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Crystalline morphology of poly(dimethylsiloxane)

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Abstract

The crystalline morphology of poly(dimethylsiloxane) was studied using a scanning electron microscope equipped with a cold stage. Samples of two different molecular weights were used. In both cases, spherulitic morphology is seen, from −70 °C, with spherulites of about 100 μ in size. Small single crystals of about a micron in size are also seen, and these are attributed to the presence of cyclics. © 2002 Published by Elsevier Science Ltd.

Keywords: Poly(dimethylsiloxane); Crystallization; Morphology

The crystalline structure of poly(dimethylsiloxane) (PDMS) has been studied previously using X-ray diffraction, below its reported melting temperature of 233–236 K. From oriented samples of PDMS filled with silica, Damaschun [1] proposed a two-fold helical conformation with six monomers per turn and a repeat distance of 8.3 Å, in a monoclinic unit cell. A recent study of Albouy [2] suggested a four-fold helical conformation, with four monomers per turn and a repeat distance of 12 Å, in a tetragonal unit cell. Molecular mechanics and molecular dynamics studies have been reported by Grigoras et al. [3] and by Qian et al. [4]. While these are related to the bulk crystallization, in 1980, Sundararajan et al. [5] reported the low temperature crystallization of PDMS from solution in *n*-heptane and toluene, using X-ray diffraction and NMR line broadening experiments. Although the *d*-spacings from the solution crystallized PDMS were similar to those reported by Damaschun, the chain conformation could not be deduced due to the lack of orientation of the crystallized sample. In a concurrent study using X-ray diffraction, Croucher et al. [6] concluded that the lower critical flocculation temperature of dispersions of PMMA particles in *n*-alkanes, stabilized by PDMS, was influenced by the crystallization of the adsorbed PDMS chains. More detailed studies of both the crystallization from solution and that of the adsorbed chains were later published by Feio et al. [7] and Ebengou and Cohen-Addad [8].

A systematic investigation of the heat of fusion for filled and unfilled PDMS was described by Aranguren [9]. Strain-induced crystallization in interpenetrating networks of epoxy resin and PDMS was reported by Sung and Wu [10]. Li and Huang [11] studied the crystallizability of PDMS segment in a series of poly(butadiene-*b*-dimethylsiloxane) block copolymers. With varying segment lengths, the crystallizability was influenced by the morphology of the phase-separated domains.

Although techniques such as X-ray diffraction, DSC and NMR have been used to study the crystallization of PDMS, it appears that microscopy studies of the morphology of crystalline PDMS, by itself, has not been reported so far.

In this paper, we describe the results of a scanning electron microscopy (SEM) study of the low temperature crystalline morphology of PDMS.

1. Experimental

Poly(dimethylsiloxane) samples of two molecular weights (M_w: 38,900, M_n: 13,700 (PDMS-1) and M_w: 182,000 and M_n: 106,000 (PDMS-2)) were purchased from Aldrich Chemical Company. These were used as received, without any added filler or cross-linking.

Scanning electron micrographs were recorded using a JEOL JSM-6400 microscope (The Facility for Cryo Scanning Electron Microscopy and Microanalysis, Carleton University) with an Oxford CT1500C cryotransfer system and cold stage. Since this is not an environmental SEM (ESEM), the samples had to be cooled to some extent before being introduced into the microscope. Otherwise, bubbling of the sample occurred with the initiation of the vacuum. Hence, the samples were first cooled with dry ice to about

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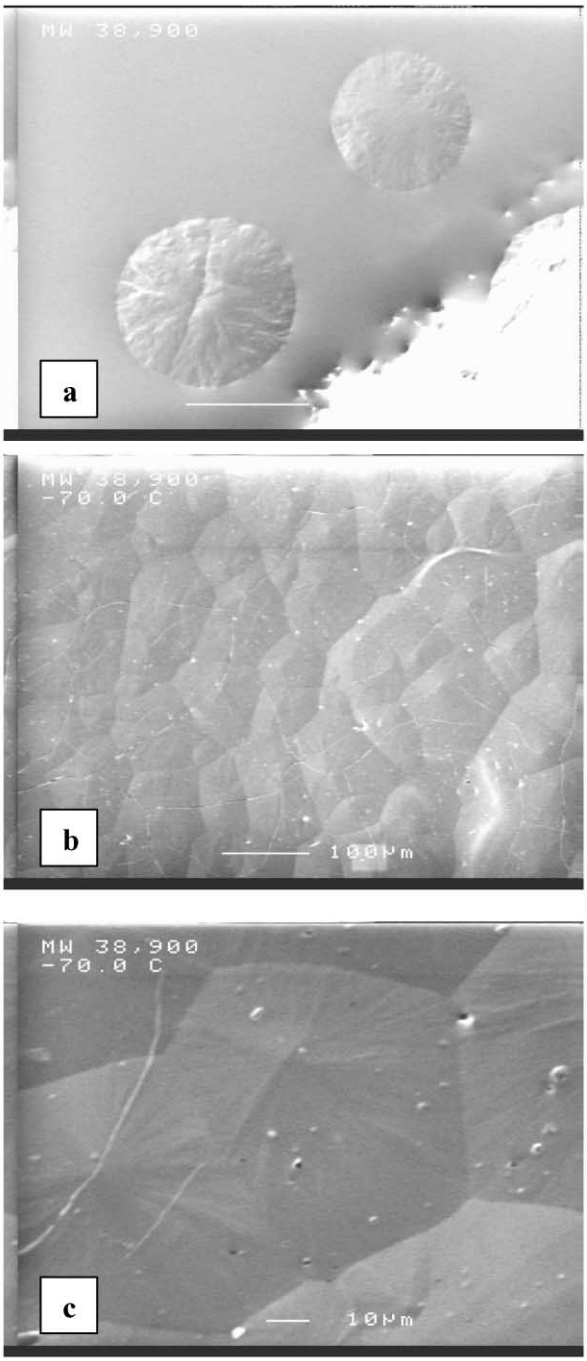

Fig. 1. SEM micrographs of PDMS-1: (a) at −70 °C at initial stage; (b) lower magnification, at −70 °C; (c) higher magnification at −70 °C.

−40 °C, transferred to the microscope, and then gradually cooled to −70 °C or below.

2. Results and discussion

Figs. 1 and 2 show the micrographs of the crystalline PDMS-1 and PDMS-2, respectively, at different temperatures and magnifications. In both cases, spherulites of nearly

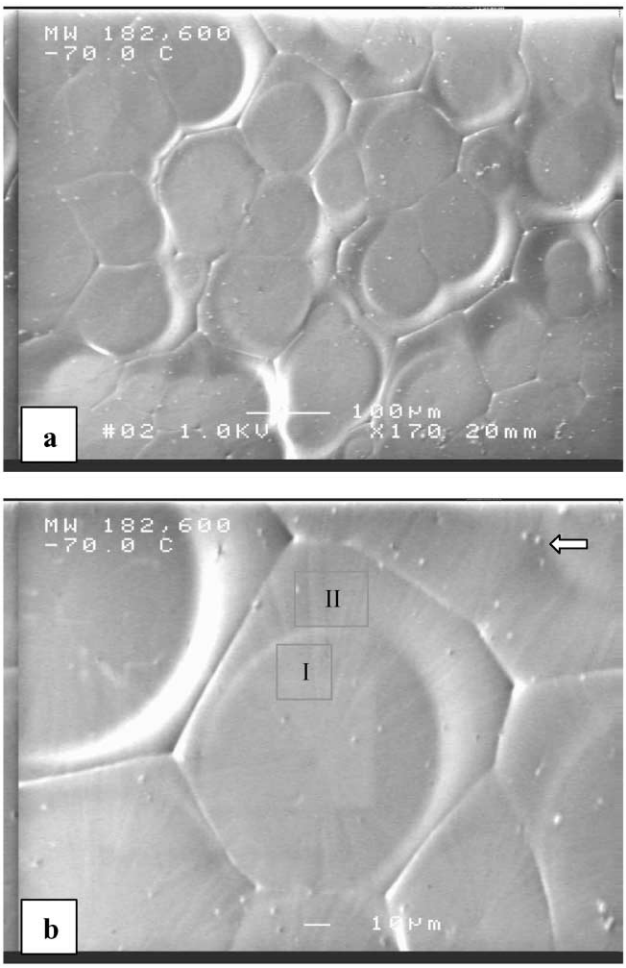

Fig. 2. SEM micrographs of PDMS-2: (a) at −70 °C; (b) higher magnification at −70 °C. The arrow shows the small crystals due to the cyclics.

100 μ in size are seen. Again, since this is not an ESEM, we have not studied the growth rate of the spherulites. However, Fig. 1(a) shows the individual spherulite as the crystallization progresses. Fig. 1(b) shows the profuse growth of the spherulites, with extensive cracks running along the sample. Fig. 1(c) shows impinging spherulites with cracks in the intra-spherulitic regions. The behavior of the higher molecular weight sample seems somewhat different. Although the size of the spherulites is about the same as for the lower molecular weight sample, extensive voids are seen in the inter-spherulitic domains. Further, it appears that two different growth patterns have occurred, as indicated by regions I and II in Fig. 2(b), although the polydispersity of this sample is not high. The reason for this morphology needs further study. However, comparing Figs. 1(a) and 2(b), it is likely that the region I in the latter corresponds to the initial growth, at about −40 °C.

Another feature observed in these micrographs is the presence of small crystals, about 1 μ in size (as indicated by the arrow in Fig. 2(b)). Hunt and George [12] analyzed the siloxane residues from PDMS elastomers by MALDI-TOF mass spectrometry. These were samples of silicone

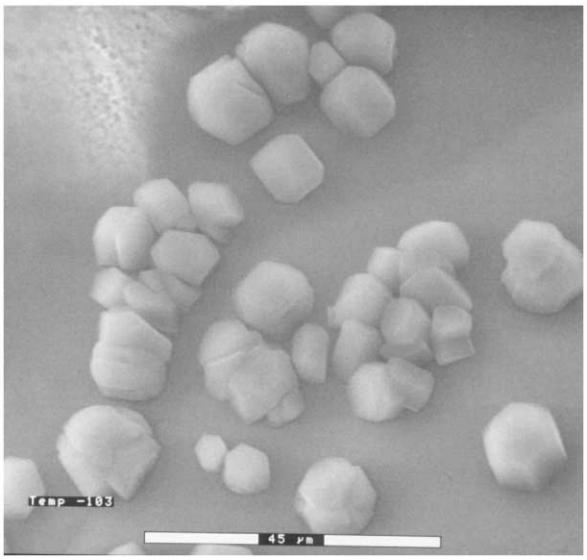

Fig. 3. SEM micrograph of a silicone wax lubricant at −103 °C.

elastomers exposed to the environment for extended periods, causing migration of low molecular weight siloxanes from the bulk to the surface. They unambiguously determined these low molecular weight materials to be predominantly cyclic siloxanes, ranging from 13 to 47 repeat units.

In view of the results reported by Hunt and George, the small crystals seen in Figs. 1 and 2 are tentatively assigned to be due to the cyclics. This is further corroborated by the micrograph shown in Fig. 3, recorded at about −100 °C, for a silicone wax commonly used for ordinary laboratory vacuum pump greasing. Single crystals of about 5–10 μ are seen in this case (the characteristics of this sample were not analyzed).

The intent of this communication is to show that PDMS samples crystallize at about −70 °C with a spherulitic morphology, with these spherulites about 100 μ in size, and that the small crystals of ~1 μ are likely to be from the crystallization of the cyclic species. Further studies on the rate of growth, the role of the crystallization temperature etc. using an ESEM will be reported in due course.

Acknowledgements

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