Oriented overgrowth crystallization on needle shaped polyoxymethylene single crystals from molten polymers

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Needle shaped single crystals of polyoxymethylene were found to provide a unique substrate for the crystallization of polymers from the molten state, as the formation of 'shish-kebabs' had been observed from solutions. When needle shaped crystals were embedded in the melt of the same polymer, polyoxymethylene, or a copolymer, the crystallization started from the surface and the growth proceeded in the form of a cylindrite, comprising a pile of chain-folded lamellar crystallites. Since the epitaxy required much smaller under cooling, transformation by this mechanism was distinct and predominated over the normal, spherulite formation. The same kind of effect was also observed for polyethylene. The feature was elucidated by means of microscopic observations, differential scanning calorimetry, small-angle X-ray scattering etc. and the mechanism, discussed.

INTRODUCTION

The crystallization behaviour of polymers is strongly influenced by the type of nucleation and peculiar morphologies frequently result from various heterogeneities in systems. So-called stress induced crystallization forms a large category and has been extensively studied because of its academic and industrial importance. Besides the oriented structures commonly involved in fibre and film makings, interest arose in the 'shish-kebab' structures created by stirring polymer solutions[1]. Another category of heterogeneous nucleation is related to the deposit of molecules on existing surfaces. The addition of foreign particles which act as nucleating agents is a popular means to modify crystallization processes, but recent attention has been focused rather on what happens on crystalline substrates, often called epitaxy. Many examples are available in a concise monograph[2].

The over-crystallization upon needle shaped polyoxymethylene crystals, reported previously from this laboratory[3], provides a unique example in that polymers (polyoxymethylene and polyethylene) from solutions form shish-kebab structures comprising a pile of lamellar crystallites around the slender core. It is remarkable that the substrate material is a polymer single crystal bearing a well defined extended chain structure[4–7]. The effect on the crystallization from melts has been of interest and, in fact, a cylindrical growth habit centred on the needles has been found instead of the normal, spherulitic growth. In this paper, the general feature of this crystallization is presented with the results of microscopic observations (optical and electron scanning) and preliminary d.s.c. (differential scanning calorimetry) runs in order to discuss the mechanism. The kinetic features of this over-crystallization, with reference to the ordinary crystallization is described in a separate article[8].

EXPERIMENTAL

Samples

Needle shaped polyoxymethylene crystals, 30 to 100 Å long, were prepared from a cyclohexane solution of trioxane with BF_3/H_2O catalysis as has been described elsewhere[5–7]. For some experiments, the crystals, obtained in the form of a radiating assembly, were isolated by the BF_3 etching technique[6].

For over-crystallization, a commercial poly(oxymethylene–diacetate) (Delrin 500X, $\bar{M}_v = 1.57 \times 10^5$, from Du Pont de Nemours Co.) was used. Other polymers tested include an acetal copolymer (Duracon, $\bar{M}_v = 1.10 \times 10^5$, containing several percent ethylene oxide units, supplied by the courtesy of Dr H. Komazawa of Polyplastics Co.), a polyethylene (Sholex 6150, $\bar{M}_v = 5.2 \times 10^4$, from Showa–Denko Co.) and various others.

Microscopy

A polarizing microscope, Ortho-pol, of Ernst Leitz gmbh, equipped with a furnace attachment and a photographing mechanism was used. Embedding needle shaped crystals in matrix polymers was performed on the microscope hot-stage. When Delrin was used, for instance, the polymer was first melted above 468K and then, between 451 and 455K, needles were pressed into the molten polymer under a cover glass. Temperature control to ±0.5K was achieved either by a manual or an on–off control method.

The scanning electron microscope used was a SMU-CSI, of Japan Electron Optics Laboratory Co. As usual, the specimens were gold-plated prior to observation.

Differential scanning calorimetry (d.s.c.)

A model, DSC-II of Perkin–Elmer Co., was used. Needle/polymer mixtures were made, with isolated needles, by the procedure mentioned above. In the d.s.c. sample-pan the matrix polymer exclusively was remelted by heating at a temperature (e.g. 455K for Delrin) below the transition/degradation temperature[9] of the needle shaped crystals.

RESULTS AND DISCUSSION

The epitaxy effect of needle-like crystals was first examined

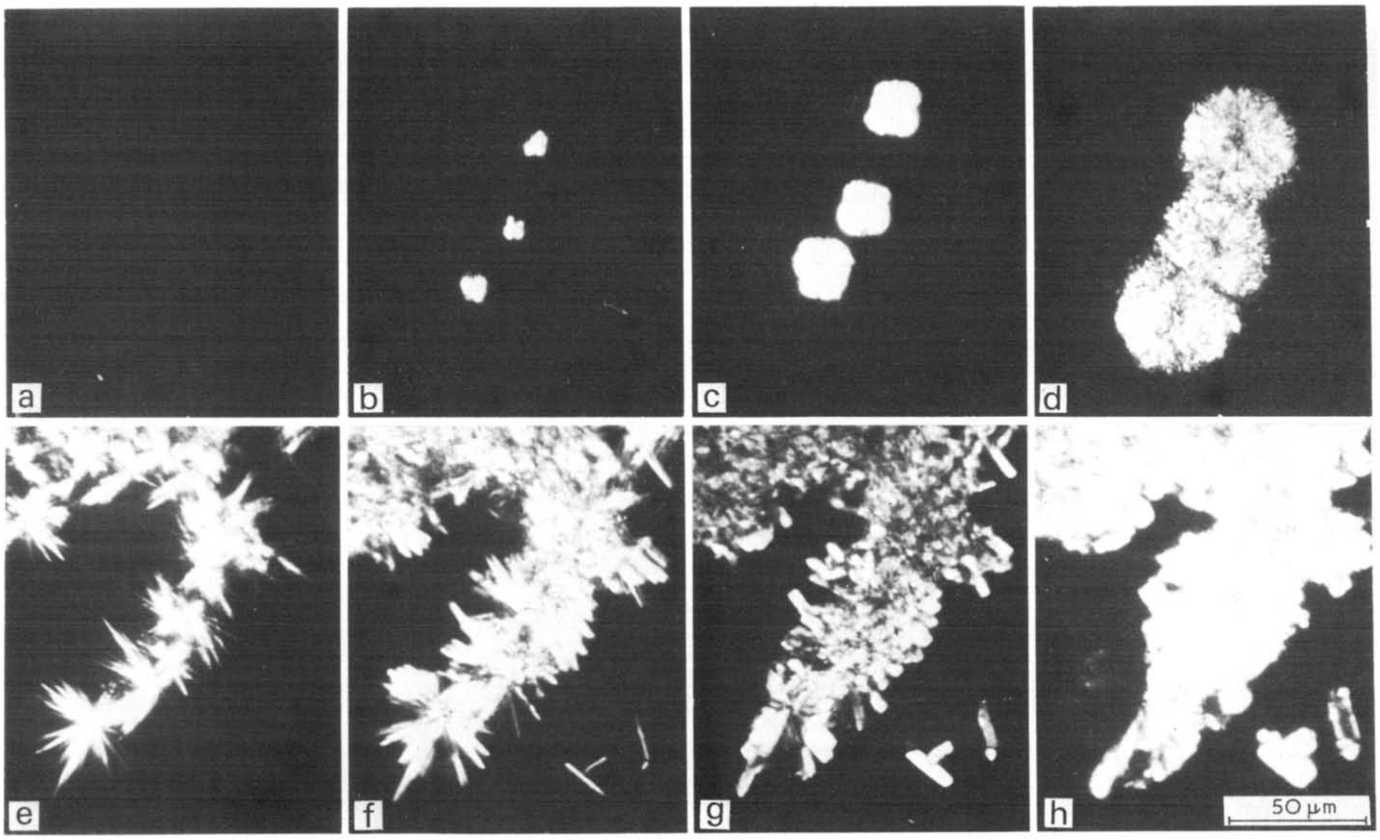

Figure 1 Polarized micrographs of Delrin crystallizing in isothermal conditions, (a)–(d) without needle shaped crystals at 432.5K and (e)–(h) with needles at 435K. (a) 0 min; (b) 5 min; (c) 8 min; (d) 12 min; (e) 0 min; (f) 2 min; (g) 4 min; (h) 6 min

for poly(oxymethylene–diacetate) (Delrin 500X) under the microscope on the transparent hot-stage. It was confirmed that, in the absence of needles, the polymer formed spherulites in a known fashion[10]. During the course of continuous cooling from the melt, nuclei appeared sporadically but almost simultaneously in a relatively narrow under cooling range (i.e. at around 430K). When the cooling was terminated at a higher temperature, some time lag or induction period was observed. In either case, the subsequent growth process seemed to be rather fast, suggesting that the initial step of the transformation was 'nucleation controlled'. *Figure 1a–1d* shows a set of micrographs taken at 432.5K.

In the presence of needles, the crystallization behaviour changed dramatically. (The single crystals persist in the molten polymer, due to their high melting temperature[5,9].) The phase change commenced from the surface of the crystals, at much lower under cooling, and developed radially in the apparent form of a cylinder. *Figure 1e–1h* shows the progress at 435K. Thus, isothermal crystallization became possible, with a practical time scale, at temperatures as high as 443K, whereas about 435K was the upper limit for spherulite formation. No induction period seemed to exist and the epitaxy was observed on every needle immediately after cooling.

In both isothermal and cooling conditions, the overgrowth was always predominant and no spherulite appeared until the last stage of the transformation, unless the holding temperature was very low (i.e. below ~431K) or the cooling was very fast. Heterogeneous and 'stress induced' crystallizations were mixed, if previous 'memory' had not been erazed, due to insufficient melting or because shear had been applied, whether accidentally or deliberately, in the molten state (see below). The radial growth rate of the cylindrite, measured under isothermal conditions, was linear with time[8].

For 'shish-kebabs' developed from solutions[3] (see *Figure 2a*), the over-grown phase has been considered to comprise chain-folded lamellae piled up around the core needle. The same type of structure is envizaged for the melt grown cylindrites. An examination of the birefringence by the use of a 530 nm test plate revealed the molecular orientation to be parallel with that in the needles. *Figure 2b* shows a scanning electron micrograph of Delrin crystallized after an aggregate of needle shaped crystals had been lightly pressed in the molten polymer. The characteristic structure, showing up parallel stripes normal to the direction of the length, is seen on the part of surface underneath which needle shaped crystals have existed not in depth. For over-crystallized specimens, a long spacing, ranging from 190 to 380 Å depending upon the crystallization condition was observed by small-angle X-ray scattering[8]. The melting temperature found by d.s.c. was between 446 and 453K[8].

These results imply that the initial deposit of chain molecules occurred on the surface lattices of needles, with chain-folding, and the same habit persisted throughout the subsequent growth process. The resultant pile of lamellae seems to be more compact than that formed from solutions. Unfortunately there was no evidence obtained to judge whether or not the original cross-sectional shape (i.e. hexagonal) of the nucleus needles was changed in the over-grown structure.

An example of laterally oriented lamellar structures formed upon an extended chain core has been reported by Amano *et al.*[11] and Reneker *et al.*[12]; the structure appearing on the surface of solid state polymerized trioxane after a partial melting would be basically the same as that by the present overgrowth, although the detailed structure of the

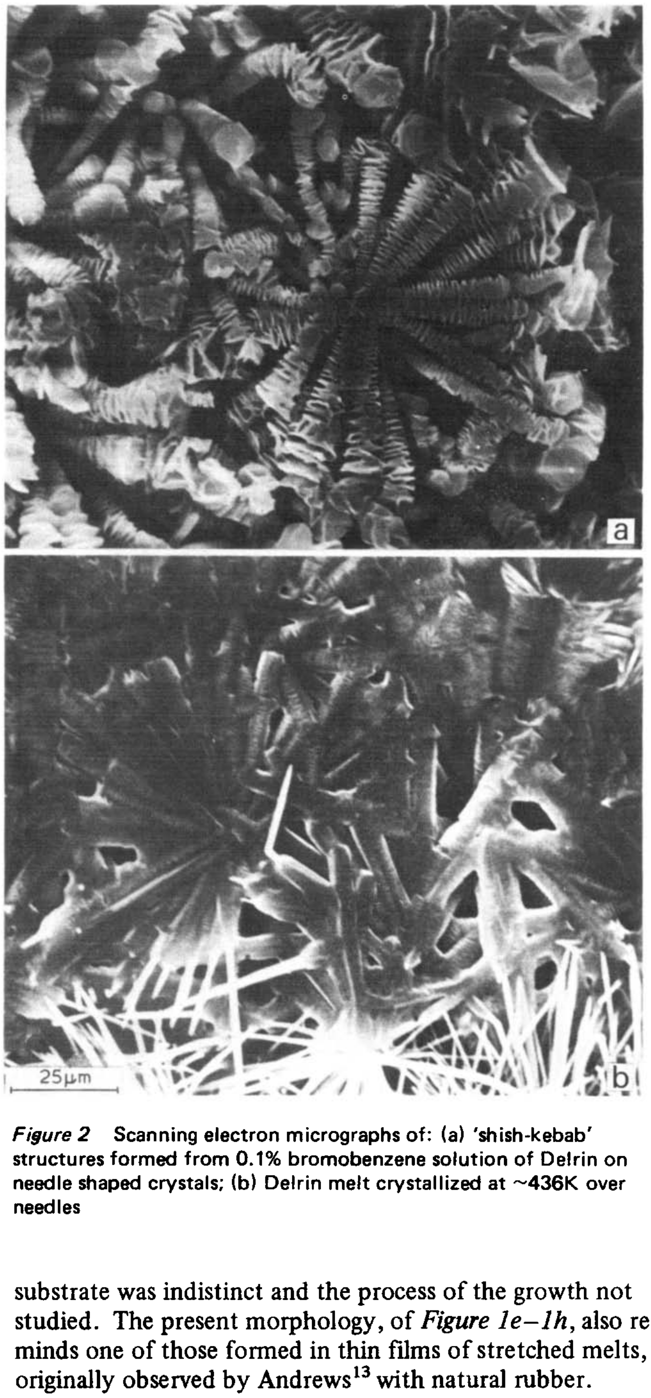

Figure 2 Scanning electron micrographs of: (a) 'shish-kebab' structures formed from 0.1% bromobenzene solution of Delrin on needle shaped crystals; (b) Delrin melt crystallized at ~436K over needles

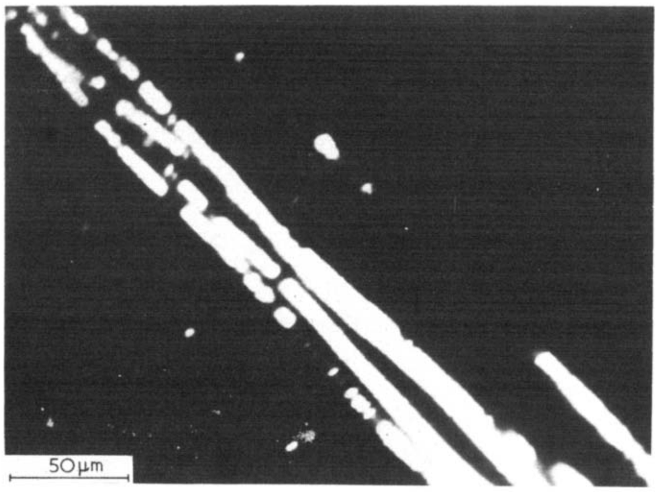

Figure 3 A polarized micrograph of shear induced crystals appearing at 437K

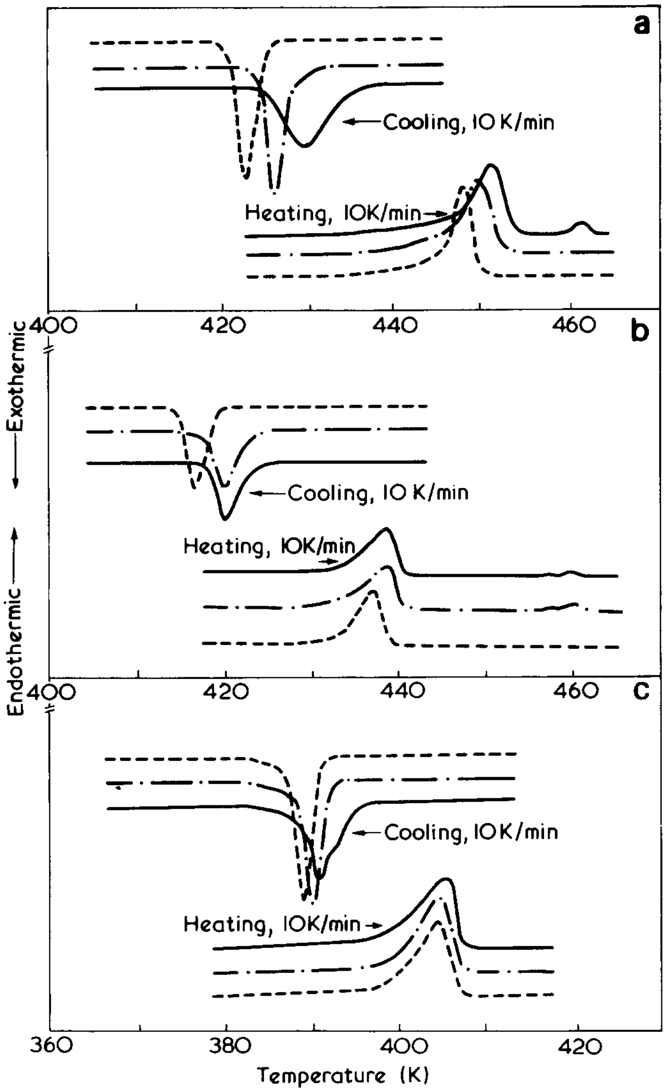

Figure 4 Cooling and heating d.s.c. curves (rate, 10 K/min) of polymers with and without embedding needle shaped crystals. (a) Poly(oxymethylene–diacetate) (Delrin 500X): — — —, Delrin only; — · — ·, Delrin/needle (trace); ——, Delrin/needle (~2%). (b) Poly(oxymethylene–ethylene oxide) copolymer (Duracon, several percent ethylene oxide units): — — —, Duracon only; — · — ·, Duracon/needle (2.5%); ——, Duracon/needle (5%). (c) Polyethylene (Sholex 6150): — — — PE only; — · — ·, PE/needle (trace); ——, PE/needle (~2%)

substrate was indistinct and the process of the growth not studied. The present morphology, of *Figure 1e–1h*, also reminds one of those formed in thin films of stretched melts, originally observed by Andrews[13] with natural rubber. *Figure 3* was produced with Delrin polyoxymethylene by shearing at around 448K and holding the melt at 437K. It is considered that the effect of an applied shear is mostly significant for the formation of the core nuclei, in which only a very minor fraction of molecules participate while the remaining structure is formed by the over-growth mechanism. Similar account was taken for the effect of stirring, forming shish-kebabs from solutions[3]. This idea may be applied more generally to crystallization under molecular orientation.

The change in the crystallization mechanism has been demonstrated conveniently by *in situ* crystallization in a d.s.c. sample cell. *Figure 4a* is for Delrin/needle systems. As seen in the cooling curves, the temperature range for crystallization was raised markedly by the presence of only a few percent needles. The return (heating) curves show a common trend for chain-folded crystallization in that crystals formed at higher temperature melted at higher temperature and *vice versa.* The melting (accompanying degradation) of needle-like crystals[9] is noticed in one of the curves by the maximum at around 463K.

Other polymers have been examined to see if they exhibit this type of epitaxy. Essentially the same behaviour was observed for the acetal copolymer (Duracon), in which the main chain structure had been disordered by several percent ethylene oxide units, although the crystallization temperatures were naturally lower than the case with the homopolymer (see *Figure 4b*). However, embedding needle shaped crystals seemed to have no effect for the crystallization of poly(ethylene oxide) and other polyethers; normal nucleation appeared and spherulite growth proceeded unaffected by the existence of the additive. An interesting polymer was polyethylene, as in the case of the solution crystallization[9]. The same type of over-crystallization took place from the surface, despite the lattice mismatch between the two polymers, though transition from spontaneous nucleation followed rather soon and disturbed the cylindrical growth as reflected in the d.s.c. curves of *Figure 4c*.

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REFERENCES

1 Penning, A. J. and Kiel, A. M. *Kolloid Z. Z. Polym.* 1965, **205**, 160
2 Wunderlich, B. 'Macromolecular Physics, Crystal Structure, Morphology, Defects', Academic Press, New York, London, 1973, Vol 1
3 Iguchi, M. and Murase, I. *J. Polym. Sci. (A-2)* 1975, **13**, 1461
4 Iguchi, M. *Br. Polym. J.* 1973, **5**, 195
5 Iguchi, M. and Murase, I. *J. Cryst. Growth* 1974, **24/25**, 596
6 Iguchi, M., Murase, I. and Watanabe, K. *Br. Polym. J.* 1974, **6**, 61
7 Iguchi, M. and Murase, I. *Makromol. Chem.* 1975, **176**, 2113
8 Iguchi, M. and Watanabe, Y. *Br. Polym. J.* to be published
9 Iguchi, M. *Makromol. Chem.* 1976, **177**, 549
10 Koch, T. A. and Lindvig, P. E. *J. Polym. Sci.* 1959, **1**, 163
11 Amano, T., Fischer, E. W. and Hindrichsen, G. *J. Macromol. Sci. (B)* 1969, **3**, 209
12 Reneker, D. H. and Colson, J. P. *J. Appl. Phys.* 1971, **42**, 4607
13 Andrews, E. H. *Proc. Roy. Soc. (A)* 1962, **270**, 232; 1964, **277**, 562