

Influence of Molecular Weight on the Thermal and Mechanical Properties of Polyurethane Elastomers Based on 4,4'-Diisocyanato Dicyclohexylmethane

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SYNOPSIS

Two series of segmented polyurethane elastomers based on 4,4'-diisocyanato dicyclohexylmethane were investigated with respect to their thermal properties and deformation behavior. We used a crystallizable soft segment, 1,4-poly(tetramethylene glycol), for one series and a noncrystallizable soft segment, 1,2-poly(propylene glycol), for the other. Both systems exhibited mechanical self-reinforcement that depended strongly on the deformation rate. We propose a mechanism for the observed stress/strain behavior in terms of two competing processes: (1) the buildup of orientation caused by deformation and (2) the loss of orientation caused by plastic slippage and segmental relaxation during deformation. The kinetics of these processes depend strongly on the deformation rate and overall molecular weight.

INTRODUCTION

We have investigated the effect of molecular weight on the mechanical and thermal properties of a linear thermoplastic elastomer. It is well known that the properties of *linear* polymers depend strongly on the molecular weight,¹ whereas the properties of *chemically crosslinked* polymers, such as vulcanized rubber, depend mainly on the molecular weight between the crosslinks (M_c).² Very few systematic investigations of the influence of polymer molecular weight on the properties of *physically crosslinked* polymers such as thermoplastic elastomers have been undertaken.

Thermoplastic elastomers consist of linear block copolymers that are phase separated into hard-segment and soft-segment regions. Even though they are linear, they can be viewed as a physically crosslinked system consisting of a soft-segment phase

that is crosslinked through the intermolecular association of hard segments from adjacent polymer chains. With polyurethane elastomers, the hard segment is composed of the reaction product of a diisocyanate and a short-chain diol, and has a glass transition (T_g) above room temperature. The intermolecular association comes through van der Waals forces and hydrogen bonding of the urethane linkages. The soft segment usually consists of a 1000–3000 molecular weight polyether or polyester diol with a T_g well below room temperature.

In this paper, we focus on the effects of elastomer composition and molecular weight. We used an aliphatic elastomer consisting of a hard segment of 4,4'-diisocyanato dicyclohexylmethane and 1,4-butanediol with two different soft-segment polyether diols. Series A used a soft-segment polyether that can crystallize, 1,4-poly(tetramethylene glycol), and Series B used a noncrystallizing polyether, 1,2-poly(propylene glycol). We discuss the effect of these factors on the degree of ordering within the hard-segment region and the surprising effect of deformation rate on the stress/strain behavior of these elastomers.

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EXPERIMENTAL

The elastomers were prepared using 4,4'-diisocyanato dicyclohexylmethane (Desmodur W, Mobay Corp.) with the following 4,4'-isomer distribution: 21% *trans,trans*; 57% *cis,trans*; and 22% *cis,cis* as determined by gas chromatography. It also contained 5 wt % 2,4'-isomers. The chain extender was 1,4-butanediol with a water content of less than 0.01 wt %. We used two different polyether diols as soft segments to prepare the two series of polyurethane elastomers:

Series A: 1000 MW 1,4-poly(tetramethylene glycol) (Terathane 1000, DuPont), a crystallizable soft segment.

Series B: 1000 MW 1,2-poly(propylene glycol) (E-9109, Mobay Corp.), a noncrystallizable soft segment.

The mole ratio of diisocyanate : 1,4-butanediol : polyether diol was 3 : 2 : 1 and the isocyanate to hydroxyl ratio was 1.00 for all the samples. We varied the elastomer molecular weight by adding different amounts of *n*-butanol as a chain terminator (see Table I).

We prepared the samples based on polytetramethylene glycol (series A) using a one-shot process with 100 ppm dibutyltin dilaurate as a catalyst. The 1000 MW polytetramethylene glycol and 1,4-butanediol were charged into a three-neck round-bottom flask equipped with a stirrer and vacuum. We stirred the solution thoroughly at 40°C and degassed the solution by using a vacuum (0.1 mm Hg) for 20

min. We then added the diisocyanate and *n*-butanol (if required). The dibutyltin dilaurate was added as a 1 wt % solution in poly(tetramethylene glycol). The solution was stirred thoroughly and vacuum degassed for another 3 min, and then cast into 6 × 6 × 1/8 in. closed molds preheated to 90°C. They were cured for at least 16 h at 90°C and then conditioned at room temperature and 50% humidity for at least 2 weeks prior to testing.

The samples based on poly(propylene glycol) (series B) were prepared using a prepolymer process. We prepared a prepolymer by reacting the diisocyanate with the 1000 MW poly(propylene glycol) at 80°C using 200 ppm of dibutyltin dilaurate as catalyst. After the reaction was complete, as determined by the percent isocyanate content, the temperature was lowered to 40°C and vacuum degassed at 0.1 mm Hg for 20 min. We weighed the prepolymer, 1,4-butanediol, and *n*-butanol (if required) into a small metal can and stirred the solution thoroughly. The solution was cast into closed molds preheated to 90°C and cured using the same conditions as the series A samples.

The molecular weights of the samples were determined by gel permeation chromatography using a Perkin-Elmer chromatograph equipped with a series 10 LC pump and a LC-25 differential high sensitivity refractive index detector. Three GPC columns from Polymer Labs, Inc. were used in series. Two of the columns had 10- μ m mixed-bed packings and the other had a gel packing of 100 Å porosity. The samples were run in tetrahydrofuran at 1 mL/min and at 30°C. The molecular weights were determined relative to monodisperse polystyrene standards.

Table I Molecular Weight Data

Sample No.	Mole Fraction of <i>n</i> -Butanol ^a	M_w (Calculated)	M_w (Experimental)
A1 ^b	0.00	∞	303,000
A2	0.01	132,300	222,000
A3	0.03	42,300	133,000
A4	0.05	25,500	79,000
A5	0.10	14,400	40,000
B1 ^c	0.00	∞	258,000
B2	0.01	132,300	150,000
B3	0.02	63,700	101,000
B4	0.03	42,300	78,000
B5	0.05	25,500	66,000
B6	0.11	13,500	25,000

^a Based on total moles of polyol.

^b Series A is based on 1,4-poly(tetramethylene glycol).

^c Series B is based on 1,2-poly(propylene glycol).

The absolute weight average molecular weights of three samples from series A were determined by light scattering at Arro Labs, Joliet, IL. They used a solvent consisting of 0.5 wt % LiBr in dimethyl formamide.

The dynamic-mechanical properties of the elastomer samples were determined with a Rheometrics dynamic spectrometer (Model 7700). Rectangular samples ($2\frac{1}{2} \times \frac{1}{2} \times \frac{1}{8}$ in.) were torqued at 1 Hz, at strains between 0.04 and 1.5%. The storage modulus (G'), loss modulus (G''), and tangent delta (G''/G') were determined as a function of temperature between 80 and 160°C.

The thermal behavior of the samples was studied using a Perkin-Elmer DSC-7. The samples (10 mg) were heated in sealed aluminum pans under a 20 cc/min dry nitrogen purge, at 20°C/min from room temperature to 240°C. After cooling to 25°C, the samples were reheated to 240°C at 20°C/min.

The stress/strain properties were determined according to ASTM D412-87 using a standard Instron testing machine. The samples were cut using a standard die (die C) and tested at room temperature using crosshead speeds of 0.25, 2.5, and 50 cm/min.

RESULTS AND DISCUSSION

Material Characterization

The molecular weights of the samples were characterized by gel permeation chromatography (GPC) using polystyrene standards. In order to determine the absolute weight average molecular weights, three of the elastomers based on poly(tetramethylene glycol) (series A) were analyzed by light scattering. We then calibrated the molecular weights of the other samples by using a plot of the GPC data versus the light scattering data. A summary of the absolute molecular weight data is given in Table I.

Surprisingly, we found that the samples that contained *n*-butanol as a chain terminator had a significantly higher molecular weight than the theoretical molecular weight as calculated using the Carother's equation (Table I). This indicates that the chain terminator was not fully utilized during the reaction. This is supported by the fact that a distinct odor of *n*-butanol was detected upon demolding the samples. See the Appendix for a more detailed discussion.

The dynamic mechanical spectra of the low, medium, and high molecular weight samples based on poly(tetramethylene glycol) (series A) are shown in Figure 1. Interestingly, the storage modulus (G')

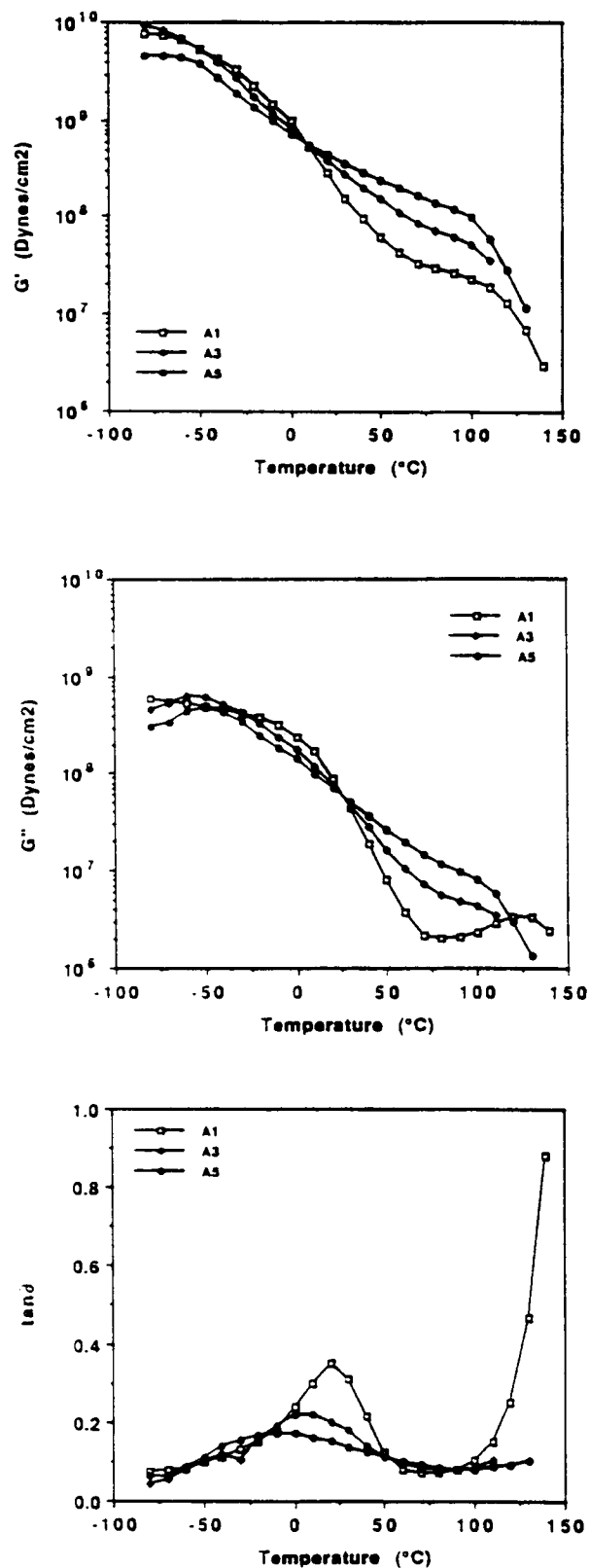


Figure 1 Shear storage modulus (G'), shear loss modulus (G''), and tangent delta (G''/G') vs. temperature of elastomers based on poly(tetramethylene glycol).

in the rubbery plateau region is highest for the lower molecular weight samples. Also, the onset of the rubbery plateau region is at a lower temperature for the lowest molecular weight sample. It begins at about 0°C for the lowest molecular weight sample and about 70°C for the highest molecular weight sample. The glass transition temperature of the soft segment as indicated by the loss modulus (G'') curve appears to be sharper for the lower molecular weight samples. These trends indicate that the lower molecular weight samples, being more mobile, are better phase-separated and have a more ordered hard-segment region.

The initial DSC scans for the series A elastomers as a function of molecular weight are given in Figure 2. The series A samples have several melt endotherms, one at about 70°C, which becomes stronger with increasing molecular weight, and several in the range of 110–160°C, which show the opposite behavior. The above trends support the previous conclusion that the lower molecular weight samples have a more ordered (i.e., higher melting) hard-segment region.

Upon rescanning the samples, the original endotherms disappear and a new endotherm appears at about 100°C. The original transitions could not be regained even after annealing at 115°C for 20 min however, the transition did shift from about 100 to 140°C. A shift of a melting transition to higher temperature upon annealing has been well documented.^{3,4}

The origin of the two endotherms observed in the first DSC runs still needs further clarification. Byrne et al. investigated a series of elastomers prepared from poly(tetramethylene glycol), 1,4-butanediol, and 4,4'-diisocyanato dicyclohexylmethane with varying amounts of the *trans,trans* isomer.⁵ They

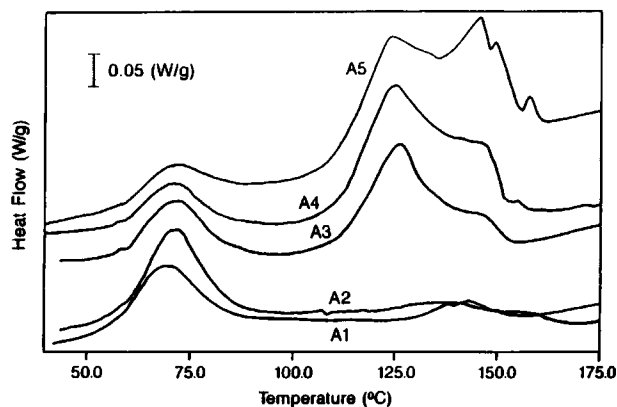


Figure 2 DSC scans of the elastomers based on poly(tetramethylene glycol) (series A).

attributed the first endotherm to the hard-segment glass transition or some related phenomenon. They found the second endotherm only in samples that had been stored for 1 year at room temperature or annealed at 100°C. They were reluctant to correlate this transition which they observed in the range between 140 and 174°C with hard-segment crystallinity. Instead, they used the term long-range order.

Our experimental data agree reasonably well with the results obtained by Byrne et al. Our post-curing conditions were similar to their annealing process at 100°C and the chemical structure of our materials is similar. However, we observed in the second heating runs only endotherms considerably above 70°C. We conclude that both endotherms observed in the first heating run represent melting transitions of hard-segment domains, but with significantly different degrees of order. The domains which melt at 110–160°C are probably formed during the post-curing of the cast samples. This “crystallization” process is certainly slower for the higher molecular weight samples.

The DMS data correlate well with the thermal data. The G' value in the rubbery-plateau region increases with decreasing molecular weight. This correlates with the higher intensity of the 140°C endotherm in the DSC scans.

Effect of the Molecular Weight on the Stress/Strain Behavior

The stress/strain curves for the series A samples at a strain rate of 2.5 cm/min are given in Figure 3. The relative effect of molecular weight on the stress/strain curves was found to be the same for strain rates of 0.25 and 50 cm/min. The lower molecular weight samples had a *higher* stress at low elongations and a *lower* stress at high deformations than the higher molecular weight samples.

The observed stress/strain diagrams can be interpreted with the following molecular picture. The modulus of a rubber elastic network is determined by the crosslink density and by the volume fraction of rigid fillers. In segmented elastomers, both of these entities are represented by the hard-segment domains. So as the degree of hard-segment crystallinity/order improves, the modulus increases. As described earlier, the lower molecular weight samples exhibit a higher degree of hard-segment order; therefore, they have a higher initial modulus.

At larger elongations, however, plastic deformations of hard-segment domains become increasingly important, especially in low molecular weight samples with relatively few chain entanglements and a

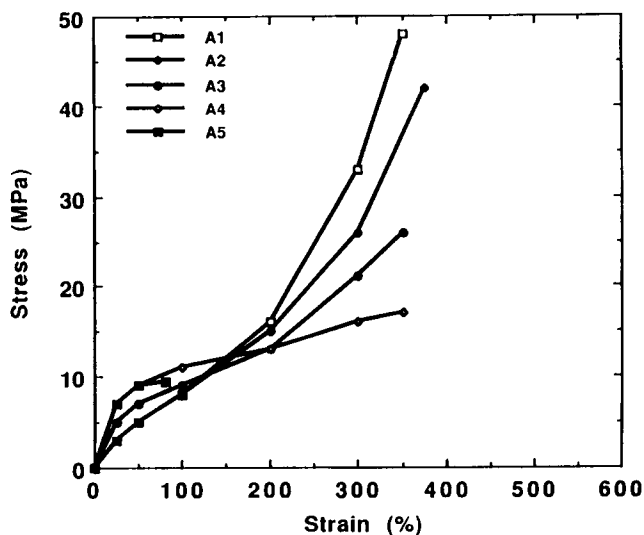


Figure 3 Stress/strain curves of the elastomers based on poly(tetramethylene glycol) (series A) at a deformation rate of 2.5 cm/min.

smaller number of hard segments per chain. The stress and also the chain orientation are rapidly reduced through relaxation processes. The stress/strain curves remain flat, and failure occurs through chain disentanglement at relatively small elongations.

With increasing molecular weight, the deformation required for total disentanglement and failure becomes much larger. At the same time, the relaxation processes are slowed down. This reasoning is in line with Schollenberg-Dinbergs stress-relaxation data on aromatic polyurethanes with different molecular weights.⁶ They found that the stress-relaxation rate was inversely proportional to the polyurethane molecular weight. A lower stress-relaxation rate ultimately leads to considerably higher tensile strengths.

The first indication of an inflection point in the stress/strain curves can be seen at weight average molecular weights of greater than 100,000 (Fig. 3). This is attributed to self-reinforcement, which becomes more pronounced at higher molecular weights. From earlier investigations it is well known that this effect can be caused by soft-segment crystallization.⁷ This generates additional physical crosslinks and leads to higher stress levels.

However, self-reinforcement (although weaker) can also be seen in the series B samples which were based on 1,2-poly(propylene glycol), a noncrystallizable soft segment (Fig. 4). So there must be additional factors which promote self-reinforcement

besides stress-induced crystallization of the soft segment.

Self-reinforcement in polyurethanes can also be understood in terms of hard-segment orientation. It is generally known that polymers exhibit a higher resistance to deformation when they are well oriented than when they are isotropic. This is true when deformation occurs in the same direction as orientation. Series A should exhibit the effects of both soft-segment crystallization and hard-segment orientation, whereas series B can only show the latter effect.

As seen in Figure 4, the hard segments develop appreciable orientation at high strains (> 150%). This causes an increase in the stress required for further deformation. As the deformation continues, more of the hard segments become aligned in the draw direction. This increases the overall orientation of the sample and hence the stress continues to increase. The resulting self-reinforcement begins at a molecular weight of about 101,000.

Effect of the Deformation Rate on the Stress/Strain Behavior

This mechanism of self-reinforcement is clearly not static and should therefore depend upon the rate of deformation. The extent of hard-segment orientation, and hence the amount of reinforcement, should depend upon the balance between two kinetic processes: (1) the buildup of orientation caused by de-

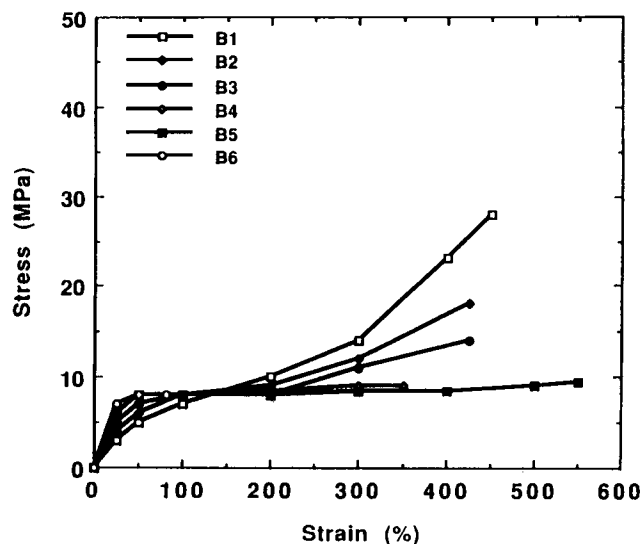


Figure 4 Stress/strain curves of the elastomers based on poly(propylene glycol) (series B) at a deformation rate of 2.5 cm/min.

formation and (2) the loss of orientation caused by plastic slippage and relaxation during the deformation process. The balance between these two processes will depend upon the time scale of the deformation.

The variation in stress-strain behavior with deformation rate for sample B2 is given in Figure 5. As can be seen, the reinforcement effect is clearly rate-dependent. At slow deformation rates (ca. 0.25 cm/min), relaxation processes dominate. In other words, there is sufficient time during the stretching experiment for a significant amount of the orientation to be lost by segmental relaxation of the polymer chains. Hence only a weak self-reinforcement effect is observed.

At intermediate deformation rates (ca. 2.5 cm/min), the buildup of hard-segment orientation dominates. There is no longer enough time during the stretching experiment for significant relaxation of the polymer chains to occur. Hence, strain-induced orientation of the hard segments dominates, resulting in a significant amount of self-reinforcement.

At higher deformation rates (ca. 50 cm/min), this self-reinforcement effect decreases due to plastic slippage of the hard segments. Since the deformation rate is now too rapid for the hard-segment domains to follow, slippage occurs as the chains are physically ripped away from the domains, thus decreasing the degree of physical crosslinking. This phenomenon is evident at high elongations.

As an aside, the deformation rate also influences the stress-strain behavior at low elongation. This

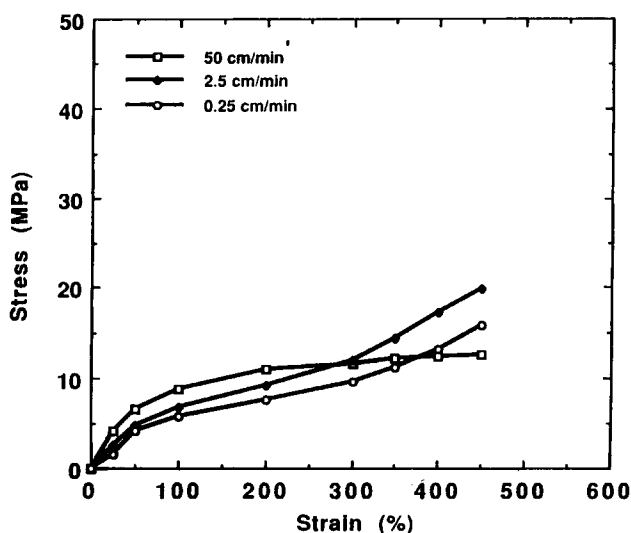


Figure 5 Effect of deformation rate on the stress/strain behavior of sample B2.

can be seen in Figure 5 at elongations of approximately 50%. This elongation is not large enough to cause plastic slippage of the hard segments, even at the highest deformation rate. Additionally, relaxation processes described earlier have less time to occur at the faster deformation rates. Hence the stress is highest at the fastest deformation rates.

To return to our model of self-reinforcement, we tested our hypotheses by performing interrupted stress-strain experiments. In order to study the balance between buildup and loss of orientation during elongation, the deformation process was briefly interrupted at either low or high elongations.

When the deformation process is interrupted at a low elongation, little or no orientation has developed and no plastic slippage has yet occurred. Hence the material can relax nearly completely during the brief resting period. As a result, little self-reinforcement is expected when the draw is resumed.

On the other hand, when the deformation is interrupted at a high elongation, a significant change in the material has occurred. Namely, the material has been drawn into an oriented state and some plastic slippage has occurred. Even though some of this orientation will relax during the interruption period, a significant fraction will remain. There will also be sufficient time for some healing of the plastic slippage to occur. This leads to the alignment of neighboring hard segments and the possibility of hard-segment domain growth. As a result of this residual orientation and possible recovery from plastic slippage, the material should exhibit strong self-reinforcement when the draw is continued.

The results of our interrupted stress/strain measurements are shown in Figure 6. Sample B2 was deformed at a rate of 50 cm/min to 50% elongation and then interrupted for 15 min (curve A). When elongation was resumed, there was only a minor effect on the stress/strain curve. When the analogous experiment was performed with interruption at 300% elongation (curve B), the stress increased dramatically upon continuation of elongation. This variation in the magnitude of self-reinforcement supports our explanation of the reinforcement mechanism.

CONCLUSIONS

The results show the dominating influence of the overall molecular weight on the mechanical properties of linear polyurethane elastomers. Consequently, the influence of the block lengths, block length distribution, chemical structure, processing

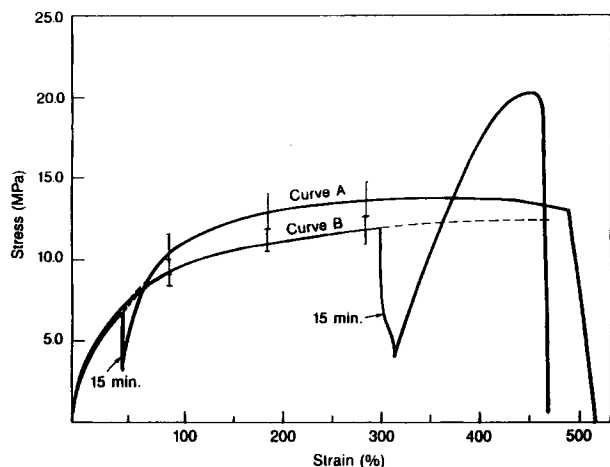


Figure 6 Stress/strain curves of sample B2 at a deformation rate of 50 cm/min: (A) interrupted at 50% elongation for 15 min; (B) interrupted at 300% elongation for 15 min.

conditions, etc. can only be evaluated when the molecular weights of the different materials are comparable.

Hard-segment crystallization kinetics have a major influence on physical properties. This is in addition to the already well-known effect of soft-segment crystallization.

These elastomers display rate-dependent, self-reinforcement effects. A mechanism for this reinforcement is proposed which includes the relative importance of orientation, plastic slippage, segmental relaxation, and soft-segment crystallization.

APPENDIX: DISCUSSION OF THE MOLECULAR WEIGHT DATA

According to the Carother's equation, the average degree of polymerization (DP) is given as

$$DP = \frac{1 + N_1/N_0}{1 - p + N_1/N_0}$$

where N_1/N_0 is the molar ratio of chain terminator to the repeating monomer units and p is the degree of conversion.

The number average molecular weight (M_n) is

$$M_n = DP \times M$$

M = molecular weight of the repeat unit
(655 g/mol series A)

i.e.,

$$M_n = DP \times 655$$

For comparison with our experimental results, we calculated M_n for the samples of series A according to the Carother's equation and converted them into weight average molecular weights (M_w) by using the polydispersity obtained by gel permeation chromatography.

The first calculation was done with sample A1 using a degree of conversion (p) equal to 1.0, which leads to an infinite molecular weight for $N_1/N_0 = 0$. The experimental molecular weight for sample A1 corresponded to a degree of conversion of 0.9942. This means that 0.6% of the isocyanate was left unreacted.

At higher concentrations of *n*-butanol, the experimental molecular weights are much higher than the theoretical. This indicates an incomplete utilization of the chain terminator.

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