Table II
Effect of Cation on the T_g of Partially Neutralized Ethylene/Acrylic Acid Copolymer

% cation concn in ionomer	β-relaxation T_g, °C	
	E′ basis	E″ basis
0	~0	-5
Ca	-24, 42	-15, 47
Mg	-30, 45	-20, 27
50	-15, 45	-13, 46
Zn	-25, 43	-18, 40
Na	-10, 39	-31, 35

and an amorphous phase of randomly mixed E and AA segments (DMA, T_g = 0 °C). Upon partial neutralization, part of the AA moieties are converted into ionic salts and these form aggregates. Depletion of free AA segments from the initial amorphous phase produces a lower T_g while simultaneously giving rise to a higher T_g due to the phase containing ionic aggregates. In the fully neutralized E/AA copolymer, the amorphous phase has no free AA units, and thus, a T_g results corresponding to the ethylene amorphous phase ($T_g \simeq -30$ °C). Simultaneously, however, another phase develops which is rich in ionic clusters, and this accounts for the higher T_g.

Finally, we wish to comment that we have only dealt with a low molecular weight (waxy) material in this work and the relaxation patterns may be quite different in a similar copolymer of high molecular weight.[15]

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Spectroscopic Analysis of Phase-Separation Kinetics in Model Polyurethanes

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Introduction

Because of their incompatible structural components, segmented polyurethanes mainly exist as phase-separated systems. The degree of phase separation as reflected in the size and perfection of the domains is the most important criterion for the determination of overall sample mechanical properties.[1-3] Although phase-separation kinetics of polymer mixtures have been active areas of study,[4-6] few investigations have been carried out to characterize the phase-separation kinetics of polyurethane block copolymers.[2,7,8] Not only is the characterization of the phase-separated structure present in segmented polyurethanes important from a practical standpoint, but also the mechanism associated with the phase separation is extremely interesting from a fundamental viewpoint as well. The connectivity between the components, the effects of chain stiffness, and the polydispersity of the hard or soft segments are all important parameters and need to be examined in greater detail in order to understand more fully the phase-separation mechanism.

In this study we have characterized the phase-separation behavior of well-defined polyurethanes consisting of the reaction product of methylenebis(*p*-phenyl isocyanate) (MDI) and butanediol (BD) as the hard segments and poly(propylene oxide) (PPO) as the soft segment. The success in utilizing vibrational spectroscopy for the study of phase separation depends on the existence of bands sensitive to mixed and phase-separated states. In a previous study,[9] we assigned spectroscopic features characteristic of urethane linkages dispersed in the soft segments as compared to interurethane hydrogen bonding confined to hard-segment domains. With a specially designed sample cell, we were able to trap a phase-mixed structure at a temperature 60 °C below the glass transition temperature of the soft segments. When this quenched sample was brought up to a higher temperature, the increase of one spectroscopic component and the corresponding decrease of the other provided a direct measurement of phase-separation kinetics.

In this paper, we report the initial findings associated with a well-defined model polyurethane. The phase separation behavior has been interpreted to proceed by a nucleation and growth mechanism with a two-dimensional growth initially, followed by a diffusion-dominated mechanism. Additional studies for the entire family of model polyurethanes will be published separately.

Experimental Section

The model polyurethanes containing monodisperse hard and soft segments used in this study have been characterized extensively.[10] The sample used in this study contains three MDI units per hard segment. All the infrared spectra were obtained with an IBM Model 98 vacuum Fourier transform infrared spectrometer. We built a "purge box" to allow ease in sample access by keeping the sampling area at atmospheric pressure and constantly purged it with boiled-off nitrogen gas. Polyurethane samples used for this infrared study were dissolved in THF (2% w/v) and then casted onto AgCl windows. After drying overnight at atmospheric pressure, the casted films were then dried in a vacuum oven for 24 h at room temperature. Finally the films were annealed at 60 °C for an additional 24 h.

As described earlier,[9] one of the most critical components in this experiment is our ability to cool the sample very rapidly. The sample in the beam area can be cooled from the molten phase (~130 °C) to -100 °C in less than 30 s. As before, we have assumed that the sample quenched from the melt is essentially phase mixed.[9] To ensure as much phase mixing as possible, the polyurethane sample was kept at 130 °C for approximately 10 min. When the sample temperature is raised above the soft segment T_g, the basically incompatible hard and soft segments phase separate.[9] Spectra in the 1700-cm^{-1} region, obtained at various annealing times at 10 °C, are shown in Figure 1. Spectral resolution is maintained at 2 cm^{-1} for all studies. Although there are multiple bands of interest in this region, we have not carried

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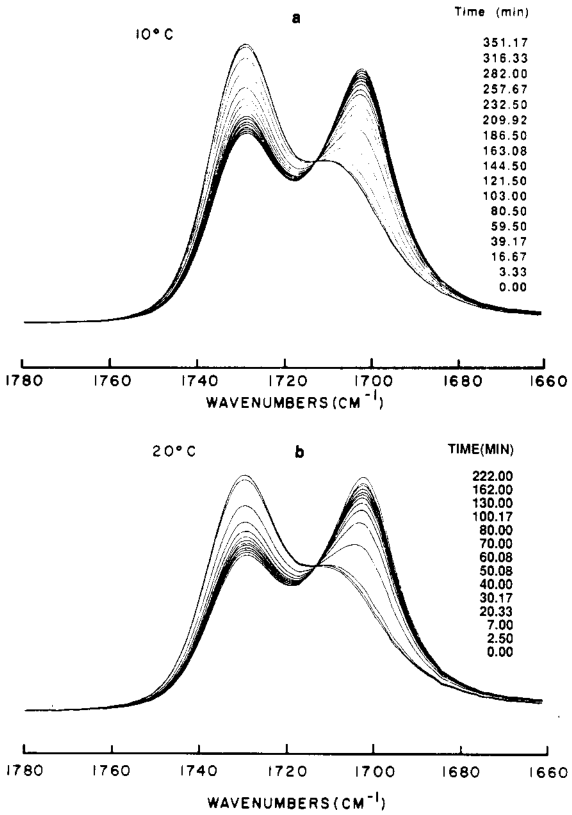

Figure 1. Changes observed as a function of time for the C=O stretching region (1700 cm^{-1}): (a) 10 °C; (b) 20 °C.

out band deconvolution because of uncertain band widths, inherent extinction coefficients, and the number of components present.[11,12] In this study, it is assumed that band height measurements can be used to represent the changing band intensity as a function of time without significant error. When more reliable band assignments become available, band deconvolution procedures may become meaningful.

Results and Discussion

The utility of using a spectroscopic technique to measure phase-separation kinetics depends very much on the ability to identify bands which are characteristic of the homogeneous state on the one hand and the phase-separated state on the other. It is generally accepted that the N–H stretching vibration in the 3300-cm^{-1} region is the one most sensitive to the hydrogen-bonding distribution in polyurethanes. However, in most observations, the usually complex broad features of this band cannot be easily analyzed. In our previous study,[9] we assigned the 3295-cm^{-1} component to the N–H stretching vibration associated with the N–H - - - -O– hydrogen bond as it is only observed in the quenched polyurethane sample maintained below the soft segment T_g and thus represents the phase mixed state. Although not observed in our quenched sample, the "free" component is usually observed at ~3450 cm^{-1}.[13,14] In most cases, the hydrogen-bonded component is observed at ~ 3330 cm^{-1}.[13,14] In our study, when the sample temperature was raised, the N–H- - - -O– band diminished in intensity and was replaced by the 3330-cm^{-1} band generally associated with N–H bonded to carbonyls. Although most observed bands can be assigned, quantitative analysis of the hydrogen bonds formed by using the N-H stretching band is complicated by the significant band overlap which may result from the large differences in the inherent extinction coefficient as a function of hydrogen bond strength.[13,14]

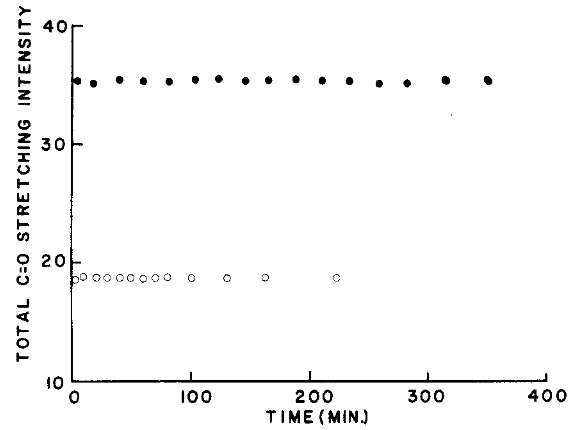

Figure 2. Integral intensity of the bands in the 1700-cm^{-1} region as a function of time: 10 °C (top); 20 °C (bottom).

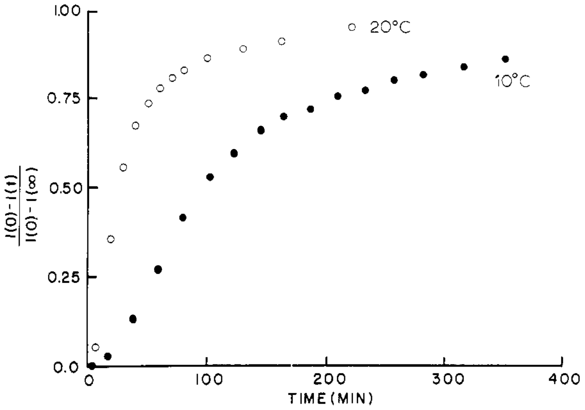

Figure 3. Decrease in the 1735-cm^{-1} component as a function of time and temperature: 20 °C (top); 10 °C (bottom).

In the 1700-cm^{-1} region, we observed two clearly resolved bands, one at 1735 cm^{-1} associated with the free C=O stretching vibration and the other at 1705 cm^{-1} associated with the hydrogen-bonded C=O stretching vibration. In the quenched sample, the dominant component is at 1735 cm^{-1}. When the sample temperature is allowed to rise, a decrease of the 1735-cm^{-1} component occurs with a corresponding increase in the 1705-cm^{-1} component as a function of time. If we accept that the quenched sample represents a phase-mixed state, then most N–H's are bonded to the ether oxygens, as expected from sample composition.[9] We should also expect a substantial number of carbonyl groups to be free from hydrogen bonding in the quenched sample before phase separation is allowed to occur. This is precisely the case as shown in Figure 1. The overall integral intensity of the two components is independent of time at a given temperature, as shown in Figure 2. The interconversion between the two principal components is considerable and can be analyzed. Because of this, the C=O stretching vibration is a suitable band for estimating the amount of hydrogen bonding present at a given time and for following the phase-separation kinetics because its inherent extinction coefficient remains relatively constant. It should be emphasized that our measurements are taken at a constant temperature, thus eliminating many of the temperature-induced spectroscopic effects.

The time dependence of the fractional decrease of the free C=O stretching vibration at 1735 cm^{-1}, using the intensity of the observed C=O stretching components as a measure of structural change, is shown in Figure 3. Even though the shape is slightly distorted at a later time, the overall sigmoidal profile for the isothermal phase separa-

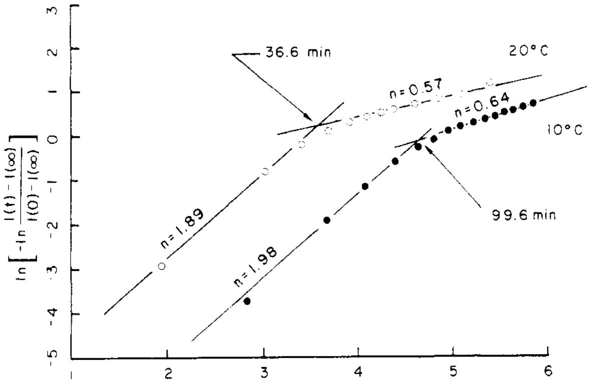

Figure 4. Avrami plot of the intensity observed for the decrease of the 1735-cm^{-1} component as a function of time and temperature. The lines drawn are fitted to the data shown.

tion behavior in this model polyurethane is very similar to the crystallization isotherm. There are no established mechanisms which can be used to explain the phase separation of copolymers. One of the possibilities is the spinoidal decomposition cited which occurs in polymer blends at the early stages of phase separation.[15-17] However, our data are not consistent with the Cahn–Hilliard expression.

As an alternative, we can model this phase-separation process as one of nucleation and growth. However, the meaning of the nucleus may not correspond to the crystallites in the usual sense. There is virtually no information regarding the crystalline structure in polyurethanes. In our case the nucleus may simply be aggregates of hard segments in the homogeneous molten phase. Then the decrease of the hard segments dispersed in the soft domains can be expressed as

$$M_t/M_0 = 1 - \lambda(1 - \exp(-zt^n)) \qquad (1)$$

where M_t and M_0 are the hard segment concentrations in the soft domains at time t and $t = 0$, respectively, and λ is the equilibrium weight fraction of hard segment in the hard-segment domains. Since the spectroscopic intensity measurements are associated with the volume fraction, eq 2 is more appropriate for analyzing the data

$$\frac{M_t - M_\infty}{M_0 - M_\infty} = \frac{I(t) - I(\infty)}{I(0) - I(\infty)} = \exp(-zt^n) \qquad (2)$$

where $I(t)$, $I(0)$, and $I(\infty)$ are the intensities associated with the free carbonyl component at time t, at $t = 0$, and after equilibrium has been achieved. This equation can be plotted by using standard conventions:

$$\ln\left[-\ln\frac{I(t) - I(\infty)}{I(0) - I(\infty)}\right] = \ln Z + n \ln t \qquad (3)$$

From Figure 4 it is clear that the phase-separation mechanism is changing as a function of time. The lines in Figure 4 have been obtained by a linear regression fit to the data. It is possible to interpret the "dimensionality" of the growth process as 2 in the early stage. In the infrared spectrum obtained for the quenched sample the 1705-cm^{-1} band can be observed next to the 1735-cm^{-1} band. We interpret the residual nuclei or aggregates which contribute to the 1705-cm^{-1} band to be associated with inhomogeneous mixing even in the molten state. Because of hydrogen bonding, there is strong anisotropic interaction between the hard segments. Therefore, the coefficient $n = 2$ can be explained by heterogeneous nucleation and two-dimensional growth in a cylindrical fashion as shown schematically in Figure 5. The hard segment domains are in the order of several hundred angstroms, fairly small in comparison to the overall sample thickness. Therefore, the "Avrami" coefficient is not strongly affected by the experimental geometry associated with the infrared technique. Even for these well-defined model polyurethanes, there may still be a very small amount of unreacted model hard segments. We do not expect the unreacted hard segments to affect the overall phase-separation behavior.

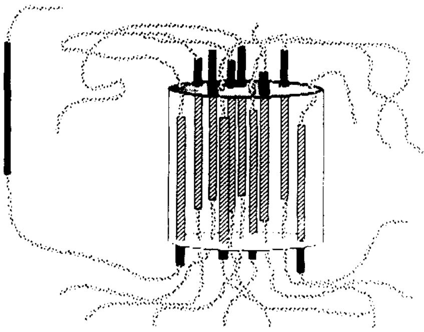

Figure 5. Schematic drawing of the growing hard-segment domain associated with a nucleation and growth mechanism.

The changing time dependence of phase separation is extremely interesting. The overall volume fraction of the hard segments in the polyurethane is approximately 30%. When phase separation starts to occur, the regions around the nuclei become depleted in hard segment content which makes it difficult for additional hard segments to reach the surface of the nuclei. On this basis, the change in dimensionality from 2 to 0.6 can be assigned to a diffusion-dominated mechanism operative at the later stages of phase separation.

In summary, we have used a spectroscopic technique to follow the phase-separation kinetics of a model segmented polyurethane. Additional experimental studies involving hard segments of different length and/or polydispersity will be reported in a separate publication. A detailed theoretical interpretation of the data remains to be developed.

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Communications to the Editor

Transition of Polystyrene in Cyclohexane from the Θ to the Collapsed State

The coil-to-globule transition has been a fascinating and fundamental problem in dilute polymer solution physics and can be classified as one of the experimental challenges in light-scattering spectroscopy. We have worked on this problem starting in the late 1970s and our experiments have encountered different stages of development.[1-5] Now, we have finally achieved our aim in reaching the globule state of polystyrene in cyclohexane based on the hydrodynamic radius. The essential experimental findings are presented in this paper, leaving the details to a later article.

The challenge can be subdivided into several standard experimental procedures: materials, solution preparation, and instrumentation as well as information on the thermodynamic state of the polymer solution under investigation. We often consider polystyrene (PS) as one of the best characterized model polymer coils with an accessible narrow molecular weight distribution (MWD), and high molecular weight PS samples are available commercially on the market (e.g., sources such as Toyo Soda, Polyscience, Pressure Chemical). What we need is an ultrahigh molecular weight PS polymer with $M_\mathrm{w} > 10^7$ g/mol and $M_\mathrm{w}/M_\mathrm{n} \leq 1.03$. None of the commercial sources could satisfy our requirements. We obtained the last of the 44 million PS sample prepared by L. Fetters, and through courtesy of H. Fujita, PS samples from the Japan Synthetic Rubber Co. The special PS samples also showed possible degradation or revealed polydispersities beyond the acceptable range for our experiment. Finally, an IK-3000 PS sample from the Japan Synthetic Rubber Co. was fractionated by Professor Ju Zuo over a period of close to 1 year. The fractionation had to be performed extremely slowly in order to be effective. With final fractions recovering only microgram quantities of high molecular weight PS samples. It should be interesting to note that although our starting material had $M_\mathrm{w} = 2.3 \times 10^7$ g/mol with $M_\mathrm{w}/M_\mathrm{n} \approx 1.2$ as reported by the manufacturer, we characterized the same PS polymer and found $M_\mathrm{w} = 2.35 \times 10^7$ g/mol with $M_\mathrm{w}/M_\mathrm{n} \approx 2.1$. The final fractions we used had $M_\mathrm{w} = 4.83 \times 10^7$ g/mol and were fractionated from the IK-3000 PS sample.

Ultrahigh molecular weight PS polymers are subject to shear and thermal degradation. Oxygen had been excluded from the fractionation and solution preparation steps. The temperature was maintained only slightly above the Θ temperature during dissolution. The polymer solution was never filtered for fear of shear degradation. Cyclohexane was filtered and made dust free directly in the light-scattering cell, which was a component of an integrated filtration circuit.[6] Small-angle light-scattering experiments could not have succeeded without such a closed filtration/dilution circulation system for solvent/solution clarification. We tried to prepare the stock polymer solution as clean as possible before its dilution by a factor of 10^3–10^4 in the filtration circuit containing dust-free cyclohexane. The excess dilution was another factor in achieving the preparation of a dust-free ultrahigh molecular weight polymer solution. To avoid shear degradation, the introduction of the polymer solution in the filtration circuit (but bypassing the filters) took a few hours.

With the ultrahigh molecular weight polymer solution, measurements of the angular distribution of solution scattered intensity and the corresponding Rayleigh line width need to be performed at small scattering angles satisfying the condition $KR_\mathrm{g} \leq 1$. This requirement cannot be met by commercial light-scattering spectrometers and translates into the need to construct a new small-angle light-scattering instrument which was perceived in the late 1970s. Furthermore, we were interested in designing an efficient spectrometer with high beating efficiency and the light-scattering cell should require only a small volume of fluid as we anticipated in advance that ultrahigh molecular weight PS samples were going to be precious and difficult to come by. After an initial demonstration,[7,8] we have now succeeded in adapting the prism light-scattering spectrometer[6] to perform light-scattering measurements for polystyrene in cyclohexane in the collapsed regime. It is sufficient to mention here that the spectrometer has a scattering angular range of $2° \leq \theta \leq 120°$ and a beating efficiency (b) of 0.9 at small scattering angles, with the theoretical limit being $b = 1$. The intensity–intensity time correlation function $G^{(2)}(K,\tau)$ has the form

$$G^{(2)}(K,\tau) = A(1 + b|g^{(1)}(K,\tau)|^2) \qquad (1)$$

where A is the base line, b is the coherence factor and represents a measure of beating efficiency, and $|g^{(1)}(K,\tau)|$ is the normalized electric field correlation function with $b|g^{(1)}(K,\tau)|^2$ $[\equiv G^{(2)}(K,\tau)/A - 1]$ being the net intensity correlation function.

Figure 1 shows a plot of $G^{(2)}(K,\tau)/A - 1$ versus τ for a fractionated PS in cyclohexane measured at 35 °C and $K^2 = 4.9 \times 10^8$ cm^{-2}. The solid line denotes $G^{(2)}(K,\tau)/A - 1 = 0.0028 \exp(-17.4\tau)$ with the delay time τ expressed in seconds. In Figure 1, we have noted three significant features. (1) The net intensity time correlation function can be fitted by using a single-exponential function, revealing that our PS fraction has a polydispersity index beyond the resolution of the dynamic light-scattering spectrometer. If we were to use a cumulants fit, $\mu_2/\bar{\Gamma}^2 \approx 0.006 \pm 0.004$ with $\mu_2 = \int G(\Gamma)(\Gamma - \bar{\Gamma})^2 \, \mathrm{d}\Gamma$ and $\bar{\Gamma} = \int \Gamma G(\Gamma) \, \mathrm{d}\Gamma$, $G(\Gamma)$ being the normalized characteristic line-width distribution. Such a PS fraction with $M_\mathrm{w} = 4.83 \times 10^7$ g/mol represents the highest narrow MWD sample ever prepared. (2) With $b \approx 0.86$, an intercept of 0.0028 represents that the ratio of PS scattering to the solution scattering is about 0.057. Measurements of polymer solution with an excess scattering intensity of 6% of the

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