Macromolecules **1980**, *13*, 1313–1314

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Trapped Entanglements vs. Dissociable Junctions in Networks Cross-Linked in Strained States

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Many rheological properties of uncross-linked polymers of high molecular weight can be interpreted in terms of a temporary network structure.[1] In most systems, there is strong evidence that the virtual network is the result of topological restraints, usually conceived as entanglements, rather than dissociable junctions between loci of specific attraction on the molecules.[1] One of the most direct manifestations of the reality of an entanglement network is the behavior of a polymer cross-linked near the glass transition temperature in a state of strain, e.g., in simple extension with a stretch ratio λ_0. After release, it retracts to a state of ease (stretch ratio λ_s) in which the elastic forces associated with the cross-links and with entanglements trapped by the cross-links are equal and opposite.[2,3] If the original temporary network consisted of dissociable junctions, the forces associated with them should disappear at equilibrium.

It was thought at first that the very existence of a state of ease demonstrated the permanence of the trapped entanglements and that the equilibrium strain would remain at λ_0 if the original temporary junctions could dissociate.[3] However, that is not quite the case. The system would correspond to that treated by Flory[4] in which two stages of cross-links are introduced, one in the unstrained and the second in a strained state, and all of the first-stage cross-links are subsequently removed. Then a memory of the first-stage cross-links remains in the structure and there is an equilibrium state of ease with a strain λ_s smaller than λ_0. Nevertheless, it can be shown from data of our previous studies[5,6] that the observed retraction to λ_s is different from that expected for dissociable junctions, so quantitatively there is still clear evidence for permanent trapping of entanglements by cross-links, as illustrated in the present note.

We utilize some of the same data for 1,2-polybutadiene that have already been interpreted in terms of the trapped entanglement model and recalculate them in terms of a model of temporary, dissociable junctions. The concentration of temporary network strands in moles per cubic centimeter in the original uncross-linked polymer, ν_e, is calculated in either case from the time-dependent Young's modulus $E(t)$ measured in stress relaxation at a standard time t = 3 min, corresponding to the relaxation period allowed at 0 °C before the stretched polymer is chilled below the glass transition temperature for cross-linking by γ irradiation. The small-strain relaxation modulus $E(t)$ is obtained by extrapolation of stress data to small strains by use of the Mooney–Rivlin equation. Assuming a front factor of unity,

$$\nu_e = E(3\ \mathrm{min})/3RT \qquad (1)$$

In the entanglement model, ν_e is the concentration of strands terminated by entanglements; in the dissociable junction model, it is the concentration of strands terminated by temporary junctions.

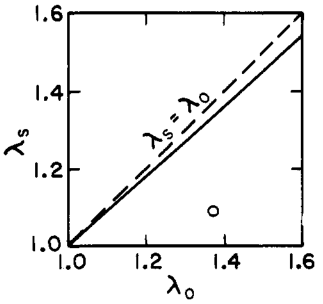

Figure 1. Plot of λ_s against λ_0 as predicted from the dissociable junction model for experiment C255 of Table I (solid curve). The open circle is an experimental point.

In the dissociable junction model, ν_e may be identified with the first-stage cross-links of the Flory theory.[4] In this theory, Gaussian statistics are assumed and there are no free ends (infinite initial molecular weight). If, after ν_x moles of strands are introduced by cross-linking while strained in simple extension with a stretch ratio λ_0, all the original junctions are dissociated, the system then behaves as though composed of ν_{1e} strands with reference state λ = 1 and ν_{2e} strands with reference state λ_0, where

$$\nu_{1e} = \Phi\nu_x \qquad (2)$$

$$\nu_{2e} = (1 - \Phi)\nu_x \qquad (3)$$

and Φ is a rather complicated function of ϕ_2, which is defined as

$$\phi_2 \equiv \nu_x/(\nu_x + \nu_e) \qquad (4)$$

We have taken the function appropriate for a random distribution of cross-linked units. The equilibrium state of ease is then calculated from Gaussian statistics[2,4] to be given by

$$\lambda_s = [(1 + \lambda_0 R_0)/(1 + R_0\lambda_0^{-2})]^{1/3} \qquad (5)$$

where $R_0 \equiv \nu_{2e}/\nu_{1e}$. From these equations, the relation between λ_0 and λ_s expected for dissociable junctions can be calculated and compared with experiments on 1,2-polybutadiene.

For this purpose, ν_{1e} is calculated from the tensile stress of the final cross-linked network when it is returned to a stretch ratio λ_0 and the strands with reference state λ_0 make no contribution to the stress. The same equation[3] is used as for calculating ν_N, the concentration of strands terminated by trapped entanglements, in the entanglement model; in the dissociable junction model, it provides the concentration of effective strands whose reference state is λ = 1. (There is a slight inconsistency in that this calculation of ν_{1e} implies certain deviations from neo-Hookean behavior[3] and the subsequent application of the Flory theory is based on neo-Hookean relations, but the difference in ν_{1e} is small (order of 15%) compared with the large difference between the predictions of the dissociable

0024-9297/80/2213-1313$01.00/0

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Table I
Comparison of Predictions of the Dissociable Junction Model with Experiment

expt no.	dose, eV/g × 10^{-20}	$\nu_{1e} \times 10^4$	Φ	$\nu_x \times 10^4$	λ_0	λ_s predicted	λ_s exptl
C236	2.3	0.85	0.47	1.82	1.556	1.235	1.098
C230	3.8	1.85	0.114	16.2	1.535	1.443	1.145
C255	4.5	2.15	0.042	51	1.370	1.348	1.091

junction model and experiment and it has very little effect on a plot such as Figure 1.)

The relation between λ_s and λ_0 for the dissociable junction model was calculated as follows. For a given pair of ν_e and ν_{1e}, a value of Φ was assumed and ν_x was calculated from eq 2; ϕ_2 was obtained from eq 4, and a revised value of Φ was obtained from eq 36 of ref 4. The process was iterated to a constant value of Φ, and then λ_s was calculated as a function of λ_0 from eq 2–4. An example is shown in Figure 1 for 1,2-polybutadiene with $\nu_e = 2.41 \times 10^{-4}$ mol/cm^3, $\nu_{1e} = 2.15 \times 10^{-4}$ mol/cm^3.[6] If the junctions dissociated leaving no trace in the configuration of the network, there would be no retraction after release and λ_s would equal λ_0 as shown by the dashed line. In fact, there is a predicted retraction to a state of ease $\lambda_s < \lambda_0$, due to the memory effect, but it is small, of the order of 10%. On the same graph, an experimentally determined point is shown for $\lambda_0 = 1.370$, and the actual retraction is much greater.

Numerical results for this and two other experiments are given in Table I. The 1,2-polybutadiene was the same identified as polymer C in earlier publications;[3,5] cross-linking was performed by γ irradiation at −10 °C as previously described[5] with the doses indicated. The strand concentrations ν_{1e} and ν_x are given in mol/cm^3. In every case the observed λ_s is much smaller than that predicted from the dissociable junction model; the memory effect does not account for the magnitude of the retraction.

It may be added that the values of ν_x in Table I are unrealistically large and would imply a Young's modulus for extension of the final network from the state of ease far larger than that observed. By contrast, the trapped entanglement model provides a prediction for the stress–strain relation in extension from the state of ease that agrees precisely with experiment.[5] It can be concluded that the properties of the networks cross-linked in strained states do confirm the presence of permanently trapped entanglements (or equivalent trapped topological restraints).

Acknowledgment. This work was supported in part by the National Science Foundation, Grant No. DMR 76-09196 and 78-16954, Polymers Program. We are indebted to Professor J. E. Willard for the use of a ^{60}Co source for irradiation and to Mr. Søren Hvidt for valuable comments.

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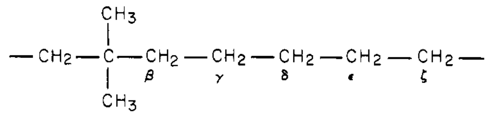
Communications to the Editor

Cationic Copolymers of Isobutylene. 4. Heptad and Octad ^{13}C NMR Signals in Isobutylene-*trans*-1,3-Pentadiene Copolymers

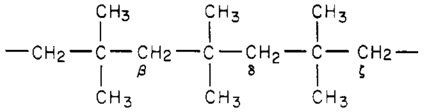
During previous investigations on the structure and the monomer distribution of copolymers based on isobutylene (I) and conjugated dienes,[1-4] we have found long-range contributions of the *gem*-dimethyl group to the chemical shifts of the carbon atoms belonging to the chain. These effects are evident only when long sequences of I are present, and they disappear when the chain segment joined to the *gem*-dimethyl group does not contain other groups of the same type. If we consider, for instance, the segment of chain labeled A, the effects of the *gem*-dimethyl group



$$-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\beta}{CH_2}-\underset{\gamma}{CH_2}-\underset{\delta}{CH_2}-\underset{\epsilon}{CH_2}-\underset{\zeta}{CH_2}-$$

A

are evident, in the spectra obtained at 25.14 MHz, only up to the methylene in the δ position while they are negligible on the ϵ and ζ carbons.[4] Conversely, large effects are observed for the carbon in the ζ position when the chain segment contains other *gem*-dimethyl groups,[3] as in B. These long-range effects allow us to distinguish pentad



$$-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\beta}{CH_2}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\delta}{CH_2}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\zeta}{CH_2}-$$

B

signals in the copolymer spectra for the quaternary carbon and methyls as well as hexad signals for the methylene of I.

A 50.3-MHz instrument allows further resolution of the peaks, and heptad signals of the quaternary carbon and methyls and octad signals of methylene become evident. Figure 1 shows some regions of the ^{13}C NMR spectrum of a hydrogenated isobutylene-*trans*-1,3-pentadiene (P) copolymer containing 32 mol % of P. Figure 1A illustrates the resonance of the CH$_2$ group of I in the homopolymeric tetrad. This signal appears as a triplet in the spectrum recorded at 25.14 MHz, corresponding to the hexads IIIIII, PIIIII + IIIIIP, and PIIIIP, i.e., to the four hexads having at the extremities two I units, one I and one P unit, and two P units.[3] A further separation of the peaks appears at 50.3 MHz, as Figure 1A shows. The peak of the homopolymeric hexad is not split, as expected, into three peaks

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