

the standards were checked against standardized thermometers (National Physical Laboratory).

Growth rates  $G_H$  (for crystals) and  $G_S$  (for spherulites) are plotted against crystallization temperature  $T_c$  in Figure 2. The curves so obtained exhibit major cusps at 51.1°C (3000H) and 51.6°C (3000E), i.e. at temperatures some 7.7°C below the dilatometric melting points of the samples. A second minor cusp is apparent in  $G(T)$  of sample 3000E at 50.6°C. Following Kovacs and Gonthier<sup>1</sup> we denote these temperatures  $T_c$  (major) and  $T_{1f}$  (minor);  $T_c$  being associated with the transition from extended-chain to once-folded-chain lamella crystallization, and  $T_{1f}$  with the transition from once-folded-chain to twice-folded-chain lamella crystallization.

For both samples crystals grown below  $T_c$  were hexagonal with  $H/W = 1.15 \pm 0.15$  (Figures 1a and 1b); those grown at or just above  $T_c$  were roughly circular (Figure 1c); and those grown much above  $T_c$  were hexagonal with  $H/W = 0.93 \pm 0.05$  (Figure 1d). Crystals grown at or below  $T_c$  had a finely decorated inner region and a coarsely decorated surround (Figures 1a and 1c). Crystals grown above  $T_c$  were essentially undecorated (Figure

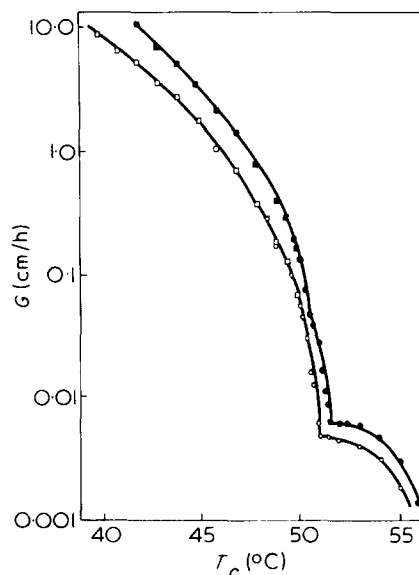


Figure 2 Semi-logarithmic plot of growth rate versus crystallization temperature ( $T_c$ ) for poly(ethylene oxide) fractions 3000H ( $\circ$ ,  $\square$ ) and 3000E ( $\bullet$ ,  $\blacksquare$ ).  $\circ$ ,  $\bullet$  Crystal growth rates ( $G_H$ ) and  $\square$ ,  $\blacksquare$ , spherulite growth rates ( $G_S$ ).

1d): however at  $T_c > 56^\circ\text{C}$  crystals were entirely coarsely decorated. No change in shape or decoration of the crystals of sample 3000E could be detected at or about  $T_{1f}$ . All these morphological observations agree with those reported by Kovacs and Gonthier<sup>1</sup> for

samples of molecular weight 3000 or lower (e.g. see ref 1, Figures 6, 10, 19, 29). They have assigned the distinct inner region to crystal thickened by a rapid chain unfolding process. The coarse decoration at high  $T_c$  is thought to be due to chain fractionation during slow crystallization.

These results serve to show that the differences in crystallization behaviour between hydroxy- and ethoxy-ended poly(ethylene oxide) fractions are slight: the only significant difference being an increased propensity for the formation of twice-folded-chain lamella crystals of 3000E compared with 3000H. This close correspondence of behaviour seems to rule out any model of the growth and thickening processes which assigns a specific role to hydrogen bonding interactions involving the hydroxy-end-group.

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## Infra-red spectra of the copolymer( $\beta$ -benzyl D- and L-aspartate) obtained by the polymerization of the *N*-carboxylic anhydride

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### INTRODUCTION

Poly( $\alpha$ -amino-acid) obtained by the polymerization of  $\alpha$ -amino-acid *N*-carboxylic anhydride (NCA) has played an important role as a model for protein. Little attention has been paid to the initiator used for the polymerization. However, the sequential distribution of D- and L-residues in the copolymer(D- and L-amino-acid) from NCA may vary depending upon the nature of the initiator. For example, poly( $\gamma$ -benzyl-DL-glutamate) obtained from racemic NCA with butylamine as initiator has an infra-red spectrum similar to those of sequential polymers such as  $(DL)_n$  or  $(DLLL)_n$ , while the spectrum of the polymer obtained from

racemic NCA with sodium methoxide substantially retains the characteristics of the L-polymers, indicating higher stereoselectivity in the sodium methoxide initiated system<sup>1</sup>.

On the other hand, in the copolymerization of D- and L-NCA of alanine<sup>2</sup> and of  $\gamma$ -benzyl glutamate<sup>3,4</sup> with primary amine type initiator,  $\alpha$ -helical conformation of the growing polymer chain has been considered responsible for the selection of one of the NCA antipodes. In contrast, no selection of the antipode of NCA was observed in the copolymerization of D- and L-NCA of valine initiated by primary amine, where the polymer formed assumes  $\beta$ -conformation<sup>5,6</sup>. However, the effect

of the secondary conformation of the polymer being formed in the NCA polymerization initiated by sodium methoxide has not been clearly elucidated.

Since poly( $\beta$ -benzyl-L-aspartate) is known to assume a left handed  $\alpha$ -helical conformation which is much less stable than the right handed  $\alpha$ -helical conformation of poly( $\gamma$ -benzyl-L-glutamate)<sup>7</sup>, it is of interest to study the copolymerization of D- and L-NCA of  $\beta$ -benzyl aspartate with different initiators. In the present report the infra-red spectra of the copolymer( $\beta$ -benzyl D- and L-aspartate) obtained with butylamine and sodium methoxide as initiators are described.

### RESULTS AND DISCUSSION

The infra-red spectra of cast film from a chloroform solution of the copolymer

( $\beta$ -benzyl D- and L-aspartate), obtained with butylamine and sodium methoxide as initiators in a mixture of 1,2-dichloroethane and tetrahydrofuran (9:1 by volume) at 30°C with a NCA to initiator ratio of 50, with various L contents are shown in Figure 1. The peak at 451  $\text{cm}^{-1}$  is assigned to the benzyl group in the side chain<sup>8</sup>, being independent of the conformation, and may be used as a standard peak.

With the decrease in the L content of the polymer, a decrease in the strength of the peak at 610  $\text{cm}^{-1}$  was observed. Similarly, the peak at 563  $\text{cm}^{-1}$  also weakened and then disappeared. On the other hand, a new shoulder peak appeared at 480  $\text{cm}^{-1}$ . The peak at  $\sim 380 \text{ cm}^{-1}$  shifted to a higher wavenumber and became sharper. These spectral changes are considered to correspond to the decrease or the perturbation in the left-handed  $\alpha$ -helical structure of the L-polymer with the introduction of the less preferred D-antipode, since the infra-red spectra in this region have been proved to offer useful information about the local conformation, reflecting the stereoregularity, of the copolymer (D- and L- $\alpha$ -amino-acid)<sup>9-11</sup>.

The comparison of polymers obtained with these initiators indicates that the spectral changes with the decrease in the L content of the polymer are very similar between the butylamine initiated system and the sodium methoxide initiated system, the changes being slightly more remarkable in the former. In other words, not much difference is observed between the spectra of the polymers with the same L content obtained with these initiator systems. Therefore, there is considered no significant difference in the stereoselectivities between the polymerization of  $\beta$ -benzyl aspartate NCA by butylamine and by sodium methoxide.

The difference in the stereochemical behaviours between the polymerization of  $\beta$ -benzyl aspartate NCA and of  $\gamma$ -benzyl glutamate NCA is considered to be related to the difference in the stabilities between the  $\alpha$ -helical conformations of the polymers from the respective NCA. Although the sodium methoxide initiated system would essentially be more stereoselective than the butylamine initiated system, the higher stereoselectivity of the former is considered to become more explicit when the growing polymer chain may assume stable  $\alpha$ -helical conformation, as in the polymerization of  $\gamma$ -benzyl glutamate NCA. On the other

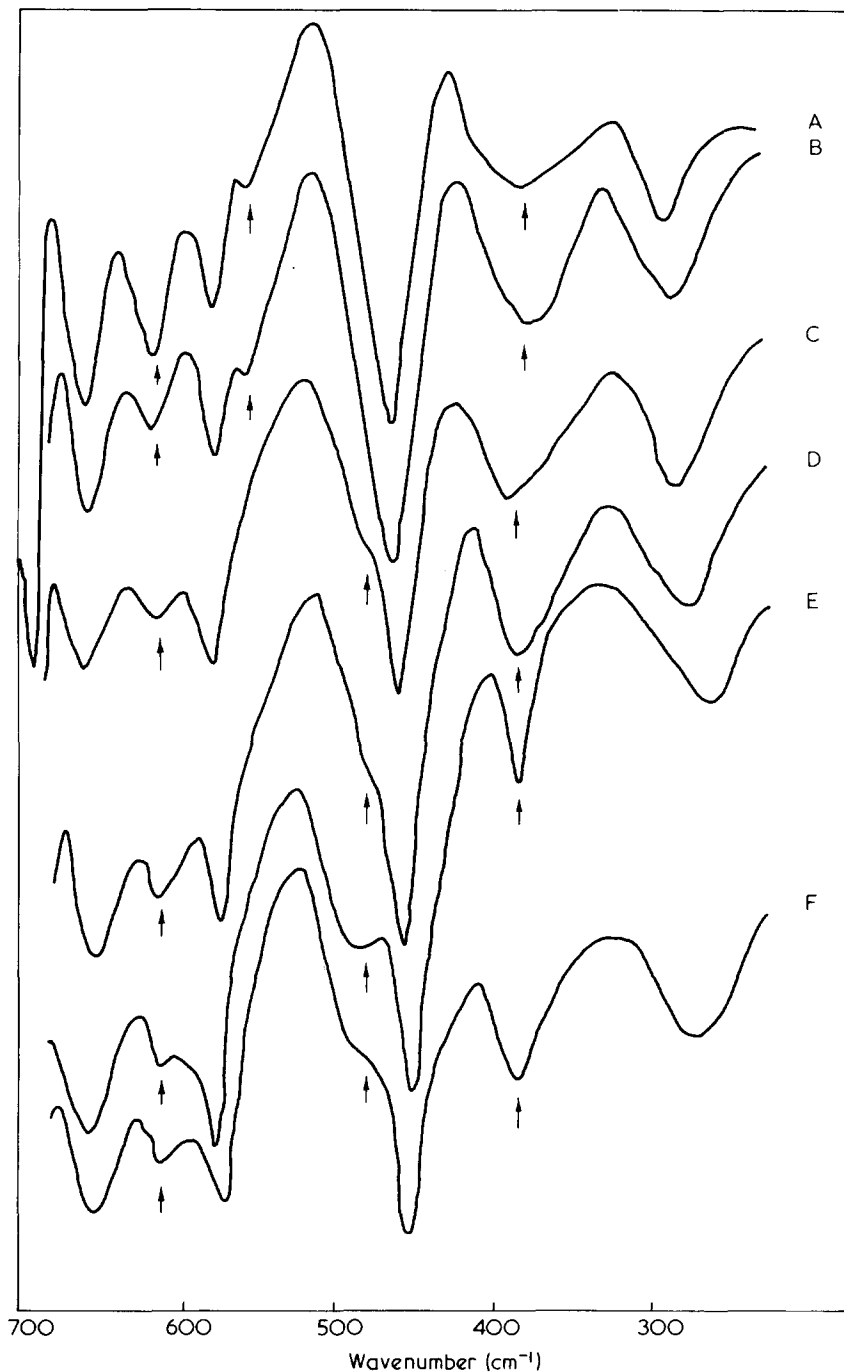


Figure 1 Infra-red spectra of copolymer( $\beta$ -benzyl D- and L-aspartate). Initiated by butylamine with L content: A, 100%; C, 75%; E, 50%. Initiated by sodium methoxide with L content: B, 100%; D, 75%; F, 50%

hand, very similar stereoselectivities for the two initiator systems in the polymerization of  $\beta$ -benzyl aspartate NCA would be related to the much lower stability of the  $\alpha$ -helical conformation of the growing polymer. The difference in the stabilities of the  $\alpha$ -helical conformation of the polymer as a whole is considered to reflect the difference in the stabilities of the local conformation around the growing terminal which plays the most important role in the selection of the NCA antipodes.

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## Letters

### Crystallization in poly(dimethyl siloxane) networks formed by $\gamma$ -irradiation

In this letter we report the observation of crystalline regions in poly(dimethyl siloxane) (PDMS) networks at temperatures up to 35°C, which is ~75°C above the melting point. Previous studies<sup>1,2</sup> of crosslinked PDMS have shown a high percentage of crystallinity in unstrained samples at -60°C and smaller percentages in strained samples at higher temperatures. The crystallization temperature increases with extension ratio<sup>3</sup> but the highest temperature at which crystallization has been observed previously is -15°C.

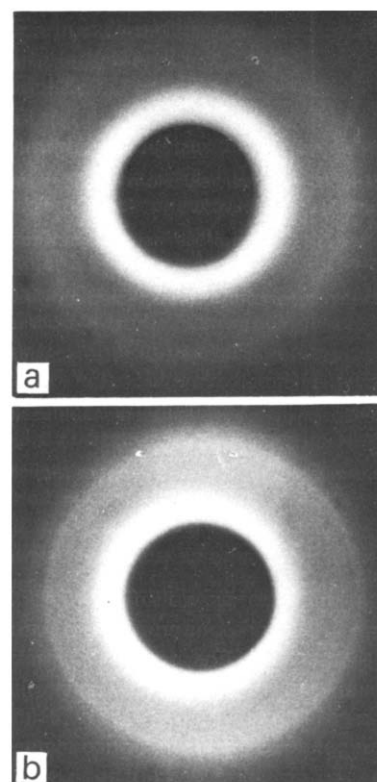
In the present work PDMS 5273-11-1 from ICI Ltd was used. The molecular weight was  $7.7 \times 10^4$  as determined by g.p.c. techniques. The crystal structure was studied using a Philips X-ray apparatus at 40 kV and 20 mA with  $\text{CuK}\alpha$  radiation and a cylindrical Debye-Scherrer camera. The networks were formed using  $^{60}\text{Co}$   $\gamma$ -irradiation at room temperature using the facility at Salford University. Doses ranged from 3.5 to 80 Mrad and the gel point was at approximately 2.4 Mrad. Before irradiation the samples were placed in glass cylinders under vacuum for approximately 20 h. The cylinders were then sealed while still under vacuum. This procedure was necessary for two reasons. First, PDMS will normally contain large amounts of dissolved gases. The presence of these gases during the radiation process is likely to cause further oxidation of the polymer resulting in possible degradation. To prevent such an occurrence as much of these gases as possible must be removed. Second, by putting the sample under vacuum much of the gas produced in the radiation process will be drawn out of the

polymer.

In spite of these precautions the crosslinked sample contained bubbles of varying size and shape, which were trapped in the network. The polymer near the surface of the bubbles took a regular polygonal form clearly visible to the naked eye. X-ray measurements demonstrated that these regions were partly crystalline. In *Figure 1* the X-ray diffraction patterns of (a) uncrosslinked and (b) crosslinked (70 Mrad dose) PDMS are shown. Two amorphous haloes are seen in each pattern corresponding to diffraction angles  $2\theta = 23.8^\circ$  and  $2\theta \approx 12^\circ$ . The sharp line, visible only in (b) indicates the presence of crystallinity. The diffraction angle is  $23.8^\circ$  and is in agreement with the results of Damaschun<sup>2</sup> corresponding to  $6_1$  helix of pitch 7.75 Å. The degree of crystallinity is estimated by density measurements to be 10% and showed no decrease at room temperature over a period of 4 months. However, heating at 45°C for 20 h caused complete disappearance and the crystalline regions did not reappear on cooling back to room temperature.

It seems probable that the crystallinity at these relatively high temperatures is associated with the strain fields around the gas bubbles. The bubbles arise from the rupture of Si-C and C-H bonds by the  $\gamma$  photons and consist of<sup>4</sup> 41%  $\text{H}_2$ , 47%  $\text{CH}_4$  and 12%  $\text{C}_2\text{H}_6$ . In the early stages of irradiation the bubbles are spherical, uniform in size and randomly distributed; at higher doses the shapes and sizes become irregular. The associated anisotropic strain fields are retained because the samples are networks<sup>5</sup>. It is well known that the crystallization is con-

trolled by the two factors nucleation and chain mobility. They are affected by the stress field<sup>6-9</sup> and the degree of crosslinking<sup>10,11</sup>. It has been observed in rubbers and other polymers that the effect of crosslinking at given strain is to lower the crystallization temperature<sup>3,10</sup>. In the present work the in-



*Figure 1* X-ray diffraction patterns in the silicone rubber PDMS at room temperature. (a) Uncrosslinked rubber; (b) crosslinked and partly crystalline after irradiation ~70 Mrad