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Polyisobutylene Model Elastomers Prepared Using Demonstrably Complete End-Linking Reactions

1. Elongation Moduli of the Trifunctional and Tetrafunctional Networks Prepared from the Linear Polymers

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Summary

Linear polyisobutylene (PIB) molecules with either hydroxyl or isopropenyl groups at the chain ends were prepared using cationic polymerizations with bifunctional initiator-chain transfer agents. Extensive spectroscopic analyses confirmed the essentially perfect difunctionality of the two types of polymers. The former polymers were end-linked using an aromatic triisocyanate, and the latter by means of a tetrafunctional silane. The resulting trifunctional and tetrafunctional model PIB networks were found to have absolutely negligible sol fractions, which demonstrates that the end-linking reactions used to prepare them were essentially complete. The networks were studied with regard to their equilibrium stress-strain isotherms in uniaxial extension at 25°C. The results thus obtained are in satisfactory agreement with theory and yield no evidence whatever for significant elastic contributions from inter-chain entanglements.

Introduction

In order to test the molecular theories of rubberlike elasticity (ERMAN, FLORY, 1978, 1982; FLORY, 1976, 1977; FLORY, ERMAN, 1982) one needs elastomeric networks of known structure, specifically networks having known values of the molecular weight M_c between cross-links. The most direct way of achieving such "model" networks is to end-link functionally terminated polymer chains having a number-average molecular weight M_n equal to the desired value of M_c (MARK, 1982). For M_c to be equal to M_n, the end-linking reaction must be essentially complete, otherwise the resulting network structure is imperfect with a reduced value of the elastic modulus.

One way in which such possible incompleteness has been gauged is through the amount of soluble polymer ("sol fraction") extractable from the network (GOTTLIEB et al.,1981). The use of such information for this purpose, however, is valid only if the sol fraction is known to consist of reactive but unreacted chains (MARK, LLORENTE, 1980; ERMAN, FLORY, 1982). Only in this case would the failure of these chains to be incorporated in the network structure indicate an incompleteness of end-linking (dangling ends) within the gel (network portion of the system). One specific difficulty with this approach is the fact that most model elastomeric networks (MARK, 1982) have been prepared from poly(dimethylsiloxane)(PDMS) $[Si(CH_3)_2O-]$. This polymer invariably contains significant amounts of cyclics (ELIAS, 1977; MARK, LLORENTE, 1980), and additional cyclics would be expected to be formed in the end-linking reaction (LEUNG, EICHINGER, 1983). DMS cyclics would of course be inert and thus remain soluble, thereby giving a significant sol fraction even in a network containing essentially no imperfections.

A system has now been found which circumvents these difficulties. Polyisobutylene (PIB) $[C(CH_3)_2CH_2-]$ has now been prepared with either hydroxyl groups (IVAN et al., 1980) or isopropenyl groups (KENNEDY et al., 1979) at the ends; these polymers have functionalities of two within experimental error, with no evidence at all for cyclics. Most important, in an observation which almost relegates chemical analyses of the reactants to secondary importance, these polymers can be used to prepare networks having essentially zero sol fraction. The present study describes the preparation and characterization of some PIB networks which are demonstrably complete in their end-linking as judged by their negligible sol fractions. The networks are then used to provide a definitive comparison between predicted and observed elastic moduli in elongation.

Experimental Details

All of the isobutylene polymers employed had been prepared using the p-dicumyl chloride/boron trichloride/isobutylene system, with cationic polymerizations carried out using the new "inifer" (initiator-transfer) technique (KENNEDY, 1977; KENNEDY et al., 1979; IVAN et al., 1980). The hydroxyl-terminated polyisobutylenes $HO-CH_2-PIB-CH_2-OH$ were prepared from α,ω-di(isobutenyl)polyisobutylene by regioselective hydroboration followed by alkaline peroxide oxidation (IVAN et al., 1980). Their characterization using infrared spectroscopy, ^{1}H-NMR analysis (of pure and silylated products), and ultraviolet spectroscopy (of phenylisocyanate-treated diols) showed the chains to have the desired functionality of 2.0(± 0.1). The two PIB samples prepared in this manner had values of M_n of 3,400 and 2,500 g mol^{-1} respectively, as determined by gel permeation chromatography (GPC) and vapor-phase osmometry (VPO). The sample of isopropenyl-terminated PIB $CH_2=C(CH_3)-PIB-C(CH_3)C=CH_2$ was obtained by complete dehydrochlorination of α,ω-di(t-chloro)polyisobutylene. ^{1}H-NMR spectroscopy showed its functionality also to be 2.0 (± 0.1), and GPC and VPO gave M_n = 2,100 g mol^{-1}.

The hydroxyl-terminated chains were end-linked using a highly purified (vacuum-distilled) sample of triphenylmethane triisocyanate (TTI) $[CH(C_6H_5NCO)_3]$. The reaction was carried out under a dry nitrogen atmosphere in a stainless steel enclosure. α,ω-Di(hydroxy)polyisobutylene was dissolved in dry tetrahydrofuran (40%, w/v), mixed with a stoichiometric amount of TTI, 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. Then the polyurethane sheet was placed in a vacuum oven and curing was completed at 85-90°C for three days under vacuum (CHANG, KENNEDY, 1982). Preliminary studies of network moduli indicated that the highest extents of reaction were obtained for the 1:1 NCO:OH stoichiometric balance used in preparing the networks to be investigated. The isopropenyl-terminated chains were end-linked using tetra(dimethylsilyl)orthosilicate $[Si(OSi(CH_3)_2H)_4]$, with chloroplatinic acid as catalyst. The mixture was placed into a Teflon®-lined aluminum mold and then heated to 80°C under vacuum to remove bubbles. The mold was then sealed and the reaction carried out at 95°C under nitrogen for approximately 24 hr. (PAN, 1982).

All three model PIB networks thus prepared were subjected to exhaustive extractions, specifically in stirred benzene and/or tetrahydrofuran at room temperature for approximately one week. 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 (MARK, ZHANG, manuscript in preparation).

Equilibrium stress-strain measurements were carried out in elongation at 25°C, in the usual manner (MARK, LLORENTE, 1980; MARK, 1981a, 1982). Portions of all three samples were studied in the unswollen state; additional portions of one of the three were studied swollen to various extents with 1,2,4-trichlorobenzene as well.

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 experimental error, which demonstrates completeness of the end-linking reaction within the network structures.

The stress-strain data were interpreted in terms of the reduced stress or modulus (FLORY, 1953; MARK, FLORY, 1966; MARK, 1975)

$$[f^*] \equiv fv_2^{1/3}/A^*(\alpha - \alpha^{-2}) \qquad (1)$$

where f is the equilibrium elastic force, v_2 is the volume fraction of polymer in the 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 sample. The values of v_2 used in the present experiment are given in column four of Table I. The values of $[f^*]$ were plotted against reciprocal elongation, as suggested by the semiempirical equation (MARK, 1975)

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

in which $2C_1$ and $2C_2$ are constants independent of α. Typical results are shown in Figure 1. The increases or

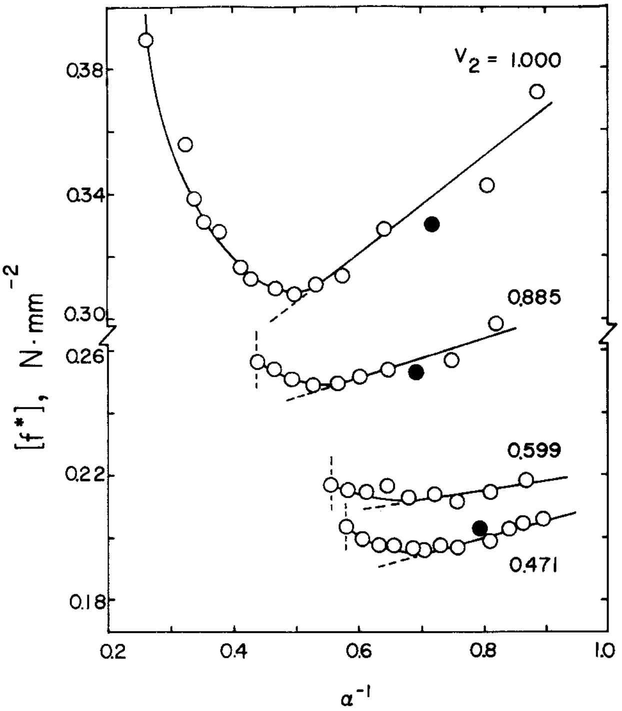

Figure 1. Stress-strain isotherms for the PIB networks having $M_c = M_n$ = 2,500 g mol^{-1}. Each curve is labelled with the volume fraction of polymer present in the network, the filled circles locate results taken out of sequence to test for reversibility, and the vertical dotted lines show the values of the elongation α at which rupture occurred.

TABLE I

Stress-Strain Results, PIB Model Networks

PIB	M_n, g mol^{-1}	End-linking Agent	v_2[a]	$[f^*]_\infty$,[b] N mm^{-2}	A_ϕ[c] Exp	A_ϕ[c] Theor
HO ∿∿∿ OH	3400	Triisocyanate	1.000	0.235	0.306	0.333
HO ∿∿∿ OH	2500	Triisocyanate	1.000	0.248	0.254	0.333
			0.885	0.216	0.238	0.333
			0.599	0.191	0.210	0.333
			0.471	0.157	0.173	0.333
Vi ∿∿∿ Vi	2100	Tetrafunctional Silane	1.000	0.390	0.360	0.500

[a] Volume fraction of polymer in the network during the stress-strain measurements.

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

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

upturns in modulus at high elongation are due to strain-induced crystallization (MARK, 1979; MOHAJER et al., 1982; BAGRODIA et al., 1982), which is of course diminished by the presence of swelling diluent (FLORY, 1953). The linear portions of the curves were extrapolated to $\alpha^{-1} = 0$ to obtain values of the elastic constant $2C_1$.

The constant $2C_1$ is used as an approximation to the modulus $[f^*]_\infty$ in the limit at high deformation. Although some error may be involved in the case of unswollen networks showing large values of $2C_2$ (FLORY, 1977; ERMAN, FLORY, 1978, 1982; FLORY, ERMAN, 1982), this is a good approximation for swollen networks. The values of $[f^*]_\infty$ thus obtained are presented in column five of the Table. They were interpreted in terms of the equation (MARK, 1982)

$$[f^*]_\infty = A_\phi \rho RTM_c{}^{-1} \tag{3}$$

where A_ϕ is the "structure factor" for the ϕ-functional network, $\rho = 0.9169$ g cm^{-3} is the density of the PIB at T = 298K, and R is the gas constant. The resulting values of A_ϕ are given in column six of the Table. Rubber elasticity theory (FLORY, 1976, 1977) 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 and 1/2 for the tetrafunctional one. As can be seen from comparisons between the last two columns of the Table, the experimental values of A_ϕ (which are proportional to the modulus) are in satisfactory agreement with theory. The fact that they are always smaller than the theoretical values indicates that inter-chain entanglements do not contribute significantly to the elastic modulus at equilibrium. The same conclusion is reached upon analogous interpretation of the low deformation modulus $[f^*]_1 \simeq 2C_1 + 2C_2$ (SUNG, 1982). It may be noted that the values of M_c investigated are significantly smaller than the molecular weight $M_{en} \simeq 8{,}900$ g mol^{-1} between entanglements in PIB, as estimated from the plateau modulus of the uncross-linked chains (FERRY, 1970). This is largely irrelevant, however, because of the chain extension which occurs in the process of forming any end-linked polymer network. In fact, any contributions from such (presumably tetrafunctional) entanglements should have been easily discernible since use of the above value of M_{en} for M_c in Eqn (3) would have yielded increments in $[f^*]_\infty$ of approximately 0.128 N mm^{-2} for the trifunctional and tetrafunctional PIB networks.

The present results strongly support the previous results obtained on PDMS networks (MARK, 1982) and on polyurethane networks (MARK, 1981 b), which were considered by some to be less than definitive because of the presence of a non-zero sol fraction. The PIB model networks are seen to be complete in their end-linking, which makes them invaluable in the study of a variety of quantitative molecular aspects of rubberlike elasticity.

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