Effect of Strain-Induced Crystallization on the Elastomeric Properties of *cis*-1,4-Polybutadiene Networks

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ABSTRACT: A number of networks of *cis*-1,4-polybutadiene were prepared using a peroxide cure, a conventional sulfur cure, and γ radiation. These networks, or portions thereof, were studied in the unfilled unswollen state to their rupture points at several temperatures in the range 5–40 °C. At the lower temperatures, high elongation generally causes strain-induced crystallization, with marked effect on the stress–strain isotherms. The modulus or reduced force was found, in general, to depart from its simple linear representation $[f^*] = 2C_1 + 2C_2\alpha^{-1}$, showing a marked increase with increasing elongation α. In addition, in some cases $[f^*]$ decreases significantly before turning upward. This complex behavior is apparently due to two opposing effects of strain-induced crystallization, viz., the increase in the spatial extension of the network chains along the axis of deformation as they form axially oriented crystallites, and the simultaneous functioning of these crystallites as physical cross-links. Very nearly the same high elongations were generally attainable at the higher temperatures, but none of these isotherms showed the anomalous increase in reduced force in evidence at the lower temperatures. This striking effect of temperature is in support of other recent evidence indicating that the marked upturn in $[f^*]$ widely observed for some polymer networks at high elongation should be attributed to strain-induced crystallization rather than to limited chain extensibility.

Polymer networks, when studied at very high elongations, frequently show anomalous stress–strain isotherms in that they exhibit values of the modulus or "reduced force" $[f^*]$[1–4] which increase markedly with increasing elongation.[5–12] Such isotherms depart appreciably from the form predicted by the molecular theories of rubberlike elasticity[13–15] and from the Mooney–Rivlin representation[16] adopted from phenomenological arguments as well. For this reason, the interpretation of the increase in $[f^*]$ at high elongations has been of great interest for a considerable period of time. For several decades now, this behavior has generally been attributed to the limited extensibility of the network chains.[5–8,10,12,17] Critical examination[18] of various published results pertinent to this question, in conjunction with more definitive experimental studies[18,19] reported recently, however, support the alternative suggestion[20–25] that such atypical isotherms are due to strain-induced crystallization.

One experiment particularly relevant to this issue is the study of the stress–strain isotherms of a polymer network as a function of temperature. Such experiments have been carried out on natural rubber,[6,7] but the relatively poor thermal stability of this polymer and the extent to which its melting point is increased by elongation make it essentially impossible to study the high elongation stress–strain relationships for this polymer at a temperature sufficiently high to ensure complete suppression of strain-induced crystallinity.[18,19] Similar experiments carried out on networks of a more suitable polymer, polyisobutylene,[19] gave stress–strain isotherms showing the upturn in the reduced force at low temperature, but not at higher temperatures, thus strongly implicating strain-induced crystallization as the origin of this anomalous behavior. These experiments, however, suffered somewhat from the one shortcoming that the increase in temperature required to suppress the upturn in $[f^*]$ also decreased the maximum extensibility of the network to below the elongation at which the upturn occurred at the lower temperatures.

Preliminary experiments on *cis*-1,4-polybutadiene (*cis*-PBD) indicated that networks of this polymer could generally be extended to very nearly the same elongations at relatively high temperatures as at lower temperatures, where crystallization was clearly in evidence. Thus, the study of these polymer networks would permit comparison of stress–strain isotherms, over a suitably wide range in temperature, obtained over essentially the same ranges in elongation. The present study reports the results of such experiments, on unfilled unswollen networks of *cis*-PBD, cross-linked using a variety of curing methods. This polymer has a melting point in the undeformed, undiluted state of 1 °C,[26] and a glass transition temperature of −102 °C.[26] Its stress–strain properties were therefore studied from 5 to 40 °C, a temperature range of particular interest to the question at hand. Stress–strain isotherms were determined for each network at several temperatures in this range, with elongations extending up to and including the rupture point. Although the subject of primary interest is the dependence of the form of the isotherm on temperature, values of the ultimate strength and the elongation to rupture are obviously also of considerable interest.

Experimental Section

Cross-Linking Techniques. (A) Peroxide-Cured Samples. The polybutadiene[27] used to prepare these networks was of high molecular weight and of at least 94% *cis*-1,4 stereochemical structure.[28] A portion of the polymer and 1% by weight of benzoyl peroxide were dissolved in benzene, and the resulting solution evaporated to dryness in a glass dish. A portion of the resulting film was pressed into an aluminum mold with internal dimensions 0.06 × 0.5 × 3.0 cm; the mold was then sealed and the polymer cured (cross-linked) at 120 °C. Two series of network strips were prepared in this way; those obtained using a cure time of 1 h were labeled P1, and those obtained using 6 h were labeled P2.

(B) Sulfur-Cured Samples. These networks were prepared from a sample[29] of polybutadiene of approximately 98% cis-1,4 content in two mixtures containing conventional curing agents. The mixtures contained, proportionally, 100 g of polymer, either 1 or 2 g of sulfur, 3.0 g of zinc oxide, 3.0 g of stearic acid, 1 g of *N*-cyclohexyl-2-benzothiazolylsulfenamide, and approximately 1.0 g of 9,9-dimethylacridane. A portion of each mixture was pressed into one of the aluminum molds described above, which was then sealed and heated at 150 °C. Two series of networks were thus prepared. The ones (S1) prepared from the mixture containing approximately 1% of sulfur were cured for 2 h, and those (S2) from the mixture containing approximately 2% of sulfur were cured for 1 h.

(C) Radiation-Cured Samples. The polymer used in the preparation of these samples was the same as that used in the peroxide cures.[27] Films of the polymer cast from benzene were sealed under vacuum in glass tubes and were than irradiated, in the vicinity of room temperature, with γ radiation from a ^{60}Co source.[15] The dose rate was 0.17 Mrad h^{-1}, and total doses were 11.2, 15.9, and 19.7 Mrad; the samples thus prepared were labeled G1, G2, and G3, respectively. They were each cut into a series of strips having approximately the same dimensions as the P series and the S series of networks.

Treatment of Samples and Swelling Equilibrium Measurements. Each network from the P series and the G series was swollen

Table I
Preparation and Characteristics of the Networks

Sample	Cross-linking conditions	v_{2m}[a]	$10^{-3}M_c$,[b] g mol^{-1}	T, °C	$2C_2$, N mm^{-2}	$2C_1$, N mm^{-2}	$10^{-3}M_c$,[c] g mol^{-1}	$10^5\ \nu/2V$, mol cm^{-3}	α at upturn	Max. upturn in [f^*], %	α at rupture
P1	Peroxide, 1%, 120 °C, 1 h	0.101	15.6	5	0.035	0.126	16.5	2.73	3.27	54.2	6.64
				10	0.024	0.154	13.8	3.26	3.48	30.1	6.22
				25	0.052	0.153	14.7	3.08	4.03	4.3	5.85
				40	0.081	0.158	14.9	3.03		0.0	5.68
P2	Peroxide, 1%, 120 °C, 6 h	0.127	10.5	10	0.043	0.172	12.3	3.66	3.57	42.5	7.38
				25	0.035	0.175	12.8	3.53	3.63	22.9	6.61
				40	0.118	0.168	14.0	3.23		0.0	6.06
S1	Sulfur, 1% 150 °C, 2 h	0.140	8.5	5	0.212	0.170	12.3	3.67	5.96	18.2	7.70
				10	0.279	0.175	12.1	3.72	6.25	9.9	7.20
				25	0.204	0.203	11.0	4.09		0.0	5.24
S2	Sulfur, 2%, 150 °C, 1 h	0.152	7.1	5	0.255	0.189	11.0	4.09		0.0	4.30
				10	0.314	0.195	10.9	4.15		0.0	4.24
				25	0.263	0.249	9.0	5.03		0.0	2.74
G1	γ radiation, 11.2 Mrad	0.110	13.6	5	0.180	0.089	23.5	1.92	8.00	13.8	8.84
				10	0.181	0.091	23.3	1.93	8.37	10.1	8.80
				25	0.182	0.102	22.0	2.05		0.0	8.61
G2	γ radiation, 15.9 Mrad	0.147	7.6	5	0.223	0.130	16.0	2.82	6.74	14.0	8.27
				10	0.201	0.151	14.1	3.20	7.01	0.0	7.65
				25	0.245	0.147	15.2	2.97		0.0	7.19
G3	γ radiation, 19.7 Mrad	0.188	4.3	5	0.228	0.160	13.0	3.47	6.39	11.3	7.23
				10	0.238	0.166	12.8	3.53	6.57	0.0	6.93
				25	0.309	0.171	13.1	3.45		0.0	6.41

[a] Volume fraction of polymer in the network, at swelling equilibrium (i.e., maximum swelling) in benzene at room temperature. [b] Calculated from v_{2m}. [c] Calculated from $2C_1$.

in benzene, at room temperature, for approximately 3 days, thereby extracting any soluble (uncross-linked) polymer. The total material thus extracted ranged from 4.7 to 12.4% of the unextracted sample. The equilibrium degree of swelling, expressed as the volume fraction v_{2m} of polymer in the swollen network,[30] was then determined for each strip at room temperature. The values of v_{2m} were calculated from the weights of the swollen and subsequently deswollen samples and the specific volumes of the benzene and the *cis*-PBD, assuming simple additivity of volumes. The dried samples were then reswollen in a benzene solution of *N*-phenyl-2-naphthylamine; subsequent drying under vacuum at room temperature thereby resulted in the incorporation of ~0.2% by weight of this antioxidant into each of the strips.

The sulfur cured (S) network strips required considerably more elaborate purification techniques.[29] Each was swollen in carbon disulfide for ~4 h, reacted with a 25% aqueous solution of dimethylamine overnight, swelled in pyridine, deswelled in ethanol, reswelled in pyridine, and then deswelled in petroleum ether. The strips thus extracted were then reswelled in pyridine containing sufficient *N*-phenyl-2-naphthylamine to constitute ~0.2% by weight of the polymer present in the swollen network. The strips were then deswelled in petroleum ether and finally dried under vacuum at room temperature. Although the amount of soluble polymer thus extracted obviously could not be estimated in these cases, values of v_{2m} for the networks at equilibrium in benzene at room temperature were calculated as described above. The precise value of the cross-sectional area A^* of each strip was obtained by the use of a micrometer.

Stress–Strain Measurements. The stress–strain isotherms were obtained on the unswollen test strips in the usual manner,[18,19] at a series of temperatures in the range 5–40 °C. Temperatures were controlled to ±0.05 °C, and all measurements were carried out under a protective atmosphere of nitrogen. Stress–strain data were taken in the direction of increasing elongation α, with occasional lower elongations employed to test for reversibility. The force f was assumed to have reached its equilibrium value when it became constant for at least 15 min; 3–12 h were required to meet this stated condition. Each sample strip was studied up to rupture, which generally occurred in regions near the sample clamps.

Results and Discussion

Different test strips identically prepared or cut from the same sample were found to have essentially the same degree of equilibrium swelling in benzene at room temperature. Values of v_{2m}, thus found to be constant to ±0.001 unit, were therefore simply averaged to obtain the result cited for each sample in the third column of Table I. The average molecular weight M_c between cross-links was calculated from the standard equation[12,24]

$$M_c = -\rho V_1(v_{2m}^{1/3} - \omega v_{2m})/[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2] \quad (1)$$

where ρ is the density (0.903 g cm^{-3}) of the unswollen *cis*-PBD, V_1 is the molar volume (88.9 cm^3 mol^{-1}) of the benzene, χ_1 is a polymer–solvent interaction parameter, and ω is a factor of somewhat uncertain magnitude,[25] which arises from a volume-dependent contribution to the entropy of network deformation.[24] The required values of χ_1 at the concentrations of interest were obtained from an experimental study[31] of vapor pressures in the polybutadiene–benzene system at 26.9 °C; these data suggest $\chi_1 = 0.32$–0.33. Although the stereochemical composition of the polybutadiene thus studied was unfortunately unspecified, the results should be sufficiently accurate for the purpose at hand. The factor ω was set equal to ½, a value consistent with experimental results obtained on networks of poly(dimethylsiloxane)[32–34] and polystyrene.[35] Values of M_c thus calculated are presented in column four of the table. (Adoption of the minimum value[25] $\omega = 0$ would increase M_c by ~12% in the vicinity of $v_{2m} = 0.10$ and by ~21% in the vicinity of 0.20. Increase in χ_1 to 0.39[36] would increase these values of M_c by approximately 38 and 36%, respectively.) The results obtained indicate that the *cis*-PBD networks prepared for this study were of a degree of cross-linking typical of those generally used in studies of rubberlike elasticity.[12,24]

In constructing the stress–strain isotherms, data taken in the direction of increasing elongation are shown as open circles and data taken to check for reversibility by the filled circles; rupture points are located by the vertical dashed lines. In the

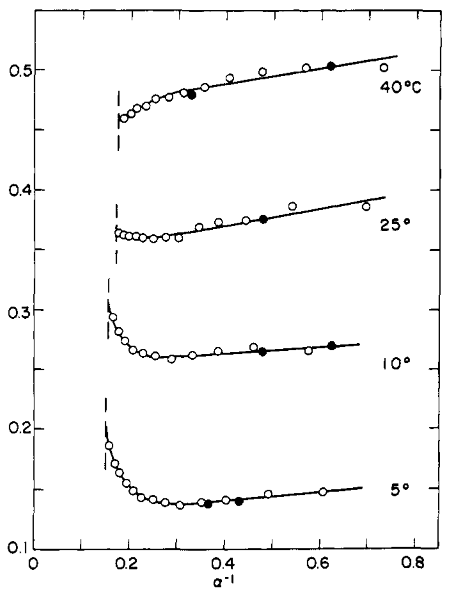

Figure 1. Stress–strain isotherms for *cis*-1,4-polybutadiene network P1 cross-linked to a relatively low degree by means of benzoyl peroxide. The following information pertains to both this figure and to the remaining figures for the other *cis*-PBD networks. All isotherms other than the one for the lowest temperature are shifted upward by adding increments of 0.1, 0.2, or 0.3 N mm^{-2} to $[f^*]$, so as to prevent overlapping of some of the data points. Filled circles show data which demonstrate the reversibility of the isotherms, and the vertical dashed lines specify the values of the elongation α at which rupture occurred.

region of low and moderate elongations, all of the data could be well represented by the linear Mooney–Rivlin relationship[16]

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

where $[f^*] = f/[A^* (\alpha - \alpha^{-2})]$ and $2C_1$ and $2C_2$ are constants independent of α. Values of $2C_2$ and $2C_1$ obtained from least-squares analysis of the linear portions of the plots of $[f^*]$ against α^{-1} are listed in columns six and seven of the table. The constant $2C_2$, generally regarded[4] as a measure of the departure of the form of the observed stress–strain isotherm from that specified by the molecular theories of rubberlike elasticity, is seen generally to increase with increasing temperature and with increasing degree of cross-linking. Previous studies[4] on a variety of polymer networks indicate that there is no general behavior which may be expected with regard to the temperature dependence of $2C_2$ but that $2C_2$ generally does increase with increase in the degree of cross-linking, as is found here, at least for networks prepared in the undiluted state and studied unswollen.

The isotherms obtained for the two peroxide-cured samples are shown in Figures 1 and 2. The values obtained for $2C_2$ for these two networks from these data are quite small. They are best viewed in terms of the ratio $2C_2/2C_1$; since $2C_1$ is thought to be proportional to the density of cross-links, this ratio represents, at least approximately, the constant $2C_2$ normalized to constant cross-link density.[4] Its value for P1 and P2 is 0.35 ± 0.15, whereas experimental values of this ratio are more typically the order of unity,[4] as recent theory[25] suggests for tetrafunctionally cross-linked networks. The value obtained for $2C_1$ may be used to obtain alternative values of M_c and the cross-link density $\nu/2V$ if, as is generally done,[4] this constant is identified with the structure factor given by the molecular theories of rubberlike elasticity, i.e., by adoption of the relationship[24]

$$2C_1 = \rho kT/M_c = \nu kT/V \qquad (3)$$

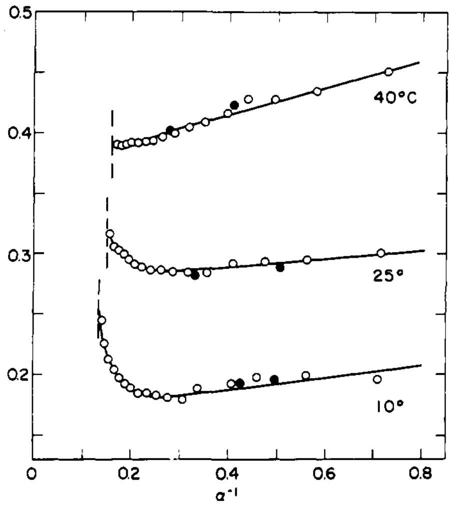

Figure 2. Results for peroxide-cured network P2, which has a somewhat higher degree of cross-linking than P1.

where k is the Boltzmann constant, T is the absolute temperature, ν is the number of network chains, $\nu/2$ is the number of cross-links (assumed tetrafunctional), and V is the volume of the network. Values of M_c thus calculated are given in column eight of the table; values of the alternate quantity, the cross-link density, are given in the following column. These values of M_c are seen to be essentially independent of temperature, as expected, and in the case of these two samples to agree within approximately ±6% with the values estimated from the swelling equilibrium measurements, as given in column four. (It should be mentioned here that recent molecular theories[25,37–39] replace ν in eq 3 by $\nu/2$ and therefore M_c by $2M_c$, as originally suggested by James and Guth.[40] This would have no effect on the good agreement obtained by the two estimates of M_c, since the M_c occurring in eq 1 would likewise have to be replaced by $2M_c$. Upon such modification, however, all values of M_c listed in Table I would of course have to be divided by two, and all values of $\nu/2V$ doubled. Which form of the structure factor is more nearly correct under a given set of experimental conditions is obviously an important general question in the area of rubberlike elasticity, but it is not directly relevant to the present issue, the *form* of the stress–strain isotherm at high elongation.)

The departures from linearity shown in Figures 1 and 2 are generally very similar to those[19] shown by polyisobutylene, another polymer which crystallizes readily at high elongation. These isotherms differ from those for polyisobutylene, however, *in that very nearly the same high elongations were attainable at the higher temperatures as at the lower temperatures*, where the upturn in $[f^*]$ is clearly in evidence. The fact that the upturn disappears with increase in temperature, *at constant high elongation*, thus clearly indicates that it is due to strain-induced crystallization. The nature and the degree of crystallinity[41] thus produced in the *cis*-PBD networks would be expected to be strongly dependent on the thermal and mechanical history of the sample. This is obviously the origin of the unusual type of reversibility exhibited by these networks at the lower temperatures. Once crystallization had occurred, as evidenced by the upturn in the reduced force, values of $[f^*]$ on the linear portion of the isotherm were no longer reproduced upon appropriate decrease in α. Such points are not shown for any of the networks since, as expected, reversibility was completely restored by returning the sample to its undeformed state, thus melting the crystalline regions, and then retracing the isotherms using a sequence of increasing values of α.

The significant decrease in $[f^*]$ in the case of sample P1 at

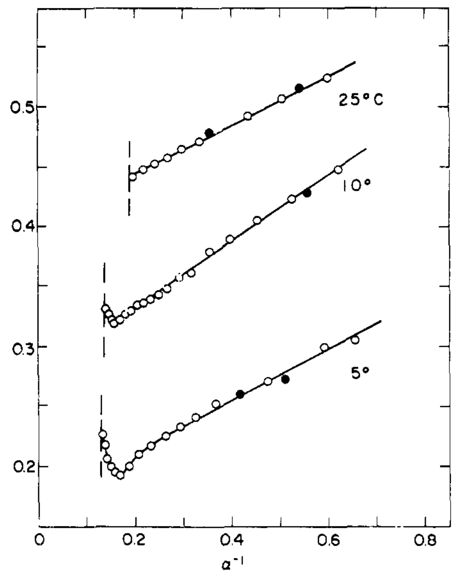

Figure 3. Results for sulfur-cured network S1, of moderate degree of cross-linking.

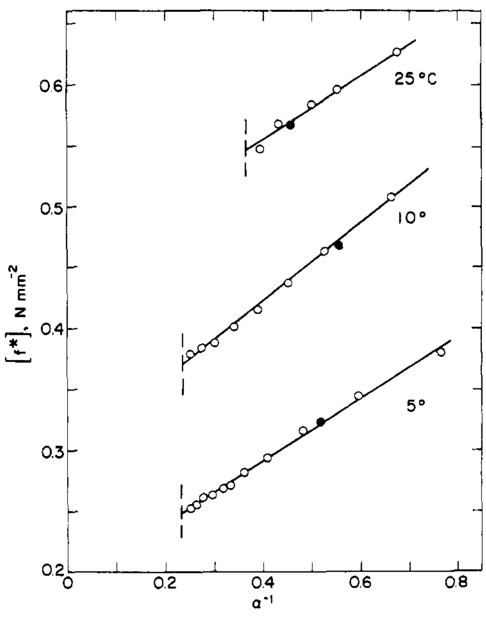

Figure 4. Results for sulfur-cured network S2, of relatively high degree of cross-linking.

the relatively high temperature of 40 °C is of particular interest. It clearly demonstrates the importance of two opposing effects[22,42] in the strain-induced crystallization. The first arises from the fact that the crystallites formed act as multifunctional cross-links, hereby increasing ν and thus also $[f^*]$. However, the chain sequences within the crystallites are in regular, highly extended conformations[43] and the crystallites themselves tend to be oriented along the axis of macroscopic deformation. This straightening out and aligning of portions of the network chains thus has the opposite effect of reducing $[f^*]$. The unmistakable decrease in $[f^*]$ shown by sample P1 at high elongation shows that this latter effect can be quite significant.

Column ten of the table lists approximate values of the elongation at which the upturn in $[f^*]$, if present, becomes discernible.[19] Although it is difficult to locate these points precisely, they appear to increase with increase in temperature, as was found to be the case for Viton fluoroelastomers.[9,18] On the other hand, the elongation at the upturn is found to decrease in general with increase in cross-link density, as has been observed for networks of polyisobutylene[19] and of natural rubber.[5,18] The following column gives a measure of the ultimate strength, the maximum upturn observed in $[f^*]$ as measured from the extension of the linear portion of each isotherm. These values decrease significantly with increase in temperature. This is due to the fact that fewer crystallites form at the higher temperatures and such crystallites have a strong reinforcing effect on the network structure.[21,24] The last column lists values of the elongation at rupture. Increase in temperature also decreases this quantity, as would be expected from the decrease in reinforcing effects accompanying the decrease in the amount of strain-induced crystallization.

Figures 3 and 4 show the isotherms obtained for the two sulfur-cured samples; results derived therefrom are again summarized in Table I. The average value of $2C_2/2C_1$ calculated from these data is 1.3 ± 0.2, which is reasonably close to the expected value of unity. The values of M_c estimated from $2C_1$ are seen to be essentially independent of temperature and to agree within ±17% with those obtained from the swelling equilibrium data. Network S1 shows a significant decrease or downturn in $[f^*]$ at the lowest temperature, and its isotherms are quite similar to those for networks P1 and P2 in that the upturn in $[f^*]$ is suppressed at the higher temperatures. Sample S2 however shows no departures at all from linearity; it was of a relatively high degree of cross-linking and could not be extended to quite as large a value of α as the other networks. The relatively high values of $[f^*]$ and the elongation to rupture, however, suggest that some crystallization probably did occur in these networks, at least at the lower temperature, but that the opposing effects of such crystallization on $[f^*]$, as described above, may have been largely offsetting under the conditions employed. In any case, values of the elongation at rupture do decrease with increase in temperature for these two networks, as was also observed for the peroxide-cured samples.

The stress–strain isotherms obtained for the three radiation-cured samples are shown in Figures 5–7 and are characterized in detail in the table. The average result $2C_2/2C_1$ = 1.69 ± 0.20 is significantly larger than the average values obtained for the other two types of samples. The values of M_c calculated from $2C_1$ are independent of temperature, as expected. They differ, however, from the values calculated from the swelling equilibrium data by a factor of 2 or 3. This could be due to nonuniformity of cross-linking, i.e., to an unusually broad distribution of chain lengths within the network structure. The extreme case of such dispersity would be regions of relatively high degree of cross-linking only lightly connected to the surrounding parts of the network. As was pointed out previously,[15] such inhomogeneous regions would be quite effective in suppressing the degree of swelling of the network (and thus the estimate of M_c derived therefrom) but would have relatively little effect on the elastic retractive force in uniaxial extension (and thus on the value of M_c obtained from the constant $2C_1$). This would explain the high values of M_c obtained from $2C_1$, but other polymers would obviously have to be studied in this manner before a definitive statement could be made regarding the relative uniformity of cross-linking obtained in different types of cures. The nonlinear portions of these isotherms are quite different from those obtained for the other two types of *cis*-PBD networks in that all of the networks showed a very pronounced downturn in the reduced force at both 5 and 10 °C. Such an influence of the curing system on the stress–strain isotherms and on the nature and degree of the crystallinity has also been observed for networks of natural rubber.[6,17] As shown in Figures 5–7, at the lower temperatures the first departure from linearity is a

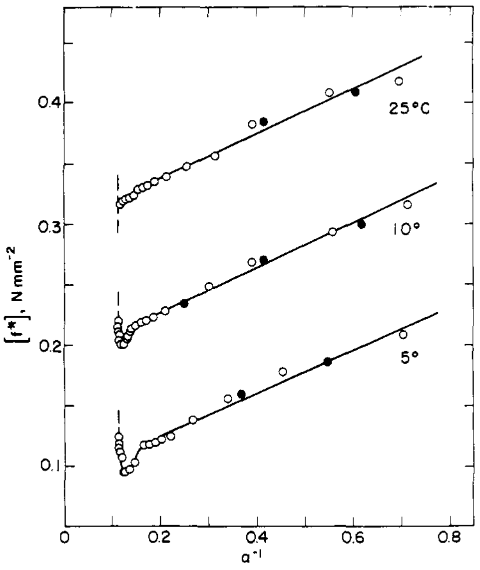

Figure 5. Results for network G1, cured to a relatively low degree of cross-linking by means of γ radiation.

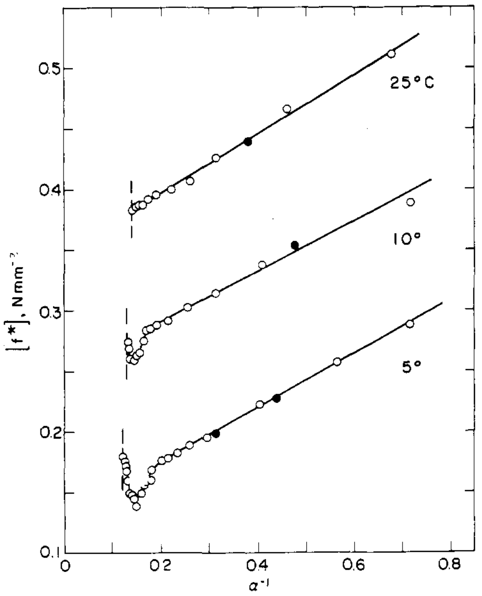

Figure 6. Results for network G2, cured to a moderate degree of cross-linking by means of γ radiation.

rather abrupt decrease in $[f^*]$. This indicates that the predominant effect in these cases is the alignment of the *cis*-PBD chains, in regular, spatially extended conformations within the crystallites, along the direction of deformation. The subsequent upturn in $[f^*]$ is then extremely abrupt, as would be expected from the presence of large amounts of strain-induced crystallization. Isotherms having somewhat similar features have been reported for some networks of natural rubber, also studied at relatively low temperatures.[6] Increase in temperature is again seen to decrease the maximum upturn in $[f^*]$ and the elongation to rupture. As was the case for the other networks of *cis*-PBD and of polyisobutylene[19] thus studied, any upturn in the reduced force is completely suppressed by increase in temperature. Again to be noted is the fact that these radiation-cured samples of *cis*-PBD have values of the maximum extensibility at the highest temperature which are not very much smaller than those at the lower temperatures employed.

All of the above results are consistent with the expected

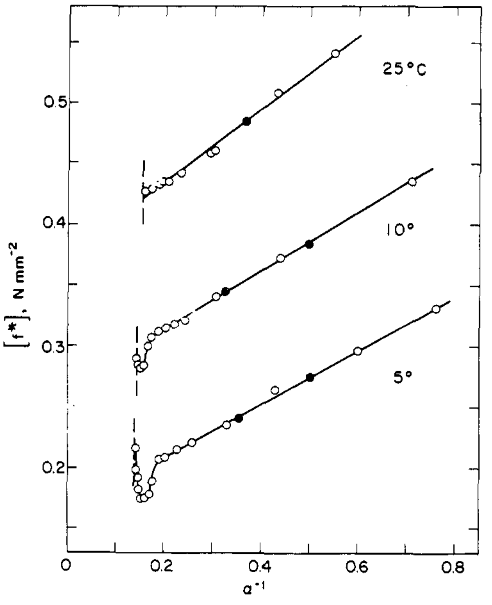

Figure 7. Results for network G3, cured to a relatively high degree of cross-linking by means of γ radiation.

effects of strain-induced crystallization on the elastomeric properties of a polymeric network. There is no apparent need to postulate significant contributions from "limited chain extensibility" as has frequently been done in the past; in fact, much of the above evidence is obviously irreconcilable with this interpretation of stress–strain isotherms at high elongation.

Important supplementary information could be provided from similar studies carried out as a function of the degree of swelling of a network. Such work is in progress.

Acknowledgments. It is a pleasure to acknowledge, with gratitude, the financial support provided by the National Science Foundation. T.-K.S. also wishes to thank the Macromolecular Research Center of the University of Michigan for a postdoctoral fellowship.

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Intrachain Reactions of a Pair of Reactive Groups Attached to Polymer Ends. 3. Intrachain Charge-Transfer Complex on Polysarcosine Chains Having Terminal Electron Donor and Terminal Electron Acceptor Groups in Chloroform Solution

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Received February 4, 1976

ABSTRACT: Polysarcosine having a terminal *p*-dimethylaminoanilide group and a terminal 3,5-dinitrobenzoyl group was synthesized. The number-average degree of polymerization $\bar{n}$ was varied from 6 to 25. In chloroform solution this polymer showed a distinct absorption band around 455 nm, which was attributed mostly to intramolecular charge-transfer interactions. The extinction coefficient of the charge-transfer complex was determined for low molecular weight model compounds. Using the same extinction coefficient, the fraction of polymers forming intrachain charge-transfer complex was evaluated at infinite dilution. The fraction was about 0.15 for $\bar{n} = 6$ and decreased asymptotically with increasing $\bar{n}$ finally to 0.03 for $\bar{n} = 25$. These values are almost 20–100 times as large as those estimated from the Monte Carlo calculation and on the basis of the intramolecularly catalyzed hydrolysis on polysarcosine chain. This indicates that the cyclized conformations of polysarcosine chain are greatly stabilized by the formation of intrachain charge-transfer complex. The fraction of the cyclized polymer was decreased with increasing temperature for short chains. The thermodynamic parameters characterizing the conformational change required for cyclization in chloroform were obtained and compared with those for the same reaction in ethanol solution, as well as those for the intramolecularly catalyzed hydrolysis on polysarcosine chain in aqueous solution.

Three-dimensional structure of protein is stabilized by intramolecular secondary valence forces, such as hydrogen bonds, electrostatic forces, hydrophobic forces, and charge-transfer interactions. The nature of these forces has been subjected to considerable investigations and their total effect on the protein structure has now been clarified to some extent.[1] However, the effect of the individual force on the protein structure seems still unclear, since these secondary valence forces are operating in a protein molecule concurrently and cooperatively. In view of this situation, it is hoped to investigate the effect of the individual secondary valence force in much simpler macromolecular systems, such as X–Y-type polymers where X and Y are interacting groups.

In this series of investigations the intrachain reactions and interactions have been studied on X–Y-type polymers.[2,3] In the first paper the intrachain reaction on polysarcosine chain was studied,[2] and the experimental results were compared with the Monte Carlo calculation of the ring-closure probability of polysarcosine chain in the second paper.[3] In the above case it was assumed that the equilibrium conformations of polysarcosine chain were not greatly affected by the incorporation of the terminal reactive groups. The assumption is reasonable, as far as no interactions exist between the pair of terminal groups. In the present study electron-donating and electron-accepting groups were attached to respective ends of the polysarcosine chain and the effects of an intrachain charge-transfer force upon the conformation of polymer chain were discussed. There are several reasons to study the charge-transfer interaction as a secondary valence force in biopolymers.[4,5] (1) The formation of charge-transfer complex can be easily detected by the characteristic absorption band of the charge-transfer complex which occurs at a longer wavelength than the component species. (2) The amount of the complex is determined directly from the intensity of the charge-transfer band, provided that the extinction coefficient is given. (3) The measurement can be carried out under a variety of conditions of the polymer concentration, solvents, and temperature.

Experimental Section

Materials. The chemical structures of compounds used in this study are illustrated in Figure 1.

Synthesis of *N*-Acetyl-*N*′,*N*′-dimethyl-*p*-phenylenediamine (I). To an ice-cooled solution of acetic anhydride (5 g) in ether (30 ml) with a small amount of pyridine (1 g) was added the ethereal solution of freshly distilled *N*,*N*-dimethyl-*p*-phenylenediamine (3.5 g/20 ml). After 1 h the precipitated product was collected, washed with ether, and recrystallized repeatedly from benzene and ethylacetate giving colorless plates of I (2.7 g): mp 133–134 °C (lit.[13] 134–135 °C). Anal. Calcd: C, 67.4; H, 7.9; N, 15.7. Found: C, 67.7; H, 8.1; N, 15.8.

Synthesis of *N*-(3,5-dinitrobenzoyl)sarcosine Dimethylamide (II). To an ice-cooled solution of sarcosine dimethylamide (1.2 g) in benzene (15 ml) was added the benzene solution of 3,5-dinitrobenzoyl chloride (2 g/55 ml) with a catalytic amount of pyridine. After 1 h the