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Reactions

Polyisobutylene Model Elastomers Prepared Using Demonstrably Complete End-Linking Reactions.

2. Elongation Moduli of the Trifunctional Networks Prepared from the Three-Arm Polymers

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Summary

Cationic polymerizations with a trifunctional initiator-chain transfer agent were used to prepare three-arm polyisobutylene $[C(CH_3)_2CH_2]$ (PIB) molecules with hydroxyl groups at all three chain ends. Extensive spectroscopic analyses confirmed the essentially perfect trifunctionality of the polymers, which were then end-linked using an aromatic diisocyanate to give trifunctional model networks. The PIB elastomers were found to have negligible sol fractions, which demonstrates that the end-linking reactions used to prepare them were essentially complete. They were studied, swollen, with regard to their equilibrium stress-strain isotherms in uniaxial extension at 25 °C. As was found to be the case for trifunctional and tetrafunctional PIB networks prepared from the linear chains, the results were in satisfactory agreement with theory and yielded no evidence that inter-chain entanglements contribute to the modulus at elastic equilibriums.

Introduction

In a previous investigation (1), model elastomeric networks were prepared from linear polyisobutylene (PIB) $[C(CH_3)_2CH_2-]$ chains having reactive groups at both ends (2-4). These difunctionally-terminated chains had been capped with either hydroxyl or isopropenyl groups, and were end-linked into network structures using an aromatic triisocyanate and tetrafunctional silane, respectively. The resulting elastomers were important for two reasons, (i) the PIB chains from which they were prepared were known to have functionalities of almost exactly two, with no evidence for inert cyclics (1-5), and (ii) they contained essentially no sol fraction (1), a circumstance widely held to indicate completeness in the reaction used to form the network (6). The demonstrated completeness in the end-linking reaction meant that these model PIB networks were of very nearly perfect structure, with values of the critically important molecular weight M_c between cross-links simply equal to the values of the number-average molecular weight M_n of the PIB chains prior to their end-linking (7). These model elastomers were therefore extremely useful (1) in testing the molecular theories (8-13) of rubberlike elasticity.

In the case of a triisocyanate, there has been some concern that the third isocyanate group to react in the molecule may do so less readily than the first two. The methodology used to prepare the telechelic PIB chains may be used to circument this possible difficulty, specifically by the use of a trifunctional initiator-chain transfer agent to prepare "three-arm" PIB chains (14). Such chains should be end-linkable with a *di*isocyanate into model elastomers in which $M_c = (2/3)\ M_n$, and the cross-link functionality is exactly three. Such trifunctional PIB networks thus have reliably known structures (15), and can therefore be used to evaluate the molecular theories of rubberlike elasticity, particularly with regard to predictions of elongation moduli.

Experimental Details

Cationic polymerizations utilizing the "inifer" (initiator-transfer) technique (2-5) were used to obtain the two isobutylene polymers employed in this study. Details on the reaction used to prepare the desired three-arm hydroxyl-terminated chains are described elsewhere (14,15). The polymers thus obtained were characterized by infrared and ^{1}H-NMR spectroscopy, and were found to have the expected functionality $\phi = 3.0$ within experimental error (5). Gel permeation chromatography and vapor phase osmometry indicated their molecular weights to be M_n = 5,600 and 11,600 g mol^{-1}, respectively.

The hydroxyl-terminated chains were end-linked using a highly purified (vacuum-distilled) sample of 4,4-diphenylmethane diisocyanate (methylene diphenylisocyanate, MDI). The reaction was carried out under a dry nitrogen atmosphere in a stainless steel enclosure. The polymer was dissolved in dry xylene (40%, w/v), mixed with a stoichiometric amount of MDI, then poured into an open Teflon® casting dish. The mixture was allowed to cure at 45° C for two weeks while the solvent was slowly evaporated. The partially cured sheet was then put into a oven, and curing was completed at 85-90° C for three days under vacuum (17).

Both model PIB networks thus prepared were subjected to exhaustive extractions, specifically in stirred benzene and/or *n*-pentane at room temperature for several days. Extraction measurements carried out on model polydimethylsiloxane networks containing known amounts of soluble chains of various molecular weights indicate that any soluble material present in the PIB networks would be entirely removed by this procedure (18).

Equilibrium stress-strain measurements were carried out in elongation at 298 K, in the usual manner (7, 19, 20). Separate portions of each network sheet were studied swollen to varying degrees so as to minimize complications from strain-induced crystallization (21-24) and to reduce uncertainties (10-13) in extrapolating elasticity data to obtain the modulus in the limit of very high elongations. The non-volatile solvent 1,2,4-trichlorobenzene was chosen as diluent.

Results and Discussion

The extraction experiments did not cause any significant change in the weights of the networks; i.e., their sol fractions were zero within a few tenths of a percent, which demonstrates near completeness of the end-linking reaction within the network structures.

The stress-strain data were interpreted in terms of the reduced stress or modulus (21, 25, 26)

$$\left[f^*\right] \equiv f v_2^{1/3}/A^*(\alpha - \alpha^{-2}) \qquad (1)$$

where f is the equilibrium elastic force, v_2 is the volume fraction of polymer in the (swollen) network, A^* is the cross-sectional area of the unswollen, unstretched sample, and $\alpha = L/L_i$ is the relative length or elongation of the swollen sample. The values of v_2 used in the present experiment are given given in column three of Table I. The values of f^* were plotted against reciprocal elongation, as suggested by the semiempirical equation

$$\left[f^*\right] = 2C_1 + 2C_2\alpha^{-1} \qquad (2)$$

in which $2C_1$ and $2C_2$ are constants independent of α (26). Typical results are shown in Figure 1. Least-squares analysis was used to obtain values of the elastic constants $2C_1$ and $2C_2$.

The constant $2C_1$ is used as an approximation to the modulus $\left[f^*\right]_\infty$ in the limit at high deformation (1,7). The values of $\left[f^*\right]_\infty$ thus obtained and the other elastic constant $2C_2$ are given in columns four and five of the Table. The values of $2C_2$ are seen to be generally very small, frequently negligibly small, as is usually the case (26) for highly swollen networks. The values of $\left[f^*\right]_\infty$ were interpreted in terms of the equation (7)

$$\left[f^*\right]_\infty = A_3\rho RTM_c^{-1} \qquad (3)$$

where A_3 is the "structure factor" for the tri-functional network, $\rho = 0.9169$ g cm^{-3} is the density of the PIB at T = 298 K, and R is the gas constant. The resulting values of A_3 are given in column six of the Table. Rubber elasticity theory (9, 10) in which contributions from inter-chain entanglements are not explicitly introduced gives $A_\phi = 1 - 2/\phi$, and thus values of 1/3 for the trifunctional networks. As can be seen from comparisons between the last two columns of the Table, the experimental values of A_3 (which are proportional to the modulus) are in satisfactory agreement with theory. The fact that they are almost always smaller than the theoretical values indicates that inter-chain entanglements do not contribute significantly to the elastic modulus at equilibrium. Very similar results had been obtained on the PIB networks prepared from the linear (two-arm) polymers (1). The present results also strongly support the previous results obtained on poly(dimethylsiloxane) networks (7), and on polyurethane networks (27), which were considered by some to be less than definitive because of the presence of a significant sol fraction.

TABLE I

Stress-Strain Results, PIB Model Networks

M_n, g mol^{-1}	M_c, g mol^{-1}	v_2^{a}	$[f^*]_\infty^{b}$, N mm^{-2}	$2C_2^{c}$, N mm^{-2}	A_3^{d}	
					Exp	Theor
5,600	3,700	0.400	0.237	0.185	0.441	0.333
		0.310	0.174	0.0287	0.323	0.333
		0.295	0.169	0.0473	0.316	0.333
11,600	7,700	0.788	0.0604	0.0367	0.207	0.333
		0.568	0.0636	0.0081	0.218	0.333
		0.506	0.0653	0.0051	0.224	0.333
		0.391	0.0656	0.0031	0.225	0.333
		0.300	0.0662	0.0043	0.227	0.333
		0.261	0.0684	0.0016	0.235	0.333

[a] Volume fraction of polymer in the network (swollen with 1,2,4-trichlorobenzene) during the stress-strain measurements.

[b] The elongation modulus in the limit at high deformation.

[c] Constant in the Mooney-Rivlin representation of the modulus.

[d] The factor relating the network modulus to the degree of cross-linking, as represented in M_c^{-1}.

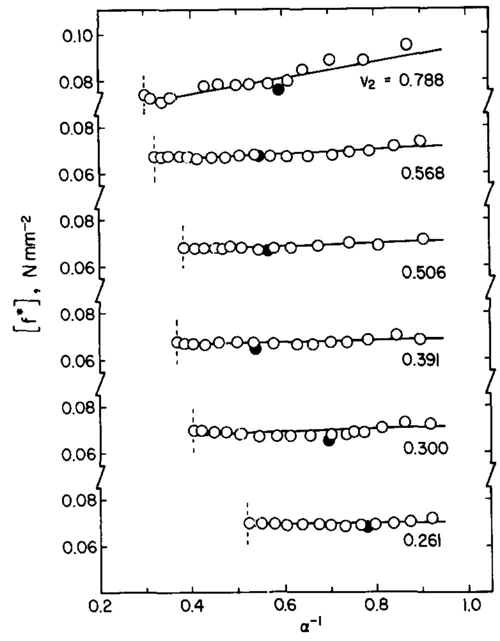

Figure 1. Stress-strain isotherms at 298 K for the PIB networks having M_c = 7,700 g mol^{-1}. Each curve is labelled with the volume fraction of polymer present in the network, the filled circles locate results taken out of sequence to test for reversibility, and the vertical dashed lines show the values of the elongation α at which rupture occurred.

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