1990

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Repository Citation

Miller, Charles E., et al. "Near-infrared spectroscopic analyses of poly (ether urethane urea) block copolymers. Part II: phase separation." Applied Spectroscopy 44.4 (1990): 581-586.

Near-Infrared Spectroscopic Analyses of Poly(ether urethane urea) Block Copolymers. Part II: Phase Separation

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Second-overtone carbonyl bands at 1918 and 2036 nm in the near-infrared (NIR) spectrum are used to monitor the phase separation of poly(ether urethane urea) (PEUU) block copolymers at 100°C. Exact positions of urea and urethane carbonyl bands are determined by NIR spectroscopic analyses of model compounds in bulk and in dilute solution. Results indicate that the carbonyl groups in the copolymers are affected by two different structural processes that occur with annealing. A faster process causes an increase in the number of free urethane groups, and a slower process causes a decrease in the number of free urea and urethane carbonyl groups. Although several structural mechanisms can be used to describe these trends, more information is necessary to identify exact structural changes that occur with annealing.

Index Headings: Near-infrared spectroscopy; Polymers.

INTRODUCTION

Segmented poly(ether urethane urea) (PEUU) copolymers are used for a variety of biomedical applications.[1] The hard-segment blocks (formed by the reaction of diisocyanate with chain extender) in these copolymers can self-associate to form hard-segment domains in a soft-segment (polyether) matrix. The hard-segment domains act as effective crosslinks and reinforce the polymers. Consequently, the physical properties of these materials greatly depend on the degree of phase separation.[2–6]

Phase separation in PEUU copolymers can be probed by several different analytical methods. Mechanical studies,[2,6] x-ray methods,[3,4,7–9] thermal analysis methods,[2,4,7,10] FT-IR spectroscopy,[5–11] and NMR spectroscopy[2] have been used to determine the nature and extent of phase separation in PEUU copolymers and similar systems. Although these methods provide specific information about phase separation, they usually require extensive sample preparation and long analysis times.

Near-infrared (NIR) spectroscopy has been used to rapidly analyze bulk materials.[12–15] It was shown in the previous paper (hereafter referred to as part I)[15] that compositions of these polymers can be determined by NIR spectroscopy. The low extinction coefficients of NIR absorption bands make possible the analysis of bulk polymers in a relatively unprepared state. NIR spectra contain vibrational overtone and combination bands from C-H, N-H, O-H, and C=O groups in a sample. As a result, much of the information obtained in infrared spectra is available in NIR spectra.

For IR analyses of phase separation in diol-extended polyurethanes,[7,8,10,11] the primary band of interest is the fundamental stretching band of the urethane carbonyl group. Changes in the relative magnitude of absorbances from free carbonyl groups and from carbonyl groups hydrogen-bonded to N-H groups are used to monitor phase separation. The carbonyl group is a good indicator of phase separation in these polymers because self-association of hard-segment blocks involves intermolecular hydrogen bonding of urethane carbonyl groups to urethane N-H groups. In contrast, the phase-mixed state has a large number of urethane N-H groups hydrogen-bonded to ether oxygens in the soft segment and a significant number of free carbonyl groups. Although other IR bands have been used to monitor phase separation,[10] the carbonyl band is the most affected by phase separation.

Spectral analysis of PEUU copolymers, or poly(ether urethane ureas), is slightly more complex than for diol-extended polyurethanes. These copolymers (Fig. 1, I) contain urea carbonyl groups, which are at the interior of hard segment blocks, and urethane carbonyl groups, which are located at the boundaries of hard- and soft-segment blocks. The urea carbonyl groups are, therefore, sensitive to hard-segment aggregation and changes in hard-segment domain structure. In contrast, the urethane carbonyl groups are more sensitive to effects at the phase boundaries. As a result, spectral analysis of urea and urethane carbonyl groups can distinguish between processes involving phase boundaries and those involving the interior of hard-segment domains.

Phase separation analysis by NIR spectroscopy relates the spectral shifts of overtone stretching bands with changes in hydrogen bonding states of urethane and urea carbonyl groups. Although the effects of hydrogen bonding on the fundamental transitions of carbonyl vibrations (observed in IR spectra) have been well-characterized,[16] effects on overtone transitions (observed in NIR spectra) are less characterized. In addition, because of the broadness of NIR bands relative to IR bands, assignment of NIR absorbances to specific functional groups is difficult. With these considerations in mind, the positions of NIR urea and urethane carbonyl bands are best determined by analysis of model compounds.

In this work, the ability of NIR spectroscopy to monitor phase separation in PEUU copolymers is investigated. Spectra of model compounds are used to assign second-overtone bands for free urethane and urea car-
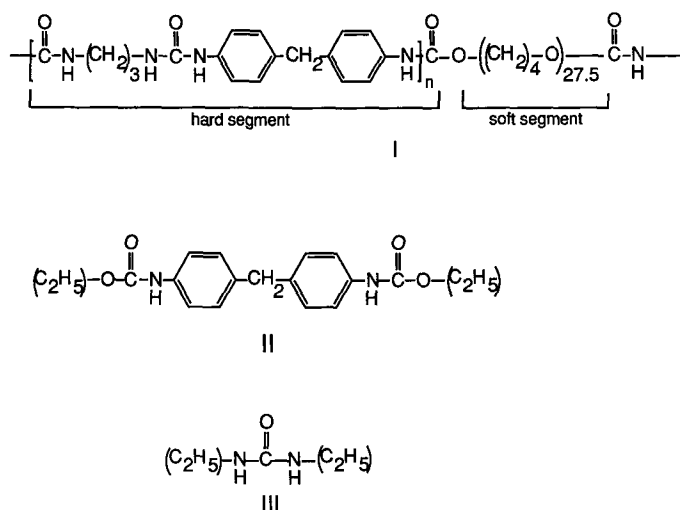
FIG. 1. Chemical structures for PEUU copolymers (**I**), the urethane model compound (**II**), and the urea model compound (**III**).

FIG. 2. Diagram of the sample cell used to contain polymer films for annealing and NIR scanning.

bonyls, and these bands are used to monitor phase separation.

EXPERIMENTAL

Sample Preparation. The synthesis of PEUU samples is discussed in part I. The chemical structure of the PEUU block copolymers used in this work is shown in Fig. 1, I. PEUU samples 2:1:1, 4:3:1, and 6:5:1 were dissolved to approximately 4% (w/v) in N,N'-dimethylacetamide (DMA). For each analysis, approximately 3 mL of solution was placed in a Teflon® casting dish and vacuum-dried for 8 to 9 days at room temperature to remove the solvent. The polymer film was then placed in a sealed sample cell with a ceramic background and a quartz window (see Fig. 2). The sample was sealed from the environment by placing a rubber O-ring between the quartz and ceramic and applying pressure on 2 stainless-steel cover rings with screws. The sample remained in the cell until the completion of annealing and NIR scanning. When necessary, the sealed sample was conveniently placed in the reflectance spectrometer for NIR analysis.

The film was annealed in an oven at 100°C. NIR scans were taken before annealing and after 11 different total annealing times (up to 70 h). After each annealing interval, the sample was removed from the oven and allowed to cool at room temperature for 30 min before NIR scanning.

Model Compounds. Model compounds were used to study the effects of hydrogen bonding on urethane and urea carbonyl groups. The urethane model was the reaction product of methylene di(phenyl isocyanate) (MDI) with ethanol (Fig. 1, II), and the urea model was 1,3-diethylurea (Fig. 1, III) (Aldrich). Diffuse reflectance NIR spectra of the model compound powders were obtained with a diffuse reflectance sampling cup that was specially designed for small samples.[17] NIR spectra of THF (Baker) solutions of the model compounds (approximately 1% w/v) were obtained with a sealed quartz cuvette. The spectra of the model compounds in THF solution were obtained by subtraction of the solvent spectrum from the solution spectrum until prominent solvent peaks dis-
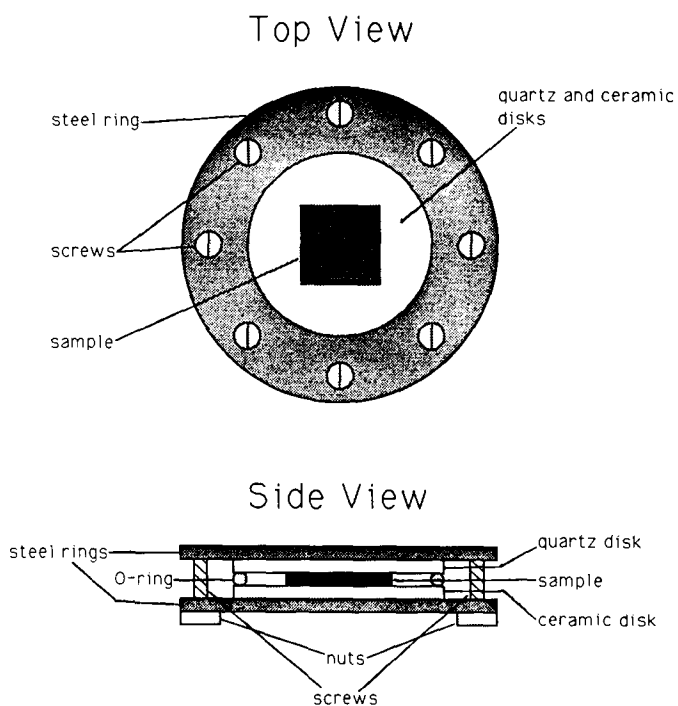
appeared. All solvent and solution spectra were obtained by averaging nine replicate scans.

Spectroscopy. All NIR spectra were obtained with a Technicon InfraAlyzer 500C NIR reflectance spectrometer. Although the total spectral range used was 1100 to 2500 nm, only the region 1800 to 2100 nm was used for phase separation analysis. The wavelength accuracy of the instrument was ±1 nm, and the nominal resolution was 10 nm. Each scan lasted about 1.5 min.

RESULTS AND DISCUSSION

NIR spectra of the urethane model compound (in the spectral region 1800 to 2100 nm) in bulk and in THF solution are shown in Fig. 3. This region of the NIR spectrum is dominated by second-overtone carbonyl stretching bands and N-H combination bands.[14,15] In the spectrum of the bulk material (Fig. 3A), the only strong absorbances are at wavelengths above 1960 nm. The band at 1980 nm might be a second-overtone band for a hydrogen-bonded carbonyl in the bulk material. Upon dissolution in THF, a strong band at 1918 nm appears, and the 1980-nm band disappears. In the dilute solution, it is assumed that all N-H groups in the material are bound to solvent molecules, and the carbonyl groups should be free from hydrogen bonding. Therefore, the 1918-nm band can be assigned to the second-overtone band of the free urethane carbonyl. Although the 1980-nm band in the bulk urethane spectrum is probably a second-overtone band from a bound urethane carbonyl, it corresponds to a specific type of hydrogen bond present in the specific structure of the bulk urethane model. Because the hydrogen-bond geometry of urethane carbonyls in the PEUU copolymers might be substantially different, use of this band for phase separation analysis is avoided.
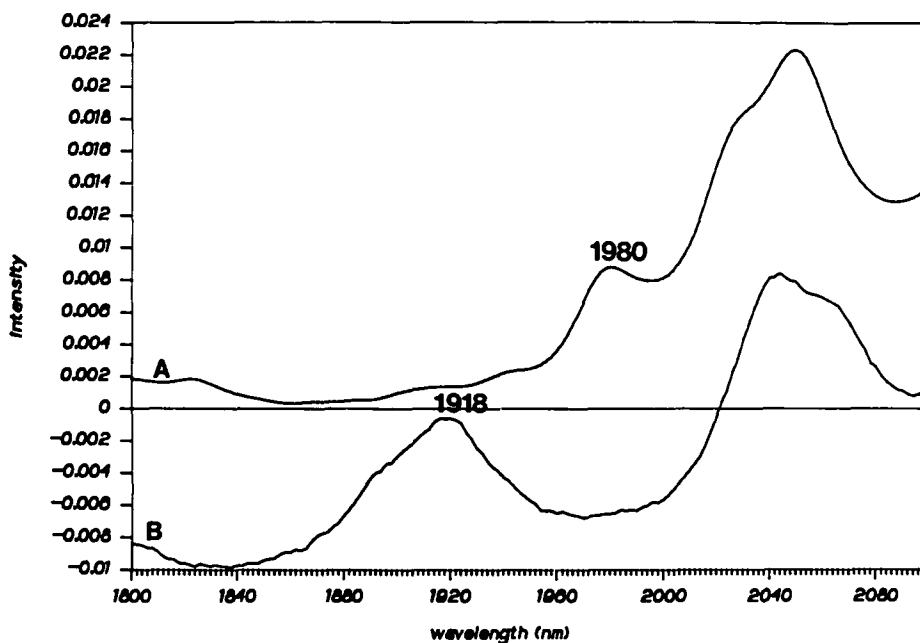
FIG. 3. NIR diffuse reflectance spectrum of the solid urethane model compound (A), and the NIR spectrum of the urethane model compound diluted 1% (w/v) in THF (B).

Similar spectra for the urea model compound are shown in Fig. 4. Overlapped bands at 2032 and 2054 nm are observed in the spectrum of the bulk urea model (Fig. 4A). However, only a single absorbance at 2036 nm is observed in the spectrum of the urea model dissolved in THF. As a result, the 2036-nm absorbance is assigned to the second overtone of the free urea carbonyl. The 2054-nm band in the spectrum of the bulk urea model compound probably corresponds to a specific hydrogen-bonded state of the urea carbonyl group.

Assignments of the NIR bands from urea and urethane carbonyls are confirmed by estimating overtone vibra-

tional frequencies from previously assigned fundamental vibrational frequencies.[5] To a first-order approximation, second-overtone bands occur at frequencies three times that of the fundamental band. Table I shows the estimated positions of second-overtone carbonyl bands (in nanometers). A close agreement with results obtained from model compound analysis is observed. The discrepancies between observed and estimated band positions are attributed to positive anharmonicity of the carbonyl vibrations, which commonly causes estimated NIR band positions to be blue-shifted from actual band positions.[12]
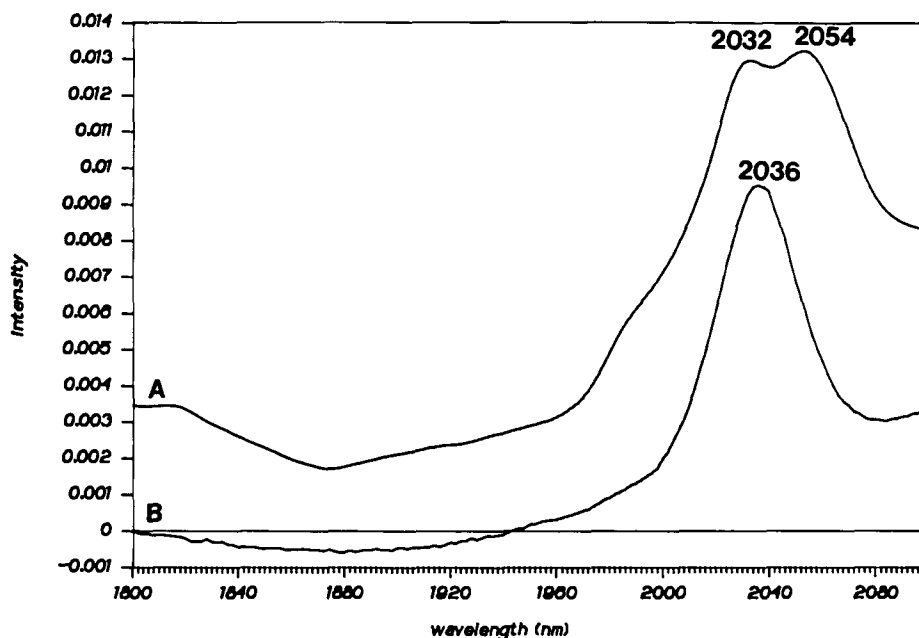

FIG. 4. NIR diffuse reflectance spectrum of the solid urea model compound (A), and the NIR spectrum of the urea model compound diluted 1% (w/v) in THF (B).
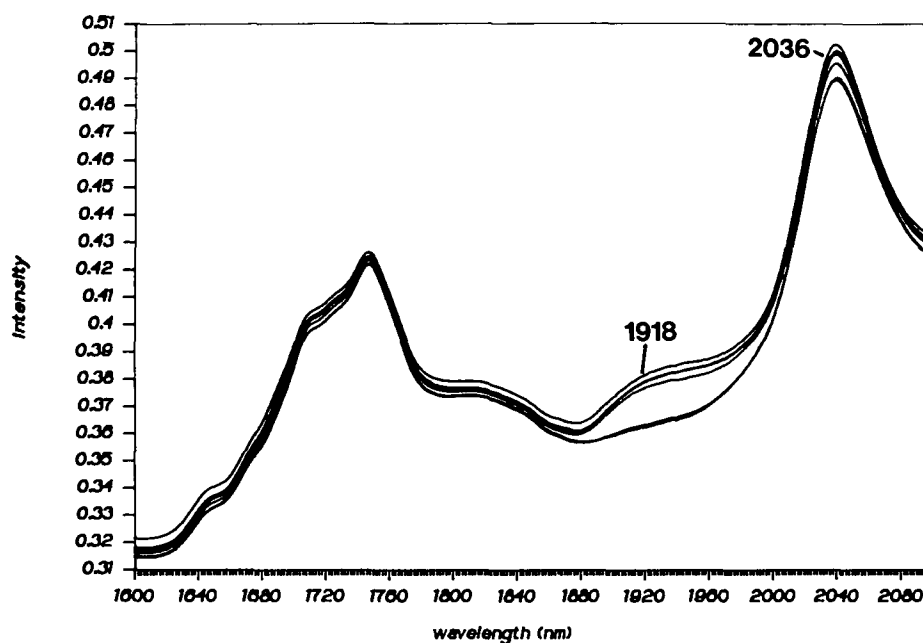
FIG. 5. NIR spectra of the 6:5:1 polymer film before annealing, and after annealing times of 20 min, 1 h, 4 h, 24 h, and 70 h.

NIR spectra of the 6:5:1 film before annealing and after several annealing times are shown in Fig. 5. Although the spectral trends with annealing are not obvious from this plot, the spectral regions that change with annealing are identified. Changes in absorbances in the region of the assigned free urethane carbonyl band (1918 nm) are quite large. Weaker changes in the free urea carbonyl absorbance at 2036 nm are also observed. In contrast, absorbances in the C-H stretching first-overtone region (1600–1800 nm) are relatively unaffected by annealing. Differences in spectral baselines are observed as caused by nonreproducible sample placement in the spectrometer or by changes in the refractive indices of the film with phase separation. As a result, the absorbance at 1800 nm is used as a baseline reference for subsequent analyses.

Figure 6 shows the free urea carbonyl absorbance at 2036 nm plotted as a function of annealing time for the three PEUU films. The absorbance for each film at time zero is arbitrarily set to zero. In each case, the free urea carbonyl absorbance decays continuously with annealing. The parameters obtained from the fit of an exponential function to these annealing profiles are shown in Table II. The A parameter, which is the magnitude of the decay, indicates the magnitude of change in the free

urea carbonyl absorbance with annealing. This parameter increases with increasing hard segment content of the film (from sample 2:1:1 to sample 6:5:1). This result is expected, because the number of urea groups in the polymer increases with the hard segment content. The decay rate constants (k_1) indicate the rate of change of the free urea carbonyl absorbance with annealing. The decay rate constants obtained from the annealing profiles of the 4:3:1 and 6:5:1 films closely agree. The decay rate constant for the annealing profile of the 2:1:1 film is highly suspect, because the magnitude of the decay is very small.

Figure 7 shows the free urethane carbonyl absorbance at 1918 nm as a function of annealing time. For all films, an increase in free carbonyl absorption is observed until a total annealing time of 2 h is reached. After two hours of annealing, the free urethane carbonyl absorption decays in a manner similar to that of the free urea carbonyl absorption (Fig. 6). This result suggests two different mechanisms occurring for urethane groups in PEUU copolymers during annealing. The parameters obtained from the fit of two exponentials to these annealing profiles are shown in Table II. These parameters indicate that the faster process has a rate constant of approxi-

TABLE I. Estimated and observed positions of second-overtone carbonyl bands for PEUU copolymers.

Group	Observed wavelength (nm)	Estimated wavelength[a] (nm)
Free urea carbonyl	2036	2020
Hydrogen-bonded urea carbonyl	2054[b]	2034
Free urethane carbonyl	1918	1922
Hydrogen-bonded urethane carbonyl	1980[b]	1960

[a] Calculated as 3 times the frequencies of assigned IR bands (Ref. 5).
[b] Denotes bands corresponding to specific hydrogen bonds in bulk model compounds.

TABLE II. Results of exponential fits to 100°C annealing profiles.

2036 nm absorbance : fit function = $A \times \exp(-k_1 t)$
1918 nm absorbance : fit function = $B \times (1 - \exp(-k_2 t))$
$+ C \times \exp(-k_3 t)$

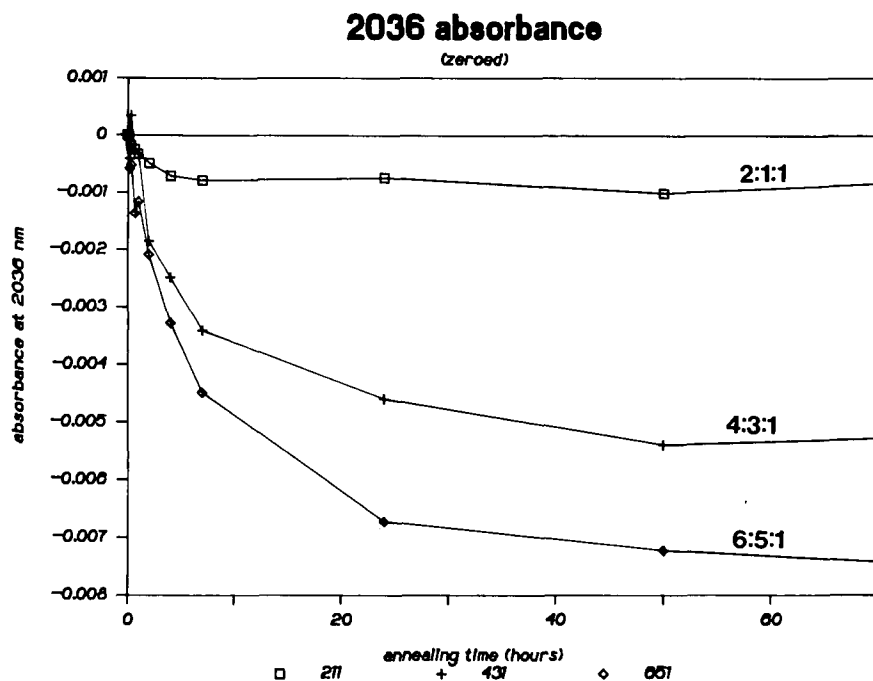| Parameter	PEUU sample		
	2:1:1	4:3:1	6:5:1
A	0.00084	0.0053	0.0069
k_1 (h⁻¹)	0.44	0.17	0.14
B	0.0072	0.020	0.011
k_2 (h⁻¹)	0.53	0.48	0.48
C	0.016	0.031	0.024
k_3 (h⁻¹)	0.14	0.20	0.13

FIG. 6. Absorbance at 2036 nm vs. annealing time at 100°C for all three PEUU copolymer films. The absorbance at time zero is arbitrarily set to zero for each sample.

mately 0.5 h^{-1}, and shows no pronounced trend with composition. The slower process (with a rate constant of 0.13 to 0.2 h^{-1}) is of larger magnitude than the faster process and shows no obvious trend with composition.

It should be noted that the A, B, and C parameters are subject to significant errors because of the uncertainty of film thicknesses and unknown degrees of phase mixing of the polymers before annealing. Smaller errors in the rate constants (k_1, k_2, and k_3) might arise from high overlap of individual absorbances that change with annealing. In this work, it is assumed that the absorbances at 1918 and 2036 nm are affected only by changes

in the free urethane carbonyl and free urea carbonyl content, respectively.

The exponential fit data in Table II suggest that three different structural processes occur as a result of annealing at 100°C. Solution-cast PEUU copolymers are assumed to be mostly phase separated, because of the high affinity of hydrogen-bond donors (N-H groups) in the hard-segment blocks towards hydrogen-bond acceptors (carbonyl groups) in the hard-segment blocks. However, a substantial amount of phase mixing, characterized by hydrogen-bonding interactions between N-H groups in the hard segment and ether oxygens in the soft seg-
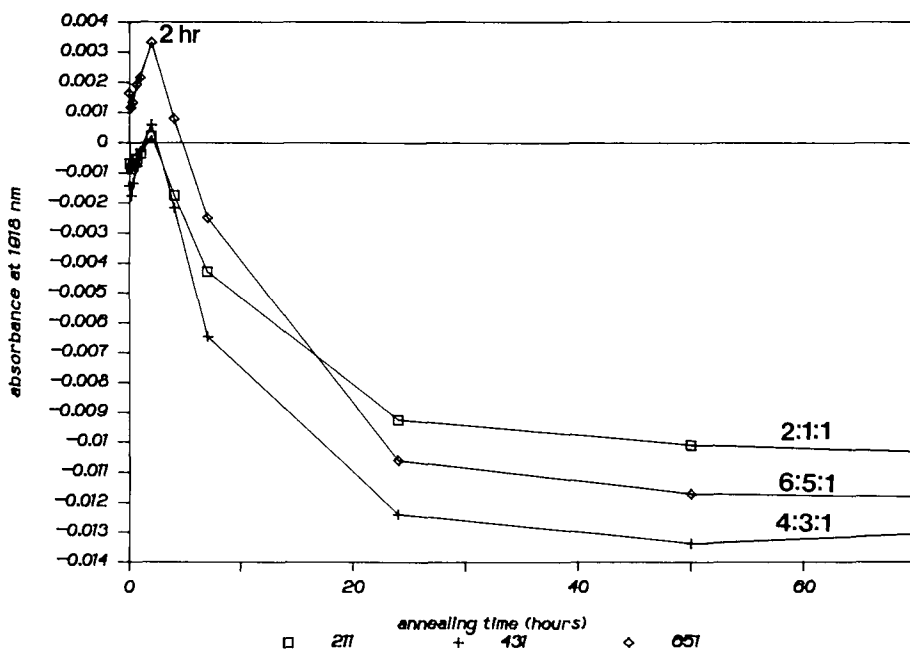

FIG. 7. Absorbance at 1918 nm vs. annealing time at 100°C for all three PEUU copolymer films.

ment, might be present. At the higher temperature used for annealing, the polymer chains can undergo substantial rearrangements that enhance phase separation by eliminating impurities in each of the phases and by maximizing hydrogen-bonding interactions in the hard-segment phases.

The annealing trend of the 2036-nm absorbance, described by A and k_1, indicates a continuous decrease in the free urea carbonyl content with annealing. This trend is consistent with a phase separation mechanism in which free urea carbonyl groups in the soft-segment phase become hydrogen-bonded to N-H groups in various hard-segment portions of the polymer. It is most likely that urea groups hydrogen-bond to each other to form hard-segment domains.

The faster trend of the 1918-nm absorbance, described by B and k_2, indicates an increase in the number of free urethane carbonyl groups with annealing. This trend is also observed in the infrared spectra of these polymers.[18] Although this result might seem anomalous, it should be noted that the urethane groups are only situated at the boundaries of hard- and soft-segment blocks in the polymers. Therefore, it is possible that as urea-urea hydrogen bonding between hard segments increases, several urethane groups at the phase boundary are forced into the soft-segment phase. This process would cause an increase in the free urethane carbonyl, because no hydrogen-bond donors exist in the soft-segment phase. Diffusion of soft-segment impurities from hard-segment domains could also explain this trend, because this process would cause expulsion of urethane groups from the interiors of hard-segment domains. Studies by Blackwell et al.[19,20] indicate that rigid hard-segment domains are present in similar polyurethane systems. If such a rigid hard-segment system is present in these polymers, it is expected that hydrogen bonding between groups at the interior of hard-segment domains is maximized, but groups at the phase boundary might be isolated in the soft-segment phase.

The slower trend of the 1918-nm absorbance, described by C and k_3, is a decrease in the free urethane carbonyl content with annealing. This trend suggests that the hard-segment domains, once they are formed, can slowly move toward each other. This process would allow free urethane carbonyls at the edges of hard-segment domains to become hydrogen bonded to N-H groups of other hard-segment domains.

Another possible source of the slower trend in the 1918-nm absorbance is the desorption of water from the samples. It is unfortunate that water has a very strong absorbance band at 1920 nm,[12] which overlaps the free urethane carbonyl absorbance at 1918 nm. Although great care was taken to avoid water contamination of the polymer samples, a very small amount of water might have been present in the samples before annealing. If this was the case, desorption of water from the sample into the surrounding space in the sample cell (most of which is not sampled by the NIR spectrometer) would cause a decrease in absorbance at 1918 nm during annealing. However, the amount of water corresponding to the observed absorbance decrease at 1918 nm would be very small. As a result, if water desorption is responsible for the slower trend at 1918 nm, other annealing trends in the spectra can still be attributed to phase separation of the polymer. In this case, the NIR results would agree with IR annealing studies of these polymers,[18] which indicate only an increase in the free urethane carbonyl absorbance with annealing.

It should be mentioned that the molecular interpretation presented here is one possible model that explains the trends in the NIR spectra. Further information from annealing studies at different temperatures, from FT-IR spectroscopy, and from x-ray diffraction is necessary in order to obtain more detailed information about the annealing process.

CONCLUSIONS

NIR spectroscopy can be used to perform rapid analyses of bulk polymers. This analysis suggests that NIR spectroscopy can characterize the degree of phase separation in PEUU copolymers and can therefore provide an accurate assessment of physical properties of these polymers. The NIR spectra indicate the presence of several structural changes that occur with annealing, but further information is required in order to fully characterize these trends.

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