

Characterization of Polyisobutylene-Based Model Urethane Networks

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Synopsis

Polyisobutylene-based model urethane networks have been prepared by crosslinking liquid α,ω -di(hydroxyl)polyisobutylenes, i.e., PIB-diols carrying exactly two $-\text{CH}_2\text{OH}$ functions, $\bar{F}_n = 2.0 \pm 0.1$, and rather narrow molecular weight distributions, $\bar{M}_w/\bar{M}_n = 1.5\text{--}1.6$, with triphenylmethyl isocyanate $\text{HC}(\text{-}p\text{C}_6\text{H}_4\text{-NCO})_3$. Networks prepared with $\bar{M}_n = 1400$ and 7500 PIB-diols, and with 90/10 and 80/20 mixtures of these PIB-diols (bimodal networks), have been characterized by extraction, by the Flory-Rehner swelling method, and by the Mooney-Rivlin equilibrium modulus method, and tested by stress-strain measurements. \bar{M}_c values of the $\bar{M}_n = 1400$ PIB-diol network obtained by swelling (1550) and by equilibrium modulus studies (1500) were in excellent agreement with the \bar{M}_n of the prepolymer. Also the C_2 parameter was negligible in comparison to C_1 , suggesting the absence of interchain entanglements. This is the first hydrocarbon-based polyurethane network that exhibits a negligible C_2 value by stress-strain measurements of unswollen samples. The \bar{M}_c values of the $\bar{M}_n = 7500$ PIB-diol were also in good agreement with the \bar{M}_n of the prepolymer; however, C_2 was larger than C_1 , indicating interchain entanglements. Evidence for strain-induced toughening was observed with both networks prepared with the $\bar{M}_n = 1400$ and 7500 PIB-diols. The ultimate properties of the two bimodal networks did not show improvement over those of the individual constituents; however, the \bar{M}_n 's of the constituents were not very different.

INTRODUCTION

Fundamental research into the mechanism of isobutylene polymerization resulted in the inifer technique,¹⁻³ which in turn led to a family of new end reactive (telechelic) polyisobutylenes (PIBs).⁴ The nature of the end groups of these PIBs can be controlled by various quantitative derivatization methods, and the molecular weight of the products can be regulated by the monomer/inifer ratio.^{2,5} A large amount of research has been devoted to developing synthetic methods for the preparation of perfectly telechelic, preferably liquid, products and on the quantitative characterization of number average end groups \bar{F}_n . Thus convenient techniques have been described for the preparation of linear PIBs carrying exactly one or two end groups, or three-arm star PIBs with three functionalities, i.e., $\bar{F}_n = 1.0, 2.0$ or 3.0 ± 0.1 .^{2,6,7} Among the many terminal functions available⁴ the $-\text{CH}_2\text{OH}$ end group is of particular significance because of its use for the synthesis of polyurethane (PU) networks.⁸⁻¹⁴ Indeed these materials are not available in semicommercial quantities.¹⁵

For the purpose of the present investigation we have prepared linear telechelic PIBs with $\bar{F}_n = 2.0$, carrying $-\text{CH}_2\text{OH}$ end groups (PIB-diols)

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and have used these intermediates in conjunction with a triisocyanate (tri-triphenylmethyl isocyanate, TTI) for the preparation of model PU networks useful for the investigation of structure-property relationships in rubberlike elasticity. The fact that we have been able to prepare such model networks (the primary objective of this work, see below) also forcefully demonstrates that perfectly telechelic PIBs can be obtained by our synthetic procedure.

PIB-based model PU networks are of theoretical and practical interest. From the academic point of view such networks are of interest because they can be prepared with predetermined molecular weights between crosslinks \bar{M}_c and with well-defined crosslink functionality ϕ ; these model networks are useful to study the molecular theories of rubberlike elasticity. From the practical point of view, PIB-based PUs should exhibit outstanding barrier properties in combination with excellent environmental, hydrolytic and high temperature resistance⁸ and with good low temperature properties (T_g of PIB = -73°C ¹⁶).

Thus the main thrust of this research was the synthesis of well-characterized liquid PIB-diols with $\bar{F}_n = 2.0$ and of narrow molecular weight distribution, the crosslinking of these prepolymers with TTI to model or "perfect" PU networks, and, ultimately, the testing of some aspects of molecular theories of rubberlike elasticity by the use of these unique materials.

EXPERIMENTAL

Materials and Instrumentation

The PIB-diol starting materials have been synthesized by first preparing α,ω -di-*tert*-chloro-PIBs using the inifer method, followed by quantitative derivatization to the $-\text{CH}_2\text{OH}$ end group.^{3,17} Both the synthetic and characterization procedures have been described in detail in a series of publications.^{3,4,6,17} To insure highest quality starting products, and to obtain reasonably narrow molecular weight distribution materials ($\bar{M}_w/\bar{M}_n \sim 1.5$), the PIB-diols were fractionated (precipitation from *n*-hexane into acetone) or by the use of preparative GPC: Waters PrepLC/System 500 A, columns, two columns each of Styragel pore size 10^3 and 500 \AA of $2.54 \text{ cm ID} \times 30.5 \text{ cm}$.

Efforts have been made to use highest quality isocyanates and solvents, and to work under driest conditions. Diphenylmethane diisocyanate (MDI, Mondur M, Mobay Chemical) was vacuum distilled. Tri-triphenylmethane isocyanate (TTI, Desmodur R, Mobay Chemical) was received as a 20% solution in CH_2Cl_2 . It was purified in a dry box under N_2 by precipitating into *n*-pentane to remove insoluble oligomers followed by distillation under high vacuum.⁸ Benzene and *n*-pentane used for swelling and extraction studies were stored over molecular sieves (4 \AA). *p*-Xylene was dried over molecular sieves (4 \AA) for a few days and then refluxed and distilled over MDI. Triethylenediamine (DABCO, Air Products) was used as received.

Molecular weights and their distribution were determined by GPC: Waters Model M-6000 A pump, μ -Styragel columns of 10^5 , 10^4 , and 10^3 \AA

and Ultragel columns of 500 and 100 Å, Model R-401 differential refractometer, flow rate 1 mL/min in THF. The calibration curve was obtained with well-fractionated PIB samples.

Tensile testing was carried out with a calibrated Instron (Model TMM).

Procedures

Chain Extension experiments were carried out in a dry box under dry N₂ atmosphere. α,ω -Di(hydroxyl)PIB and MDI were dissolved in *p*-xylene separately, and predetermined amounts of the solutions were mixed at room temperature by vigorously shaking for a few minutes. The polymer concentration was 46% by volume after mixing. After 24 h at room temperature samples were withdrawn for molecular weight determination. One sample represents one NCO/OH ratio.

Network Preparation was carried out in a dry box under N₂.⁸ PIB-diol and DABCO were dissolved in *p*-xylene (0.02% DABCO to the PIB=diol) and mixed with stoichiometric amounts of TTI dissolved in *p*-xylene. The concentration of the polymer in the mixture was 46 vol %. The mixture was thoroughly mixed by a glass rod and poured in the cavity of open Teflon molding pans, dimension 7 × 6 × 0.5 cm, floating on a bath of mercury placed on a heating plate. The cure schedule was as follows: For the $\bar{M}_n = 1400$ sample 2 days at 70°C in the dry box followed by 3 days at 70°C in a vacuum oven; for the $\bar{M}_n = 7500$ sample 1 day at ambient temperature, 1 day at 70°C, 10 days at 100°C in the dry box followed by 2 days at 90°C in a vacuum oven; for the mixed samples of $\bar{M}_n = 1400$ and $\bar{M}_n = 7500$ 1 day at ambient temperature, 10 days at 70°C, 7 days at 100°C in the dry box, followed by 2 days at 90°C in a vacuum oven. The $\bar{M}_n = 1400$ sample became gradually purple after 1 day at 70°C. This discoloration may be due to traces of water in our system, however, the mechanism of discoloration is unknown.

Swelling and Extraction studies were carried out by the use of benzene and *n*-pentane. Preweighed samples (2 × 0.5 × 0.1 cm) were immersed in the solvents at room temperature. The swollen samples were blot-dried and weighed every 24 h until the equilibrium weight was attained. At this point the samples were dried in vacuum and the equilibrium dry weight was determined. \bar{M}_c was calculated by the Flory-Rehner equation.¹⁸ Cracking of dried samples may occur by the use of relatively thick specimens (> 1 mm), low \bar{M}_c networks (< 2000), and low boiling good solvents.

Dynamic Stress-Strain measurements have been carried out by the use of microdumbbells (5 × 0.25 × 0.1 cm) under continuous strain at 5 cm/min at 25°C.

Equilibrium Stress-Strain measurements for the Mooney-Rivlin analysis were carried out at 25°C in the usual manner.¹⁹ Specifically the samples were stretched and held (every ~10% for the $\bar{M}_n = 1400$ and every ~20% for the $\bar{M}_n = 7500$ sample) until equilibrium modulus was reached. The reverse experiment was done to determine the nonrecoverable deformation (crystallinity) by relaxing the samples and holding (every ~20% for the $\bar{M}_n = 1400$ and every ~40% for the $\bar{M}_n = 7500$ sample) until equilibrium.

RESULTS AND DISCUSSION

 \bar{F}_n by Chain Extension

Perfectly telechelic starting materials (i.e., prepolymers with $\bar{F}_n = 2.0$) are absolutely essential for the preparation of model networks.²⁰ The \bar{F}_n of our PIB diols has been quantitated by determining their \bar{M}_n by GPC, and their equivalent $-\text{OH}$ concentration by IR spectroscopy.¹⁷ According to these measurements, the \bar{F}_n of our materials was consistently 2.0 ± 0.1 .

Independently of these \bar{M}_n plus spectroscopic characterization methods, we have also determined \bar{F}_n by chain extension experiments. Thus we have reacted a series of PIB-diol/MDI mixtures with various $[-\text{NCO}]/[-\text{OH}]$ ratios and determined the molecular weights of the "extended" products by GPC. Figure 1 shows the results. Ideally the maximum \bar{M}_n is expected to arise at $[-\text{NCO}] = [-\text{OH}]$. According to the data the systems approach the ideal case, i.e., maximum chain extension was obtained at $\bar{F}_n = 2r$, where $r = [-\text{NCO}]/[-\text{OH}]$. Specifically, we obtained $\bar{F}_n = 2.04$ for the $\bar{M}_n = 1400$ PIB-diol, and $\bar{F}_n = 2.15$ for the 7,500 PIB-diol. Since it is physically impossible for \bar{F}_n to be higher than 2.0 in these systems, these data strongly suggest $\bar{F}_n = 2.0$, i.e., perfect and functionality for both prepolymers.

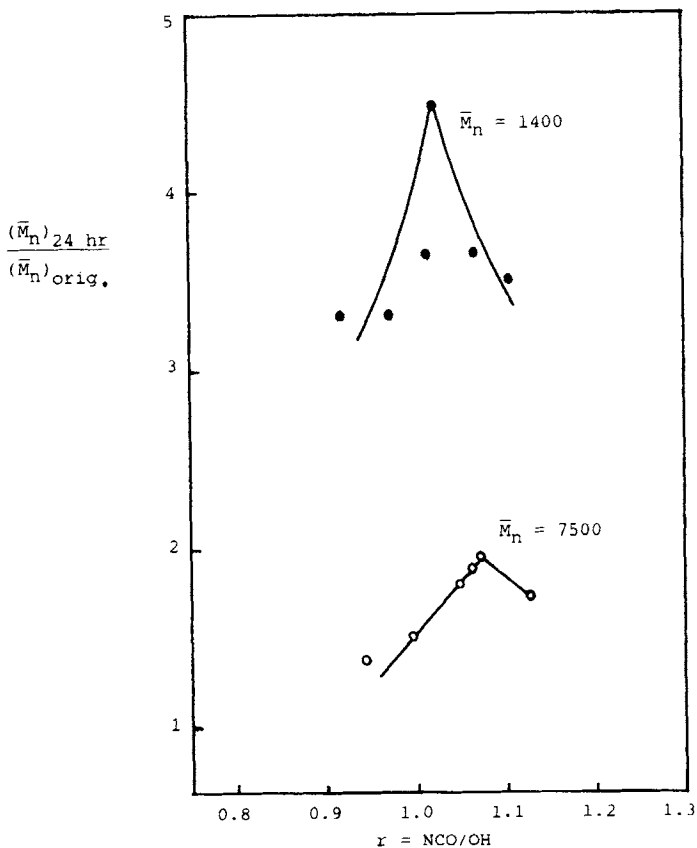


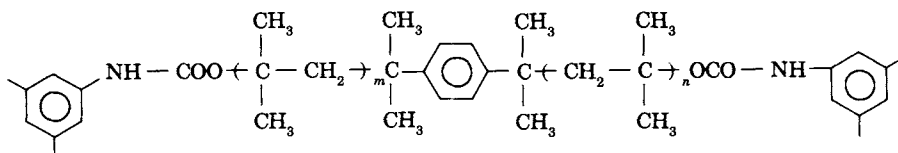
Fig. 1. Chain extension with various NCO/OH ratios.

Swelling and Extraction

Swelling and extraction data provide important insight into network characteristics.¹⁸ We have determined \bar{M}_c of our networks by the Flory-Rehner swelling method together with the percent extractables (sol fraction). Table I shows the data.

The extractable (sol fraction) of the $\bar{M}_n = 1400$ PIB-diol determined by the use of benzene solvent is very low (2%), indicating essentially complete network formation, and the \bar{M}_c calculated from swelling data is close to the theoretical value within experimental error. The results obtained with the $\bar{M}_n = 7500$ PIB-diol are less satisfactory (5% sol) but still marginally acceptable. The same general comments also hold for the two bimodal networks. The higher mol wt PIB-diol crosslinked very slowly (see Experimental), and a somewhat shorter cure-schedule gave completely unacceptable networks.

Swelling and extraction experiments have also been carried out by the use of *n*-pentane as solvent; however, the data obtained were completely unexpected. For example, the \bar{M}_c calculated for the $\bar{M}_n = 1400$ PIB-diol network was 2300 and that for the $\bar{M}_n = 7500$ PIB-diol was 3200 (both with negligible sol fractions). These data are quite puzzling considering that the interaction parameter χ is almost identical for PIB-benzene ($\chi = 0.5$) and PIB-pentane ($\chi = 0.49$).¹⁶ Evidently, in contrast to benzene, *n*-pentane is not a good solvent for a network that contains relatively short PIB segments together with significant amounts of urethane linkages:



m and $n \sim 11$ for the network prepared with $\bar{M}_n = 1400$ prepolymer.

Stress-Strain Properties

Figure 2 shows the stress-strain curves of the networks investigated. As expected, the modulus decreases while the elongation at break increases with increasing \bar{M}_n of the prepolymer (\bar{M}_c of the network). Overall, the stress-strain properties of the fully crosslinked network obtained from the $\bar{M}_n = 1400$ prepolymer are sufficient for many applications where high strength is not a mandatory requirement, i.e., medical applications (according to Ref. 21 PIB is hemocompatible), coatings, membranes. The properties of the network prepared from the $\bar{M}_n = 7500$ PIB-diol are of course lower because its crosslink density is too low.

Bimodal networks comprise a mixture of relatively long and very short chains²² and were found to combine high tensile strength with high elongation.²³ It was of interest to prepare bimodal networks with our $\bar{M}_n = 1400$ and 7500 PIB-diols and to investigate their ultimate dynamic properties. We have prepared two bimodal networks containing 90/10 and an 80/20 mole mixtures of $\bar{M}_n = 1400$ and 7500 PIB-diols, and determined

TABLE I
 Network Characterization Data

\bar{M}_n^a	Swelling and extraction		Mooney-Rivlin analysis				
	\bar{M}_w/\bar{M}_n^a	\bar{M}_c^b	Extractables (%)	$2C_1$	$2C_2$	C_2/C_1	\bar{M}_c^c
1400	1.5	1550	2	0.300	0.016	0.053	1500
7500	1.6	8640	5	0.05	0.06	1.2	9000
Bimodal Networks							
2000 ^d		1860	3				
2600 ^e		2960	5				

^a By GPC.

^b Calculated by the Flory-Rehner equation,¹⁸ benzene solvent.

^c Calculated from $2C_1 = A_p \rho R T V_{2C}^{2/3} M_c^{-1}$, where $A_p = 1 - 2/\phi = 1/3$, $\rho = 0.9169 \text{ g cm}^{-3}$ = density of PIB at $T = 298 \text{ K}$, R = gas constant, and $\bar{V}_{2C} = 0.46$ = volume fraction of polymer present during crosslinking.

^d Calculated average \bar{M}_n of a 90.4/9.6 mol mixture of $\bar{M}_n = 1400$ and 7500 PIB-diols.

^e Calculated average \bar{M}_n of a 80.8/19.2 mol mixture of $\bar{M}_n = 1400$ and 7500 PIB-diols.

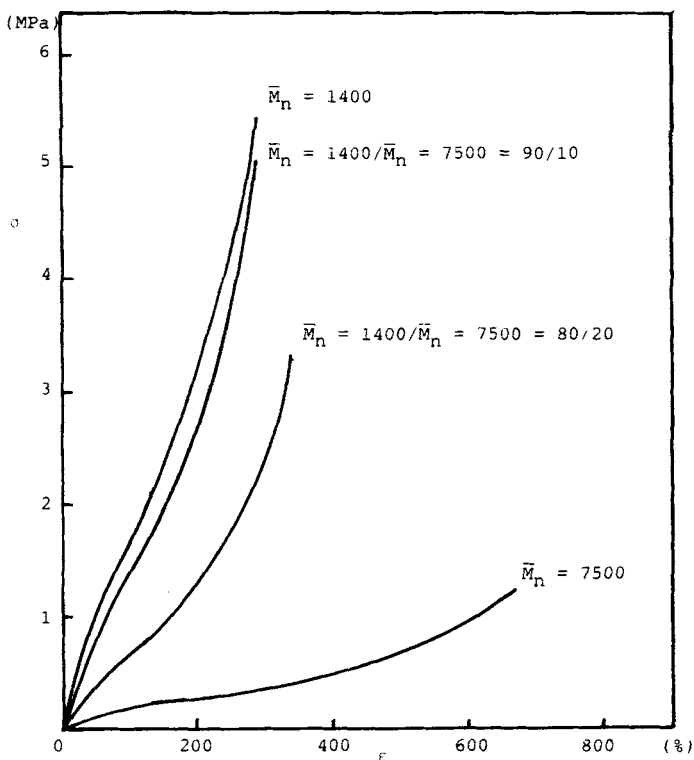


Fig. 2. Stress-strain curves of PIB networks.

their sol fractions and \bar{M}_c by swelling, as well as their stress-strain behavior. Table I and Figure 2 show the results. According to the percent extractables (cf. Table I), a satisfactory (3%) and a marginally acceptable (5%) network has been obtained. The \bar{M}_c values calculated from swelling data are very good for the 90/10 mixture and marginal for the 80/20 bimodal network. In contrast, the ultimate properties of these networks (cf. Fig. 2) did not show improvement over those of the components. Indeed, the stress-strain curve of the 90/10 bimodal network was almost superimposable with that of the pure $\bar{M}_n = 1400$ PIB-diol network, while that of the 80/20 mixture exhibited much lower ultimate values. It should be pointed out that the disparity in mol wts used by us was much smaller (only a factor of 5) than that used by the previous workers.^{22,23}

Network Analysis by Mooney-Rivlin Treatment

Figure 3 shows the $[f^*]$ vs. $1/\alpha$ (Mooney-Rivlin) plot, and Table I summarizes the data calculated from the plot. The solid line represents the initial elongation data. Evidently the \bar{M}_c of the network prepared with the $\bar{M}_n = 1400$ PIB-diol calculated from the high deformation modulus $2C_1$ for the deformation of a phantom network is in excellent agreement with the \bar{M}_n of the prepolymer. C_2 is negligible in comparison to C_1 . According to these data, this network may be essentially "perfect," i.e., the modulus of this network is most likely affected only by crosslink density and not by

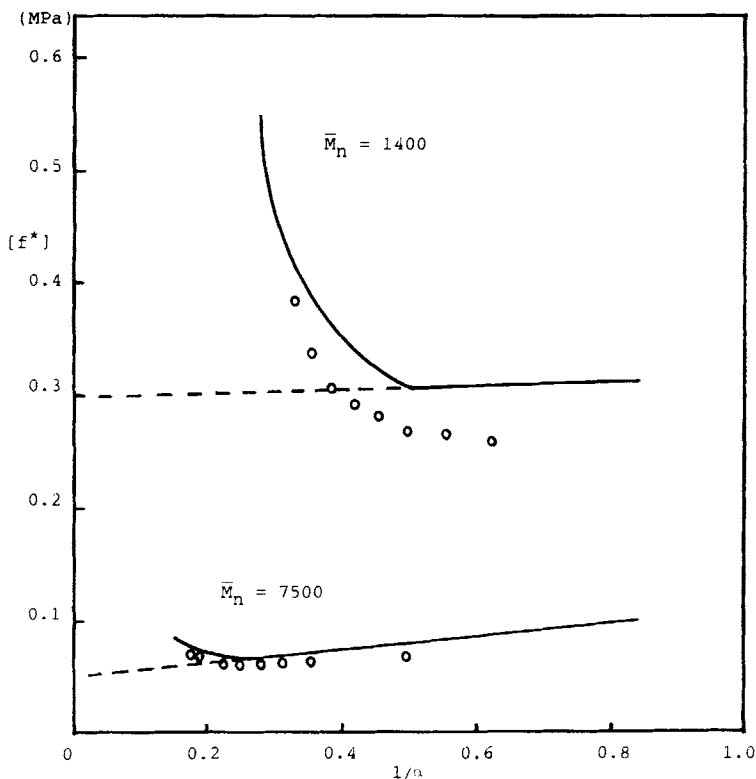
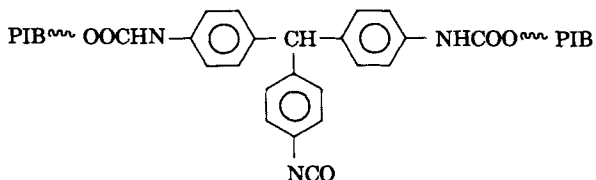


Fig. 3. Stress-strain isotherms for unswollen PIB networks at 25°C: (○) obtained out of sequence to test for reversibility; the initial elongation data.

other structural factors, for example, interchain entanglements. This is the first hydrocarbon-based PU network that exhibits a negligible C_2 value by stress-strain measurement of an unswollen specimen. The preparation of this network became possible only because of the availability of a perfectly telechelic ($\bar{F}_n = 2.0 \pm 0.1$) PIB-diol with \bar{M}_n much lower than the entanglement molecular weight ($\bar{M}_{en} \approx 12000$ for PIB²⁴) and of sufficiently narrow molecular weight distribution.

In contrast, the network obtained with the $\bar{M}_n = 7500$ PIB-diol had a C_2 higher than C_1 , although the absolute value of C_2 was still quite low. According to the theory of rubberlike elasticity²⁵⁻²⁸ the ratio C_2/C_1 is a measure of the extent to which the elongational deformation changes from essentially affine to the phantom limit with increasing stress and is related to the firmness with which the crosslinks are constrained in the network. Interchain entanglements act as configurational restraints on crosslinks which decrease with elongation (transition from affine to phantom behavior). Therefore, it is suggested that interchain entanglements are present in the networks obtained with the $\bar{M}_n = 7500$ PIB-diol. These networks exhibit a larger C_2/C_1 ratio than those made with the $\bar{M}_n = 1400$ PIB-diols due to interchain entanglements. The \bar{M}_c of the $\bar{M}_n = 7500$ diol network calculated by the Mooney-Rivlin analysis is higher by factor of 1.2 than \bar{M}_n which, in view of the experimental difficulties involved, is still considered to be a satisfactory agreement.

Very long curing times and high temperatures were employed (cf. Experimental) to obtain acceptable networks, particularly with the higher molecular weight PIB-diols. We speculate that the rate of crosslinking is much reduced in these systems because of the decreased mobility of the third unreacted isocyanate group during molecular weight build-up:



This undesirable phenomenon is absent with lower molecular weight linear prepolymers (i.e., $\bar{M}_n \lesssim 2000$) and may be minimized by the use of higher molecular weight three-arm star PIB-triols. Experimentation along these lines is continuing.

Finally, as shown by the data in Figure 3, both Mooney–Rivlin plots exhibit a strong upturn at increasing elongations. Also, the equilibrium moduli obtained in a reverse experiment, i.e., with a series of decreasing elongations (open circles in Fig. 3), are much smaller than those obtained with increasing elongations. According to these observations, strain-induced toughening (whose origin remains obscure in this system) commences at $\sim 100\%$ (0.5 on the $1/\alpha$ scale) elongation for the $\bar{M}_n = 1400$ PIB-diol network, and part of it remains irrecoverable. The data for the $\bar{M}_n = 7500$ network are more difficult to interpret in this regard.

Financial support by the National Science Foundation (Grant DMR 84-18617) is gratefully acknowledged. One of us (T. M.) is grateful to the Japan Synthetic Rubber Co. for an educational leave.

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Received July 26, 1985

Accepted January 5, 1986