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Effect of deformation ratio on fibril deformation in fatigue of polystyrene

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Small-angle X-ray scattering has been used to measure the deformation of craze fibrils during mechanical fatigue of polystyrene. The maximum deformation of the sample in the fatigue cycle was kept constant while the minimum deformation was varied. When the minimum deformation was 50% or more of the maximum, the load on the craze fibrils remained tensile. When the minimum deformation was reduced below this, the load on the fibrils became compressive and they buckled. The main effect of minimum sample deformation on fatigue life occurred in the regime where the fibrils remained straight. In this regime a decrease in minimum sample deformation caused a considerable decrease in fatigue life. At low minimum sample deformations the effects of minimum deformation on fatigue life were not large. These effects probably stem from the fibril strains involved in the deformation processes.

1. Introduction

The basic mechanism of fatigue in polymers is the growth and breakdown of crazes. Under cyclic loading crazes experience considerable deformation, with the fibrils buckling as the sample is unloaded and straightening as the sample is reloaded [1, 2]. Logically this microscopic deformation process would be expected to accelerate the macroscopic failure processes of craze breakdown and crack propagation. It seems likely that fibril lifetime, and hence fatigue lifetime, would be considerably affected by the plastic strain range experience by the fibrils. The aim of the current work was to examine in more detail the relationship between the craze deformation during fatigue and the fatigue lifetime of the sample.

The number of fatigue cycles to failure, N_f, of an unnotched sample is a function of both the minimum and maximum stresses in the fatigue cycle. It is often assumed that only the difference between maximum and minimum stress, $\Delta\sigma$, controls the rate of failure so N_f is often plotted against $\Delta\sigma$ only. (Fatigue is often characterized by studying crack growth rate as a function of stress intensity range, ΔK. Results for polystyrene using this approach have been published by Mai and Williams [3] using a wide range of both ΔK and mean K. It is clear, however, from the results of Sauer *et al.* [4] that the majority of the fatigue lifetime of an unnotched polystyrene is spent in crack initiation, so unnotched fatigue lifetime is the more relevant parameter for comparison with the SAXS data presented here.) As such data are normally obtained using a constant ratio of minimum to maximum deformation or stress (R-ratio) they cannot be used to address directly the question of the effect of craze fibril deformation on fatigue lifetime. There do exist a number of studies where the effects of mean stress or stress intensity have been examined. Sauer *et al.* [4] have examined the effects of stress amplitude and mean stress on fatigue lifetime for polystyrene. They found that, at constant maximum stress, the value of the minimum stress, or equivalently the R-ratio has a profound effect on N_f with the lifetime increasing strongly as the minimum stress (R-ratio) was increased. In this paper we use real-time small-angle X-ray scattering to determine the craze fibril deformation as a function of R-ratio and correlate this deformation with the fatigue lifetime.

2. Experimental technique

Specimen bars 90 mm long (z-axis) by 12 mm wide (x-axis) by 1.5 mm thick (y-axis) were machined from polystyrene (Dow Styron 685®) which contained no mineral oil lubricant and had a weight average molecular weight of 300 000 Daltons. The bars were deformed in bending about the y-axis in a three-point bending jig having two extra loading points which allowed the sample to be forced back to a straight line or even to be bent in reverse. The displacement of the two halves of the jig, and hence the bending of the bar, was driven by a stepping motor. A load cell mounted within the jig allowed the bending force to be monitored continuously during the cycling.

The X-ray beam from the Cornell High Energy Synchrotron Source (CHESS) was directed along the y-axis and irradiated the sample just under the tension (upper) surface above the centre load point. The position of the X-ray beam on the sample did not change as the sample was bent and straightened. A fibre-optic imaging system coupled to a video camera was used to observe the sample *in situ* and hence to align it with respect to the X-ray beam. The jig, including the specimen bar, could be displaced rigidly either horizontally or vertically by separate stepping motors to accomplish this alignment.

To begin the fatigue experiment, the sample was bent by a constant displacement which corresponds to a maximum elastic strain of 0.7%. Under this displacement the craze growth was monitored both by the SAXS pattern and the optical image of the bar as observed by the fibre-optic imaging system. When no further change in the extent of crazing could be observed, the fatigue experiment was started. The displacement was decreased to a minimum value at a constant rate then increased back to a maximum value at the same rate, forming a triangular displacement cycle with a period of from 2 to 12 sec, depending on the minimum displacement. After ten cycles the test was ended at the maximum displacement; the ratio of the minimum displacement to the maximum is defined as the R-ratio of the test. Eight such tests were conducted sequentially on the same bar starting at an R-ratio of 0.875 and decreasing to zero in steps of 0.125. The measured ratio of the minimum to maximum load, or L ratio, was typically less than the R-ratio due to the non-linear response of the crazed sample.

Monochromatic 8 keV X-rays (wavelength $\lambda = 0.154\,\text{nm}$) from CHESS were collimated using a 0.3 mm pinhole to produce a beam of $\sim 2.5 \times 10^{10}$ photons sec^{-1}. An oversize circular beam stop was mounted asymmetrically to permit recording of one side of the X-ray scattering pattern from the fibrils as close as possible to the primary beam. The data were collected using a TV camera/image intensifier system [2] whose output was recorded on a $\frac{3}{4}$ in. Sony U-matic video recorder. A character inserter was used to simultaneously record the load, time, frame number and primary beam intensity on each frame.

The data on each frame were digitized from the tape using a Deanza image processing system described earlier [2]. The response of the image intensifier/TV camera system was deliberately made non-linear by adjusting the contrast (gamma) of the TV camera in order to increase its dynamic range. The response of the camera plus other video components was measured using an optical step wedge and a calibration curve produced. This curve was used in the image processing stage to correct the data for the non-linearity of the camera. The corrected data were plotted as contour maps to allow visualization of the craze fibril alignment. Row averaging was also used to produce the equivalent of slit-collimated data for input to a Porod analysis [5, 6].

In a separate experiment, the fatigue lifetime, N_f, of the same polymer was measured as a function of R-ratio in tension starting from a constant maximum tensile strain of 0.7% (30 MPa maximum tensile stress). The tensile displacement was controlled by a MTS servo-hydraulic testing machine operating at a cyclic frequency of 0.1 Hz. At this frequency the thermal heating of the polystyrene sample was negligible.

3. Results and discussion

The aim of this experiment was to examine the deformation of craze fibrils as a function of the R-ratio of the fatigue. As the microstructure of craze fibrils is known to change rapidly during the first few cycles of fatigue (at least for R-ratio's of 0) [2], the results were initially examined for stability of the pattern over several cycles. It was clear that in the first two or three cycles the patterns at maximum and minimum load changed rapidly but after about five cycles they stabilized so that, for example, the pattern at maximum load changed only slightly over the second five cycles. The reason for this rapid change of the pattern is not clear but may be related to fibril coalescence or slight sample movement over the first few cycles. The patterns displayed below were all taken on the last fatigue cycle of each set of ten.

Figs 1 to 4 show contour plots of the SAXS patterns

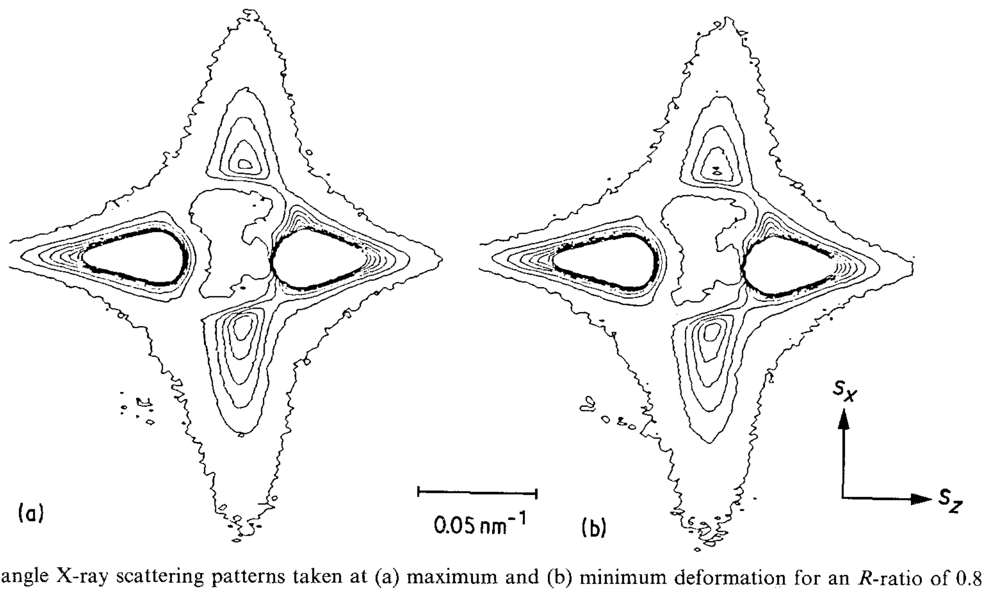

Figure 1 Small-angle X-ray scattering patterns taken at (a) maximum and (b) minimum deformation for an R-ratio of 0.875.

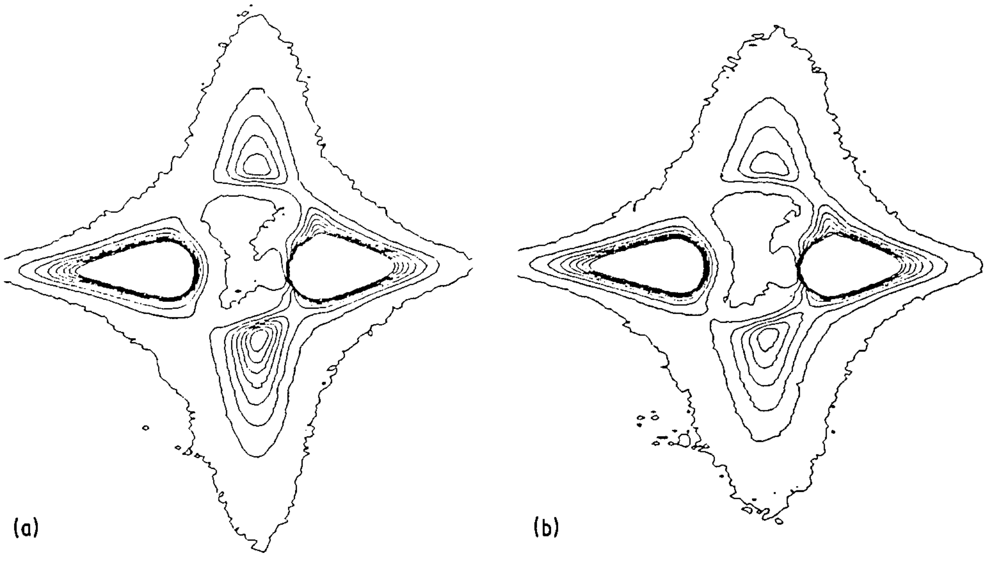

Figure 2 As Fig. 1 for an R-ratio of 0.5.

taken at maximum and minimum displacements at R-ratios of 0.875, 0.5, 0.375 and 0.25, respectively. The basic interpretation of patterns of this type has been discussed in detail in previous publications [1, 2, 5]. The vertical streak along the s_x direction is caused by diffraction from the craze fibrils whereas the very intense horizontal streak along the s_z direction comes mainly from X-ray reflection at the craze–matrix interface. It has been demonstrated that the increase in width of the diffraction streak on unloading the specimen can be related to the buckling of the craze fibrils [1, 2]. The SAXS patterns taken at maximum displacement show only relatively small changes of the type that have been observed previously [2] and interpreted as evidence for fibril coalescence. On the other hand, patterns taken at minimum displacement change dramatically with R-ratio. It is immediately clear that fibril buckling, which causes the increase in the width of the vertical streak on unloading, is insignificant for R ratios greater than 0.5 but increases rapidly for R-ratios smaller than that figure. When the R-ratio had decreased to 0.25, the fibril diffraction pattern was nearly isotropic (ignoring the reflection component) implying that the fibrils are so bent and have so many contacts that the fibril–void microstructure is essentially isotropic. It is not possible to model this structure as independent, parallel, sinusoidally bent fibrils as was done in the previous work [1].

Calculation of the SAXS invariant, Q, defined as

$$Q = \int_0^\infty i(s_x) 2\pi s_x \, \mathrm{d}s_x \qquad (1)$$

where i is the row averaged scattered intensity, $s_x = 2 \sin \theta/\lambda$ and 2θ is the scattering angle measured along the x-axis, is a good way of obtaining more quantitative data from patterns of this sort. This is because

$$Q = V v_f (1 - v_f) \Delta\varrho^2 \qquad (2)$$

where V is the volume of crazed matter in the beam, $\Delta\varrho$ is the difference in electron density between the voids and the fibrils and v_f is the volume fraction of fibrils in the craze. The product Vv_f, which represents the total volume of fibrils in the craze, should be constant for the sets of cycles considered here. (The craze volume does not grow during these sets.) Q may be combined with the Porod constant, k_1, obtained from the tail of the scattering curve to give a mean

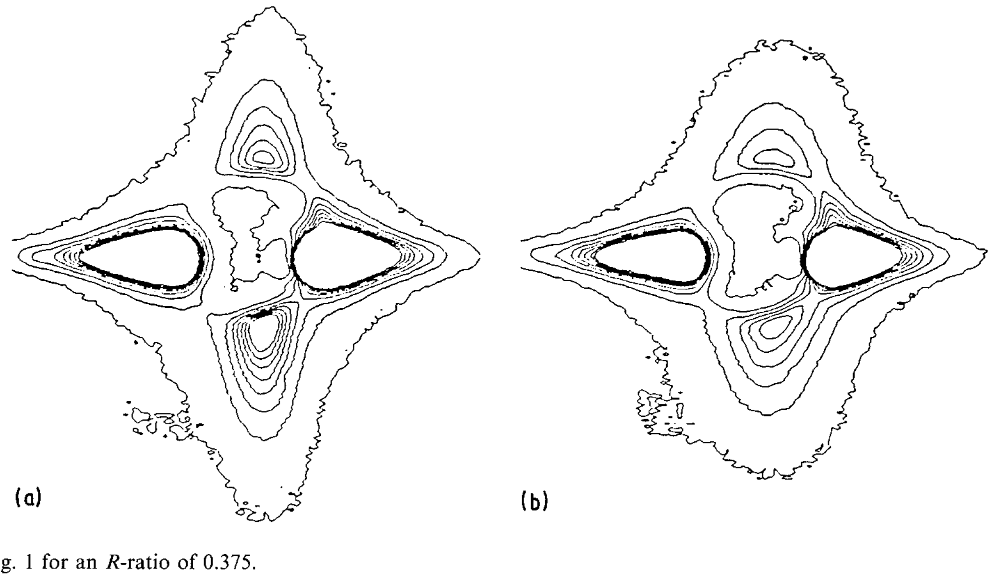

Figure 3 As Fig. 1 for an R-ratio of 0.375.

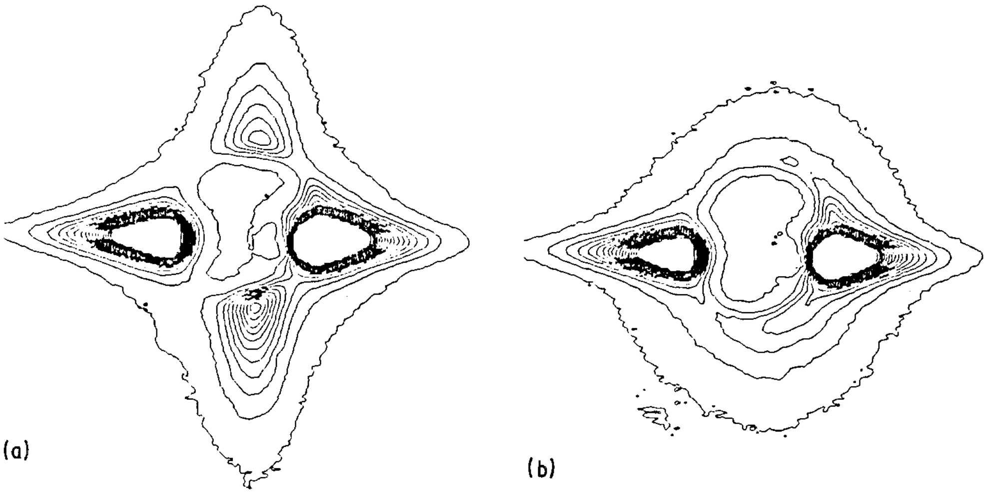

Figure 4 As Fig. 1 for an R-ratio of 0.25.

fibril diameter, D, as has been described in detail in previous publications [5, 6].

Table I gives values of Q in arbitrary units for the fully loaded crazes and also ΔQ, the change in invariant between the maximum and minimum deformation, as a function of R-ratio. It is evident from this table that there was no significant change in Q at maximum deformation except for the final point at an R-ratio of 0.25. The decrease of invariant at this R-ratio is most likely due to the fibrils having coalesced to such an extent that a significant portion of Q is at such low angles that it is lost under the beam stop. The lack of change in Q at maximum deformation shows that new craze matter did not grow during fatigue in the area of the sample that was examined by the beam. Because under conditions of no craze growth Vv_f is a constant in Equation 2, the change in Q on unloading is directly proportional to $(1 - v_f)$. Table I shows the changes in v_f calculated from ΔQ and Equation 1, assuming that the fully loaded craze always had a v_f of 0.25. Also shown is the craze compression ratio, Λ, which is defined as

$$\Lambda = \frac{0.25}{v_f}. \tag{3}$$

These results are also shown in Fig. 5 from which it is clear that for an R-ratio of greater than 0.5, which corresponds to an L ratio of 0.25, there was only slight craze compression. In this region the total craze compression, which was only about 10%, occurred mainly by the contraction of the fibrils with only a small amount of fibril misorientation and bending. As the minimum deformation was decreased below 0.5 of the maximum the craze compression increased rapidly and the fibrils began to buckle. By an R-ratio of 0.125, where the load had already dropped to zero, the crazes had been compressed to 40% of their original width.

For the large R-ratios the deformation of the craze fibrils can also be estimated from the change of the Porod constant k_1. We assume that the fibrils remain straight on partial unloading an assumption that is only valid for $R = 0.5$ and above. The mean fibril diameter, $\bar{D}$, is given by [5, 6]

$$\bar{D} = \frac{AQ}{(1 - v_f)k_1} \tag{4}$$

where A is a constant. Because from Equation 2 and the reasoning above, Q varies as $(1 - v_f)$ during these fatigue cycles, D must vary as $1/k_1$. If the fibrils deform at constant volume then, assuming small deformations,

$$\Lambda = \left(1 + \frac{\Delta k_1}{k_1}\right)^{-2} = \left(1 + \frac{\Delta D}{D}\right)^2 \tag{5}$$

Values of Δk_1 were obtained from Porod plots of the difference between the diffraction patterns in the fully loaded and unloaded crazes. The results for Λ obtained in this way are also given in Table I; there is no value given for R of 0.875 as the errors in the data were too large to obtain a value in this case. These values for Λ are similar to those obtained from the invariant. We believe that the value of Λ obtained from the invariant, Q, is somewhat more accurate than that obtained from the Porod constant because Q is an integral over the whole of the scattering curve. The agreement between the two values confirms that

TABLE I Results from SAXS

R-ratio	L-ratio	$Q_{\max}$	ΔQ	v_f	Λ from Q	Λ from k_1
1	1			0.25	1	1
0.875	0.710	51 100	800	0.26	0.96	
0.75	0.556	49 700	1 200	0.27	0.93	0.95
0.625	0.397	49 000	1 400	0.27	0.92	0.95
0.5	0.250	45 900	1 750	0.28	0.90	0.92
0.375	0.132	52 300	5 700	0.35	0.71	
0.25	0.013	47 600	16 300	0.53	0.47	
0.125	0	30 300	12 700	0.63	0.40	

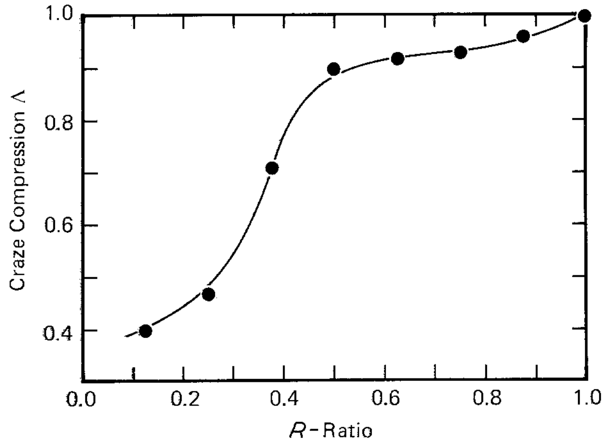

Figure 5 The variation of craze compression with R-ratio.

the basic model of craze fibril contraction is correct, though the data are not sufficiently accurate to test the assumption that the fibrils deform at constant volume.

In previous work [2] we have argued that, as the average stress on a craze in polystyrene before unloading is about 17% less than the average stress on the section [7], one may expect that the stress on a craze will become compressive when the section stress is decreased below 17% of its original value. This argument assumes that the craze compression during unloading is insignificant. From Table I it can be seen that this compression before fibril buckling is approximately 10%, which implies that the fibrils will buckle when the section stress is below 14% of its original value. This revised figure agrees very well with the results presented above in which the fibril diffraction patterns showed a small spreading at an L ratio of 0.25 indicating a small amount of fibril buckling and showed considerable spreading at an L ratio of 0.13.

Fig. 6 shows the effect of R-ratio on the fatigue lifetime at a constant maximum deformation of the same polystyrene. At R-ratios above 0.6, increases in the R-ratio produce a large increase in the fatigue lifetime, N_f, while at R-ratios below 0.6 similar increases produce much smaller changes in N_f. These results are entirely consistent with those of Sauer *et al.* [4]. The SAXS results presented above offer an explanation of this difference. At higher R-ratios the unloading and reloading is accommodated by changes in the tensile strain of relatively straight fibrils, changes which from Table I are in the range of 5 to 10%. At low R-ratios the additional unloading and reloading is accommodated by fibril buckling, a process that produces relatively small further changes in the strain in the fibrils due to their large aspect ratio, changes in strain that for typical fibrils might be 1 to 2%. If one hypothesizes that it is the magnitude of the strain in the fibrils themselves that is responsible for the initiation of fibril breakdown in fatigue, it is reasonable to expect that the fatigue lifetime should be more strongly affected at large R-ratios than at small R-ratios as observed.

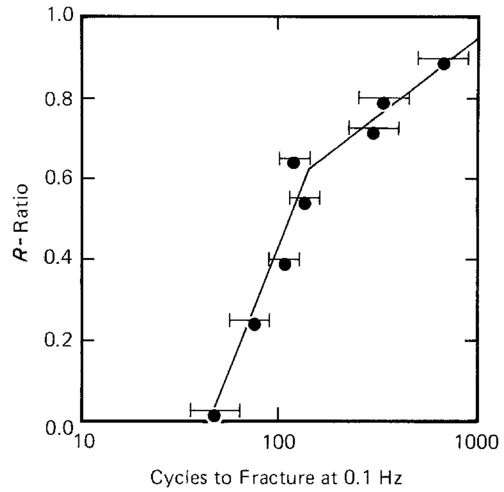

Figure 6 The effect of R-ratio on fatigue lifetime for this polystyrene.

4. Conclusions

We have shown that the mode of deformation of craze fibrils during fatigue differs according to the R-ratio of the deformation. If the minimum deformation is 50% or more of the maximum then the load on the fibrils remains tensile, they remain relatively straight and they contract in length and increase in diameter as the load is decreased. When the minimum deformation is less than 50% of the maximum the load on the fibrils becomes compressive and they begin to buckle. The main effect of R-ratio on fatigue life occurs in the high R ratio regime where the fibrils remain straight. A decrease in R-ratio in this regime causes a considerable decrease in fatigue life. At lower R-ratios the decreases in fatigue life for the same decrease in R-ratio are not as large. These differences between the large R-ratio regime and the small R-ratio regime probably stem from the fact that the fibril strains involved in the buckling process are considerably smaller than those that occur when the fibrils are straight.

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References

1. P. J. MILLS, E. J. KRAMER and H. R. BROWN, *J. Mater. Sci.* **20** (1985) 4413.
2. H. R. BROWN, E. J. KRAMER and R. A. BUBECK, *J. Polym. Sci. Polym. Phys. Edn.* **25** (1987) 1765.
3. Y. W. MAI and J. G. WILLIAMS, *J. Mater. Sci.* **14** (1979) 1933.
4. J. A. SAUER, A. D. McMASTER and D. R. MORROW, *J. Macromol. Sci. Phys.* **B12** (1976) 535.
5. H. R. BROWN and E. J. KRAMER, *ibid.* **B19** (1981) 487.
6. E. PARADES and E. W. FISCHER, *Macromol. Chem.* **180** (1979) 2707.
7. B. D. LAUTERWASSER and E. J. KRAMER, *Phil. Mag.* **A39** (1979) 469.

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