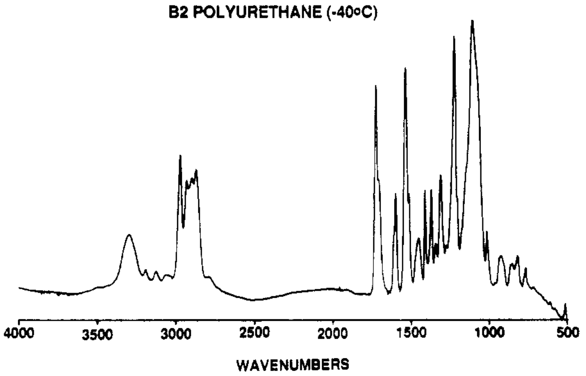

Figure 6. Infrared spectra obtained for B2 polyurethanes: 2-cm^{-1} resolution; 200 scans; -40 °C.

exhibit bands which are characteristic of localized chain conformation of packing. Most of the attention has been given to the characterization of the band intensity and shape of the localized vibrations associated with specific functional groups, i.e., N—H, —O—, or C=O, which participate in specific hydrogen bonding in the various domains. Most studies recognize this two-phase system, i.e., hard domains dispersed in soft segment matrix, which is too simplistic a picture. A morphological model incorporating a highly ordered lamellar structure, amorphous regions (e.g., interphase), and regions of soft phase with few hard segments dispersed within it should be considered.[22,25] It is well established that the position and intensity of these vibrations are extremely sensitive to the strength and specificity of the hydrogen bonds formed.[26] The phase separation in polyurethanes can be characterized by measuring the intensity and position of the hydrogen-bonded N—H stretching vibration.[8,9,14-16,24] If there is significant N—H- - -O=C hydrogen bonding, since both units are associated with the hard segments, it has usually been interpreted that extensive phase sepration has occurred. It has also been suggested that N—H can form strong hydrogen bonding with the oxygen of the ether groups associated with the soft segments when available.[4-7] The observation of these hyrogen bonds suggests the existence of a dispersed phase consisting of hard segments mixed with soft segments. The converse of this statement, i.e., the existence of a dispersed phase, does not necessarily mean there are well-defined N—H- - - —O— hydrogen bonds. A significant number of studies have attempted to quantitatively assess the amount of hydrogen-bonded vs. free species, undoubtedly some of the difficulties in the interpretation of spectroscopic data are complicated by the two types of hydrogen bonds available and other second-order spectroscopic effects involving the N—H stretching fundamental and combinations of lower lying amide vibrations.[10,11]

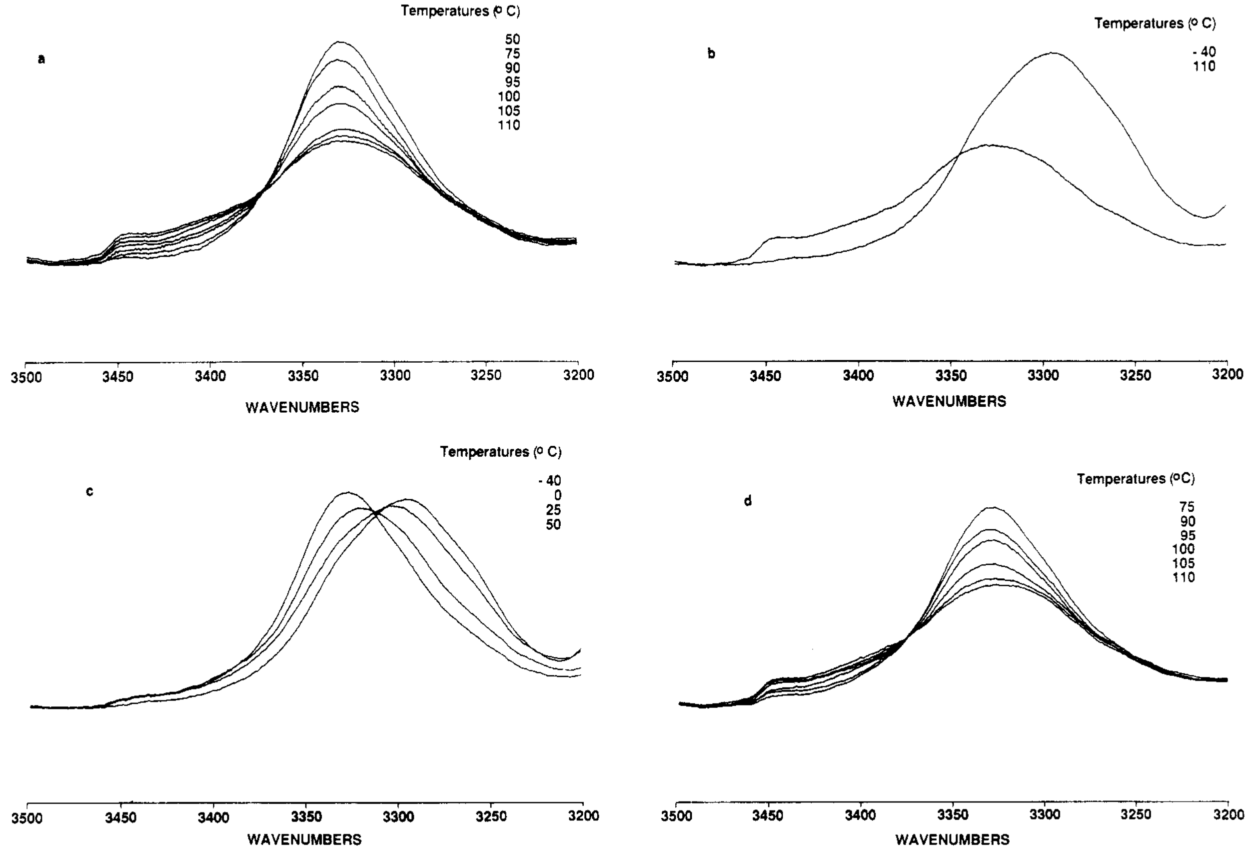

Figure 7. Temperature variation of the N—H stretching region: (a) stage 1 as shown in Figure 4; (b) stage 2; (c) stage 3; (d) stage 4.

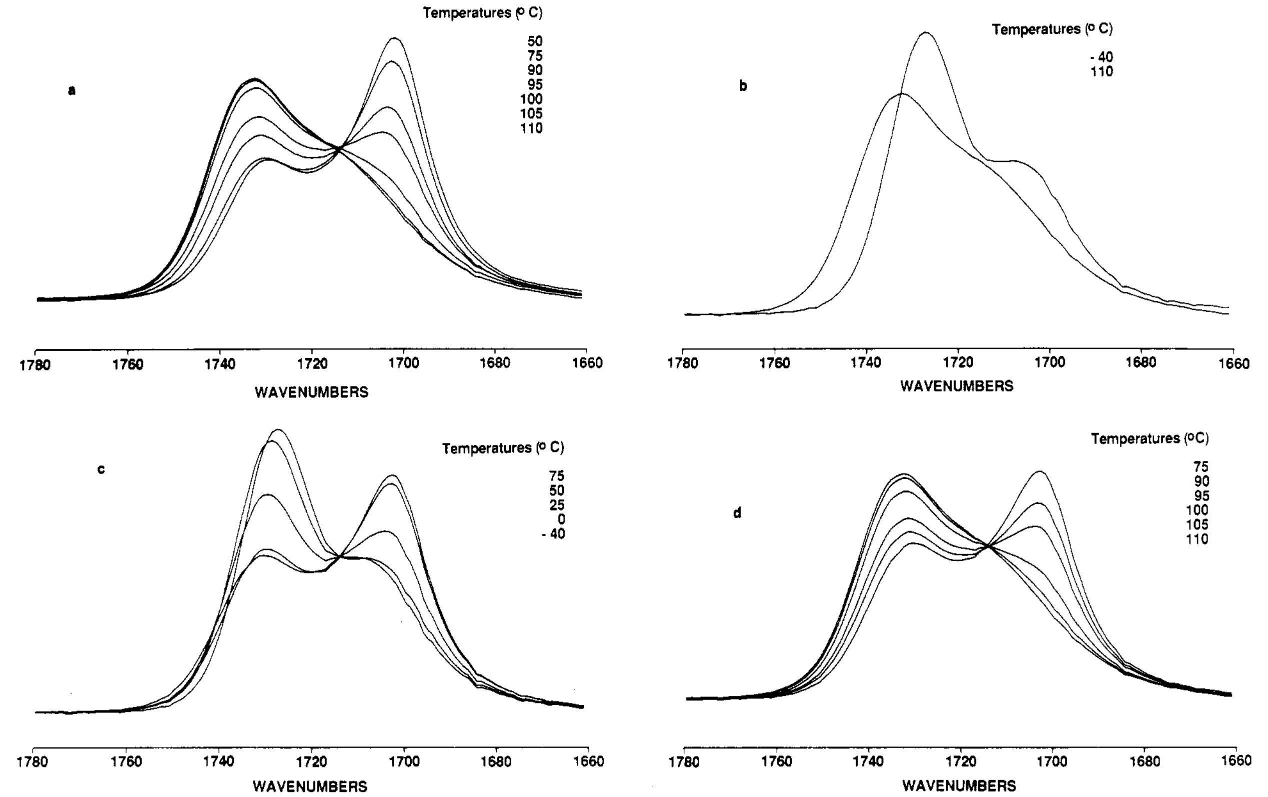

Figure 8. Temperature variation of the C=O stretching vibration: (a) stage 1 as shown in Figure 4; (b) stage 2; (c) stage 3; (d) stage 4.

The frequency shifts associated with both N—H and C=O vibrations when hydrogen bonds are formed can be understood intuitively. For the N—H stretching vibration, the formation of the hydrogen bonds alters the electronic distribution associated with the N—H bond.[27] For the C=O stretching vibration, there is the added contribution of transition dipole–dipole coupling.[28] Generally speaking, the N—H groups free from hydrogen bonding have a stretching vibration at 3450 cm^{-1}. In contrast, the groups involved in hydrogen bonding have much lower frequencies, ranging from 3300 to as low as 3200 cm^{-1}. The exact position depends very much on the strength of the hydrogen bonding formed,[29] and this bond strength strongly depends on the local geometry,[30] such as the linearity of the bonds involved and the distance between the groups. The general approach is to treat the spectroscopic data as having two components, one free and one hydrogen bonded, even though the frequency maxima for the hydrogen-bonded component varies significantly as a function of composition or thermal history.[2]

Amide I vibration is usually referred to as a relatively localized normal vibration with the largest potential energy contribution from the C=O stretching internal coordinate. Similarly, since the C=O stretching vibration is sensitive to the specificity and magnitude of hydrogen bonding, it is plausible that the amide I vibration actually consists of several components associated with C=O groups in various environments. The amide I as a function of temperature obtained for our samples is shown in Figure 8. Similar to the N—H stretching region, two clearly discernible components can also be found. The 1732-cm^{-1} component is assignable to the carbonyls free of hydrogen bonding, and the lower frequency component, at approximately 1703 cm^{-1}, is associated with hydrogen-bonded carbonyls. The increase or decrease of the two components as a function of temperature reflects the changing hydrogen bonding properties in these phase-separated polyurethanes. However, a number of studies have also found a third component.[8,31] Interpretation of this additional feature will be published separately.[31]

One must accept that the hydrogen bonds formed are not uniform and a distribution must exist. The exact form of this distribution is dependent on various parameters such as chemical composition, sample preparation, or temperature. Quantitative analysis of the amount of each is complicated by the fact that the absorptivity coefficient of the hydrogen-bonded component is dependent on the strength of the hydrogen bonds formed.[9,29] However, the dipole moment change or band intensity need not be associated with the inductive effect but rather is dominated by the changing resonance structure.[27] Although the difference in the absorptivity coefficient for the amide I band has not been observed to be significant,[8,27] the same cannot be said for the N—H stretching vibration. The ratio of the absorptivity coefficient, R, is described as

$$R = \epsilon_{\mathrm{b}}^{\mathrm{N-H}} / \epsilon_{\mathrm{f}}^{\mathrm{N-H}}$$

where ϵ denotes the absorptivity coefficient and b and f stand for bonded and free components, respectively. The relative intensities of these two components can and have been used to determine the degree of phase separation in polyurethanes. However, recent studies have demonstrated that this simplistic analysis can be misleading.[8,9]

Spectral Observations. The room-temperature spectra in the 3300- and 1700-cm^{-1} regions of a B2 polymer are as expected. In each region dominant peaks are characteristic of hydrogen-bonded components. The N—H groups free of hydrogen bonds cannot be seen easily. When we allow the temperature to rise in stage 1 of Figure 4, the hydrogen-bonded component diminishes in intensity and shifts upward. This frequency shift reflects a change in hydrogen bond strength but does not imply that the hydrogen bonds have disassociated as Skrovanek et al. correctly pointed out.[9] At melting, the hydrogen-bonded component diminished considerably in intensity as compared to the room-temperature spectrum as expected. In the carbonyl region the 1735-cm^{-1} component is the dominant one. Because of the significant difference in the absorption coefficient, the N—H stretching at 3450 cm^{-1} did not change as dramatically as the 3330-cm^{-1} hydrogen-bonded component.

Except for relatively minor band intensity and frequency changes, the infrared spectrum obtained by cooling the polyurethane sample directly from room temperature to low temperatures is quite similar to the spectrum obtained at room temperature. What are most interesting are the spectra obtained for the quenched B2 polyurethane. For simplicity, the N—H and C=O stretching regions will be described separately. For the quenched sample measured at low temperatures, in the N—H stretching region, the dominant peak is at 3295 cm^{-1} with very weak shoulders at 3330 and 3260 cm^{-1}. The N—H stretching vibration free from hydrogen bonding seems to be totally absent. When we slowly raised the temperature of the sample from -40 to 50 °C, the 3330-cm^{-1} component changed continuously and gradually became dominant. When the sample was heated beyond 70 °C in stage 4, this region changed as described in stage 1. The shifting of the N—H band for the quenched sample cannot be attributed to the different temperature dependence between N—H- - -O=C and N—H- - - —O— hydrogen bonding because the changing characteristics of the quenched sample are irreversible.

As can be seen in Figure 8, the carbonyl stretching region obtained for the quenched sample is totally unexpected. We see the dominant peak at low temperature is the 1730 cm^{-1}, representing free C=O stretching with the weaker component being the 1705-cm^{-1} one. The relative intensity of the two components of this quenched sample again change significantly between -45 and 50 °C. The temperature-induced changes in stage 4 are similar to what is observed in stage 1 for the N—H stretching vibration as well. As stated previously, the existence of a homogeneous phase is difficult to establish. The fact that the 1705-cm^{-1} component is much weaker than the 1730-cm^{-1} band also suggests that most C=O's are not bonded to N—H groups as expected for a dispersed phase.

Discussion. One of the most critical assignments in our analysis is the 3295-cm^{-1} band. Our data suggests this component to be associated with N—H bonded to the ether oxygen. The structure of the quenched sample reflects the phase-mixed behavior of the melt and is preserved in the "frozen" state at -70 °C, well below the glass-transition temperature of the soft segments. We feel this "frozen" state is a well-dispersed phase containing few isolated N—H groups. All the N—H groups participate in hydrogen bonding either with the C=O or the —O— groups. This interpretation can be supported from basic concepts associated with the thermodynamics of these polyurethanes.

Previous studies have suggested that the glass-transition temperatures of the soft and hard segments are approximately -40 and 110 °C, respectively. In our experiment, we have quenched the melt with sufficient speed to trap the morphology of the melt state, preventing phase separation to take place. There are approximately 34 ether units per soft segment and six carbonyl units per hard segment. From stoichiometry, it is highly likely for ether oxygen to be around the N—H groups. The conformation around the soft segments allows a great deal of chain flexibility, making it sterically favorable to form hydrogen bonds as well. The change in the rotational energy barrier is in the neighborhood of 1 kcal/mol;[32] and the gain for each hydrogen bond formed is approximately 5–10 kcal/mol.[29] Thus the disappearance of the free N—H band and the strong 3295 cm^{-1} in the "frozen" sample can be explained. There are other explanations for the observed components in the 3200-cm^{-1} region. The possibility that additional components arise from the Fermi resonance interaction between the N—H stretching fundamental and combination of low-lying amide vibrations does exist, and some well-defined vibrations have been observed in polypeptides.[10,11] However, these weak Fermi resonance components should not alter our interpretation. Christenson and his co-workers have argued for the assignment of an N—H- - -O– band below the 3350 cm^{-1} component and concluded the 3260-cm^{-1} component is the appropriate one.[24] Their arguments, based on steric considerations and model compound studies, for the existence of such a component are rather persuasive. However, on the basis of our results, we feel the component at 3295 cm^{-1} is the correct assignment and the one at 3260 cm^{-1} may be assignable to the second-order effects associated with Fermi resonance interactions.[10,11] Our assignment is consistent with earlier analsyis.[4] When the temperature is increased above -40 °C, we see that the soft segments gain sufficient mobility, excluding hard segments, for separation to occur, disrupting the N—H- - -O– hydrogen bonds. This process dominates in stage 3 in our schematic diagram shown in Figure 4.

The spectroscopic changes observed for the carbonyl stretching vibration are consistent with this interpretation. Initially as can be seen in Figure 7, the 1735-cm^{-1} band dominates in the quenched state, although the presence of the 1705-cm^{-1} band can definitely be observed clearly. There is an insufficient number of N—H groups for most of the C=O groups to be bonded to. When the temperature is raised, phase separation occurs and the hydrogen bonds between hard segments begin to form with other N—H groups. Finally, beyond 70 °C, these hydrogen bonds weaken but do not necessarily break, until the entire sample melts at 110 °C. Therefore, transformation of NH- - - —O— bonds in the phase-mixed state into NH- - -O=C bonds in phase-separated state is clearly supported by the spectroscopic changes observed in both the N—H and C=O stretching regions. We wish to reiterate that as temperature increased, a clear indication of transformation of phase-mixed state into the phase-separated state was observed.

In our analysis, one of the critical premises is that at high temperatures, phase mixing and/or an incomplete domain structure of polyurethanes exists. This has been suggested by a number of investigators. The DTA or DSC endotherm near 80 °C has initially been interpreted to be the disassociation of hard segment–soft segment hydrogen bonds.[33] That transition has since been reinterpreted to be morphological in origin.[14] Wilkes noticed that the T_g of soft segments quenched to 20 °C from high temperature increased significantly.[34] Sung and her co-workers also measured the T_g of soft segment as a function of urethane hard segment concentration.[17] They found T_g values for the amorphous 2,4-TDI and polyester soft segment polyurethanes to be higher than expected.[17] In both cases, the increases in T_g values were explained as a result of increased hard segments dissolved in soft segment matrix and result in hydrogen bonding of hard and soft segments, i.e., N—H- - -O=C, when polyesters were used as soft segments.

Conclusion

Infrared spectroscopy has been widely used to study the microstructure of polyurethanes. The changing distribution of hydrogen-bonding properties in each domain can be assessed by this technique. In spite of its inherent selectivity for studying each functional group separately, there are some vague assumptions in the application of the spectroscopic data to better understand structural changes such as phase mixing or phase separation upon thermal treatment. This has been mainly due to the lack of direct spectroscopic evidence which is unique to each macroscopic phase structure.

In this study, new spectroscopic evidence identifying hard segment–hard segment hydrogen bonding (N—H- -O=C) in hard domains and hard segment–soft segment (N—H- - -—O—) hydrogen bonding in phase-mixed states has been presented. As far as we know, these direct spectroscopic features have been sought but not found. If properly assigned, most of the spectroscopic data can then be correlated to the macroscopic structural transformation, mainly the degree of phase mixing or the separation kinetics. In this study the qualitative structural pictures shown in Figure 1 are proven by the experimental evidence obtained.

It is now feasible to follow the phase-separation kinetics at the segmental level. Our initial experimental work along the line presented here shows this possibility. If the thermodynamic arguments about equilibrium temperatures of hydrogen bonding between hard and soft segments given are not grossly erroneous, then our results suggest a new way of studying hydrogen bonding thermodynamics, i.e., establishing the equilibrium state at elevated temperatures followed by detailed characterization of the low-temperature structures. These will be published separately.

Acknowledgment. This research has been supported by a grant from Dow Chemical Corporation. We deeply appreciate that Professor Y. K. Wang has been granted a leave to carry out the spectroscopic research here at the University of Massachusetts with the support of the National Science Foundation, US–China Cooperative program, Grant 8407130. Samples used in this study have been kindly supplied by Dow Chemical Corporation.

Registry No. (MDI)(BD)(PPO) (copolymer), 109801-12-9.

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