

Study of Domain Structure in Linear and Crosslinked Polyurethanes Using Pulsed Proton NMR*

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Synopsis

Pulsed proton magnetic resonance was used to study the domain structure of a series of polyurethanes which had been crosslinked to various degrees at 210°C. The difference between segmental mobility of the hard and soft phases decreases with crosslinking. The fraction of rigid segments in the linear material decreases in two distinct stages as the temperature increases, while the fraction of rigid segments in the crosslinked material decreases in a continuous fashion as the temperature increases. Crosslinking also decreases the rate of domain formation following thermal treatment. These effects are attributed to the inability of the segments in the crosslinked material to completely segregate into domains.

INTRODUCTION

Polyurethanes are segmented (short-block) copolymers composed of soft rubbery segments joined by hard glassy segments containing urethane linkages. Because the two types of segments are typically incompatible at the use temperature, the material often undergoes microphase separation, with the resultant formation of soft and hard domains. Many of the thermal and mechanical properties of polyurethanes can be understood in terms of this domain structure. The hard domains, which generally contain strong dipole-dipole interactions and are hydrogen bonded, act as fillers or virtual crosslinks in the material and increase its modulus. While many studies have focused on the effects of hard- and soft-segment chemistry and on the nature of domain textures,¹⁻⁷ there have been few studies on the influence of chemical crosslinking on the physical properties of segmented polyurethanes.⁸⁻¹¹ In this study, we examined the microscopic dynamical properties of a series of polyurethanes with varying crosslink densities.

The polyurethanes used in this study have been recently characterized by Ophir and Wilkes.^{10,11} The polyurethanes were crosslinked at elevated temperatures where the hard and soft segments are mixed to a substantial degree. By examining the materials with small-angle x-ray scattering (SAXS), differential scanning calorimetry, and stress-strain techniques, they were able to correlate time dependent mechanical behavior with structural changes. They established that crosslinking prevents complete phase separation in quenched samples and that the domain structure which does form is more easily disrupted at elevated temperatures. The rate at which domains are formed after quenching decreases as the degree of crosslinking increases.

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In this study, we examined the microscopic dynamical properties of these polyurethanes by pulsed proton magnetic resonance. The rate at which a proton signal decays depends on the mobility of the segments containing the protons. The proton-free induction decay of polyurethanes consists of a fast component from the glassy domains and a slow component from the rubbery or soft domains.^{12,13} Thus, proton magnetic resonance can establish when a polyurethane has separated into domains and determine the relative amount of material in each domain.

The difference between the hard- and soft-phase mobilities at room temperature was found to decrease with crosslinking. Moreover, the temperature behavior revealed that the mobilities of segments in separate domains are relatively independent of each other in a linear polyurethane, while the mobilities of segments in separate domains are closely coupled in a crosslinked polyurethane. The rate of recovery of the domain structure after annealing decreases as the degree of crosslinking increased. Each of these observations on the microscopic dynamical properties was consistent with the study of Ophir and Wilkes, which showed that the segments were in a mixed state when the material was crosslinked and that crosslinking under those conditions prevented complete phase separation from occurring.

EXPERIMENTAL

Instrumentation

The proton-free induction decay measurements were made on a Bruker SXP broadband spectrometer operating at 100 MHz in the phase-sensitive detection mode. The external field was that imposed by a Varian V-3800-1 high-resolution magnet stabilized by a ¹⁹F external lock. The decays were captured by a Biomation 610 transient recorder at a 1-MHz digitization rate. A PDP-11/34 computer was used to accumulate and numerically analyze the decays.

Materials

The materials used in this study were based on a single linear polyester urethane crosslinked by different weight percentages of peroxide, see Table I. The hard segments contained *p,p'*-diphenylmethyl diisocyanate and 1,4-butanediol. The soft segment was poly(tetramethylene adipate) glycol (MW ca. 1100). The diisocyanate, diol, and glycol were mixed and "melt reacted" randomly to yield a polyurethane containing 30 wt % hard segments (30 wt % diisocyanate and diol). Next, a conventional aromatic organic peroxide was mixed into the polymer, and the films were then compression molded at 210°C for 10 min while curing took

TABLE I
Important Characterization Parameters of ESX Series of Segmented Urethane Films

Peroxide	0.0 wt % (ESX 0.0)	0.5 wt % (ESX 0.5)	1.0 wt % (ESX 1.0)	2.0 wt % (ESX 2.0)
Swelling in DMF, %	soluble	275	205	165
Young's modulus, MPa, (aged at ambient for several days)	12.8	11.5	10.3	7.2

place. Four samples were prepared in this way: ESX 2.0 (contains 2.0% peroxide by weight), ESX 1.0, ESX 0.5, and ESX 0.0 (contains no peroxide). The exact location of the induced covalent crosslinks is not known, but it is expected that they will likely occur between similar as well as between dissimilar segments. The data to be discussed indirectly support this view.

The films were swelled in dimethylformamide (DMF) to obtain a measure of their crosslink density. Table I shows that, as expected, the crosslink density increases as the peroxide content increases. Also shown in Table I are the Young's moduli of aged films obtained by stress-strain measurements. Although classical rubber elasticity theory predicts an increase in modulus for an increase in crosslink density, for these films the modulus is seen to decrease as peroxide content increases. This behavior has been discussed previously^{10,11} and, as will be seen in this work, is related to the decrease in domain formation with increasing peroxide content.

Procedure and Analysis

The homogeneity and strength of the magnetic field were frequently adjusted on a water sample. Sixteen free induction decays, using a 5- μ s, 90° pulse, were collected at repetition rates varying from 1 to 4 s. A nonlinear least-squares fit of the form

$$M(t) = M_f e^{-t/T_{2f}} + M_s e^{-t/T_{2s}} \quad (1)$$

was then applied to the data, where $M(t)$ is the magnetization as a function of time, M_f and M_s are the initial magnetizations of the fast and slow components, and T_{2f} and T_{2s} are the spin-spin relaxation times of the fast and slow components. The root-mean-square deviation of the experimental points from the theoretical fit was typically 0.5 to 1.0 % of the initial magnetization.

The initial magnetizations of the fast and slow component, M_f and M_s , are proportional to the number of hydrogens in the hard and soft phases, respectively. The spin-spin relaxation times increase in a complex way as the mobility of the corresponding hard and soft segments increase.¹⁴ Thus, T_{2f} and T_{2s} are related to the mobility of segments in a particular phase. In previous studies,^{12,13} we used a Gaussian function to describe the rapidly decaying component. The Gaussian function is a good approximation for the decay of a material whose nuclear dipoles are fixed rigidly in space while an exponential decay is observed for motionally narrowed materials.^{15,16} As will be seen, the hard phase exhibits significant mobility when the polyurethane is chemically crosslinked. Thus, although the early part of the linear material's free induction decay is fit marginally better by a Gaussian function, the early part of the crosslinked material's free induction decay is fit significantly better by an exponential function. In order to make meaningful comparisons between the linear and crosslinked materials, an exponential function was used for the rapidly decaying component of all materials.

The frequency by which a hydrogen's dipole-dipole interactions are perturbed determines whether that hydrogen contributes to the fast or slow component of a decay. For typical polymers, the characteristic frequency is near 10^4 Hz.^{16,17} This is several orders of magnitude above the characteristic frequencies of the scanning calorimetry and stress-strain techniques which were used by Ophir

and Wilkes in their study of these materials. Thus, it is expected that the transitions which are reported in this paper will be shifted to higher temperatures.

The kinetics of domain formation were measured by observing the material's free induction decay as a function of time after annealing. Samples were placed in a 0.7-cm-diameter tube and heated for 5 min in an oil bath at 170°C. Ophir and Wilkes have shown that the hard and soft segments are extensively mixed at this temperature. The samples were quenched in liquid nitrogen and then brought rapidly to 28°C in a water bath. Samples were found to reach equilibrium with the water bath in less than 2 min. After the sample had reached equilibrium, free induction decays were recorded as a function of time. For short times after annealing, the materials exhibited complex decays which did not appear to have a simple functional form. These decays undoubtedly represent a polyurethane whose segments have undergone extensive mixing. As the domains reform with time, the decays begin to take on a two component nature as described by eq. (1).

The progress of domain formation was quantified by defining T_2^+ as the time it takes for the magnetization of the annealed sample to reach $1/e$ of its initial value and T_2^0 as the time it takes for the decay of the original unannealed (well-aged) sample to reach $1/e$ of its initial value. The deviation from equilibrium is then $T_2^0 - T_2^+$, which approaches zero with time. Since T_2^0 depended on the crosslink density of the sample, a normalized deviation from equilibrium was defined as

$$\frac{T_2^0 - T_2^+}{T_2^0} \quad (2)$$

so that the behavior of the various samples could be compared.

RESULTS AND DISCUSSION

Free Introduction Decays

The free induction decays of ESX 0.0 and ESX 2.0 at 28°C are displayed in Figure 1. Only one experimental point in five is shown for clarity. The solid lines are nonlinear least-squares fits of the data using the two exponential function described by eq. (1). The two samples exhibit several notable differences. The initial portion of the ESX 2.0 signal decays less rapidly than the initial portion of the ESX 0.0 signal, indicating that crosslinking has led to an increase in mobility of the hard phase. The final portion of the ESX 2.0 signal decays more rapidly than the final portion of the ESX 0.0 signal, indicating that crosslinking has led to a decrease in mobility of the soft phase. As expected, the free induction decays of ESX 0.5 and ESX 1.0 exhibit characteristics intermediate to those observed for ESX 0.0 and ESX 2.0.

The spin-spin relaxation times and the fraction of hydrogens associated with the hard phase at 28°C for all of the samples as summarized in Table II. T_{2f} shows an increasing trend with crosslinking, while T_{2s} shows a decreasing trend with crosslinking. The ratio of the fast to slow relaxation times, T_{2s}/T_{2f} , is a measure of the difference in mobilities of the two phases. This difference is seen to decrease as crosslinking increases. Note that for a homogeneous material there

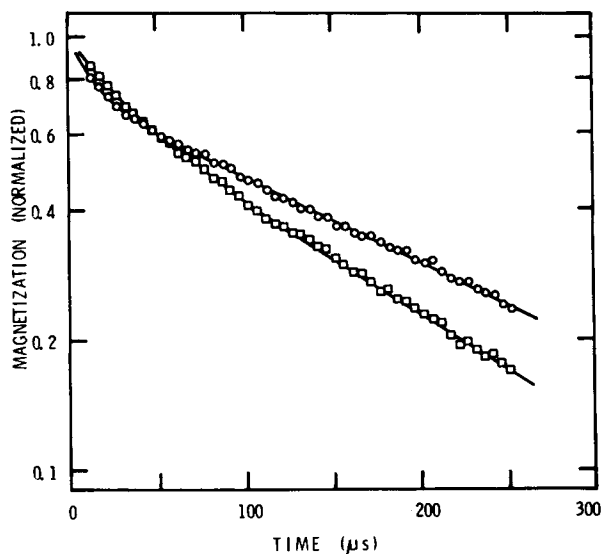


Fig. 1. Free induction decays of the linear (ESX 0.0) and crosslinked (ESX 2.0) polyurethanes at 28°C: (O) ESX 0.0; (□) ESX 2.0. Solid lines are least-squares fits of the form described by eq. (1).

would only be one relaxation time, and the ratio could be defined as 1.0. The fraction of hydrogens associated with the hard phase at 28°C appears to be relatively independent of crosslink density. We will see in the next section, however, that the temperature dependence of this fraction is different for different levels of crosslinking. Thus, at temperatures significantly above or below 28°C, the fraction of hydrogens associated with the hard phase does depend on crosslink density.

Crosslinking can affect a segmental polyurethane in two principal ways. First, crosslinking can cause a decrease in the mobility of segments in each phase analogous to the decrease in mobility observed when a single phase polymer is crosslinked.¹⁴ This would result in a decrease in both the hard- and soft-phase relaxation times. Second, crosslinking at elevated temperatures is expected to lead to less complete phase separation. Previous studies have shown that the hard and soft segments are mixed at elevated temperatures.^{12,18} If new constraints are introduced by crosslinking the material in a mixed state, then it is reasonable to assume that the ability of the segments to segregate would be impaired. The mobility of the hard phase would be increased because of the presence of flexible soft phase segments, while the mobility of the soft phase would be decreased because of the presence of rigid hard-phase segments. Such

TABLE II
Spin-Spin Relaxation Times and Fraction of Hydrogens Associated with Hard Phase at 28°C for Materials Crosslinked at Various Levels

Material	T_{2f} , μs	T_{2s} , μs	T_{2s}/T_{2f}	Rigid hydrogens, %
ESX 0.0	14.7	218.	14.8	26.2
ESX 0.5	16.2	187.	11.5	29.3
ESX 1.0	20.2	183.	9.1	27.4
ESX 2.0	32.6	175.	5.4	28.6

a mixed state would then result in a longer relaxation time for the fast component and a shorter relaxation time for the slow component.

A decrease in soft phase mobility with crosslink density is expected for both effects discussed in the preceding paragraph; thus, no conclusion can be drawn from the behavior of the soft-phase mobility. The hard-phase mobility increases with crosslink density, which is expected only if the second effect dominates. Thus, it appears that the increase in phase mixing caused by crosslinking is more important in determining phase mobility than is the simple increase in crosslink density. This result is analogous to the finding by Ophir and Wilkes that the Young's moduli of these materials after aging decreased with crosslink density contrary to what is observed for typical elastomers (see Table I). They concluded that crosslinks reduce the extent of phase separation and thereby disrupt the ability of the hard domains to effectively serve as a rigid filler or as physical crosslinks. Thus, the increase in phase mixing caused by crosslinking can affect both the microscopic and macroscopic properties of a polyurethane to a greater degree and in an opposite sense compared to changes normally associated with increases in crosslink density.

Temperature Behavior

The temperature behavior of the phase structure of the linear and crosslinked materials was compared by recording their free induction decays as a function of temperature. The initial magnitudes, M_f and M_s , of the fast and slow components correspond to the number of hydrogens in each phase. Figure 2 shows the fraction of hydrogens attributed to the hard phase as a function of temperature. Below -20°C , both phases are below their glass transition temperatures, and the entire signal decays rapidly. Above 80°C , both phases are above their glass transition temperatures, and the entire signal decays slowly. At inter-

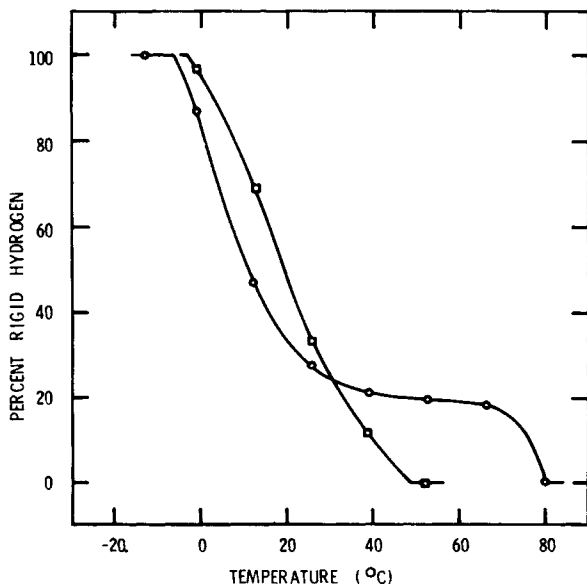


Fig. 2. Fraction of hydrogens attributed to the hard phase for the linear (ESX 0.0) and crosslinked (ESX 2.0) polyurethanes as function of temperature: (O) ESX 0.0; (□) ESX 2.0.

mediate temperatures, the two-phase nature of both materials is apparent. The behavior of the linear and crosslinked material in this intermediate range is quite different.

If the primary effect of crosslinking was to decrease the mobility of each phase, we would expect the curve for the crosslinked material to be similar in shape but shifted to a higher temperature compared to the curve for the linear material. We see, however, a qualitative difference in the shape of the curves with no overall shift of the crosslinked material's curve to a higher temperature. The soft phase of the linear material undergoes a transition at approximately 10°C, and its hard phase undergoes a transition at approximately 75°C. Between these two transitions, the fraction of hydrogens corresponding to the hard domains remains relatively constant. The crosslinked material does not exhibit distinct transitions for the hard and soft phases. Its fraction of hard-domain hydrogens decreases in a continuous fashion over a relatively small temperature interval.

We believe that these differences in temperature behavior are further evidence of the inability of the segments in the crosslinked material to segregate completely into two phases. The shift of the soft-phase transition to a higher temperature indicates that the crosslinked material does not contain regions which are as pure in soft-phase segments as does the linear material. At elevated temperatures, the situation is reversed. The crosslinked material becomes completely mobile approximately 30°C below the temperature at which the linear material becomes completely mobile. Thus, the crosslinked material does not contain regions that are as pure in hard-phase segments as does the linear material. The absence of a plateau indicates that the composition of the crosslinked material varies in a continuous fashion from regions rich in hard segments to regions rich in soft segments. These conclusions are supported by previously reported SAXS studies.^{10,11}

Kinetics of Domain Formation

Crosslinking may be expected to affect not only the equilibrium state of the material but also the rate at which the material approaches equilibrium. To study the kinetics of domain formation, we observed the materials as a function of time after subjecting the samples to the annealing and quenching procedure described earlier. Figures 3 and 4 show the free induction decays before annealing and as a function of time after annealing for the linear and crosslinked materials. The normalized deviation from equilibrium defined by eq. (2) in terms of effective relaxation times is shown in Figure 5 for the four materials of this study.

The materials appear to regain their phase structure on a short and a long time scale. The linear material recovers almost entirely on a short time scale and hence after 20 min is nearly completely recovered, as observed by the magnetic resonance technique. As crosslinking increases, the amount of recovery associated with the long time scale increases. Thus, for EXS 2.0, the normalized deviation from equilibrium defined by eq. (2) reaches 80% of its initial value after only 7 or 8 min but is still less than 90% of its initial value after 60 min. The short time-scale recoveries appear very similar for the linear and crosslinked materials. It is impossible to make a meaningful comparison of the rates of recovery for the long time-scale components because this component decays so slowly and rep-

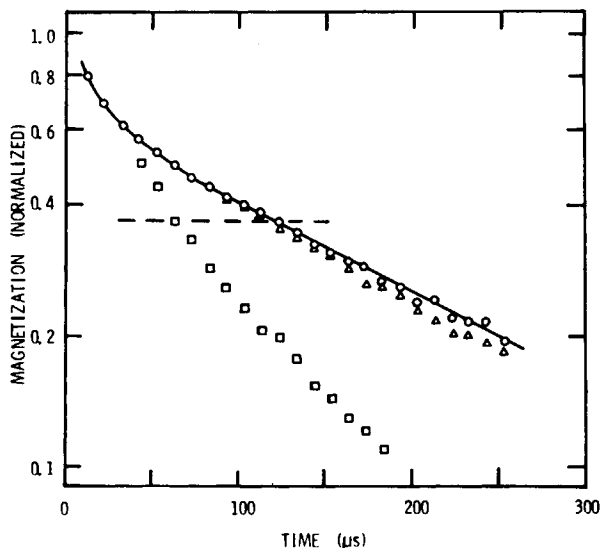


Fig. 3. Free induction decay of the linear polyurethane (ESX 0.0) before annealing and as function of time after annealing: (O) before annealing; (□) 120 s; (Δ) 1200 s. Dashed lines indicate the point at which the signal has decayed to $1/e$ of its initial value.

resents only a fraction of the total recovery. Although we cannot provide a physical interpretation for the short and long time-scale recoveries, we can conclude that high-temperature crosslinking reduces the overall rates at which the phase structures of these materials recover. This same trend is also observed by thermal, mechanical, and SAXS studies of these polymers.^{10,11}

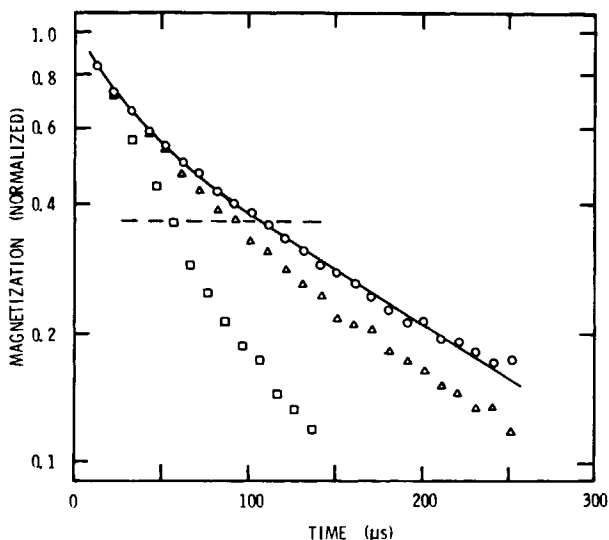


Fig. 4. Free induction decay of the crosslinked polyurethane (ESX 2.0) before annealing and as function of time after annealing: (O) before annealing; (□) 120 s; (Δ) 1200 s. Dashed line indicates the point at which the signal has decayed to $1/e$ of its initial value.

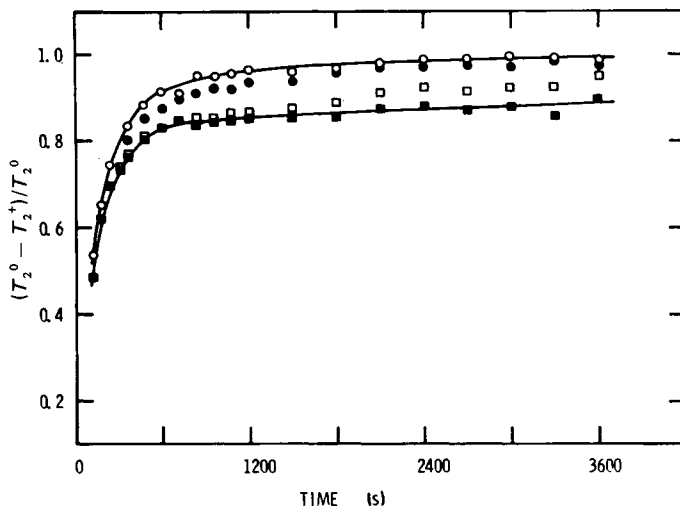


Fig. 5. Normalized deviation from equilibrium as function of time after annealing for the polyurethane crosslinked to various degrees: (○) ESX 0.0; (●) ESX 0.5; (□) ESX 1.0; (■) ESX 2.0.

CONCLUSIONS

Since mechanical properties depend so strongly on the material's phase structure, it is important to understand the various factors that can modify phase structure. An earlier study has shown that the domain size of a two-phase material can affect its properties.¹⁹ The segments in a material with large domains displayed independent transitions, while the segments in a material with small domains displayed transitions which were closely coupled. In this study, we found that crosslinking the material when the phases are in a mixed state at elevated temperatures impairs the ability of the material to regain complete phase separation at lower temperatures. The inability to attain complete phase separation was seen to have a major effect on the material's room-temperature properties, on the way the material behaves as a function of temperature and on the rate at which the domains reform after a temperature pulse. Analogous behavior is expected for network polyurethanes which are prepared by reactive molding, since crosslinks in such materials are induced at temperatures for which the domains are mixed.

The segments in a crosslinked polyurethane that displays incomplete phase separation were found to become completely mobile at a lower temperature than segments contained by a linear polyurethane that displays well-formed phases. This is expected to reduce the temperature for which the material retains its useful mechanical properties. It is interesting to consider whether crosslinking the material when its domains are well formed at room temperature could result in a material with a more stable domain structure. This is expected to increase the temperature for which the material retains its useful mechanical properties. Such materials are now being studied.

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