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Polysulfide containing *s*-triazine rings as a new thermoplastic elastomer: spherulite morphology and strain recovery behaviour

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A new polymer, polysulfide containing *s*-triazine rings, was found to be crystalline but it showed an excellent strain recovery after large deformation; residual strain was less than 10% after 25–400% elongation. The elastic recovery was much better than low density polyethylene (LDPE), a typical rubber-like crystalline polymer. As in the case of LDPE, a four-leaf clover pattern in H_v (cross-polarized) light scattering was observed, suggesting the formation of spherulites. The H_v pattern deformed with bulk deformation and recovered to the original pattern after releasing, without any change in the disorder parameter of orientation correlation. The reversible change in scattering pattern suggests that the spherulite itself is highly elastic and it may render the elastomeric character in bulk. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polysulfide; thermoplastic elastomer; spherulite)

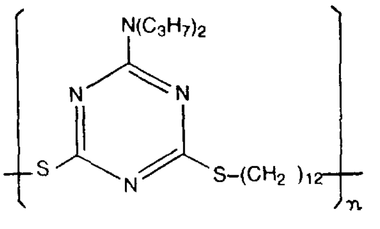
INTRODUCTION

It is well known that there are two groups of thermoplastic elastomers (TPEs): the block copolymers consisting of rigid and soft segments and the plastic–rubber blends by dynamic vulcanization[1]. A new polymer, polysulfide containing *s*-triazine rings, recently explored the potential for new TPEs[2]. The crystalline polymers usually undergo the plastic deformation which is often utilized for fibre and film processings. In contrast, the new crystalline polysulfide shows nice strain recovery after large deformation, i.e. the residual strain caused by the plastic deformation is very small. Hence, it is interesting to investigate the relationship between the crystalline morphology and the strain recovery.

In this paper, we investigate the crystalline morphology and its change with bulk deformation by H_v (cross-polarized) light scattering. The results are compared with those for a typical rubber-like crystalline polymer, low density polyethylene (LDPE), to elucidate the origin of strain recovery mechanism in the new crystalline polymer.

EXPERIMENTAL

The polysulfide, containing *s*-triazine rings, used in this study was prepared by the phase-transfer catalysed polycondensation[2] ($M_w = 2 \times 10^5$, $M_n = 7.8 \times 10^4$).



It shows a glass transition at -25°C and a melting temperature at about 100°C. The LDPE used was a commercial polymer supplied by Mitsubishi Chemicals Co., Ltd. (J30281; $M_w = 3.3 \times 10^4$, degree of branching: 2.7).

The polysulfide is processable as a thermoplastic above the melting temperature. The thin film specimens (ca. 90–110 μm thick) were prepared by pressing the molten polymer between two polyimide sheets at 150°C and cooling gradually in a press machine. The pressed films were allowed to crystallize at room temperature for 1 day. The thick film specimen (ca. 0.5 mm thick) was also prepared for wide-angle X-ray diffraction (WAXD) arrangement in the same way.

The WAXD pattern was observed using a Rigaku Denki RU-200 diffraction apparatus. The radiation from the Cu anode was reflected from a graphite monochromator to obtain monochromatic Cu Kα radiation with a wavelength of 0.1541 nm. The generator was operated at 50 kV and 180 mA.

The stress–strain curve of the film specimen was measured using a tensile testing machine (Tensilon UTM-II-20, Toyo Baldwin Co., Ltd.) at constant strain rate of 20% min^{-1} at room temperature, both for stretching and releasing processes. During the deformation processes, the H_v light-scattering pattern with the deformation was recorded by the classic photographic technique[3]. The

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stretching direction was vertical. The polarization direction was set vertical, while the optical axis of analyser was set horizontally.

Strain recovery was evaluated as follows. The film specimen was stretched at an elongation rate of 100% min^{-1} to a certain strain. The stretched specimen was held at this strain for 1 min and then released to shrink back. The residual strain was calculated by measuring the gauge length after the shrink back:

$$\text{Residual strain }(\%) = \frac{L_r - L_0}{L_a - L_0} \times 100 \qquad (1)$$

where L_a is the gauge length in the stretched state, L_0 is that of the unstretched state, and L_r is after shrink back.

To estimate the orientation angle fluctuation of the crystalline axis in a spherulite, the angular distribution of scattering light at an azimuthal angle $\mu = 45°$ was measured by using a highly sensitive CCD (charge-couple device) camera with 576 × 382 pixels in a sensor of 13.3 × 8.8 mm^2 (Princeton Instruments, Inc.). The details of this apparatus have been reported elsewhere[4].

RESULTS AND DISCUSSION

Figure 1 shows WAXD profiles of the polysulfide. One sees broad amorphous halos for the quenched sample (broken line). After annealing at 20°C ($< T_m = 100°\mathrm{C}$) for 1 day, three sharp diffraction peaks appeared, as shown by the solid line, suggesting that crystallization had taken place.

The elastomeric character could be demonstrated by the results of the uniaxial cyclic tensile test, as shown in *Figure 2*. Here, the sample was stretched up to 100% elongation and released to shrink back. On the second cycle, the sample was stretched immediately after the first cycle. In the first cycle, the stress–strain curve of the polysulfide is closer to that of a plastic than that of a rubber: a yield point at about 25% elongation and a large residual strain (25%). For the second cycle the hysteresis loop becomes much smaller and the residual strain also decreases. During the third and the subsequent cycles (we performed seven cycles), the behaviour was typical of a rubber with a small hysteresis loop and residual strain ($\leq$10%). The results clearly show that after the second cycle the strain recovery property is much improved. The results may suggest that the higher-order structure, e.g. crystalline lamellae, is broken to yield smaller crystallites after the first cycle and the fragmented crystallites could play the role of junction points for rubbery chains in the following cycles. In contrast, LDPE shows a large residual strain for each cycle, as seen in *Figure 3*. The large residual strain of LDPE should be caused by the plastic deformation.

When the film specimen was released from the clamps after the shrink back of the stress–strain measurement, the specimen shrank further during resting at room temperature. The typical shrinkage behaviour is shown in *Figure 4*. Residual strain after resting for 1500 min is plotted as a function of the applied strain in *Figure 5*. One can see a big difference in strain recovery behaviour between the polysulfide and LDPE. In the case of polysulfide, the residual strain is less than 10% for the entire experimental range, 25–400%

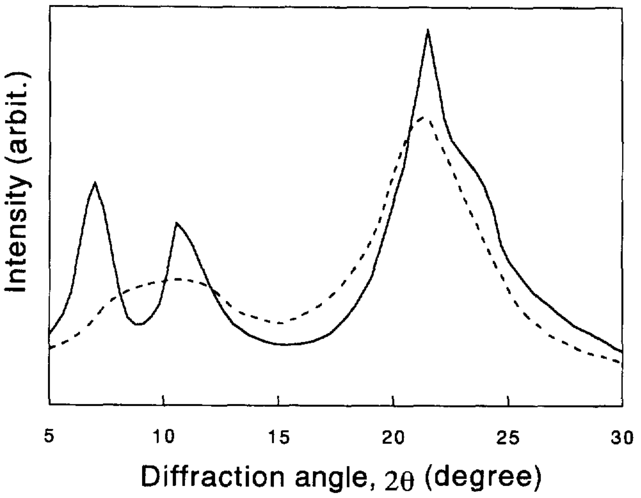

Figure 1 WAXD profiles for a quenched polysulfide (quenched in iced-water, broken line) and for an annealed one (annealed at 20°C for 1 day, solid line)

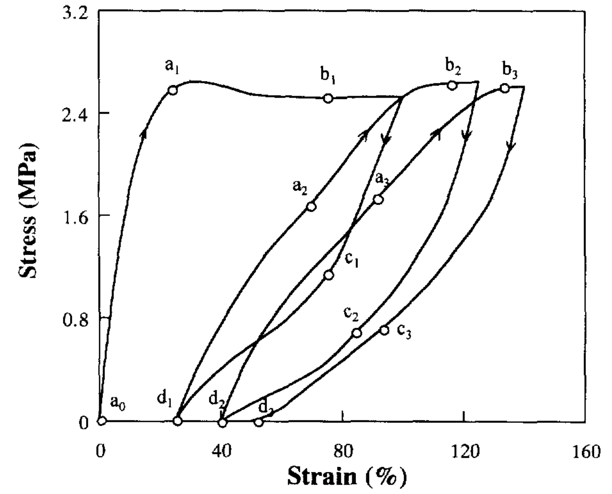

Figure 2 The cyclic stress–strain behaviour of polysulfide. Symbols (a_i,b_i,...) indicate the deformed states at which H_v light-scattering patterns were observed

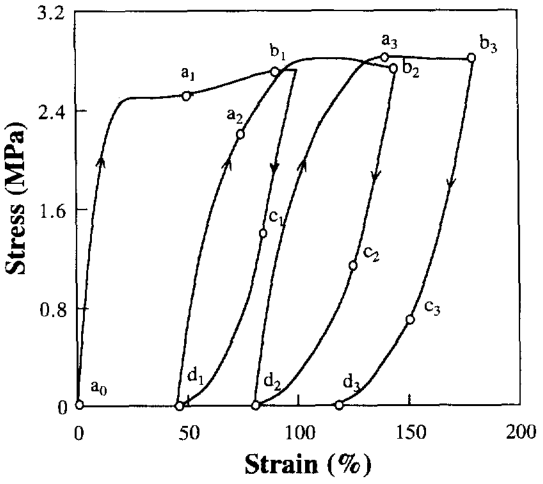

Figure 3 The cyclic stress–strain behaviour of LDPE. Symbols (a_i,b_i,...) indicate the deformed states at which H_v light-scattering patterns were observed

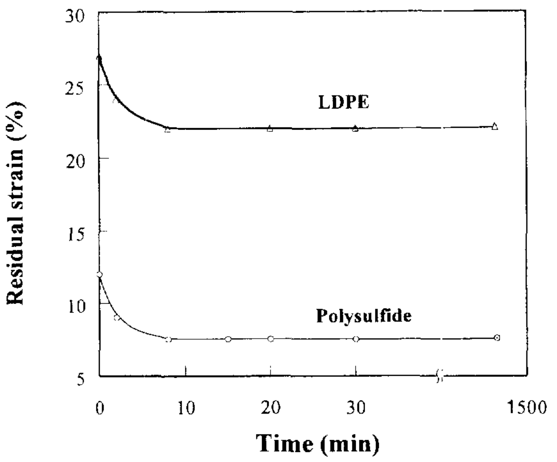

Figure 4 Residual strain as a function of resting time after stress–strain measurement (up to 100% elongation) and releasing from clamps

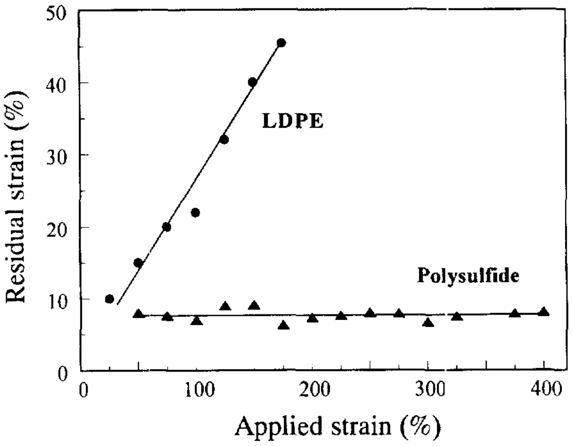

Figure 5 Residual strain after resting 1500 min *versus* applied strain

elongation*, while the residual strain of LDPE is larger and it increases with increasing applied strain.

The H_v light-scattering pattern from the polysulfide was the four-leaf clover type (see *Figure 6*). This suggests that the spherulite formation is as in the case of LDPE. *Figure 6* represents the change in the H_v light-scattering pattern with bulk deformation for the polysulfide. The stretching direction is vertical. In the undeformed state, the clover leaves are at azimuthal angles of ± 45° (*Figure 6a$_0$*). The azimuthal angles increase with bulk deformation to yield an elliptical clover pattern (*Figure 6a$_1$,b$_2$*). According to the model proposed by Van Aarten and Steins[5] or by Samuels[3], the change in the H_v pattern indicates the deformation of the spherulite to an ellipsoidal shape with the long axis parallel to the stretched direction. One can also see in *Figure 6* that after releasing the sample, the H_v pattern can heal back to a nearly original one (*Figure 6d$_1$*). A more complete recovery was observed after releasing and resting for several minutes at room temperature. The elastic recovery of the H_v pattern was also observed for the second and subsequent cycles (*Figure 6d$_2$,d$_3$*). In contrast, the elastic recovery of the pattern was not observed in LDPE, as shown in *Figure 7*.

To discuss the pattern recovery in more detail, we analysed the angular dependence of scattering intensity along the azimuthal angle $\mu = 45°$. As is expected from the H_v patterns of unstretched samples in *Figures 6 and 7*, the one-dimensional H_v scattering profile at $\mu = 45°$ shows a peak. The peak angle θ_m is related to the average spherulite radius R_{H_v}[6]:

$$4.1 = 4\pi(R_{H_v}/\lambda)\sin(\theta_m/2) \qquad (2)$$

where λ is the wavelength of light in the medium, 632.8 nm. According to Stein and Chu[7], the relative intensity of scattered light at small angles ($\theta < \theta_m$) is enhanced by the disordering of the orientation fluctuation in the tangential direction, whereas at wide angles ($\theta > \theta_m$) it is by disordering in the radial direction. Then, one could discuss the degree of disordering from the relative intensity of scattered light, but it should be given as a function of the reduced

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* As mentioned in the experimental section, the residual strain was estimated by releasing after holding the stretched specimen for 1 min at the applied strain. When the holding time is zero, the test becomes very mild and yields smaller residual strain. For example, when the polysulfide was stretched to 300% elongation and released immediately, the residual strain was 3%

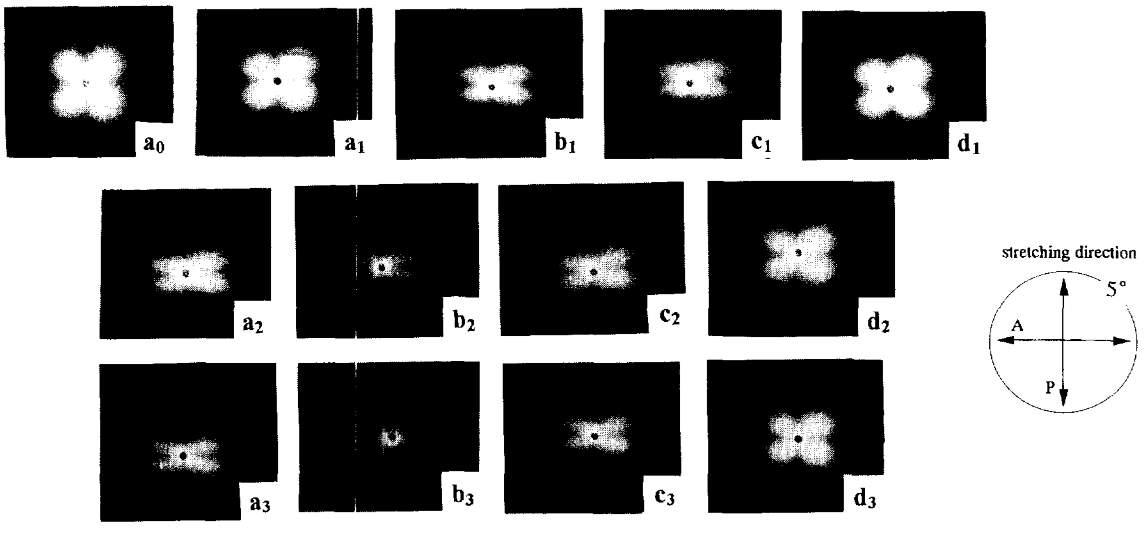

Figure 6 The variation of H_v light-scattering pattern with bulk elongation during uniaxial cyclic stress–strain test of polysulfide (symbols: see *Figure 2*)

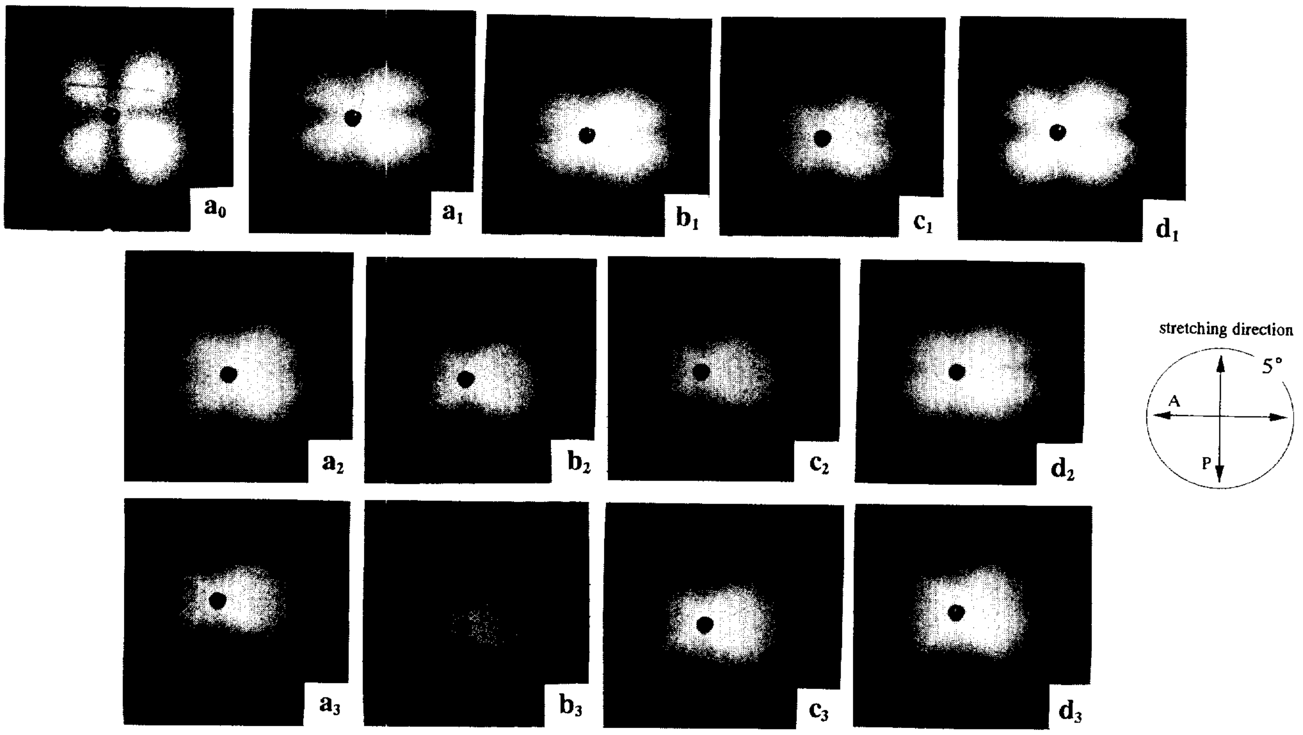

Figure 7 The variation of H_v light-scattering pattern with bulk elongation during uniaxial cyclic stress–strain test of LDPE (symbols: see *Figure 3*)

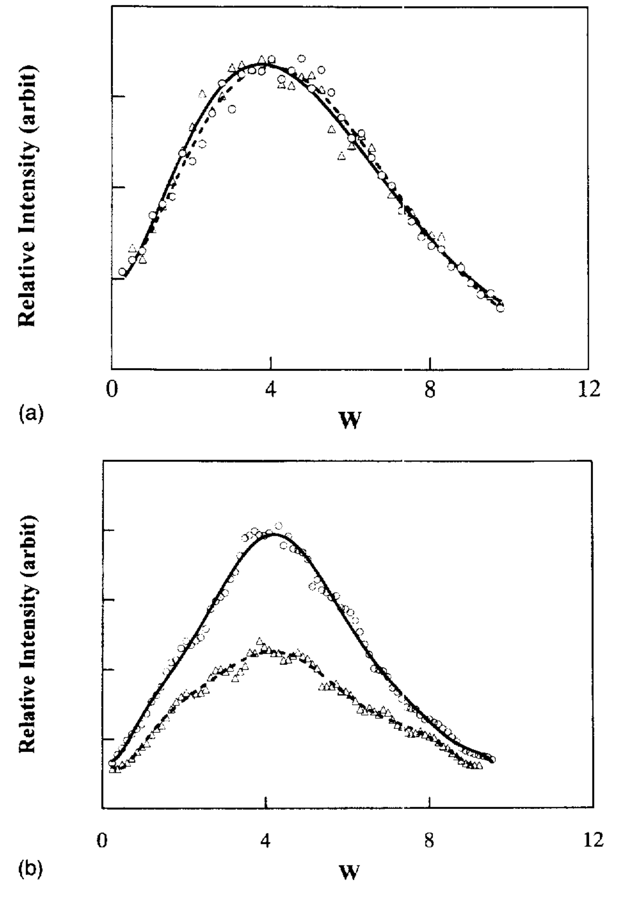

Figure 8 The reduced light-scattering profiles, (○) before stretching and (△) after recovery from 100% elongation: (a) polysulfide, (b) LDPE

Table 1 The disorder parameters in the radial direction before and after stretching to 100% elongation

Sample	Unstretched	Recovered
LDPE	0.31	0.44
Polysulfide	0.45	0.45

scattering angle w

$$w = \left(\frac{2\pi}{\lambda}\right)\bar{R}_{H_v}\sin\theta \qquad (3)$$

where θ is the scattering angle. The reduced scattering profiles in the radial direction are shown for the polysulfide and LDPE in *Figure 8a* and *Figure 8b* respectively. To discuss quantitatively the degree of disordering, it is convenient to employ the disorder parameter ζ, defined by[8]

$$\zeta = I_{H_v}(w=8)/I_{H_v}(w=4) \qquad (4)$$

The ζ values calculated from the reduced scattering profiles in *Figure 8* are shown in *Table 1*.

In *Table 1*, one sees that the disorder parameter of LDPE increases with the bulk deformation, suggesting that the radial orientation correlation becomes worse. This means that the plastic deformation of crystallites inside the spherulite takes place and it hardly heals back. This is a well-known behaviour for crystalline polymers. However, the situation is quite different for the polysulfide. The value of ζ for the recovered polysulfide is almost the same as the undeformed one. This suggests a very unique behaviour of polysulfide.

CONCLUSION

The light scattering studies show that the spherulite of polysulfide is highly elastic and it will provide a key mechanism of the nice bulk strain recovery. In the other words, the spherulite itself has a unique internal structure, probably caused by the strong intermolecular interaction of *s*-triazine rings in the crystalline region, which is free from the local plastic deformation.

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