

Networks

Optical Properties of Some Isoprene-Styrene Networks Cross-Linked Through Metal-Acetylacetonate Chelation

Y.-P. Ning* and J. E. Mark

Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH 45221, USA

Summary

A styrene-isoprene random copolymer containing 80 mol % isoprene, and acetylacetonate groups attached to some of the styrene repeat units was cross-linked by chelation of these groups with a Pd(II) salt. The resulting elastomers were studied in both the unswollen state and swollen with the relatively symmetrical solvent 1,2,4-trichlorobenzene. Their birefringence-strain isotherms were found to be highly reversible, with deviations from linearity due to limited chain extensibility being even more marked than those exhibited by the stress. The stress-optical coefficient obtained is close to that previously reported for natural rubber, as might be expected.

Introduction

In preparing elastomeric materials, it can be highly advantageous to control the network structure by introducing the cross-links at only certain sites present on the polymer chains. Linking end-reactive chains with a multifunctional reactant is an example of such a specific cross-linking reaction (1). Another example, only recently developed (2-4), involves covalently attaching acetylacetonate (acac) groups $[-C(COCH_3)(COHCH_3)]$ to a polymer backbone, and then chelating some of these ligands with metal atoms to form complexes which can function as cross-linkages. Judging from published stability constants for acac complexes (5), it should be possible to form a series of network structures in which the cross-links range from highly permanent (giving elastomers of good stability and reversibility) (6) to highly transient (giving materials with potentially very novel viscoelastic properties).

The present investigation involves some chelation networks prepared from an acac-substituted styrene isoprene copolymer by cross-linking it with a palladium salt. Since the Pd-acac complex has a very large stability constant (5), the resulting networks are highly stable elastomers (6). Measurements of their birefringence are used to obtain additional information on their stability and the reversibility of their isotherms, and their non-Gaussian behavior due to limited chain extensibility. Also of interest are their values of the stress-optical

*Permanent address: Shangdong Institute of Chemical Engineering, Quindao City, People's Republic of China.

coefficient and the optical configuration parameter, for comparison with other results in the literature and for later interpretation in terms of rotational isomeric state theory.

Experimental Details

The polymer employed (3,6) consisted of 80 mol % isoprene (approximately 10:1 1,4:1,2 units), 12.6 mol % styrene, 6.0 mol % chloromethylstyrene, and 1.4 mol % acac-methylstyrene ($\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{CH}_2\text{acac})$). It was generously provided by Professor B. E. Eichinger of the University of Washington. The concentration of acac groups was 1.4×10^{-4} mol (g polymer) $^{-1}$ which corresponds to an average spacing along the chains of 7.14×10^3 g mol $^{-1}$. Portions were chelation cross-linked into network strips using Pd(II) acetate at room temperature as is described elsewhere (6). FT-NMR measurements carried out on a Bruker WM500 spectrometer at 500 MHz (3) indicated that well over 50% of the acac groups were successfully incorporated into network cross-links. The samples, even after extensive extractions, were brown, which somewhat complicated the measurements of their birefringence described below.

In brief, small strips were cut from the crosslinked sheets and mounted between clamps. The upper clamp was attached to a pressure transducer, while the lower one could be moved downwards so as to impose the desired elongation. A 3mw He-Ne laser ($\lambda = 632.8$ nm) was used as light source for all the experiments; a detailed description of the apparatus used is given elsewhere (7,8). In order to keep the temperature constant at 25°C during the experiments, the sample was surrounded by a double-walled jacket in which an ethylene glycol-water mixture was circulated from a thermostat. The networks were studied both unswollen, and swollen with the non-volatile diluent 1,2,4-trichlorobenzene (boiling point 214°C) to values of the volume fraction v_2 of polymer ranging from 1.000 to 0.207. The index of refraction n was determined for the unswollen network using an Abbe refractometer, and estimated for the swollen networks using the relationship given by Huglin (9).

The first optical property of interest is the stress-optical coefficient

$$C = \Delta n / (f/A) \quad (1)$$

where Δn is the birefringence, f the elastic force and A the deformed cross-sectional area of the sample. The other, related property is the optical-configuration parameter

$$\Delta_a = (45kTC/2\pi) [n/(n^2 + 2)^2] \quad (2)$$

where k is the Boltzmann constant, and T the absolute temperature. The elastomeric quantity of primary interest is the reduced stress or modulus defined by (10-13)

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

where A^* is the cross-sectional area of the unstretched and unswollen sample, and $\alpha = L/L_1$ (where L and L_1 are the stretched and unstretched lengths, respectively, in the swollen state).

Results and Discussion

A typical plot of the birefringence against reciprocal elongation is shown in Figure 1; included for purposes of comparison is the reduced

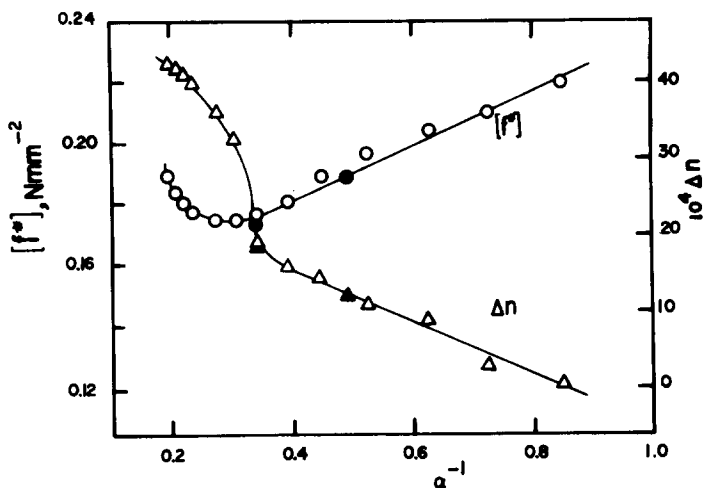


Figure 1. Typical stress-strain and birefringence-strain isotherms for an unswollen chelation network at 25°C. The filled symbols locate results obtained out of sequence to test for reversibility.

stress, as defined in Equation (3). As is obvious from the isotherms, the networks showed very good reversibility. They thus are seen to have excellent stability (6), which is consistent with the large stability constant of the Pd-acac complex (5). There are significant deviations from linearity at high elongations, with the changes being particularly pronounced in the case of the birefringence. The deviations of the birefringence were found to persist even upon swelling or increase in temperature, as is also the case with the reduced stress (6). This indicates that they are due to the limited extensibility of the network chains (1,14) rather than to strain-induced crystallization (15). The achievement of sufficiently high elongations to observe such an effect attests to the relatively high degree of perfection in these network structures.

The most reliable values of the stress-optical coefficient and the optical-configuration parameter are those obtained using networks highly swollen with a relatively symmetrical diluent (7). Typical results

obtained for the chelation networks swollen to a volume fraction $v_2 = 0.207$ with 1,2,4-trichlorobenzene are shown in Figure 2. Both C and Δa

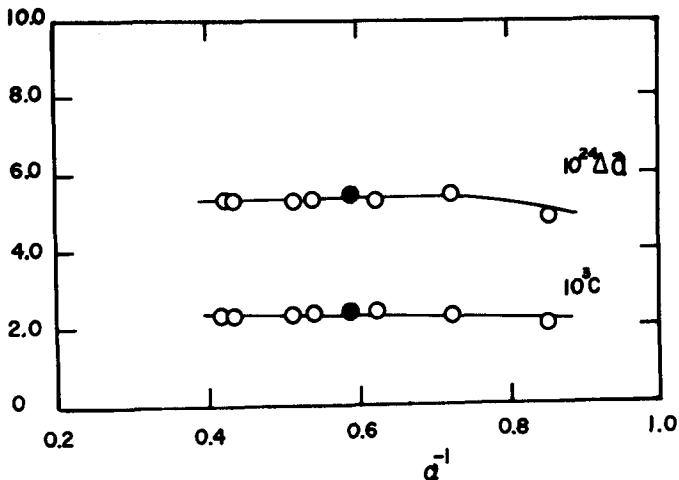


Figure 2. Values of the stress-optical coefficient C and the optical-configuration parameter Δa shown as a function of reciprocal elongation for a chelation network swollen with 1,2,4-trichlorobenzene to a volume fraction v_2 of polymer of 0.207.

are seen to be essentially independent of elongation. The value obtained for C , $2.3 \times 10^{-3} \text{ (N/mm}^2\text{)}^{-1}$, is close to the value $2.0 \times 10^{-3} \text{ (N/mm}^2\text{)}^{-1}$ reported for natural rubber. The similarity in the values is perhaps not surprising in view of the high isoprene content in the chelation polymer studied. The value of Δa obtained is $5.3 \times 10^{-24} \text{ cm}$, a result which should be quite suitable for interpretation in terms of the rotational isomeric state theory of chain configurations (17).

Acknowledgement

It is a pleasure to acknowledge the financial support provided J.E.M. by the National Science Foundation through Grant DMR 79-18903-03 (Polymers Program, Division of Materials Research).

References

1. J. E. Mark, Adv. Polym. Sci., **44**, 1 (1982).
2. H. C. Yeh, B. E. Eichinger and N. H. Andersen, J. Polym. Sci., Polym. Chem. Ed., **20**, 2575 (1982).

3. N. Iwamoto, B. E. Eichinger and N. H. Andersen, ms. submitted to Rubber Chem. Technol.
4. N. Iwamoto, Ph.D. Thesis in Chemistry, University of Washington, 1983.
5. A. E. Martell and R. M. Smith, "Critical Stability Constants: Vol. 3", Plenum Press, New York, 1977.
6. Y.-P. Ning, J. E. Mark, N. Iwamoto, and B. E. Eichinger, ms. submitted to Macromolecules.
7. M. A. Llorente and J. E. Mark, J. Polym. Sci., Polym. Phys. Ed., **19**, 1107 (1981).
8. J. E. Mark and M. A. Llorente, Polymer J., **13**, 543 (1981).
9. M. B. Huglin, J. Appl. Polym. Sci., **2**, 3963 (1965).
10. P. J. Flory, "Principles of Polymer Chemistry", Cornell Univ. Press, Ithaca, NY, 1953.
11. M. A. Llorente, A. L. Andraday and J. E. Mark, J. Polym. Sci., Polym. Phys. Ed., **18**, 2263 (1980).
12. J. E. Mark and P. J. Flory, J. Appl. Phys., **37**, 4635 (1966).
13. J. E. Mark, Rubber Chem. Technol., **48**, 495 (1975).
14. J. E. Mark and J. G. Curro, J. Chem. Phys., **79**, 5705 (1983).
15. J. E. Mark, Polym. Eng. Sci., **19**, 409 (1979).
16. L. R. G. Treloar "The Physics of Rubber Elasticity", Clarendon Press, Oxford, 1975.
17. P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, 1969.

Accepted June 1, 1984