2 Tsuruta, T., Inoue, S. and Matsuura, K. *Biopolymers* 1967, **5**, 313
3 Inoue, S., Matsuura, K. and Tsuruta, T. *J. Polym. Sci. (C)* 1967, **23**, 721
4 Akaike, T., Makino, T., Inoue, S. and Tsuruta, T. *Biopolymers* 1974, **13**, 129
5 Akaike, T., Aogaki, Y. and Inoue, S. *Biopolymers* 1975, **14**, 2577
6 Akaike, T., Inoue, S. and Itoh, K. *Biopolymers* 1976, in press
7 Fasman, G. D. in 'Poly-α-amino Acids', (Ed G. D. Fasman), Marcel Dekker, New York, 1967, p 499
8 Miyazawa, T. in 'Poly-α-amino Acids', (Ed G. D. Fasman), Marcel Dekker, New York, 1967, p 69
9 Itoh, K., Oya, M. and Shimanouchi, T. *Biopolymers* 1972, **11**, 1137
10 Itoh, K. and Katabuchi, H. *Biopolymers* 1972, **11**, 1593
11 Itoh, K., Ozaki, T., Nagayama, K., Wada, A. and Tsuboi, M. *Macromolecules* 1973, **6**, 654

Letters

Crystallization in poly(dimethyl siloxane) networks formed by γ-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[1,2] 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[3] 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 7.7×10^4 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 CuKα radiation and a cylindrical Debye–Scherrer camera. The networks were formed using ^{60}Co γ-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 $2\theta = 23.8°$ and $2\theta \simeq 12°$. The sharp line, visible only in (b) indicates the presence of crystallinity. The diffraction angle is 23.8° and is in agreement with the results of Damaschun[2] 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 γ photons and consist of[4] 41% H_2, 47% CH_4 and 12% C_2H_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[5]. It is well known that the crystallization is controlled by the two factors nucleation and chain mobility. They are affected by the stress field[6–9] and the degree of crosslinking[10,11]. It has been observed in rubbers and other polymers that the effect of crosslinking at given strain is to lower the crystallization temperature[3,10]. In the present work the in-

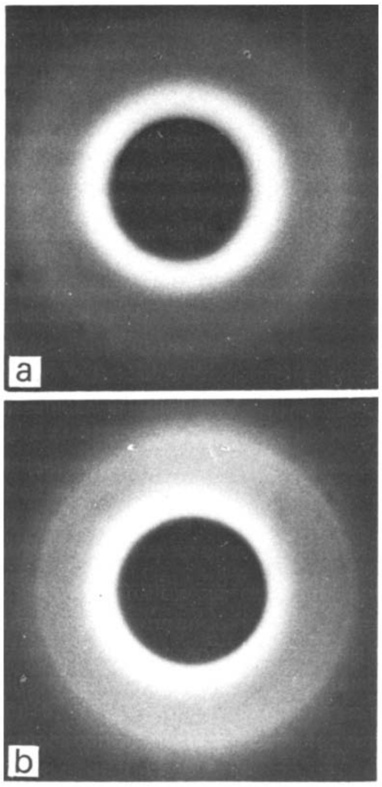

Figure 1 X-ray diffraction patterns in the silicone rubber PDMS at room temperature. (a) Uncrosslinked rubber; (b) crosslinked and partly crystalline after irradiation ~70 Mrad

crease in crosslink density is presumably accompanied by increases in internal strain sufficient to increase the crystallization temperature. Another possible effect may arise from the fact that the formation of crosslinks inhibits the extreme flexibility of the PDMS chains and thus may help to promote the formation of nuclei. At high crosslink densities the chain segments are sufficiently constrained to prevent any further crystallization. This occurs above ~70 Mrad radiation dose where the chain length between links is 35 monomer units. The non-reappearance of crystallinity at room temperature following heating to 45°C is believed to be due to relaxation of the strain field.

The free energy of formation of a crystalline cluster, ΔF, is given by[12]:

$$\Delta F = \sum_{i} n_i \alpha_i \sigma_i + \frac{n}{N_\alpha}(\mu_c - \mu_a) \quad (1)$$

where the sum is over all the faces of the cluster. Referring to faces of type i, n_i is the number of molecules or molecular segments, α_i is the molecular cross-sectional area and σ_i is the interfacial tension. N_α is Avogrado's number, n is the total number of molecules in the cluster and μ_c and μ_a the chemical potentials in the crystalline and the amorphous state, respectively. The crosslinking process and associated strain field is expected to affect both terms in equation (1), the major effect through the parameter μ_a and a lesser effect through σ_i.

Extension of this work to lower temperatures in samples with different degrees of crosslinking will help understanding of the detail of this high temperature crystallization.

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References

1 Ohlberg, S. M. *et al. J. Polym. Sci.* 1958, 27, 1
2 Damaschun, G. *Kolloid Z.* 1962, **180**, 65
3 Warrick, E. L. *J. Polym. Sci.* 1958, 27, 19
4 Charlesby, A. *Nature* 1954, 173, 679
5 Delides, C. G. *Diploma Report* University of Manchester (1976)
6 Treloar, L. R. G. 'The Physics of Rubber Elasticity', 3rd Edn, Oxford, 1973, p 16
7 Peterlin, A. *Polym. Eng. Sci.* 1976, **16**, 126
8 Yeh, G. S. Y. *Polym. Eng. Sci.* 1976, **16**, 138
9 Yeh, G. S. Y. *Polym. Eng. Sci.* 1976, **16**, 145
10 Slowikowska, I. and Daniewska, I. *J. Polym. Sci. Polym. Symp.* 1975, **53**, 187
11 Andrianov, K. A. *et al. Dokl. Akad. Nauk SSSR Ser. Khim.* 1976, **226**, 85
12 Geil, P. H. 'Polymer single crystals', Interscience, New York, 1963, p 376

The nature of the initiation process in the photo-oxidation of polypropylene

Two quite distinct initiation processes have been suggested to explain the sensitivity of polyolefins to light[1,2]. Both invoke the presence of adventitious photosensitive impurities formed in the polymer either during manufacture or as a consequence of oxidation during high temperature fabrication processes. The first class of sensitizing impurities encompasses the macromolecular peroxides which readily photolyse to give initiating free radicals[1,3–6]. The second class comprises the in-chain ketones[4,7–10] which are the major derived products formed by thermolysis or photolysis of hydroperoxides[1].

It has previously been shown[3] that polypropylene is markedly sensitized to photo-oxidation by the thermal processing sequence involved in its conversion to fabricated products. The absence of significant carbonyl formation during the early stages of this thermal oxidative treatment suggests that hydroperoxides rather than carbonyl compounds are responsible for the photoactivation process. Similar conclusions have been reached in the study of other polyolefins[5,6]. Other work has indicated[11], however, that conjugated carbonyl compounds formed as a result of thermal oxidation could be involved in the initiation step during the early stages of photo-oxidation and a relationship has been found between fluorescence intensity due to conjugated carbonyl initially present in the polymer and u.v. lifetime of polypropylene samples[12].

There is little doubt that carbonyl compounds may participate in photoinitiation processes in extensively photo-oxidized polyolefins which contain a substantial concentration of ketonic carbonyl[13]. However, the evidence is much less unequivocal during the early stages of photo-oxidation and it has been shown that in low density polyethylene allylic hydroperoxides are the primary photoinitiators[14].

An analogous study of polypropylene has shown a similar relationship between the rate of photo-oxidation and hydroperoxide concentration. *Figure 1* shows that the latter (measured by a chemical method), grows

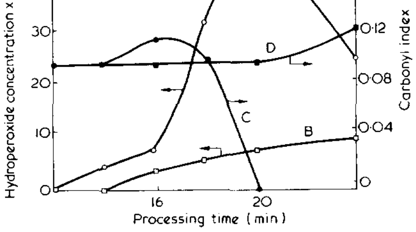

Figure 1 Effect of processing of polypropylene at 180°C in open mixer (○, ●) and closed mixer (□, ■) on peroxide concentration and conjugated carbonyl index (1685 cm^{-1})