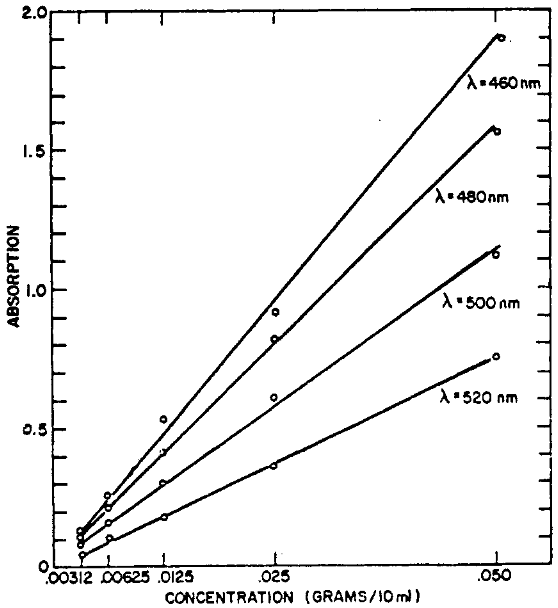

Figure 3. Linear dependence of absorption of concentration for poly(TNFMA-*co*-AEMA) charge-transfer band, THF, 25 °C, 1-cm cell.

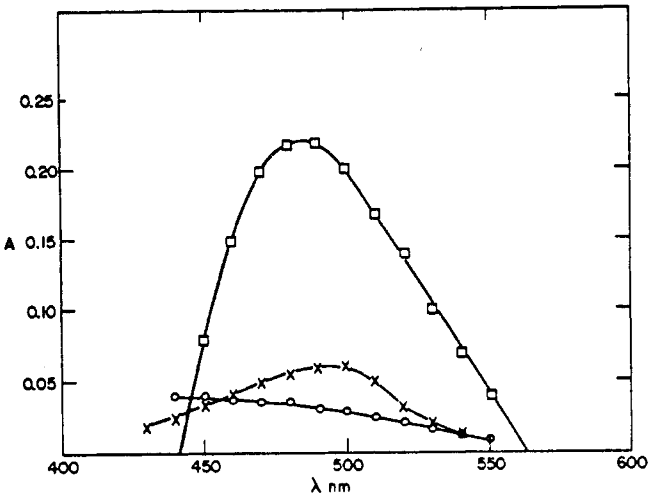

Figure 4. Charge-transfer spectra of (○) anthracene/2.47-trinitro-9-fluorenyl acetate; (×) anthracene/poly(TNFMA); (□) poly(TNF-*co*-AEMA)] 5×10^{-3} M in each chromophore, THF, 25 °C and 1-cm cell.

Polymerization. TNFMA (0.2 g, 5×10^{-3} M) and AEMA (1.5 g, 5×10^{-3} M) were dissolved in 20 mL of reagent grade acetone. AIBN (0.5 wt %) was added as the free-radical initiator. The polymerization tube was sealed under vacuum after two freeze–thaw cycles and the polymerization was carried out for 18 h at 60 °C. The product was isolated by precipitation into methanol followed by reprecipitation from THF into hexane. Approximately 2.0 g (57% conversion) of an orange powder, freely soluble in THF, DMF, and Me_2SO, was obtained. The IR spectrum of the copolymer showed "inter alia" a broad carbonyl band at 1730 cm^{-1}, nitro group bands at 1340 and 1540 cm^{-1}, and aromatic bands at 1600 and 730 cm^{-1}. GPC analysis in THF gave a single peak and $\bar{A}_n = 280$, $\bar{A}_w = 560$, with MWD = 2.0. An intrinsic viscosity of $[\eta] = 0.062$ was measured in THF at 30 °C.

Anal. Calcd for $C_{37}H_{29}O_{10}N_3$ (1:1 copolymer): C, 65.80; H, 4.30; N, 6.20. Found: C, 65.79; H, 4.40; N, 6.29.

Results and Discussion

Spectral Studies. Measurements were made on a Cary 14 spectrophotometer using standard techniques. Charge-transfer bands were determined by subtracting out the contribution due to the acceptor from the absorption of the donor/acceptor mixture in all cases except the 2,4,7-trinitro-9-fluorenylacetate–anthracene model system where the acceptor solution was used in the reference beam and the difference read directly. As reported earlier,[8] THF was found to react slowly with the acceptor polymer, therefore, all spectra were determined from freshly prepared solutions.

Copolymer Composition. Elemental analysis showed that the copolymer had an equimolar composition. This composition was confirmed using UV analysis by comparing the absorption of the trinitrofluorenyl group of the copolymer to that of poly(2,4,7-trinitro-9-fluorenyl methacrylate) at 345 nm. The UV spectrum of the copolymer to 400 nm is shown in Figure 1. Figure 2 shows the UV spectrum of poly(TNFMA) (note the absence of the anthracene band at ca. 260 nm). The weight percent of II in the equimolar copolymer is 57. At equal weight concentrations, the absorption from the trinitrofluorenyl group of the copolymer was 57% of that of the homopolymer.

Charge-Transfer Interactions. The intramolecular character of the charge-transfer interaction of the pendant anthracene and trinitrofluorenyl groups was established by showing that the absorption of the charge-transfer band varied linearly with concentration (see Figure 3) at several different wavelengths. An intermolecular interaction would be expected to vary in a nonlinear fashion with concentration because of the equilibrium between the donor and acceptor components.

Comparison of the charge-transfer spectra of the copolymer with the model systems, anthracene/2,4,7-trinitro-9-fluorenyl acetate (IV), and anthracene/poly(2,4,7-trinitro-9-fluorenyl methacrylate),[8] shows an enhanced absorption for the copolymer (see Figure 4). The intensity of the charge-transfer band in the 490-nm range is about an order of magnitude greater than the charge-transfer band in the model systems. This enhancement is attributed to the influence of the polymer environment on the interacting chromophores. A constrained intramolecular chromophoric interaction thus results and therefore a higher effective concentration of complex, in comparison to the model systems, is obtained. Such an effect is consistent with the observation of donor–acceptor cyclophane systems where strong charge-transfer complexes are formed despite little if any interactions being observed in the model components.[1,9]

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Chain Deformations in Rubber

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Small-angle neutron scattering (SANS) has made possible direct determinations of the chain dimensions of polymers in

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the bulk amorphous state.[1-3] The technique takes advantage of the isotopic difference in neutron scattering cross sections of deuterium and hydrogen. In this note, we give a brief preliminary account of a study of the chain dimensions in rubber networks by the SANS technique. We ask what happens to the linear dimension of a chain upon cross-linking its ends into a network and how this dimension changes when the network is stretched. In the theory of rubber elasticity, it has generally been hypothesized that the macroscopic extent of stretching of a network is affinely transformed to the extension ratio of each adjoining pair of cross-links.[4] We are now able to test this hypothesis. We could effect the experiment because we were able to prepare uniform networks,[5] whose elastic strands are of monodisperse chain length and cross-links are of uniform functionality. Incorporating a small fraction of perdeuteriopoly(butadiene) (3% or less)[6] in its hydrocarbon matrix, we have performed SANS measurements on the uncross-linked mixtures and on the cross-linked networks with and without an axial strain.

Experimental Section

Uniform poly(butadiene) networks were synthesized following the scheme of Rubio.[5] Butadiene or butadiene-d_6 was polymerized in a sealed glass reactor using high-vacuum techniques.[7] The "living" polymer was initiated with a difunctional isoprene oligomer,[8] terminated with ethylene oxide, and washed with water to give a dihydroxy liquid prepolymer. Gel permeation chromatography showed a single narrow peak and number average molecular weights determined by vapor pressure osmometry agreed with the predicted values. Chain microstructure was estimated by infrared analysis.[9] Uniform networks were prepared by mixing the stoichiometric amount of the cross-linking agent, purified triphenyl methane triisocyanate, in a small amount of solvent (tetrahydrofuran) with the liquid polymer, pouring into a Teflon mold (0.5 cm × 4 cm × 7 cm), and leaving at 80 °C for several days under nitrogen.

Each network was extracted several times with hexane containing a small amount of antioxidant; the sol content was under 2%, indicating[10] that the end linking reaction went to at least 90% completion.

Two independent sets of samples were used. Set A contained a deuterated polybutadiene of $M = 10^4$ at nominal concentrations of 0, 1, 2, and 3% by weight in a protonated matrix of mol wt 6.4×10^3. For the second set, set B, the deuterated chains (3% of the sample by weight) had $M = 6 \times 10^3$; the butadiene matrix had $M = 6.7 \times 10^3$.

The small-angle neutron-scattering experiments were carried out at the NBS research reactor with the instrument similar to the one reported earlier.[11] An extra 10 cm of Pb was used in the chilled filter to cut down γ rays to prevent counting noise as well as possible sample degradation. The scattering geometry and strain axis are such that we extract only one of the three components of radius of gyration $\langle S_y^2 \rangle$, and the structure factor is given by

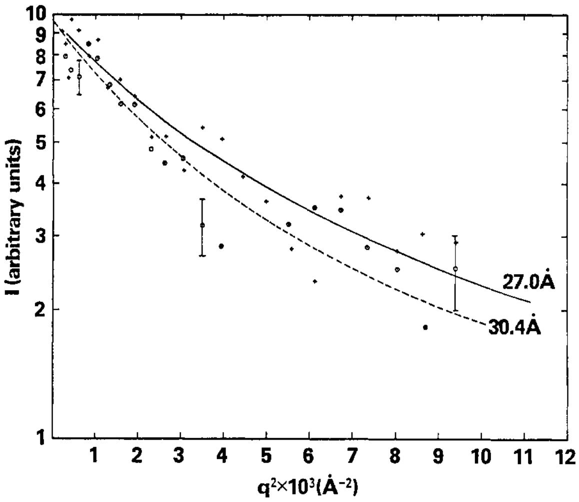

Figure 1. Excess scattered intensity in log scale vs. q^2(Guinier plot where the ordinate is in arbitrary units) for samples containing 3% deuterated chains: (+) for bulk mixture and (⊙) for network. Error bars, standing for one standard deviation, are given only for a few representative data points. The two curves are drawn according to the Debye form factor which gives the best fit for the mixture (solid curve) and for the network (chained curve).

$$P(\mathbf{q}) = 1 - q_y^2 \langle S_y^2 \rangle + \ldots \qquad (1)$$

where the y component (parallel to the strain axis) q_y of scattering vector $\mathbf{q}$ is given by $(2\pi/\lambda') \sin \theta$ with the neutron wavelength $\lambda' = 5.75$ Å and the scattering angle range $0.9° \leq \theta \leq 5.1°$. Sample and blank were alternately measured with strain released in between. Extension ratios were selected in random order, and the absence of any detectable permanent set indicated that sample degradation was not significant. The 3% bulk as well as network samples from set B were also studied.

Results and Discussion

We first present the results for the determination of chain dimensions in bulk samples. The root mean square radius of gyration $\langle S^2 \rangle^{1/2}$ (henceforth, just called the radius of gyration) is extracted from the excess scattered intensity, $I(q)$, in two ways. The first method is to fit the data at small q to a least-squares straight line. Because the scattering profile is in fact curved for the observed range of $q_y^2 \langle S_y^2 \rangle$, this method systematically overestimates $\langle S_y^2 \rangle$. A simulation study shows that the error is about 20% for the range of q used. Inasmuch

Table I
The Apparent Root-Mean-Square Radius of Gyration, $\langle S^2 \rangle^{1/2}$ Å, of Poly(butadiene-d_6) in Amorphous Bulk Mixtures and in Uniform Networks

Perdeuteriochain content, %	Method 1[a]		Method 2[b]	
	A[c]	B[c]	A	B
	Mixtures			
3	40.6 ± 3.9	35.4 ± 4.4	27.0 ± 4.0	26.3 ± 3.5
2	42.7 ± 4.8		28.8 ± 3.8	
1	40.8 ± 6.3		35.3 ± 8.5	
Infinite dilution			36.9 ± 10.5[d]	
	Networks (3% perdeuteriochain)			
Extension ratio λ				
1	39.4 ± 4.1	40.6 ± 4.8	30.4 ± 4.8	26.0 ± 6.7
1.22	41.5 ± 5.4			
1.25	43.8 ± 7.6			
1.43	54.8 ± 3.4			
1.53	58.6 ± 12.2			
1.55	53.0 ± 6.2			

[a] From the limiting slope of small q. [b] Fitting to the Debye form factor. [c] Two sets of samples described in the Experimental Section. [d] The only value extrapolated to infinite dilution.

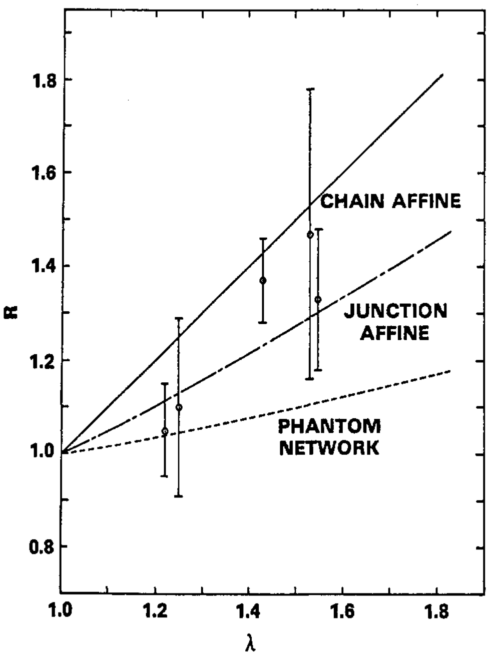

Figure 2. Ratio of the apparent radius of gyration to that in the unstrained state vs. extension ratio. $R \equiv \langle S_y^2\rangle^{1/2}/\langle S_y^2\rangle_{\lambda=1}^{1/2}$. The error bars are estimated from the sum of relative errors of slope and intercept of the linear extrapolation procedure without taking into account possible correlation between the two. Three curves are drawn respectively for the chain affine model (—) where $R = \lambda$, for the junction affine model (— · —) where $R = [(1 + \lambda^2)/2]^{1/2}$, and for the phantom chain model (- - -) where $R = [(5 + \lambda^2)/6]^{1/2}$ when the cross-link functionality is three.

as chain conformations in the bulk amorphous state have been shown to be well described by the Gaussian coil model,[1-3] we have also fit the $I(q)$ data to the Debye form factor for a Gaussian coil. The results of both fitting procedures are collected in Table I. The radius of gyration at infinite dilution derived from the second method is 36.9 ± 10.5 Å. This agrees with the unperturbed radius of gyration of 35 Å calculated from the literature values[12,13] taking into account the variation with microstructure.

The study of the chain dimension in a rubbery network is restricted to networks containing 3% (by weight) of deuterated chains, hence we represent the radius of gyration as the apparent one which is not corrected for its possible concentration dependence. On the basis of a plausible assumption that the concentration dependence of $\langle S^2\rangle$ for the free chain in the bulk state does not differ from that for the network chain in the unstrained state, we can now compare the chain dimensions in the two states. In Figure 1, Guinier plots for the 3% mixture and the 3% network are presented. Within the experimental uncertainty, the apparent radii of gyration are indistinguishable. We therefore conclude that the chain dimension of polybutadiene in the free state is the same as in the unstrained network. An identical experiment on set B samples gave the same result (see Table I).

The results for the study of chain dimensions in a network under unaxial strain are also collected in Table I. We summarize the data by plotting in Figure 2 the ratio of apparent radius of gyration at a given λ to that at the unstrained state ($\lambda = 1$) against λ. The experimental data are compared against three different models in Figure 2. The first is that of chain affine deformation, whereby every pair of chain segments within an elastic strand moves affinely with the macroscopic strain.[14] The second model is the classical one which we call the junction affine deformation, descriptive of the case when only the cross-link junctions deform affinely with the macroscopic strain. This is the model that is commonly invoked in the statistical mechanical description of elastic free energy of an isolated chain in a network.[15-19] The third is the model of the phantom network proposed by James[20] and others.[21-25] Given the experimental uncertainty and the limited range of λ covered, we can conclude only that our preliminary data are in qualitative accord with the prediction of the model of junction affine deformation.

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