Mechanical Relaxations of Nylon–Polyurea Block Copolymers

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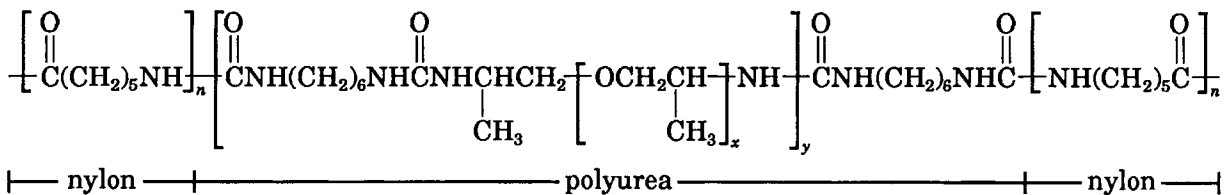
SYNOPSIS

Dynamic mechanical analysis from −150 to +150°C has been carried out on seven block copolymers that were prepared by the *in situ* anionic polymerization of caprolactam in the presence of a preformed polyurea. The various relaxations have been identified and activation energies calculated. Some polymer–polymer miscibility of the polyurea and amorphous nylon copolymer segments is indicated by the compositional dependence of the α relaxation.

INTRODUCTION

Although many nylon block copolymers have been reported in the literature, little work has been done on studying the mechanical relaxations and moduli of these copolymers. Van der Loos and van Geenen[1] determined the dynamic mechanical properties of a nylon 6 block copolymer with polyurethane segments based on poly(propylene oxide) at 0.2 Hz. Although composition of the copolymer was unspecified, the size of the copolymer β relaxation indicated a 70/30 composition. The block copolymer displayed two loss maxima; one at −62°C that was ascribed to the polyurethane glass relaxation and one at $\simeq$ 70°C due to the nylon glass relaxation. Hedrick, Gabbert, and Wohl[2] reported a series of nylon 6 block copolymers with a polyesteramide based on poly(propylene oxide). Over a range of 0–60% polyesteramide the α relaxation of 55–60°C due to the amorphous nylon segments did not appear to change with composition. This lack of an appearance of compositional dependence could be due to the extreme broadness of the α relaxation peak. At a concentration of 37% polyesteramide the α relaxation was too broad to accurately determine a relaxation temperature. This broadening could indi-

cate interphase mixing between the nylon and polyesteramide but an accompanying compositional dependence of the relaxation temperature would also be expected. The tan δ of the copolymer β relaxation due to the glass transition of the polyesteramide increased in magnitude but not width with increased amounts of polyesteramide. The temperature remained constant in the range of −60°C. Kurz[3] supplied more details about the dynamic mechanical properties of the polyesteramide copolymer including the fact that a frequency of 1 Hz had been used as the test frequency. The glass transition temperature of the polyesteramide portion of the block copolymer was the same as that of a polyesteramide homopolymer. A nylon–polybutadiene copolymer was reported by Borggreve and Gaymans.[4] The dynamic mechanical analysis was again done at a single frequency, 1 Hz in this case. The composition of the copolymer had an effect, though small, on the copolymer α relaxation temperature. Transmission electron microscopy showed some of the nylon to be encapsulated in the polybutadiene domains. The β relaxation was not affected by copolymer composition.

The copolymers described here were prepared by the *in situ* anionic polymerization of caprolactam in the presence of a hexamethylene carbamyl caprolactam terminated polyurea. The general structure of the block copolymers is shown below.

$$\left[\begin{array}{c}O\\\parallel\\C(CH_2)_5NH\end{array}\right]_n\left[\begin{array}{c}O\\\parallel\\CNH(CH_2)_6NHCNHCHCH_2\\|\\CH_3\end{array}\right.\quad O\quad\left.\begin{array}{c}O\\\parallel\\OCH_2CH\\|\\CH_3\end{array}\right]_x NH\left.\begin{array}{c}O\\\parallel\\CNH(CH_2)_6NHC\\\end{array}\right]_y\left[\begin{array}{c}O\quad\quad O\\\parallel\quad\quad\parallel\\NH(CH_2)_5C\end{array}\right]_n$$

|— nylon —|————————————— polyurea —————————————|— nylon —|

These copolymers, ranging from 0 to 40% polyurea, are designated as 100/0, 90/10, 80/20, 75/25, 70/30, 65/35, and 60/40. Since the copolymers were prepared as plaques in the presence of an activator in addition to the activator incorporated as end groups on the polyurea, composites of nylon–polyurea and nylon were formed. Previous work[5] has shown that the copolymers undergo phase separation during polymerization.

This paper describes dynamic mechanical studies of the relaxations and moduli of *in situ* polymerized nylon–polyurea copolymers. Accompanying insights into polymer–polymer miscibility are discussed.

EXPERIMENTAL

Preparation of Nylon–Polyurea Copolymers

The synthesis and characterization of reactants and copolymers have been described in detail.[5] The plaques were stored in a vacuum desiccator over calcium chloride until used. The copolymers were maintained in a dry condition and the concentration of residues was very low for all the copolymers. The crystallinities of the nylon portions of the copolymers ranged between 42 and 48%.

Preparation of DMTA Samples

The dry plaques were cut into 1.2 × 3.5 × 0.3 cm pieces and were affixed to a small wooden block. The samples were sliced to a thickness of 0.012–0.014 cm with a Reichert–Jung Polycut S microtome. Slicing was done from both sides of the sample to remove any possible skin effects. Final sample widths were in the range of 0.5–0.9 cm.

Dynamic Mechanical Analysis

Analysis was done with a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) in the single cantilever mode. A temperature range of −150 to +150°C and a heating rate set at 1°C/min were used with a nitrogen atmosphere. The DMTA operates extremely efficiently over the temperature range of −50 to +150°C with heating rates of 1°C/

min. Efficient operation was also obtained at lower temperatures; however, the heating rate could not be controlled at 1°C/min in the −150 to −100°C range. Rather, rates of 4 to 5°C/min were observed. These rapid heating rates, together with the difficulty in obtaining a good temperature equilibrium at −150°C, make less reliable the precision with which the nylon γ relaxation could be determined.

RESULTS

Frequency Effects on Loss Moduli

The loss and dynamic moduli of several nylon–polyurea copolymers (100/0, 90/10, 80/20, 75/25, 70/30, 65/35, and 60/40) have been determined over a temperature range of −150 to +150°C at six frequencies (0.3, 1, 3, 10, 30, and 100 Hz). Measurements of tan delta correlate with changes in loss moduli while the dynamic modulus E' was computed directly.

In Figure 1 are shown the temperature versus tan δ traces for the *in situ* polymerized copolymer 100/0 (nylon 6) at several specific frequencies. These curves are similar in appearance[6] to those usually obtained for nylon 6, regardless of the mechanical test method used. A progression of the α relaxation temperature from 69 to 87°C with increasing frequency from 0.3 to 100 Hz is seen. The β and γ relaxation temperatures also increase with frequency. The β progressively changes from −63 to −35°C and the γ from ≃ −125 to ≃ −105°C. All relaxation temperatures were obtained from the digital readouts. The reliability of the α temperatures is 1–2°C. Due to the broadness of the relaxations the variability in the β temperature is about 2°C. The low temperature γ relaxation is less reliable, in the range of ± 3–4°C, due to the broadness of the relaxation and the incapability of the DMTA to maintain a slow heating rate below −100°C.

The effects of frequency and temperature on the loss mechanisms in a typical nylon–polyurea copolymer, the 80/20 copolymer, are shown in Figure 2. The high temperature relaxation (i.e., the α relaxation), changes with frequency in a manner sim-
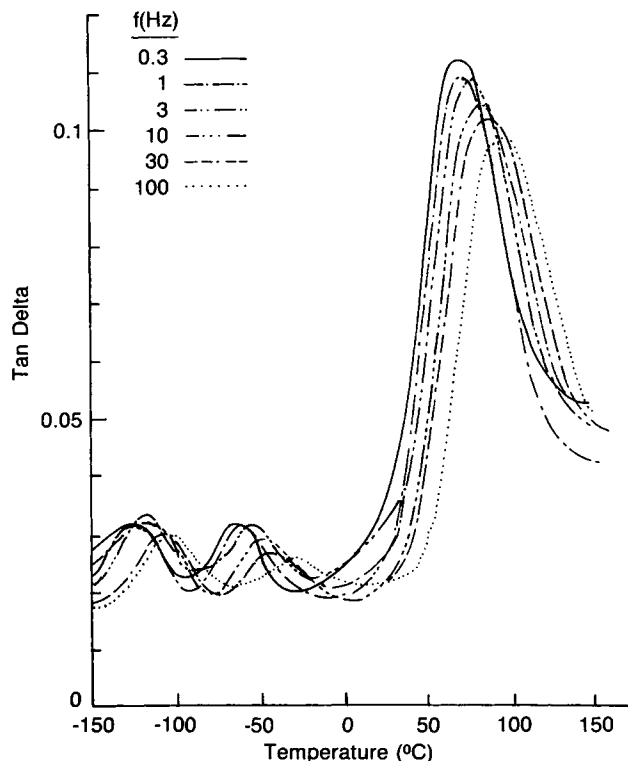
Figure 1 Tan δ of nylon–polyurea 100/0 as a function of temperature at various frequencies.

ilar to that of the pure nylon. This relaxation, which is the glass transition of the amorphous nylon, increases in temperature from 61 to 78°C and decreases in maximum tan δ value. The next lower temperature maximum is in the same region as the β relaxation found in nylon 6 (100/0 copolymer), although much larger. In fact, this is not a nylon relaxation but rather the glass relaxation of the polyurea portion of the nylon–polyurea copolymer. This designation will be more obvious when the effect of copolymer composition is discussed later. This β relaxation of the nylon–polyurea copolymer ranges from −57 to −48°C and increases in total value with increasing frequency. The lowest relaxation is again a nylon relaxation and not well defined. This very broad γ relaxation, depending on frequency, is in the range of $\simeq$ −127 to $\simeq$ −104°C.

Figure 3 summarizes the effects of changing frequency and temperature on the loss mechanisms in the 65/35 copolymer. The α relaxation changes in the same manner as the 100/0 and 80/20 copolymers; albeit over a slightly different temperature range, i.e., 55–67°C. The β relaxation is much larger in magnitude, exceeding even the α relaxation with a larger maximum with increasing frequency, a trend

that is opposite that of the α relaxation. The temperature range is very close to that of the 80/20 copolymer, namely −57 to −48°C. The γ relaxation is again very broad and in the range of $\simeq$ −128 to $\simeq$ −109°C.

Compositional Effects on Loss Moduli

Copolymer compositional effects are shown in Figure 4. In this figure the frequency of the test was held constant at 30 Hz and tan δ is plotted versus temperature for each of the copolymers. The high temperature relaxation is that of the amorphous nylon parts of the copolymer and any nylon homopolymer. The temperature of the α relaxation maximum is found to decrease from 83 to 59°C with increasing polyurea content. There is also, in general, a trend to larger tan delta values for the α relaxation at higher polyurea contents. The tan delta value for the next lower relaxation, the β relaxation of the copolymer, increases markedly with increased polyurea content. The temperature of the relaxation varies around −45°C. In fact this is not one relaxation, but two, the glass relaxation of the polyurea and the β relaxation of the nylon. For the 100/0
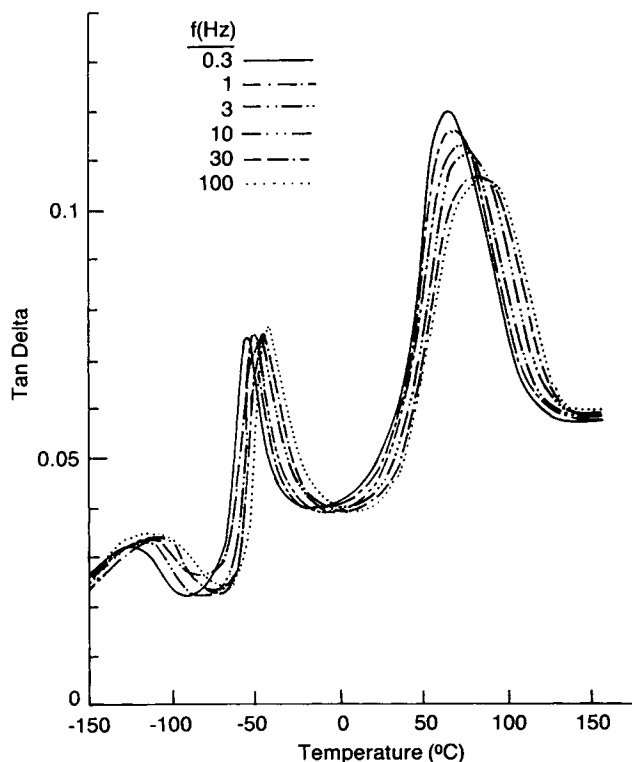

Figure 2 Tan δ of nylon–polyurea 80/20 as a function of temperature at various frequencies.
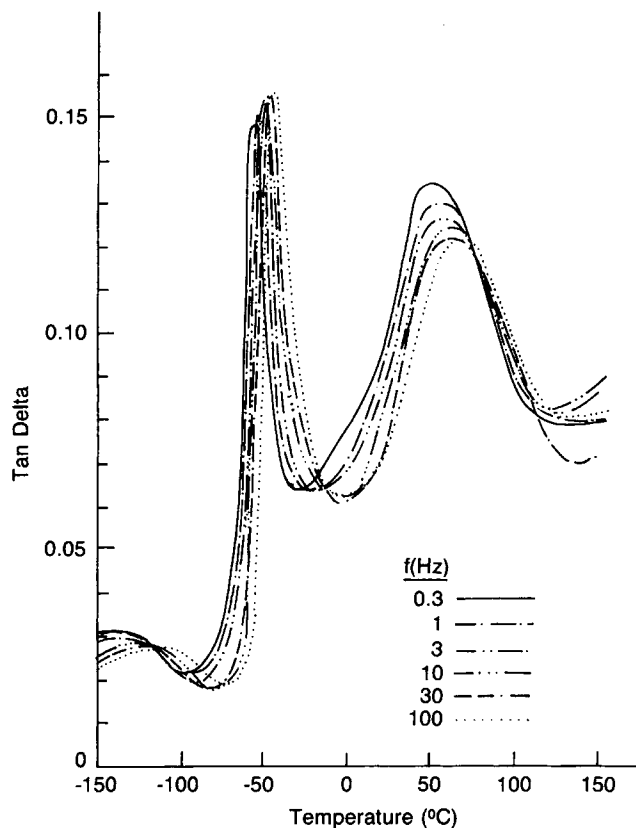
Figure 3   Tan δ of nylon–polyurea 65/35 as a function
of temperature at various frequencies.

and 90/10 copolymers the maximum is due to the
β relaxation of the nylon. In the 80/20 copolymer
the maximum is predominately due to the polyurea
glass transition but a slight shoulder can be seen
which is attributed to the nylon component. At
higher polyurea contents the nylon β relaxation is
completely masked and only the polyurea relaxation
is observed. The lowest temperature relaxation is
again the γ relaxation of the nylon. This very broad
maximum is centered about −110°C and shows no
trends.

Activation Energies of α, β, and γ Relaxations

Plots of log frequency versus the inverse relaxation
temperature in degrees Kelvin allow determination
of the activation energies (E^*) of the relaxations.
Figure 5 shows the plot for the α relaxation in each
of the copolymers. Although not immediately ob-
vious from the plot, the slopes of the lines generated
for the 100/0, 90/10, 80/20, and 75/25 copolymers
are the same but different from the remaining co-
polymers. This difference is readily seen when the

activation energies are calculated (Table I). An av-
erage E^* of 350 kJ mol^{-1} is obtained for the 100/
0 to 75/25 copolymers. A higher average E^* of 460
kJ mol^{-1} was found for the 70/30, 65/35, and 60/40
copolymers.

Figure 6 consists of plots of frequency versus the
inverse of the β relaxation temperature in degrees
Kelvin. The identity of the β relaxation in the co-
polymers becomes more obvious. The plots for the
β relaxations of copolymers 100/0 and 90/10 almost
coincide. An average E^* of 85 kJ mol^{-1} was calcu-
lated (Table I). The activation energies of the 80/
20 to 60/40 β relaxations were also very consistent
($\simeq$ 240 kJ mol^{-1}).

As described previously, the accurate determi-
nation of the γ relaxation temperature in these co-
polymers was not possible with a precision of more
than ± 3–4°C. With this limitation in mind the in-
verse of the γ relaxation temperature as a function
of log frequency is shown in Figure 7. A family of
lines with similar slopes is observed. An average E^*
of 65 ± 10 kJ mol^{-1} was obtained.

Dynamic Modulus

The dynamic modulus (E') was determined as a
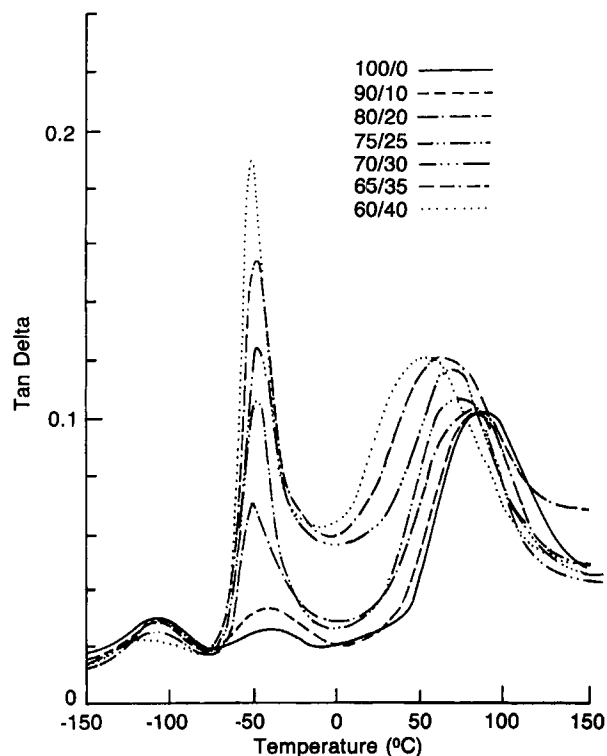function of temperature. Figure 8 shows the plots

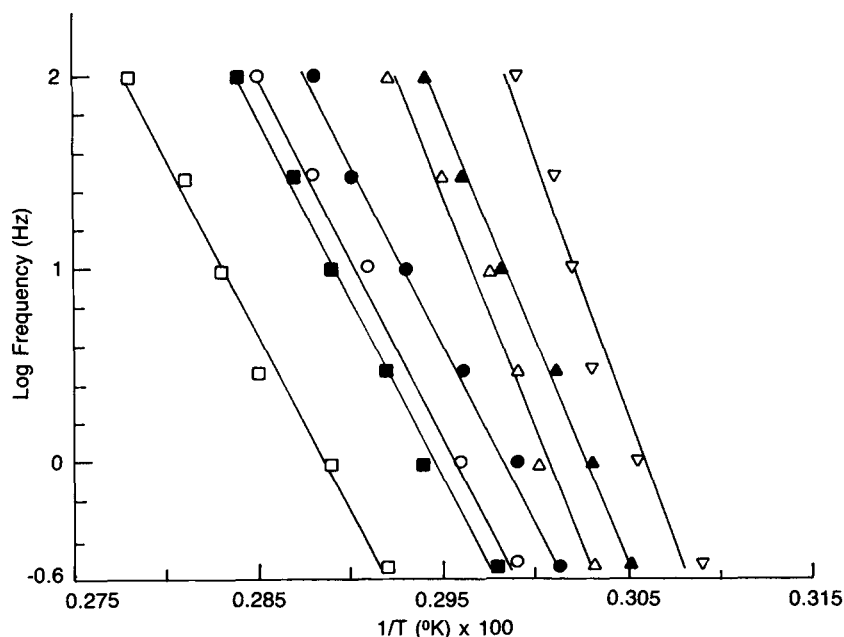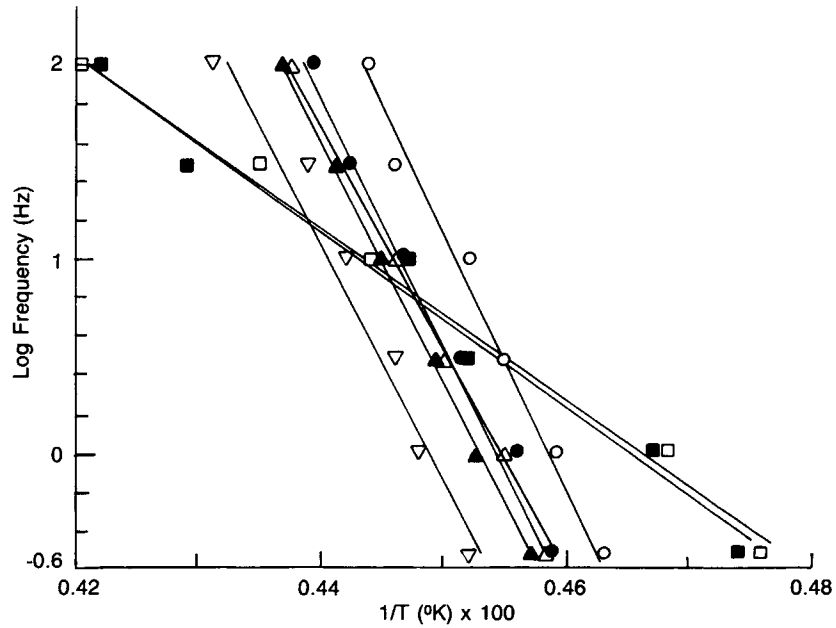**Figure 4**   Effect of copolymer composition on tan δ at
30 Hz.

Figure 5 α relaxation: log frequency versus the inverse of absolute temperature (K):
(□) 100/0; (■) 90/10; (○) 80/20; (●) 75/25; (△) 70/30; (▲) 65/35; (▽) 60/40.

of log E' versus temperature at 100 Herz for the various block copolymers. All the copolymers exhibit a slight decrease in E' between −150 and −75 to −50°C. The 100/0 copolymer shows only a slight loss in modulus with increasing temperature until a temperature of ≃ 70°C is reached, where the modulus drops off sharply. The 90/10 copolymer is very similar to the 100/0 but the plateau modulus between −50 and 60°C is ≃ 8.8 Pa as compared to ≃ 8.9 Pa. The remaining copolymers undergo a sharper decrease in modulus at ≃ −40°C. Above −40°C the 80/20 copolymer has a modulus plateau somewhat similar to the 90/10, again at a slightly lower value. The 75/25, 70/30, 65/35, and 60/40 copolymers show larger changes in modulus over the −40 to 40°C range and sharp decreases in modulus above 40°C.

DISCUSSION

Copolymer 100/0 (Nylon 6)

The predominant relaxation, the α relaxation of nylon 6, is caused by the onset of large segmental motions in the amorphous regions of the polymer. The next lower temperature relaxation, the β, is ascribed to the motions of nonhydrogen bonded amide groups in the polyamide chain. The low temperature γ relaxation arises from motions of methylene sequences in the polyamide backbone. Even though the various nylon relaxations have been determined by numerous investigators, little has been reported on the same dry samples from the same source at several frequencies. Figure 9 is a summary of literature data together with that obtained in these experiments

Table I   Activation Energies[a] of the α, β, and γ Relaxations as Functions of Copolymer Compositions

Relaxation	Copolymer						
	100/0	90/10	80/20	75/25	70/30	65/35	60/40
T α	345	355	350	350	455	425	500
T β[b]	82	87					
T β[c]			240	240	225	245	235
T γ	56	72	54	84	77	60	55

[a] Units for activation energy = kJ mol⁻¹.
[b] Nylon β relaxation.
[c] Polyurea α relaxation.

Figure 6 β relaxation: Log frequency versus the inverse of absolute temperature (K):
($\square$) 100/0; ($\blacksquare$) 90/10; ($\bigcirc$) 80/20; ($\bullet$) 75/25; ($\triangle$) 70/30; ($\blacktriangle$) 65/35; ($\triangledown$) 60/40.

(the DMTA results are designated by open squares). In general the data are in good agreement. All α relaxation temperatures fall on the same straight line. The β relaxation temperatures have been determined over a wider frequency range and also all fall on the same line. The reported relaxation temperatures for the γ relaxation are more disperse but the lines have the same general slopes. Due to a lack of other data at several frequencies with samples with the same origin, the results of a dielectric study have been included (filled circles).

The activation energies of α, β, and γ relaxations are shown in Table I. Glass transitions are major changes and always have large activation energies.
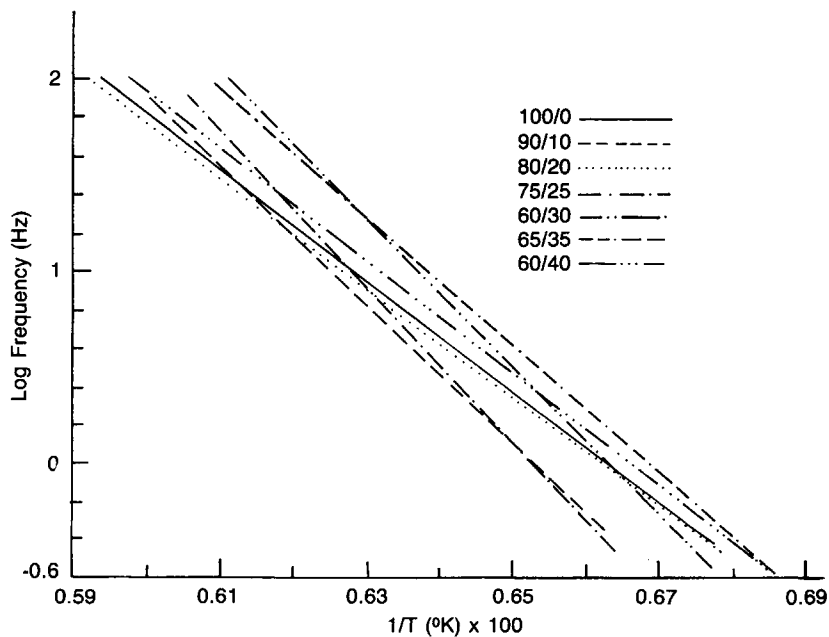

Figure 7 γ relaxation: log frequency versus the inverse of absolute temperature (K).
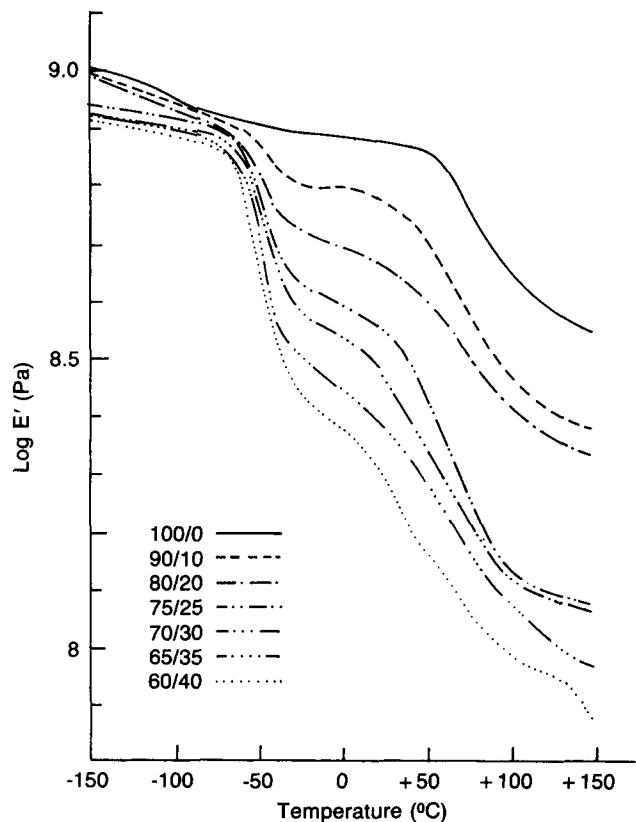
Figure 8 Log dynamic modulus (E') at 100 Hz as a function of temperature.

An activation energy (E^*) for the α relaxation of nylon 6 (100/0) of 345 kJ mol^{-1} compares well with the 400 kJ mol^{-1} of Prevorsek, Butler, and Reim-

schuessel.[7] In contrast to the *in situ* prepared polymer, Prevorsek's polymer had been isolated, precipitated to remove unreacted caprolactam, melt pressed at 210°C and quenched in dry ice/acetone. Leung, Ho, and Choy[8] reported an E^* for the α relaxation of 255 kJ mol^{-1}. Although the sample had been dry oriented by drawing. E^* for the β and γ relaxations were also reported by Leung, but again with oriented samples. The activation energies of the β and γ relaxations (i.e., 82 and 56 kJ mol^{-1}), of the *in situ* polymer are small as expected for second order relaxations.

Copolymers Containing Polyurea

In the nylon–polyurea system the effect of composition on the α relaxation temperature is readily seen in Figure 4. The tan delta response progressively moves to lower temperatures with increasing polyurea content. This response to change in composition results from an intermingling of the polyurea with the amorphous nylon portions of the copolymer. There is a broadening of the tan delta that is indicative of phase mixing. The movement to lower temperatures is also seen in Figure 5 where the plots of inverse temperature versus frequency show a definite progression for each copolymer of increased polyurea content. For the β relaxation the movement of data from left to right in Figure 6 implies some compositional effects. However, contrary to the α relaxation where temperature differences in the range of 18°C at 0.3 Hz to 25°C at 100 Hz were observed
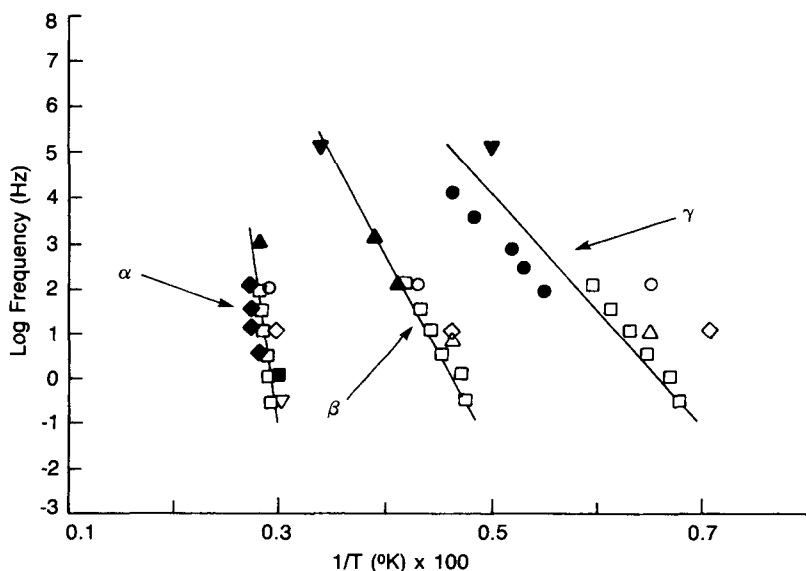

Figure 9 Summary of α, β, and γ transition temperatures for the 100/0 copolymer[10]: (□) this work; (■) 3; (△) 10; (▲) 11; (○) 12; (●) 13; (▽) 14; (▼) 15; (◇) 8; (◆) 7.

between 0 and 40% polyurea content, much smaller differences were observed with the β relaxation. The change in β relaxation temperature between copolymer 80/20 and copolymer 60/40 was only 4 to 5°C. (Note the difference in the size of the X axes in Figures 5 and 6.) In the case of the γ relaxation, the slopes of the lines in Figure 7 are similar but no composition correlations can be made.

In a polymer system where there is an indication of miscibility it is interesting to look at the predictions given by the Fox equation.[9] In polymer systems where the components are completely miscible the Fox equation can be used to predict the α relaxation temperature

$$\frac{1}{T_g} = \frac{W_a}{T_{g_a}} + \frac{W_b}{T_{g_b}}$$

when the composition of the blend or copolymer is known. Figure 10 shows the predicted temperature dependence on copolymer composition. The actual observed α relaxation temperatures are also plotted versus nylon weight fraction. Although not completely miscible the plot does predict some miscibility of the polyurea component in the nylon. (Complete immiscibility is indicated by the dashed lines.)

The activation energies of the α, β, and γ relaxations are shown in Table I. The E^* of the α relaxation is constant for the 100/0, 90/10, 80/20, and

75/25 copolymers but increases to an average value of 460 kJ mol^{-1} for the 70/30, 65/35, and 60/40 copolymers. It is interesting that the 70/30, 65/35, and 60/40 copolymers, as well as the 75/25 copolymer, show direct evidence of polyurea phase separation.[5] This change in activation energy implies a change in environment for the nylon components that undergo the α relaxation, and correlates with the phasing out of the polyurea segments of the nylon–polyurea block copolymers during the polymerization. As was shown previously,[5] the phase separation of the polyurea segments begins early in the polymerization with the 75/25, 70/30, 65/25, and 60/40 copolymers. Phase separation in the 75/25 copolymer was slightly slower than the other three copolymers. The activation energies of the β relaxations are consistent. The β relaxation of the 100/ 0 and 90/10 copolymers which is due to the nylon β relaxation is 82–87 kJ mol^{-1}, in agreement with the identification as a second order relaxation. The β relaxation of the 80/20 to 60/40 copolymers is between 225 and 245 kJ mol^{-1}, which is consistent with being identified as the α relaxation of the polyurea segments of the copolymers. The γ relaxation, as discussed earlier, is difficult to determine precisely.

Dynamic Modulus

Kurz[3] and Hedrick et al.[2] as well as Borggreve and Gaymans[4] reported dynamic moduli for their block
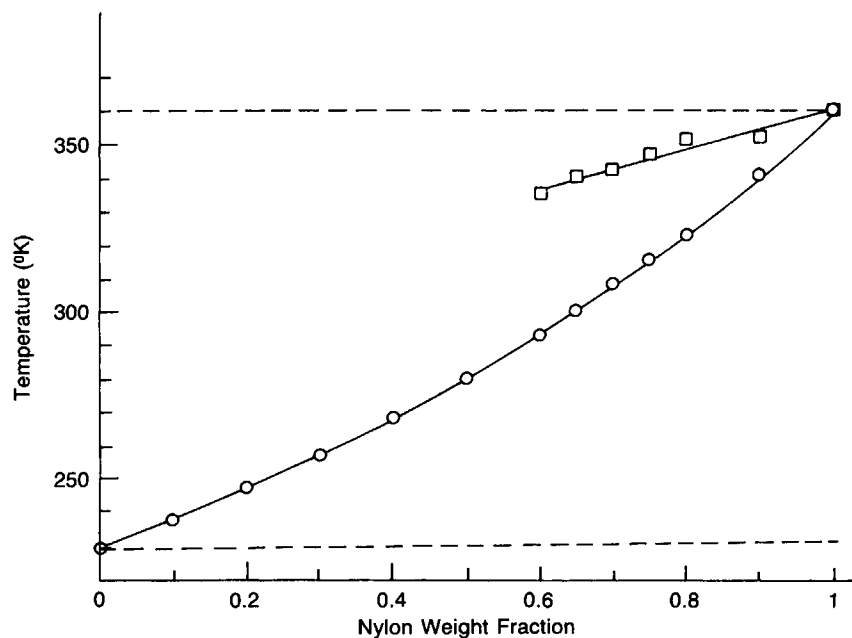

Figure 10 α Transition temperatures of nylon–polyurea copolymers versus nylon weight fraction: ($\square$) observed glass transition temperature; ($\bigcirc$) T_g calculated by the Fox equation.

copolymers. In general, as is the case with the *in situ* polymerized nylon–polyurea copolymers, two pronounced decreases in the dynamic modulus curves were observed. With the polyesteramide copolymers[2,3] as well as with the nylon–polyurea copolymers (Fig. 9), the 100/0, 90/10, and 80/20 copolymers have very similar curves. With concentrations of 25% polyurea and above as well as with 37.3% polyesteramide and above, the low glass relaxation temperature segments have large effects on the dynamic modulus. E' is related to the rigidity of the polymer. All polymers undergo a large change in E' in the region of the glass transition temperature. These nylon–polyurea copolymers show two changes in E'. The copolymers first have a small change in E' in the range of the copolymer β relaxation. This is due to a change in the polyurea segments from the glassy to rubbery state with a resultant small change in polymer rigidity. The second change in E' is large in the region of the glass transition temperature of the copolymer. This corresponds to the relaxation of the amorphous nylon from the glassy state to the rubbery state.

SUMMARY

The mechanical relaxations of several nylon–polyurea block copolymers have been determined over a large temperature range at several frequencies. The various relaxations have been identified and activation energies calculated. The change in the temperature of the α relaxation with changes in copolymer composition indicates that there is some miscibility between the nylon and polyurea. The intermixing of the copolymer segments can become important when the transfer of impact energy is necessary. The mechanical properties, including impact strengths and morphologies of these copolymers will be discussed in a subsequent paper.

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