J. Biochem., **63**, 591 (1976).
(3) A. Abuchowski, J. R. McCoy, N. C. Palczuck, T. van Es, and F. F. Davis, *J. Biol. Chem.*, **252**, 3582 (1977).
(4) V. P. Torchilin and A. V. Maksimenko, *Biochim. Biophys. Acta*, **522**, 277 (1978).
(5) The following abbreviations are used in the text: PEG, poly(ethylene glycol); *t*-Boc, *tert*-butyloxycarbonyl; Ac, acetyl; NHEt, ethylamino; Bzl, benzyl; OMe, methoxy; Ala, alanine; Val, valine; Gly, glycine; Glu, glutamic acid; Met, methionine; CD, circular dichroism; TFE, 2,2,2-trifluoroethanol; IR, infrared.
(6) M. Mutter, H. Hagenmaier, and E. Bayer, *Angew. Chem.*, **83**, 883 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 811 (1971); M. Mutter and E. Bayer, *Angew. Chem.*, **86**, 101 (1974); *Angew. Chem., Int. Ed. Engl.*, **13**, 88 (1974); M. Mutter, R. Uhmann, and E. Bayer, *Justus Liebigs Ann. Chem.*, 901 (1975).
(7) M. Mutter, H. Mutter, R. Uhmann, and E. Bayer, *Biopolymers*, **15**, 917 (1976).
(8) M. Mutter, *Macromolecules*, **10**, 1413 (1977).
(9) C. Toniolo, G. M. Bonora, and M. Mutter, *J. Am. Chem. Soc.*, **101**, 450 (1979).
(10) G. M. Bonora, C. Toniolo, and M. Mutter, *Polymer*, **19**, 1382 (1978).
(11) G. M. Bonora, M. Palumbo, C. Toniolo, and M. Mutter, *Makromol. Chem.*, **180**, 1293 (1979).
(12) C. Toniolo, G. M. Bonora, S. Salardi, and M. Mutter, *Macromolecules*, **12**, 620 (1979).
(13) C. Toniolo, G. M. Bonora, and M. Mutter, *Int. J. Biol. Macromol.*, **1**, 188 (1979).
(14) D. A. Brant, W. G. Miller, and P. J. Flory, *J. Mol. Biol.*, **23**, 47 (1967).
(15) P. J. Flory and P. R. Schimmel, *J. Am. Chem. Soc.*, **89**, 6807 (1967).
(16) P. J. Flory in "Statistical Mechanics of Chain Molecules", Interscience, New York, 1969, p 258.
(17) R. T. Ingwall, E. A. Czurylo, and P. J. Flory, *Biopolymers*, **12**, 1137 (1973).
(18) M. Mutter and P. J. Flory in "Peptides", M. Goodman and J. Meienhofer, Ed., Wiley, New York, 1977, pp 288-291.
(19) M. Mutter, *J. Am. Chem. Soc.*, **99**, 8307 (1977).
(20) T. Miyazawa in "Poly-α-Amino Acids", G. D. Fasman, Ed., Marcel Dekker, New York, 1967, pp 69-103.
(21) M. Avignon and C. Garrigou-Lagrange, *Spectrochim. Acta, Part A*, **27**, 297 (1971).
(22) M. Avignon and J. Lascombe in "Conformation of Biological Molecules and Polymers", E. D. Bergmann and B. Pullmann, Eds., Academic Press, New York, 1973, pp 97-105.

Small-Angle Neutron Scattering from Stretched Polystyrene Networks

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Several papers discuss small-angle neutron-scattering (SANS) experiments on the response of polymer chains to elongation of the specimen. Picot et al.[1] studied uncross-linked polystyrene by using samples containing 1% deuterated polystyrene (PS-d_8) which had been subjected to rapid stretching above the glass transition temperature and then frozen at room temperature. The deformation of the radius of gyration, R_g, of the tagged molecules in both the longitudinal and transverse directions did not quite follow affine behavior. Benoit et al.[2] measured the separation of chain ends (crosslink points) for a swollen polystyrene network uniaxially stretched to low elongations. Hinkley et al.[3] measured the change in R_g for polybutadiene networks, where the tagged chains connected two network junctions. Scatter in the data prevented the making of a firm statement as to whether the predictions of the junction affine theory were closely followed.

In the study reported here, SANS measurements were made on stretched, tagged polystyrene networks cross-linked by irradiation. The samples were elongated above T_g, held while the stress relaxed, and then cooled to room temperature. Determination of R_g was made in directions both parallel and perpendicular to the stretch direction by using data analysis techniques developed especially for anisotropic scattering.[4] Since the time required to collect sufficient data on anisotropic samples is long compared to that of the isotropic samples,[4] measurements in the transverse direction were also made by cutting films perpendicular to the stretch direction. Thus, the neutron beam was effectively parallel to the elongation direction, and isotropic scattering resulted.

Experimental Section

The PS-d_8 was prepared by anionic polymerization: $\bar{M}_w = 1.63 \times 10^5$, $\bar{M}_n = 1.23 \times 10^5$. This was mixed in toluene with normal protonated polystyrene characterized by $\bar{M}_w = 2.91 \times 10^5$ and $\bar{M}_n = 0.74 \times 10^5$ to give 1.95% tagged molecules. After precipitation and drying, bars were compression molded with cross-sectional dimensions of 2.0 cm by 1.2-2.0 cm. The bars were sealed under vacuum in tubes and cross-linked by ^{60}Co γ radiation. Two samples were irradiated to slightly different total doses. After irradiation the samples had swell ratios in toluene of 11.0 and 14.0, giving average molecular weights between cross-links,[9] $\bar{M}_c$, of 2.3×10^4 and 2.7×10^4, respectively.

The bars were elongated at 145 °C on an Instron tensile tester and held at the final elongation α for 10 min to allow some stress relaxation. $\alpha = l/l_0$ where l is the final length of the sample after elongation and l_0 is the initial length. After cooling, 1.5 mm thick specimens were cut in both the longitudinal and transverse directions. Identical samples without the tagged molecules were prepared for background data. A range of elongations from $\alpha = 1.44$ to 2.34 was investigated.

The SANS experiments were performed on the small-angle diffractometer D11[5] at the Institut Laue-Langevin, Grenoble, France. Two sets of experimental conditions were used: (1) for the "end-on" experiments, where the scattering is isotropic, the normal velocity selector with $\Delta\lambda/\lambda$ of 10% was used and the sample to detector distance was 10 m (λ_0 was 8.0 Å); and (2) for the anisotropic measurements a velocity selector with $\Delta\lambda/\lambda$ of 50% was used thereby increasing the neutron flux by a factor of about 3 compared with the 10% selector. Because of the very broad wavelength distribution the value of λ_0 used in the analysis was calculated by using the expression[6]

$$\lambda_0 = (\overline{\lambda^{-2}})^{-1/2}$$

The value of λ_0 used in the analysis was 7.0 Å. The sample to detector distance was 20 m.

Scattering Theory

The scattering law, $S(\mathbf{Q})$, for a polymer coil is

$$S(\mathbf{Q}) = N^{-2}\sum_{ij}^{N} e^{i\mathbf{Q}\cdot\mathbf{r}_{ij}} \tag{1}$$

where $\mathbf{r}_{ij}$ is the vector joining the segments i and j in a coil with N segments, $\mathbf{Q}$ is the momentum transfer equal to $(4\pi/\lambda)\sin\theta/2$, λ is the neutron wavelength, and θ is the scattering angle. For a coil embedded in a matrix the total scattered intensity is a combination of coherent and incoherent scattering of the form

$$I(\mathbf{Q}) = A + BS(\mathbf{Q}) \tag{2}$$

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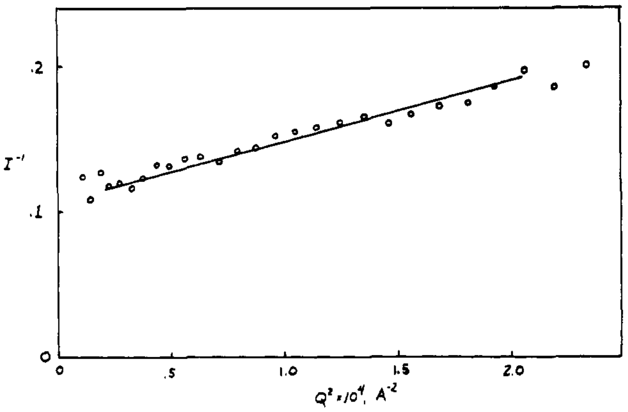

Figure 1. I^{-1} vs. Q^2 for the transverse anisotropic scattering from a sample with α = 2.18.

where A is the incoherent scattering which should be Q independent at low angles and B is an intensity factor. In order to obtain $S(\mathbf{Q})$ the incoherent signal must be subtracted. For an undeformed polymer in a matrix the scattering from the matrix alone is subtracted and in the case of a deformed chain the equivalent deformed matrix should be subtracted.

For a deformed coil the scattering law can be divided into two components depending upon whether Q is parallel or perpendicular to the stretch direction and in the Guinier range ($QR_g < 1$)

$$S(\mathbf{Q}_{\|}) \propto 1 - \frac{Q_{\|}{}^2 R_{\|}{}^2}{3} \qquad (3)$$

$$S(\mathbf{Q}_{\perp}) \propto 1 - \frac{Q_{\perp}{}^2 R_{\perp}{}^2}{3} \qquad (4)$$

If the chain deformation is affine, then the radii of gyration parallel, $R_{\|}$, and perpendicular, $R_{\perp}$, to the stretch direction should be related to the radius of gyration of the undeformed chain R_0, thus

$$R_{\|}{}^2 = \alpha^2 R_0{}^2$$

and

$$R_{\perp}{}^2 = \alpha^{-1} R_0{}^2$$

Results and Discussion

Figure 1 shows a I^{-1} vs. Q^2 plot (where I is the scattered intensity) for the transverse direction of the anisotropic scattering from one of the samples having α = 2.18. The quality of these data are comparable with those obtained from normal isotropic systems. The data for the "end-on" systems achieved the same quality in a quarter of the experimental time required for the anisotropic systems. The R_g values for the α = 1 specimen were within 5% of the value 111 Å obtained[7] from $R_g = 0.275(M_w)^{1/2}$.

In Figure 2 the ratio $R = R_g(\text{stretched})/R_g(\text{unstretched})$ is plotted against the macroscopic elongation ratio α. Results obtained on the two samples of different cross-link density are very similar. The transverse anisotropic data and the transverse "end-on" data, which are isotropic, are closely similar. In neither instance is there a detectable change in $R_{\perp}$ until the elongation exceeds 100%, i.e., α = 2.0. It certainly does not follow the behavior $R = \alpha^{-1/2}$. A constant value $R_{\perp} = 1$ is predicted for junction affine behavior.[1]

In the direction of elongation the values of R increase with increasing elongation but not according to the chain affine transformation of the end-to-end distance for which the line corresponding to $R = \alpha$ is drawn. The experimental points lie much closer to the line corresponding to $R = [(\alpha^2 + 3)/4]^{1/2}$, the dependence predicted for a tetrafunctional phantom network.[8] Figure 2 also includes the $R_{\|}$ curve for the junction affine case, $R = [(\alpha^2 + 1)/2]^{1/2}$.

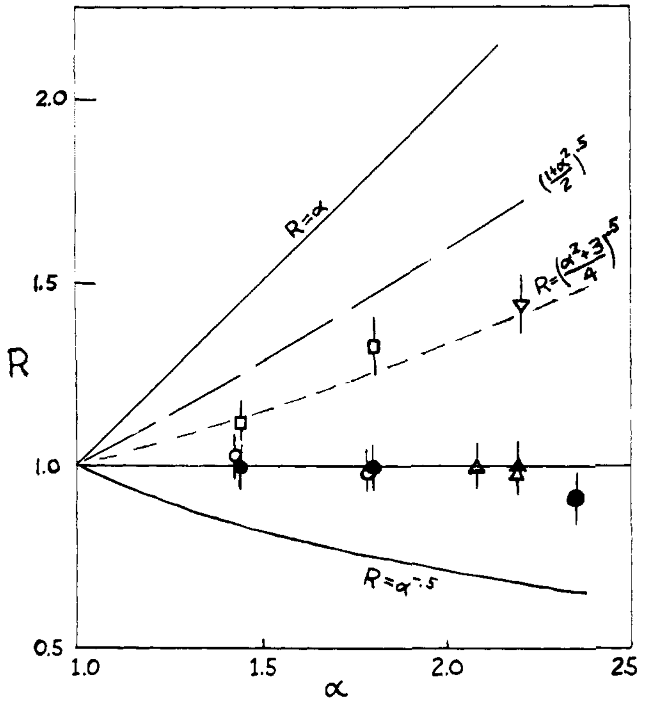

Figure 2. $R = R_g(\text{stretched})/R_g(\text{unstretched})$ as a function of sample elongation. See text for an explanation of the theoretical curves drawn on the figure.

	direction	anisotropic or "end on"	$\overline{M}_c \times 10^4$
□	longitudinal		2.3
▽	longitudinal		2.7
○	transverse	anisotropic	2.3
●	transverse	"end-on"	2.3
△	transverse	anisotropic	2.7
▲	transverse	"end-on"	2.7

Thus, our results on the polystyrene networks are in qualitative agreement with the results obtained by Benoit et al.,[2] that chain affine behavior is not followed.

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References and Notes

(1) C. Picot, R. Duplessix, D. Decker, H. Benoit, F. Boué, J. P. Cotton, M. Daoud, B. Farnoux, G. Jannink, M. Nierlich, A. J. deVries, and P. Pincus, *Macromolecules*, **10**, 436 (1977).
(2) H. Benoit, D. Decker, R. Duplessix, C. Picot, P. Remp, J. P. Cotton, B. Farnoux, G. Jannink, and R. Ober, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 2119 (1976).
(3) J. A. Hinkley, C. C. Han, B. Mozer, and H. Yu, *Macromolecules*, **11**, 836 (1978).
(4) A. Maconnachie and R. W. Richards, *Polymer*, **19**, 739 (1978).
(5) K. Ibel, *J. Appl. Crystallogr.*, **9**, 296 (1976).
(6) J. P. Cotton, D. Decker, H. Benoit, B. Farnoux, J. Higgins, G. Jannink, R. Ober, C. Picot, and J. des Cloiseaux, *Macromolecules*, **7**, 863, (1974).
(7) J. S. Higgins and R. S. Stein, *J. Appl. Crystallogr.*, **11**, 190 (1978).
(8) D. S. Pearson, *Macromolecules*, **10**, 696 (1977).
(9) Calculated assuming χ = 0.44.