Block Polymers from Isocyanate-Terminated Intermediates.   III. Preparation and Properties of Cured Diene–Urea Block Polymers

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Synopsis

Isoprene–urea and butadiene–urea block polymers have been prepared by reaction of iso-cyanate-terminated prepolymers with diamines and diisocyanates. It was found that the per cent of blocked urea in these copolymers is dependent on the isocyanate–diamine stoichiom-etry. Stress–strain data were obtained on sulfur-cured copolymers. Stress levels at any given extension were directly dependent on the urea content, however, ultimate strength was maxi-mized at about 35 wt-% urea. Slight variations in urea structure produced rather dramatic changes in the modulus of these cured elastomers. Diamine–diisocyanate stoichiometry did not affect the physical properties of these cured copolymers at equal or excessive diamine con-centrations. However, at excess diisocyanate levels, elastomeric properties deteriorated rapidly. Finally, stress–strain properties were affected by polymerization solvent. Copoly-mers prepared in hexane gave higher values of stress at low strains than corresponding elas-tomers prepared in toluene. These latter results are explained in terms of the nonaqueous emulsion in which the urea blocks form.

INTRODUCTION

In earlier work,[1] we described the preparation of isocyanate-terminated pre-polymers. We have since demonstrated the utility of such intermediates in the preparation of butadiene–ε-caprolactam, styrene–ε-caprolactam, and butadiene–imide block polymers.[2] We report here the synthesis and evaluation of diene–urea block polymers from similar intermediates. The polydiene portion of these diene–urea copolymers is either polyisoprene or polybutadiene. The urea portion is prepared through a condensation reaction involving toluene diiso-cyanate and diamines or water.

The present study concerns itself with copolymers which are elastomeric. The diene portion contains a high proportion ($\geq 85\%$) of 1,4-units, and the com-positional range was limited to $\leq 50\%$ by weight urea. These copolymers were sulfur vulcanized, and the influence of various parameters on physical properties was then investigated.

EXPERIMENTAL

Reagents

Isoprene was distilled from a mixture of sodium metal and fluorene (1 part of sodium to 24 parts of fluorene per 500–600 cc of isoprene), stored under refrigera-

tion, and used as needed. Butadiene was treated with a sodium–fluorene mixture (molar ratio 0.022 sodium, 0.066 fluorene, and 6.5 butadiene) in 28-ounce bottles and was flash distilled as needed.

Hexamethylenediamine (HMDA) and m-phenylenediamine (MPDA) were both distilled under reduced pressure. The HMDA was distilled at 100°C and 2.67 kPa, while MPDA was distilled at 130°C and 0.93 kPa. Toluene diisocyanate (TDI) and toluene diamine (TDA) were obtained from E. I. du Pont Company as 97% 2,4-isomers. Both were used without further purification.

Toluene, hexane, and tetrahydrofuran (THF) were all purified by distillation in the presence of sodium metal. A solution of n-butyllithium in hexane was obtained from Lithium Corporation of America and used without further purification.

Polymerization

Polymerization of the diene portion of these copolymers was run at room temperature. TDI was added to the converted polydienyllithium solutions at room temperature, followed immediately by the prescribed amount of diamine. Molar ratios of TDI to polydienyllithium (PDL) varied somewhat depending on the molecular weight of the polydiene portion. However, this ratio was always, 10, ensuring a low degree of coupling which occurs when a TDI molecule reacts with two molecules of polydienyllithium.[1] Unless otherwise specified, a 10 mole-% excess of diamine over diisocyanate was employed in all syntheses. Reaction of the diisocyanate and diamine to form polyurea required 2–3 hr at 150°C or overnight at 80°C to reach about 98–99% conversion. This reaction was followed quantitatively by comparing the optical density ratio of —NCO absorption (2280 cm^{-1}) to —CH$_2$— absorption (2850 cm^{-1}) in the infrared[3] before and after the addition of the diamine. Copolymers were recovered by precipitation with methanol and were dried in a vacuum oven at 25°C to constant weight.

Compounding and Molding

Copolymers were compounded by milling with the required ingredients at 66–93°C. Copolymers whose urea portion was prepared from an aromatic diamine were compounded according to the following recipe: copolymer, 100; sulfur, 2; stearic acid, 2; zinc oxide, 5; and N-t-butyl-2-benzothiazole sulfenamide, 1.2. Copolymers whose urea portion was prepared with HMDA did not require accelerator, and the following recipe was used: copolymer, 100; sulfur, 1.4; stearic acid, 1.4; and zinc oxide, 3.5. All compounded elastomers were cured for 30 min at 149°C.

Physical Property Measurements

Tensile modulus and strength were measured on 1.905 mm dumbbells according to ASTM Method D 412-68.
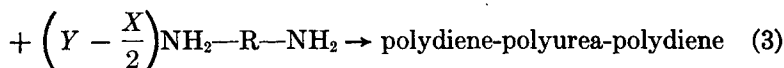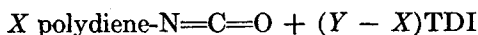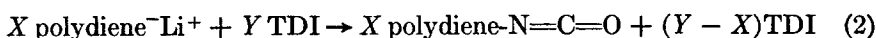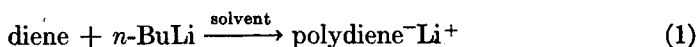
Polymer Characterization

NMR spectra were measured at 60 MHz on the diene portion of all copolymers in CCl$_4$ at room temperature to investigate the microstructure of the diene segments. Peak areas of signals for terminal and nonterminal olefinic protons were determined and analyzed according to the method of Senn.[4] Copolymer com-

positions were determined by elemental analysis on a Hewlett-Packard Model 185 Analyzer. Viscosity-average molecular weights were determined on the polydiene portion of these copolymers. This was accomplished by employing Mark-Houwink relationships determined in these laboratories for anionically prepared polyisoprenes and polybutadienes. The K and a values used for polyisoprene were 1.9×10^{-4} and 0.73, respectively. Those used for polybutadiene were $K = 7.25 \times 10^{-5}$ and $a = 0.86$. Both relationships depend on viscosities measured in toluene at $25°C$.

RESULTS AND DISCUSSION

Copolymer Synthesis

These diene–urea copolymers were prepared according to the reaction scheme outlined below:

$$\text{diene} + n\text{-BuLi} \xrightarrow{\text{solvent}} \text{polydiene}^-\text{Li}^+ \qquad (1)$$

$$X \text{ polydiene}^-\text{Li}^+ + Y \text{ TDI} \rightarrow X \text{ polydiene-N}=C=O + (Y - X)\text{TDI} \quad (2)$$

$$X \text{ polydiene-N}=C=O + (Y - X)\text{TDI}$$

$$+ \left(Y - \frac{X}{2}\right)\text{NH}_2\text{—R—NH}_2 \rightarrow \text{polydiene-polyurea-polydiene} \quad (3)$$

The first two steps above involve homogeneous reactions. However, when the diamine is added in step 3, a nonaqueous emulsion or latex forms immediately. This is true for all diamines which we have examined, i.e., HMDA, TDA, and MPDA. In many instances, these milky emulsions show a bluish fluorescence, indicating a rather small particle size formation. When the stoichiometry between isocyanate and amine is carefully controlled as indicated in the above reaction scheme, a triblock polymer is obtained. In most cases, however, we purposely added a slight excess of diamine over TDI to guard against biuret crosslink formation. In this case, both diene–urea diblock polymer as well as unblocked homopolyurea can form. The amount of blocked urea can be calculated from the relationship shown below:

$$\text{blocked urea } \% = \left[\frac{(100) \text{ moles RLi}}{\text{moles RLi} + \text{moles diamine} - f(\text{moles diisocyanate})}\right]. \quad (4)$$

In (4) above, RLi represents a polydienyllithium chain. Thus, the amount of blocked urea depends on both the RLi concentration and the difference between the moles of diamine and diisocyanate. The factor f is the fraction of diisocyanate molecules which have reacted. We include this factor since we have observed that, even at extremely long reaction times, there is always a small amount of diisocyanate which does not react. This is true even in the presence of excess diamine. It should be pointed out that eq. (4) above is valid only when moles diamine $\geq$ moles diisocyanate. When excess diisocyanate is present, the possibility of isocyanate groups reacting with urea linkages exists. Such reactions quickly lead to the formation of a network via biuret crosslinks.
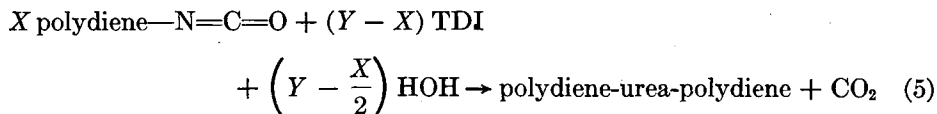
In an effort to verify the influence of diamine–diisocyanate stoichiometry on the percent blocked urea, we extracted some cured copolymers for several days with hot dimethyl sulfoxide. Elemental analysis showed the extracted mate-

TABLE I
Variation of Blocked Urea with Diamine–Diisocyanate Stoichiometry in
Isoprene–Urea Block Polymers

Sample no.	Moles RLi $\times 10^3$	Moles MPDA	Moles TDI	f	% Blocked urea	
					Calcd.	Found
1	4.7	0.551	0.507	0.988	8.7	16
2	4.7	0.453	0.454	0.986	48.5	54

rial to be homopolyurea. Table I lists the results obtained from two such extractions. The values reported for f in column 5 were determined by infrared measurements. The calculated values for percent blocked urea in column 6 were then obtained from eq. (4) above. In both cases, the values obtained by extraction for per cent blocked urea were slightly higher than the corresponding calculated values. This is probably due to the fact that some homopolyurea is imbibed by the copolymer in the network making it difficult to remove even after long extraction times. Nevertheless, the data in Table I do illustrate the dependence of blocked urea upon diamine–diisocyanate stoichiometry.

As an alternative synthetic route to the addition of diamine for urea formation, we have prepared these diene–urea copolymers by substituting water for the diamine. In this case, step 3 in the reaction scheme described above becomes

$$X \text{ polydiene—N=C=O} + (Y - X) \text{ TDI}$$

$$+ \left(Y - \frac{X}{2}\right) \text{HOH} \rightarrow \text{polydiene-urea-polydiene} + CO_2 \quad (5)$$

The major difference in using water in place of diamine is reaction rate. The uncatalyzed reaction between diisocyanate and water to form urea was much slower than corresponding reactions with diamines. However, various catalysts have proven effective where reactions involving isocyanate and hydroxyl groups take place.[5] Such catalysts improved the rate of urea formation considerably in our systems.

Polymer Evaluation

The relationship between stress–strain properties and copolymer composition is demonstrated in Figure 1 for four cured butadiene–urea copolymers of varying urea content. The urea portion of these copolymers was derived from TDI and HMDA. Molecular weight was kept relatively constant throughout this series. The viscosity-average molecular weights for the polybutadiene portion of these copolymers ranged from 60 to 73×10^3 g/mole. The stress levels at any given extension show a dependence on the urea content, or hard phase, as might be expected. Furthermore, the ultimate strength is maximized at about 35 wt-% urea. At low urea contents, these elastomers are both low in modulus and strength, while high urea levels give very short materials.

The nature of the urea segments also plays an important role in determining the physical properties of these elastomers. Figure 2 illustrates the stress–strain behavior of two cured isoprene–urea copolymers having similar molecular weights and urea contents but different urea structures. In one copolymer, the diamine portion of the urea segments was TDA while the other contained MPDA. Vis-
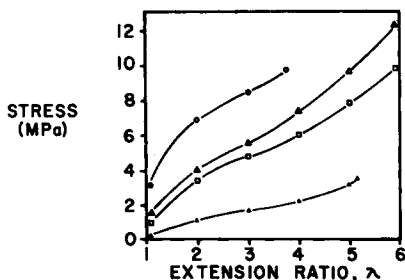
Fig. 1. Effect of copolymer composition on stress–strain properties for polybutadiene–urea copolymers. Urea portion is TDI + HMDA: (▲) 20% urea; (□) 30% urea; (△) 37% urea; (○) 40% urea.
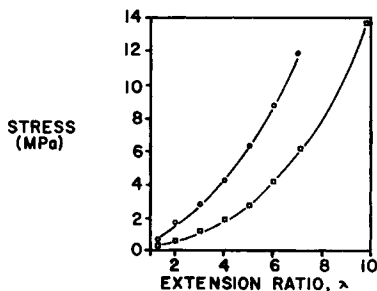

Fig. 2. Effect of urea structure on stress–strain properties: (○) urea portion is TDA + TDI; (□) urea portion is MPDA + TDI.

cosity-average molecular weights of the polyisoprene portion was 73×10^3 g/mole and 78×10^3 g/mole for the TDA and MPDA copolymers, respectively. Both copolymers contained 30% urea by weight. It is readily seen that the stress–strain curve for the TDA copolymer runs higher than that of the MPDA copolymer. Tensile strengths, however, are similar. It is difficult to see why such large differences in modulus occur in these copolymers whose urea segments are quite similar in structure. Apparently, the domains formed by the urea segments containing TDA require higher stresses for deformation than the corresponding domains whose urea segments are derived from MPDA. In any case, the data serve to illustrate the importance of urea structure and the dramatic influence this variable can have on physical properties.

It was pointed out above that the percent blocked urea is dependent on the diamine–diisocyanate stoichiometry. We tested the influence of this variable on the physical properties of the cured copolymers by preparing a series of polymers in which the diamine–diisocyanate stoichiometry was varied. Figure 3 illustrates the stress–strain behavior of butadiene–urea block polymers having equivalent compositions and similar molecular weights but prepared at different diamine–diisocyanate stoichiometries. Viscosity-average molecular weights of the polybutadiene portion varied from 62 to 70×10^3 g/mole. Each copolymer contained 30% urea by weight. The urea portion was derived from HMDA and TDI. It can be seen from Figure 3 that physical properties are unaffected by stoichiometry when moles diamine $\geq$ moles diisocyanate. However, as the molar concentration of diisocyanate exceeds that of the diamine, elastomeric properties deteriorate rapidly. Both ultimate elongation and tensile strength
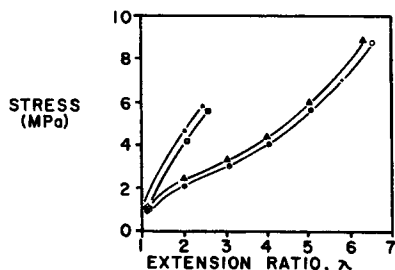
Fig. 3. Effect of diamine-diisocyanate stoichiometry on stress strain properties for polybutadiene urea copolymers. Urea portion is TDI + HMDA: (▲) 4.2% molar excess TDI; (□) 2.8% molar excess TDI; (O) moles TDI = moles HMDA; (△) 7.3% molar excess HMDA; (●) 14.7% molar excess HMDA.
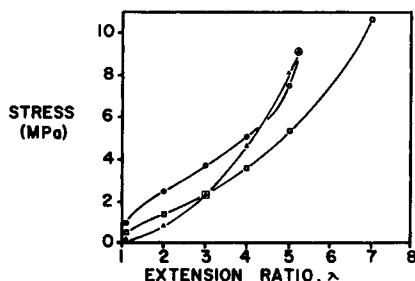

Fig. 4. Effect of polymerization solvent on stress strain properties for polyisoprene–urea copolymers. Urea portion is TDI + MPDA: (O) hexane; (▲) toluene/THF (85/15 vol ratio); (□) toluene.

are markedly decreased in those copolymers containing excess diisocyanate. This phenomenon is explained in terms of biuret crosslink formation which occurs in the urea segments when excess diisocyanate is available. The fact that physical properties are not affected by variation in stoichiometry when moles diamine ≥ moles diisocyanate is not surprising. The effect of increasing the diamine over the diisocyanate is to decrease the amount of blocked urea as discussed above. Reinforcement of the polydiene portion of these copolymers by the urea segments most likely occurs via urea domain formation. Morton[6] has shown that the addition of homopolystyrene to styrene–diene–styrene (S—D—S) triblock polymers does not affect tensile strength although it does raise the stress–strain curve. He contends that the added homopolymer finds its way into the block polystyrene domains and the net result is the same as having an S—D—S polymer of higher styrene content. This is analogous to what is happening in our block polymers. Since we are maintaining equal urea contents but varying the amount of blocked urea present, the stress–strain curves are expected to remain unchanged. The results in Figure 3 show this to be the case.

We mentioned earlier that, although the polydiene portion of these copolymers is formed under homogeneous conditions, the urea portion is not. In fact, upon addition of the diamine a nonaqueous emulsion forms almost immediately. One might suspect, therefore, that the polymerization solvent in which these fine urea particles are formed could influence physical properties. Figure 4 shows the effects obtained by the use of three different polymerization solvents on the modulus of the cured copolymers. All three copolymers contain isoprene in the

polydiene portion and 30% urea by weight. The urea portion was derived from MPDA and TDI. The molecular weights were kept relatively constant ($\bar{M}_v$ of polyisoprene segments ranged from 85 to 98×10^3 g/mole) throughout this series. For the copolymer prepared in the toluene/THF mixture, the THF was added along with the diamine after the polymerization of isoprene was completed. In this way, a microstructure high in 1,4-structural units for the polyisoprene portion was ensured. The modulus values for the copolymer prepared in hexane are considerably higher, particularly at low strains ($\leq \lambda = 3$), than similar values for the other two copolymers. It is also interesting to note the differences in modulus values at high strains ($\geq \lambda = 3$) between the copolymer prepared in pure toluene and that prepared in the toluene/THF mixture. The modulus is considerably higher for the copolymer prepared in the solvent mixture than that prepared in pure toluene. Although no latex particle size measurements have been made, we suspect that particle size varies with polymerization solvent. This factor in turn apparently has some influence on the modulus values of these materials.

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