Polymer Bulletin 11, 319–324 (1984)

Polymer Bulletin

Models

The Use of Model Polyisobutylene Networks to Study Strain-Induced Crystallization

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Summary

Model elastomeric networks were prepared by trifunctionally end linking hydroxyl-terminated chains of polyisobutylene having number-average molecular weights in the range $10^{-3}M_n = 2.4 - 10.7$ g mol^{-1}. Their stress-strain isotherms in elongation at 25°C in the unswollen state showed significant increases or upturns in modulus at high elongations, due to strain-induced crystallization. Increase in degree of cross-linking (decrease in M_n) was found to decrease the elongation required to initiate crystallization and the maximum extensibility, but to increase the magnitude of the upturn in modulus.

Introduction

Elongation of an elastomer causes alignment of some of the polymer chains of which it is composed, thus lowering their configurational entropy (1,2). This decreases the magnitude of the additional decrease in entropy ΔS_{cr} required for crystallization and therefore increases the melting point, since it is inversely proportional to ΔS_{cr} (1-4). Such "strain-induced" crystallization is of great importance with regard to the mechanical properties of an elastomer since the crystallites thus formed reinforce the network structure with an associated increase in ultimate properties, particularly the ultimate strength (1,5,6). For this reason, it is of considerable importance to characterize the dependence of strain-induced crystallization on network structure.

In studying elastomeric properties in general, it is very advantageous to use "model" networks, i.e., those formed in a way which provides independent information on the network structure. Such a network can be prepared, for example, by end linking functionally-terminated chains (7); in this case the number-average molecular weight M_n of the chains prior to their end linking becomes the molecular weight M_c between cross-links, and this is an inverse measure of the degree of cross-linking (1). The same relationship pertains, of course, to the molecular weight distribution as well. Finally, there is the additional advantage of very low incidence of dangling chains (7), which could interfere with the crystallization process.

Most model elastomeric networks prepared to date have consisted of chains of poly(dimethylsiloxane) (PDMS) $[-Si(CH_3)_2O-]$ (7). Its very low melting point ($-40^{o}C$) (8) and low rate of crystallization, however, have prevented its use in characterizing the dependence of strain-induced crystallization on network structure. Much more suitable for this purpose are model networks of polyisobutylene (PIB) [$-C(CH_3)_2CH_2-$], which has a melting point of 5 ^{o}C (8) and crystallizes quite readily (9). For this reason, PIB was chosen for the present investigation, which focuses on the effects of degree of cross-linking on strain-induced crystallization.

Experimental Details

The polymer samples employed were PIB diols (10,11) having the number-average molecular weights given in the first column of Table I. To facilitate mixing of the PIB chains with the triphenylmethane triisocyanate end-linking agent, the former was dissolved in a small amount of xylene and the latter in a small amount of dimethylformamide. Amounts of the two solutions corresponding to a stoichiometric balance between hydroxyl groups and isocyanate groups were then stirred together at 70-75^{o}C for 20 min.® The resulting solution was then poured into prewarmed 6 x 7 cm Teflon molds to a depth of approximately 0.1 cm and held at 70-75 ^{o}C for one day. All of the above steps were conducted in a "dry box" under dry nitrogen. The final step in the cure consisted of holding the samples at the same temperature under vacuum for an additional two days. Strips cut from the network sheets were then extracted at room temperature in tetrahydrofuran for two days. The amounts of material thus extracted gave the values of the sol fraction listed in the second column of Table I.

The cross-sectional area A^* of each unswollen strip was measured at room temperature. In order to facilitate the approach to elastic equilibrium, each strip was then stretched to the desired first value of the elongation or relative length $\alpha = L/L_i$ at $50^{o}C$. After the force f became constant, the temperature was reduced to $25^{o}C$. When f again became constant, it was recorded, and the temperature increased again for the next value of α. This scheme was continued to obtain the complete $25^{o}C$ stress-strain isotherm up to the rupture point of the sample.

Results and Discussion

Values of the reduced force on modulus defined by (5,12,13)

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

were plotted against reciprocal elongation in the usual Mooney-Rivlin representation (2,13) of the modulus, $[f^*] = 2C_1 + 2C_2\alpha^{-1}$. The resulting stress-strain isotherms are shown in Figure 1. The general shape shows an initial low-elongation portion linear in α^{-1}, followed by a marked upturn in $[f^*]$ at higher elongations. Least-squares analysis was used to locate the linear portions of each isotherm and the resulting values of the constants $2C_1$ and $2C_2$ are given in columns three and four of Table I.

The values of the elongation α_u at which the strain-induced crystallization becomes discernible, as judged by the non-linear upturn

TABLE I

PIB Network Characteristics and Stress-Strain Results at 25°C

M_n, g mol^{-1}	Sol Fraction	$2C_1$,[a] N mm^{-2}	$2C_2$,[a] N mm^{-2}	α_u[b]	α_m[c]	α_r[d]	$[f^*]_r$,[e] N mm^{-2}	$\Delta[f^*]_r$,[f] N mm^{-2}	$\Delta[f^*]_r/[f^*]_r$
2,400	0.020	0.0553	0.0494	1.59	1.66	4.29	0.132	0.0649	0.969
2,500	---	0.0456	0.0280	1.46	1.87	4.47	0.091	0.0510	0.784
8,550	0.020	0.0320	0.0521	1.70	2.60	4.53	0.074	0.0304	0.695
8,600	0.048	0.0279	0.0397	1.61	2.20	4.89	0.069	0.0331	0.922
9,200	0.050	0.0378	0.0236	1.84	2.27	4.41	0.067	0.0240	0.556
10,700	0.048	0.0290	0.0522	1.65	3.05	5.33	0.073	0.0344	0.891

[a] Constants in the Mooney-Rivlin representation of the modulus.

[b] Elongation at the upturn in the stress-strain isotherm.

[c] Elongation at the minimum in the stress-strain isotherm.

[d] Maximum extensibility.

[e] Ultimate strength, as represented by the modulus at rupture.

[f] Magnitude of the upturn in the modulus.

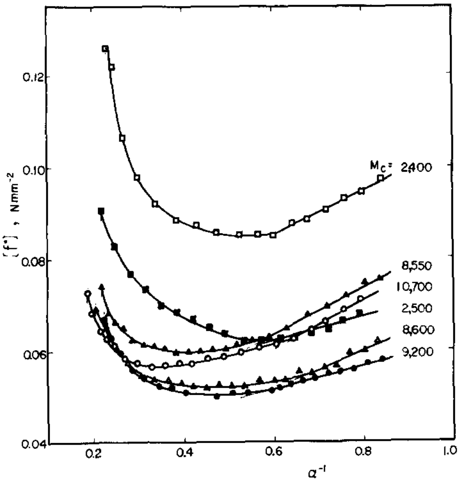

Figure 1. Stress-strain isotherms for the unswollen PIB networks at 25°C. The vertical dashed lines locate the values of the elongation at rupture.

in $[f^*]$, are given in column five of Table I. The following column gives values of a related quantity, the elongation α_m at which the stress-strain isotherm exhibits a minimum, i.e., the point at which the decrease in $[f^*]$ due to the increasing non-affineness of the deformation (14-17) is just balanced by the increase in $[f^*]$ due to the crystallite reinforcing effect. Both α_u and α_m decrease with increase in degree of cross-linking (decrease in $M_c = M_n$), as is shown in Figure 2. Thus network crystallization is induced at lower elongations in the more heavily cross-linked elastomers, presumably because of the increased orientation of the chains (9,18).

As expected, the maximum extensibility or elongation α_r at rupture decreases with increase in degree of cross-linking, as is shown by the values presented in column seven. Values of the ultimate strength, as represented by the modulus $[f^*]_r$ at rupture, are given in column eight, and the fractional increase $\Delta[f^*]_r/[f^*]_r$ (relative to what $[f^*]_r$ would have been with no upturn at all) are given in the final column. These quantities scatter considerably more than α_u and α_m since $[f^*]$ is changing much more rapidly as the rupture point is approached (6). Nonetheless, the results shown in Figure 3 do suggest that both the total increase and fractional increase in $[f^*]$ increase with increase in degree of cross-linking. Eventually these quantities must of course decrease with further increase in degree of cross-linking, as has been pointed out by Flory (9).

Since non-crystallizing PDMS model networks exhibit unusually good mechanical properties when they have a bimodal distribution of chain lengths (7), it would be extremely interesting to determine whether such bimodality would affect the strain-induced crystallization in PIB model networks.

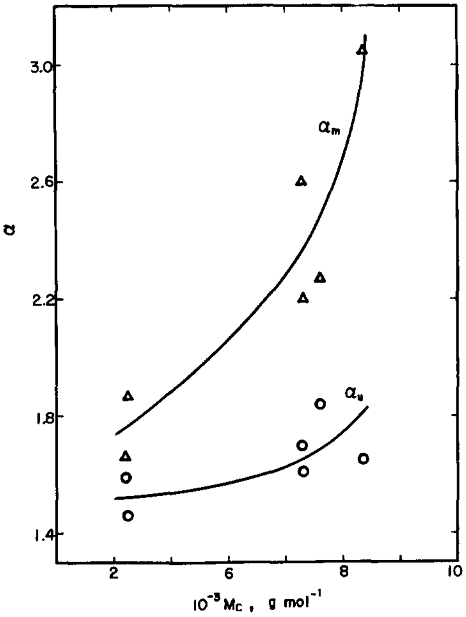

Figure 2. The effect of degree of cross-linking on the elongation α_u at which the modulus shows an upturn, and the elongation α_m at which the modulus exhibits a minimum.

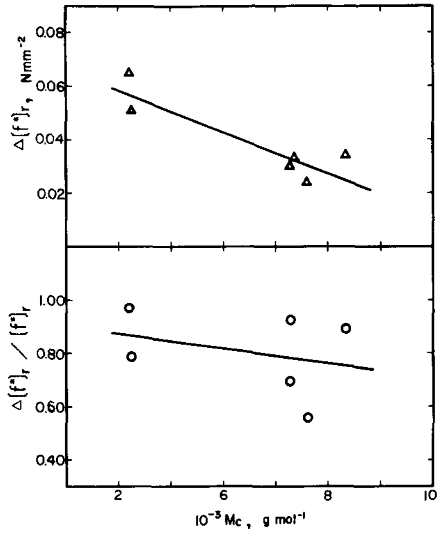

Figure 3. The effect of degree of cross-linking on the total increase and fractional increase in modulus arising from strain-induced crystallization.

Acknowledgements

It is a pleasure to acknowledge the financial support provided JEM and JPK by the National Science Foundation (Polymers Program, Division of Materials Research). C.-Y.J. also wishes to thank the Dow Corning Corporation for their financial support.

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Accepted February 7, 1984