Elastomeric Properties of Some Isoprene–Styrene Networks Cross-Linked through Metal–Acetylacetonate Chelation[†]

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ABSTRACT: Emulsion polymerization was used to prepare an isoprene–styrene copolymer having 80 mol % isoprene and 1.4 mol % acetylacetonate (acac) groups attached to some of the styrene units. The copolymer was cross-linked by chelation of acac groups with palladium acetate, giving highly elastomeric networks. These chelation elastomers were studied in elongation at 25 and 50 °C, both unswollen and swollen with various amounts of the nonvolatile diluent 1,2,4-trichlorobenzene. They were found to be stable, with reversible stress–strain isotherms, and to have very good ultimate properties. Their moduli in the limit at high elongation were found to be in satisfactory agreement with theoretical predictions for tetrafunctional networks. The increases in modulus they generally exhibit at high elongations are apparently due to limited chain extensibility.

Introduction

There are a variety of ways to localize segments of chain molecules to give the three-dimensional network structure required for (reversible) rubberlike elasticity.[1–4] Examples of physical interactions acting as such cross-links are the formation of very small crystallites in a partially crystalline elastomer, adsorption of chains onto high surface area particles in a filled system, ionic aggregation in an ionomer, and phase separation to give small glassy domains in a triblock copolymeric elastomer. Cross-links of a chemical nature are, of course, introduced in processes such as sulfur vulcanization, high-energy irradiations, peroxide cures, and the end-linking of functionally capped (telechelic) polymers.[5]

An additional, very novel cross-linking technique has recently been developed.[6,7] In brief, it involves covalently attaching acetylacetonate (acac) groups to a polymer backbone and then chelating some of these ligands with metal atoms to form complexes which (at least in some cases) should function as permanent cross-linkages. There are a number of potential advantages[6] for forming elastomeric networks in this manner. For example, the cross-links thus formed are in effect also labels, which should be quantitatively determinable using any of a variety of spectroscopic methods. Also, if desired, the use of competing ligand exchange reactions should make the cross-linking process highly reversible. Finally, judging from published stability constants for acac complexes,[8] it should be possible to form a series of network structures in which the cross-links range from highly transitory to highly permanent (thus rivaling covalent linkages in their stability).

The present investigation focuses on the preparation of such chelation networks using an acac-substituted styrene–isoprene copolymer which is cross-linked with a palladium salt. Since the Pd–acac complex has a very large stability constant,[8] the resulting elastomers should yield stress–strain isotherms which can be correlated with chemical information on the network structure.

Experimental Details

The polymer employed was prepared by copolymerizing isoprene, styrene, and styrene substituted with chloromethyl (CH_2Cl) groups in the meta and para positions. The reaction was a standard emulsion polymerization (199 parts of water, 5 parts of sodium dodecyl sulfate, 2 parts of potassium persulfate, 0.3 part of dodecyl mercaptan, 68.5 parts of isoprene, 23.9 parts of styrene, and 7.6 parts of (chloromethyl)styrene) carried out at 50 °C to a conversion of approximately 90%, and the resulting polymer had a molecular weight the order of 10^5. A known small number of acac groups were bonded to the chains through displacement of the Cl atoms with the sodium salt of acetylacetone at some of the chloromethyl groups. According to its NMR spectrum, the polymer thus modified consisted of 80 mol % isoprene (approximately 10:1 1,4:1,2 units), 12.6 mol % styrene, 6.0 mol % (chloromethyl)styrene, and 1.4 mol % acac–methylstyrene ($CH_2CHC_6H_4CH_2$(acac)). The concentration of acac groups was 1.4×10^{-4} mol (g of polymer)$^{-1}$, which corresponds to an average spacing along the chains of 7.14×10^3 g mol^{-1}.

The polymer was diluted with a small amount of chloroform to facilitate mixing. An amount of palladium acetate giving a 1:2 molar ratio between Pd(II) atoms and acac groups was kneaded into the polymer, which was then dried and pressed between two Teflon-lined stainless steel plates to a thickness of approximately 1 mm. The reaction was allowed to proceed at room temperature,[6,7] for 1 h in the press and then overnight at atmospheric pressure. The resulting network was extracted at room temperature for 3 days using benzene containing a small amount of the antioxidant N-phenyl-β-naphthylamine. The sample was then dried under vacuum, and the constant weight thus obtained was used to calculate the volume fraction v_{2C} of polymer successfully incorporated in the network structure. Three batches of networks were made in this way and their values of v_{2C} are given in the first column of Table I. They had a density ρ, as determined by pycnometry, of 0.966 g cm^{-3}. FT-NMR measurements carried out on a Bruker WM500 spectrometer at 500 MHz[7] indicated that well over 50% of the acac groups were successfully incorporated into network cross-links.

The networks were studied both unswollen and swollen with the nonvolatile diluent 1,2,4-trichlorobenzene (boiling point 214 °C) to the values of the volume fraction v_2 of polymer given in the second column of Table I. The stress–strain measurements were carried out in elongation at 25 and 50 °C in the usual manner,[5,9–11] using strips which had the approximate unswollen dimensions 1 mm × 3 mm × 30 mm. The elastomeric quantity of primary interest was the reduced stress or modulus defined by[1,11–13]

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

where f is the elastic force, A^* is the cross-sectional area of the unstretched and unswollen sample, and $\alpha = L/L_i$ (where L and L_i are the stretched and unstretched lengths, respectively, in the swollen state). The measurements were carried out to the rupture points and were generally repeated several times to test for reproducibility.

Results and Discussion

The rather different values of v_{2C} obtained for the three batches of networks are almost certainly due the difficulty

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Table I
Characteristics of the Networks and Their Elasticity Constants and Ultimate Properties

v_{2C}[a]	v_2[b]	T, °C	$2C_1$,[c] N mm^{-2}	$2C_2$,[c] N mm^{-2}	$2C_2/2C_1$	α_r[d]	$[f^*]_r$,[e] N mm^{-2}	increase in f^*,[f] N mm^{-2}
0.918	1.000	50	0.097	0.110	1.13	3.59	0.157	0.288
		50	0.123	0.041	0.33	3.69	0.160	0.265
		50	0.106	0.015	0.14	3.71	0.132	0.220
	0.585	25	0.093	0.050	0.54	5.04	0.143	0.039
	0.284	25	0.069	0.044	0.64	3.36	0.117	0.033
	0.207	25	0.097	0.043	0.44	2.39	0.140	0.022
0.823	1.000	25	0.114	0.088	0.77	4.91	0.157	0.025
		25	0.101	0.139	1.38	5.04	0.146	0.020
		25	0.113	0.110	0.97	4.47	0.170	0.031
		25	0.090	0.153	1.70	5.47	0.146	0.029
		25	0.131	0.114	0.87	5.13	0.187	0.034
0.758	1.000	25	0.136	0.107	0.79	5.14	0.189	0.028
		25	0.108	0.064	0.59	5.67	0.135	0.018
		25	0.104	0.083	0.80	5.88	0.151	0.033
		25	0.101	0.083	0.82	5.32	0.139	0.017
	0.525	25	0.100	0.039	0.39	3.28	0.139	0.027
	0.404	25	0.129	0.038	0.30	3.48	0.176	0.036
	0.377	25	0.113	0.037	0.35	2.66	0.146	0.018

[a] Volume fraction of polymer successfully incorporated in network. [b] Volume fraction of polymer in network during stress–strain measurements. [c] Constants in the Mooney–Rivlin representation of the modulus. [d] Elongation at rupture. [e] Ultimate strength, as represented by the modulus at rupture. [f] Magnitude of upturn in modulus.

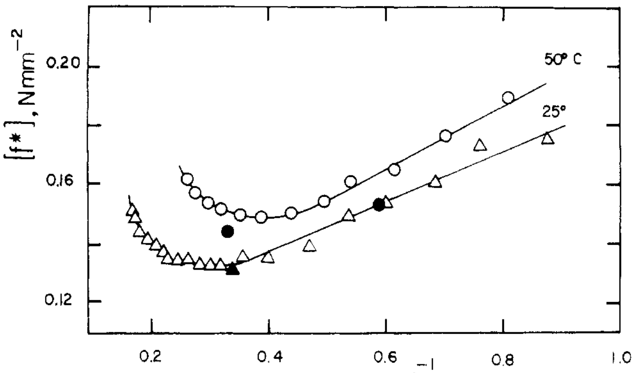

Figure 1. Typical stress–strain results showing the effect of temperature on the isotherms. The filled symbols locate results obtained out of sequence to test for reversibility.

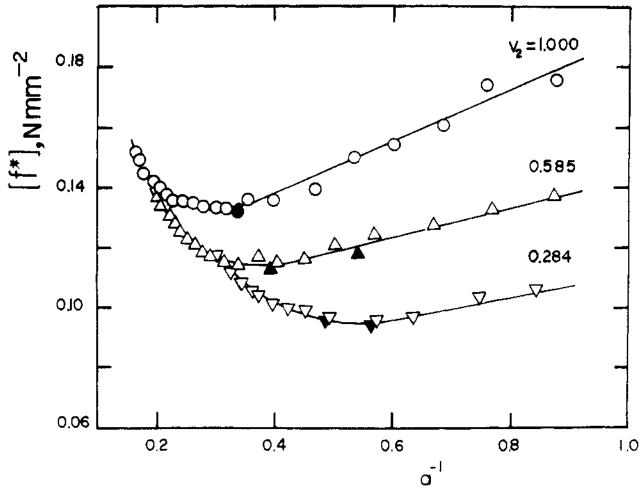

Figure 2. Typical stress–strain results showing the effect of swelling on the isotherms, at 25 °C. Each curve is labeled with the volume fraction of polymer present in the network, the (nonvolatile) diluent employed being 1,2,4-trichlorobenzene.

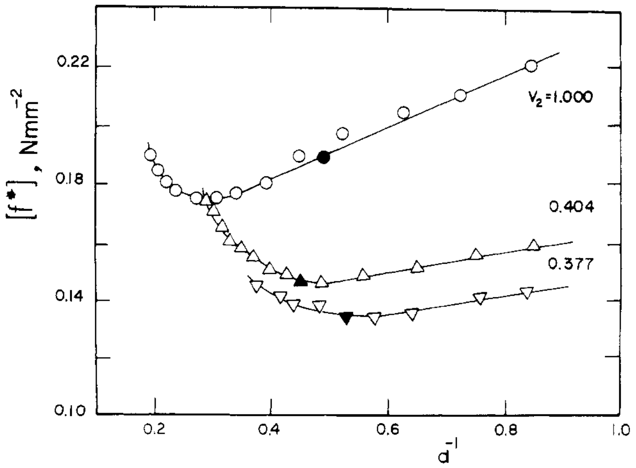

Figure 3. Additional results showing the effect of swelling on the isotherms; see legend to Figure 2.

of uniformly dispersing the palladium salt in this extremely viscous polymeric medium. It may be possible to ameliorate this problem by carrying out the reaction in the presence of significant amounts of diluent.[14]

The representation of the stress–strain data was based on the Mooney–Rivlin equation[2,13]

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

where $2C_1$ and $2C_2$ are constants. Typical plots of the reduced stress against reciprocal elongation are shown as a function of temperature in Figure 1 and as a function of degree of swelling in Figures 2 and 3. As can be seen from the isotherms, the networks showed very good reversibility, even in the highly swollen state. They thus are seen to have excellent stability, which is consistent with the large stability constant of the Pd–acac complex.[8] Least-squares analysis was used on the linear portions of the curves, and the resulting values of $2C_1$, $2C_2$, and $2C_2/2C_1$ are given in columns four through six of Table I. The reproducibility is seen to be fairly good, considering the synthesis problem already mentioned. The values obtained for $2C_1$ can be used to calculate the structure factor defined by[5]

$$A_4 = 2C_1M_c/\rho RTv_{2C}^{2/3} \qquad (3)$$

where M_c is the molecular weight between cross-links, and RT has its usual significance. If it is assumed that all the acac groups react to form cross-links (i.e., $M_c = 7.14 \times 10^3$), then the average value of A_4 is 0.36 in the case of all the results and 0.34 if only the more reliable[15] results on the swollen networks are included. On the other hand, if for example the reaction were only 50% complete (partly because of Pd-oxidized removal of acac groups), then M_c would be effectively doubled and A_4 would be 0.72 or 0.68. These values are in satisfactory agreement with the theoretical value 0.50 predicted for tetrafunctional networks;[5,15-17] none of the values provides evidence for significant contributions from interchain entanglements, which is in agreement with results obtained on a variety of other elastomeric systems.[5,15,18] The values obtained for the ratio $2C_2/2C_1$ average to 0.86 for the unswollen networks and 0.44 for the swollen ones and are of the same magnitude as values reported for a variety of other tetrafunctional networks.[13]

Values of the elongation at rupture (maximum extensibility) and ultimate strength (as represented by the reduced stress at rupture) are given in columns seven and eight of Table I. These values of the ultimate properties indicate that the chelation networks are quite good elastomers. Increases in reduced stress above the linear continuations of the curves are given in the final column of Table I. As can be seen from these tabulated results and from Figures 1 and 2, the reinforcing upturns in [f^*] are little affected by increase in temperature or increase in degree of swelling. This indicates that they are due to the limited extensibility of the network chains[5,19] rather than to strain-induced crystallization.[20] The achievement of sufficiently high elongations to observe such an effect attests to the relatively high degree of perfection in these network structures. The present results thus encourage additional investigations of other elastomeric properties of these and other chelation networks.

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Development of Modulated Structure during Solution Casting of Polymer Blends[†]

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ABSTRACT: We have found the development of regularly phase-separated structure in solution-cast films of polymer blends. Characteristic features of the structure are periodicity and dual connectivity of phases. Here we call it "modulated structure". The casting process from ternary solution, consisting of A polymer, B polymer, and solvent, to dry film was studied by using the light scattering technique. The regular structure that developed at relatively low polymer concentration was maintained as a whole at higher concentrations until the modulated structure was frozen in the cast film. More than ten pairs of dissimilar polymers formed the modulated structure. These pairs had fairly small differences in solubility parameters between the component polymers. Faster rates of solvent evaporation yielded a smaller periodic distance in the modulated structure. The rate of phase separation became lower and the periodic distance of the modulated structure became shorter as the blend ratio deviated from 50/50. When the molecular weight of polymer was very high, the system failed to phase-separate during the fast casting, resulting in a homogeneous blend without appreciable composition fluctuations. These results on development of modulated structure were interpreted through thermodynamic and kinetic discussion in terms of molecular and processing variables such as polymer–polymer interaction parameters, blend ratio, degree of polymerization, and rate of solvent evaporation.

Introduction

The solution casting of an incompatible polymer blend generally results in the two-phase morphology having irregular shape and size of domains. Quite recently, we studied the morphology of poly(vinyl chloride)/poly(acrylonitrile-*co*-butadiene) (NBR) blends cast from tetrahydrofuran (THF) solutions. A regularly phase-separated structure with a periodic distance of 1.4 μm was found in a 50/50 blend of PVC and NBR having 26 wt % acrylonitrile.[1,2] Characteristic features of the structure were the periodicity and the dual connectivity of the phases. They are similar in appearance to the phase

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