Small-angle neutron scattering from a polymer coil undergoing stress relaxation

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Small-angle neutron scattering measurements have been made on samples of polystyrene in which the stress has been allowed to relax at a constant strain. The radii of gyration parallel and perpendicular to the stretch direction have been measured as a function of time after the strain has been applied. After an initial rapid change, the radii of gyration tend towards asymptotic values which are close to those for the undeformed chain. The deformation appears to behave as if the affine deformation theory holds only for distances separating effective crosslinks. It is proposed that after the initial change in radii of gyration the stress is relieved by reorientation of the chain segments.

INTRODUCTION

During the past few years small-angle neutron scattering (SANS) has been increasingly employed for observing the conformation of polymer chains in the bulk under a variety of conditions. No other technique is able to distinguish one particular chain from those surrounding it without resorting to labelling the chain with heavy atoms, as in X-ray scattering, which can change the conformation of the chain. Deuterium labelling gives a large contrast between the labelled chain and its surroundings without affecting the conformation of the chain to any measurable extent. A number of studies have been carried out on the behaviour of stretched[1-3] or swollen[4] rubbers and networks using SANS.

In an early paper, Benoit *et al.*[4] studied polystyrene networks in which (a) some of the chains between crosslinks were labelled and (b) just the ends of the chains connected to the crosslinks were labelled. These networks were subjected to uniaxial extension and to swelling. It was concluded that the chain ends deformed affinely but that the radius of gyration of the chain between the crosslinks did not. An 'end-to-end' pulling deformation mechanism was postulated to explain this behaviour. Picot *et al.*[1] studied the uniaxial deformation of uncrosslinked polystyrene, where chain entanglements act as temporary crosslinks, at different temperatures. At high elongations deviations from affine behaviour were found. A model was fitted to the data which combined affine and non-affine deformation of the coils. Hinkley *et al.*[2] and Clough *et al.*[3] studied uniaxially deformed end-crosslinked and randomly-crosslinked networks, respectively, and again observed that the affine principle did not hold.

Here, we present the results of an investigation into the way in which uncrosslinked polymer chains relax during a stress relaxation experiment.

SCATTERING THEORY

The static 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 segments i and j of a coil with N segments; $\mathbf{q}$ is the momentum transfer equal to $(4\pi/\lambda)\sin\theta/2$, where λ is the neutron wavelength and θ 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:

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

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 $\mathbf{q}$ is parallel or perpendicular to the stretch direction and in the Guinier range ($qR < 1$):

$$S(\mathbf{q}_\parallel) \propto 1 - \frac{q_\parallel^2 R_\parallel^2}{3} \tag{3}$$

and

$$S(\mathbf{q}_\perp) \propto 1 - \frac{q_\perp^2 R_\perp^2}{3} \tag{4}$$

If the coil is deformed affinely then each vector $\mathbf{r}_{ij} = (x_{ij}, y_{ij}, z_{ij})$ joining any two segments of the coil should be

Table 1 Experimental conditions

Sample	Relaxation time (s)	Wavelength (Å)	Detector distance (m)	q range (Å^{-1})
1	0	4.6 ± 0.1	20.53	0.66×10^{-2} to 2×10^{-2}
2	1800	5.7 ± 0.1	19.7	0.56×10^{-2} to 1.7×10^{-2}
3	4500	5.5 ± 0.1	20.53	0.56×10^{-2} to 1.7×10^{-2}
4	10 800	4.6 ± 0.1	20.53	0.66×10^{-2} to 2×10^{-2}

transformed to $\mathbf{r}'_{ij}=(\alpha x_{ij}, \alpha^{-1/2}y_{ij}, \alpha^{-1/2}z_{ij})$, then the radii of gyration parallel, $R_{\parallel}$, and perpendicular, $R_{\perp}$, to the stretch direction should be related to the radius of gyration of the undeformed chain R_0, thus:

$$R_{\parallel}{}^2=\alpha^2 R_0^2 \quad (5)$$

and

$$R_{\perp}^2=\alpha^{-1}R_0^2 \quad (6)$$

where $\alpha=L/L_0$, the macroscopic draw ratio, L_0 is the initial length of the sample and L is the final length after stretching.

EXPERIMENTAL

Sample preparation

The deuterium-tagged samples were a mixture of 2% by wt perdeutero-polystyrene (PSD) ($M_w=1.44\times10^5$, $M_w/M_n=1.7$) and 98% polystyrene (PSH) ($M_w=1.08\times15^5$, $M_w/M_n=2.2$). The matrix samples were 100% PSH. Films with approximate dimensions 6 × 1.2 × 0.2 cm were compression moulded at 200°C. The samples were uniaxially stretched at 120°C. The final thickness of the samples was about 1 mm and the draw ratio was 1.9. After stretching, the length of the samples was fixed and the stress allowed to relax. When a measured interval of time had elapsed the samples were cooled rapidly to below T_g (~100°C) by blowing methanol/solid CO_2-cooled compressed air over them. Pairs of samples comprising a PSD tagged film and a PSH film were stretched, allowed to relax and cooled in the same way. One pair of films was left in the unstretched state.

SANS

The experiments were carried out at the Institut Laue–Langevin in Grenoble, France, using the small-angle scattering diffractometer D11. The details of the instrument have been given elsewhere[5]. The velocity selector produced a broad distribution of wavelengths with a value of $\Delta\lambda/\lambda$ of about 50% with a consequent increase in flux of a factor of about 3 compared with the usual 10% selector. The experimental conditions are listed in *Table 1*. The measurement time for each stretched sample was of the order of 6 h and for the unstretched sample of the order of 0.5 h. All the measurements were carried out at room temperature.

Data analysis

The data were corrected for background scattering and detector response before being analysed for anisotropy. Picot *et al.*[1] subtracted the scattering from an undeformed matrix which is probably valid if there is no coherent scattering from the deformed matrix. However, it was noted by them that the matrix gave small-angle scattering probably due to orientation of the matrix chains and perhaps voids. As this effect was observed for our samples it was considered essential to subtract the scattering from a deformed matrix. Sectors of the data at 90° to each other were analysed using the programme ANARCH[6]. 30° sectors parallel and perpendicular to the deformation axis were chosen, see *Figure 1*. It was found that smaller sectors gave essentially the same values for $R_{\parallel}$ and $R_{\perp}$but the statistics were much poorer. If sector angles greater than 30° were used then the values of $R_{\parallel}$ decreased and $R_{\perp}$ increased since the averaging process included data from other parts of the coils.

Since the velocity selector which was used produced such a broad wavelength distribution it was necessary to calculate a mean wavelength for use in the calculations of R. The following average was used[7]:

$$\lambda_0=\langle\lambda^{-2}\rangle^{-1/2}$$

where $\langle\lambda^{-2}\rangle$ is the mean value of λ^{-2}. The scattering from the unstretched sample was analysed in the usual way for isotropic scattering[6].

RESULTS AND DISCUSSION

In *Figure 2* $I_{\parallel}^{-1}$ and $I_{\perp}^{-1}$ are plotted against q^2 for samples 1 and 4. The values of $R_{\parallel}$ and $R_{\perp}$ calculated for all the samples are listed in *Table 2* together with the value of R_0 obtained from the undeformed material. All the Zimm polts are linear over the q range used except that of $I_{\perp}^{-1}$ for sample 1. Equations (3) and (4) are valid for $qR<1$ whereas in this case $qR\leqslant2$. However, if the molecular weight distribution is assumed to have a Zimm–Schulz form[8], which is a reasonable assumption for anionically-polymerized polystyrene, then $S(\mathbf{q})$ can be calculated using the expression

$$S(\mathbf{q})\propto\frac{2}{(U+1)Y^2}[(1+UY)^{-1/U}-1+Y] \quad (7)$$

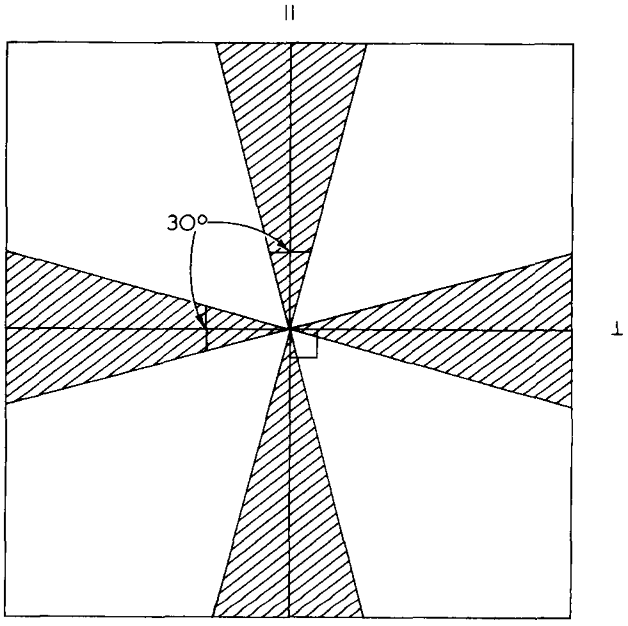

Figure 1 Hatched sectors show the position on the area detector of the data used in the ANARCH analysis

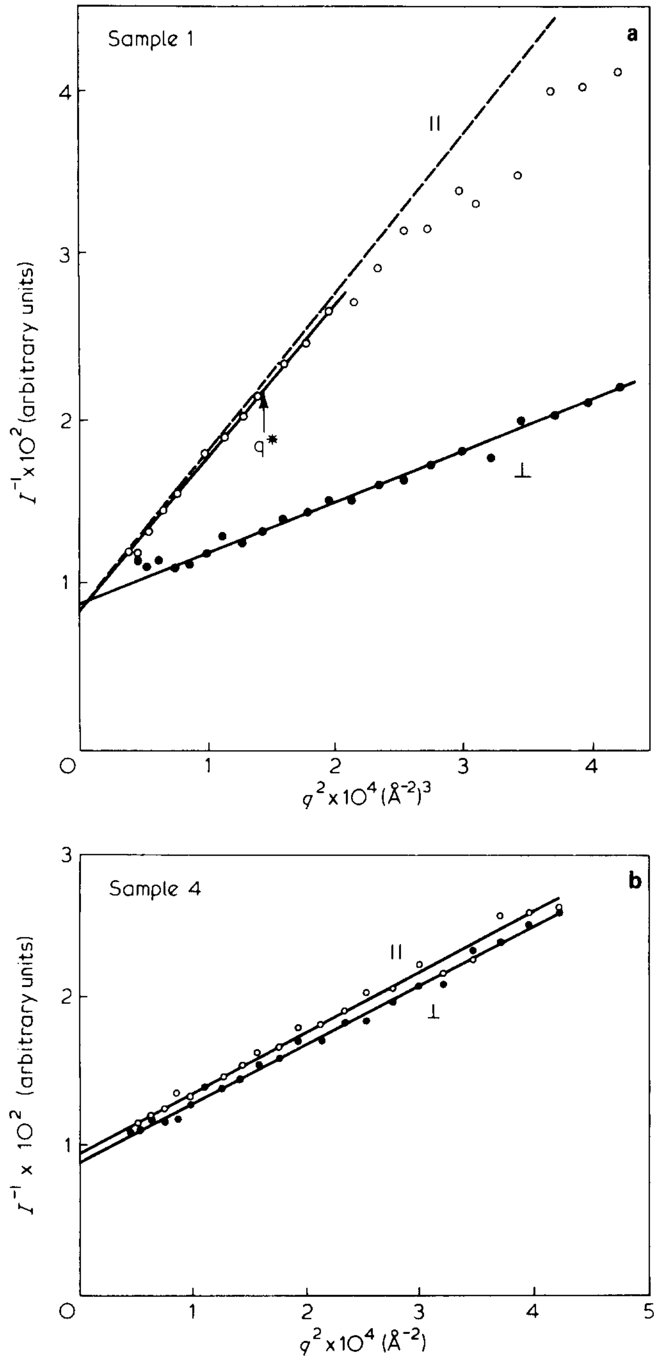

Figure 2 Plots of I^{-1} vs. q^2 for samples 1, (a) and 4, (b). The theoretical curve, – – – –, calculated using equation (7) is shown for sample 1

where $Y = q^2R^2/(1+2U)$ and $U = M_w/M_n - 1$. Using this expression the line shown in *Figure 2a* has been calculated and is a good fit to the data below $q^2 \approx 2 \times 10^{-4}$.

α has been calculated for sample 1 using expressions (5) and (6), from $R_{\|}$, $\alpha_{\|} = 1.74$ and from $R_{\perp}$, $\alpha_{\perp} = 1.09$. The value of $\alpha_{\|}$ is fairly close to the macroscopic value of 1.9 although smaller, but $\alpha_{\perp}$ is much smaller and indicates that R is virtually unchanged in the direction perpendicular to the deformation. Similar behaviour has been observed with a randomly-crosslinked polystyrene network[3] where, for macroscopic values of α of between 1.4 and 2.3, the data were in closest agreement with the phantom network theory[9]. Measurements by Picot *et al.*[1] on an almost identical system to that discussed in this paper show that the chains behave essentially affinely at elongations up to $\alpha = 1.7$. At higher draw ratios the chains no longer behaved affinely and an explanation was put forward in terms of a non-affine deformation model in which the affine deformation theory only holds for distances separating effective crosslinks. According to Picot *et al.*[1], the scattering law for a uniaxially-deformed chain can be described in terms of affine and non-affine draw ratios α_A and α_B, respectively. Equations (3) and (4) become:

$$S(\mathbf{q}_{\|}) \propto 1 - \left[q_{\|}{}^2 R_0^2(\alpha_A^2 + (\alpha_B^2 - 1))/2 \right] /3 \qquad (8)$$

$$S(\mathbf{q}_{\perp}) \propto 1 - q_{\perp}^2 R_0^2 \alpha_A^{-1}/3 \qquad (9)$$

Using equations (8) and (9) values of α_A and α_B for sample 1 have been calculated ($R_0 = 105.1$ Å) and are, respectively, 1.09 and 2.17. According to ref 2 if $\alpha_B > 1$ there is a value of $q_{\|}$, $q_{\|}^*$ such that for $q > q^*$ the scattering tends to an asymptotic limit. q^* can be calculated from the expression:

$$q^*_{\|} = (\alpha_B^2 - 1)^{1/2}/(2^{1/2}\alpha_A R_0) \qquad (10)$$

For sample 1, q^* is calculated to be ~ 0.012 Å^{-1} ($q^2 \approx 2 \times 10^{-4}$) and, as can be seen in *Figure 2a*, is close to the point where the data becomes non-linear in q^2.

The variation of $R_{\|}$ and $R_{\perp}$ with relaxation time is shown in *Figure 3*. After an initial sharp decrease $R_{\|}$ tends to an asymptotic limit which is close to that of R_0, although slightly higher. $R_{\perp}$ increases slightly, then tends towards the same limit as $R_{\|}$. In *Figure 4* a plot of modulus *versus* t is shown for polystyrene ($M = 125\,000$) at 121°C[10] which is expected to behave in a similar way to the samples used in this work; marked on the curve are the points at which samples 1 to 4 were frozen. It can be seen that using a freezing technique, which it is estimated takes 60 to 120 s to cool the whole sample below T_g, that it is not possible at this temperature to study the beginning of the curve, but only the conformation in the plateau and terminal regions can be observed. The data seem to indicate that by the time the terminal region is reached the chains have nearly attained their equilibrium conformation. Although the modulus is dropping rapidly, little or no change occurs in the radius of gyration of the coils. Possibly the stress is now relieved by reorientation of the segments and not a change in end-to-end distance. If this were so then values of α_A and α_B calculated for these samples should indicate what is happening. In terms of the theory, α_A ought to change whilst α_B should stay unchanged (see *Table 3*).

The α_A values do seem to show a steady downwards trend whereas the α_B values are basically unchanged after the initial drop. The values of α_B are all greater than 1 and may indicate that there is a slightly expanded conformation.

Table 2

Sample	$R_{\|}^*$ (Å)	$R_{\perp}^*$ (Å)
1	183.2 ± 11.7	100.8 ± 5.2
2	125.1 ± 7.4	106.6 ± 5.2
3	116.1 ± 11.0	111.2 ± 7.3
4	113.4 ± 4.8	116.0 ± 5.0
	Unstretched 105.1 ± 4.4	

* All values of R are z-averages

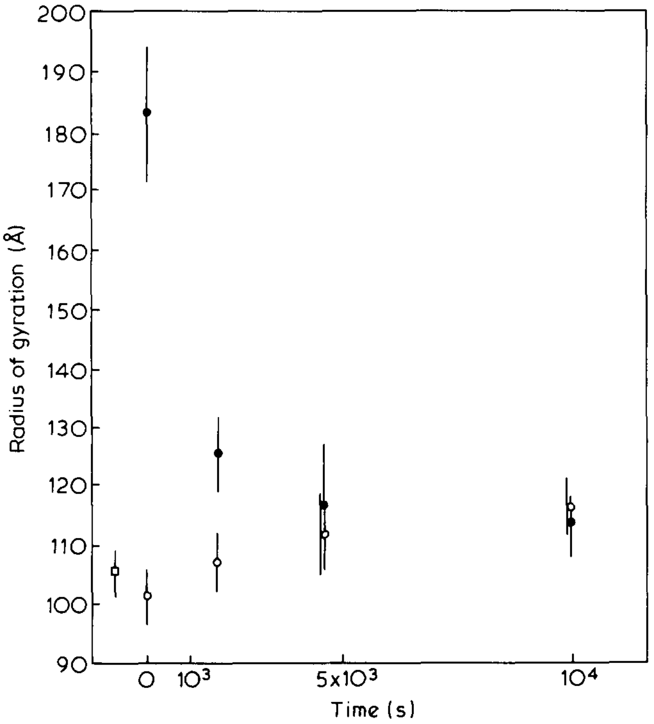

Figure 3 Plot of $R_{\parallel}$ (●) and $R_{\perp}$ (○) as a function of time. The value of R for the unstretched polymer is also plotted (□)

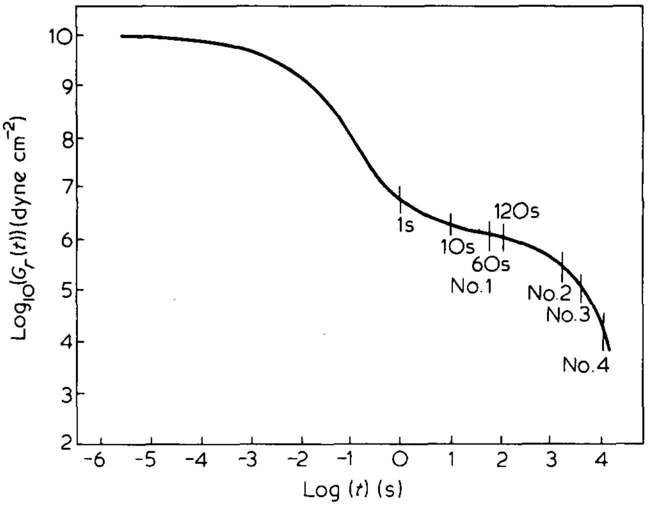

Figure 4 Plot of modulus (G) vs. time for a polystyrene fraction (M_w = 125 000) calculated using data from ref. 10

Table 3 Values of α_A and α_B calculated using equations (8) and (9) (R_0 = 105.1 Å)

Sample	α_A	α_B
1	1.09	2.17
2	0.97	1.40
3	0.89	1.36
4	0.82	1.41

CONCLUSION

Many techniques have been used to follow stress relaxation and flow, including birefringence studies. Most of the molecular techniques monitor segmental anisotropy. SANS has great merit in that it can monitor chain conformation. Therefore comparison of SANS data with the stress–time curve has special significance. On the time scale of our experiment, stress measurements show that relaxation of stress is complete after about 5 min and is followed by flow. Experimental difficulties made it impossible to follow the time variation of the anisotropy of R in the time interval 0 to 2 min where stress relaxation occurs. Nevertheless the initial measurement demonstrates clearly the chains are highly anisotropic. Within the time-scale of our first measurement or $R_{\parallel}$ and $R_{\perp}$ (i.e. after 60 s) there is still anisotropy in the samples comparable to the excess stress. After 30 min or more have elapsed, anisotropy of R has virtually disappeared, corresponding to almost complete stress relaxation.

In the period from 30 min onwards, flow occurs and this is sustained under conditions in which the chains have virtually isotropic dimensions. Nevertheless, the previous analysis indicates that full isotropy is not quite attained which may be the origin of the slow relaxation tail observed over long periods of time in some stress relaxation measurements.

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