Studies on comb-like polymers: 5* A d.s.c. investigation of samples of poly(octadecylethylene) with different history

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The crude product of the stereospecific polymerization of octadecylethylene shows, on d.s.c. analysis, two enthalpy changes associated with the melting or the crystallization of two immiscible crystalline phases. It is shown that the crystallization of the crude polymer from dilute heptane solutions leads to a satisfactory separation of supposedly isotactic from atactic material. Contrary to previous statements, it is demonstrated that both these materials display single melting and crystallization phenomena. It is also shown that appropriate annealing treatments lead to a narrow distribution of the crystallite sizes for all the crystalline structured formed by poly(octadecylethylene).

Key words Polymerization; crystallization; calorimetry, poly(octadecylethylene); enthalpy changes

INTRODUCTION

Previous calorimetric studies[1-6] carried out on higher isotactic poly(alkylethylene)s in their most stable crystalline form (Type II)[7] have indicated that these polymers display a main melting phenomenon at a temperature which depends on the length of the side chains, and a minor thermal effect, at a lower temperature, the origin of which has been variously interpreted. Some authors[1,5] attribute this effect to the fusion of a crystalline phase built up mainly by atactic material; others[2-4,6] claim that the effect is present also in purely isotactic samples and ascribe it to a secondary transition taking place in the Type II crystalline structure of the polymers as a result of conformational changes of the side polymethylene chains.

In this paper we provide direct evidence in favour of the first interpretation, using poly(octadecylethylene) as representative of this class of polymers. The d.s.c. traces of several samples of this polymer having different history are also discussed.

EXPERIMENTAL

Poly(octadecylethylene) was prepared as already described[5]. The crude polymerization product, after complete monomer separation, was fractionated either by extraction with solvents or by crystallization from solutions.

According to the technique adopted in previous studies of this series[5], a powder sample of crude polymer was placed in a Kumagawa apparatus and extracted with boiling ethyl ether for 36 h. The residue was dried at room temperature under vacuum to constant weight. The dissolved polymer was recovered by precipitation in excess methanol and dried.

Fractionation by crystallization was carried out dissolving a sample of polymer in the selected hot solvent and letting the solution cool down slowly to room temperature. After standing for a sufficient time, the polymer gel was separated from the solution by centrifugation, washed repeatedly with portions of fresh solvent and dried. The material in solution was recovered by precipitation with methanol.

The d.s.c. traces were obtained on a Perkin–Elmer DSC-1B instrument, with scanning speeds of 16 K min^{-1}. Annealing was carried out placing the samples with their d.s.c. holders in a thermostatically controlled oven.

RESULTS AND DISCUSSION

The work of Aubrey and Barnatt[1] as well as ours[5] has shown that the solvent extraction of the crude product of the stereospecific polymerization of higher olefins leads to a substantial separation of atactic, lower-melting material with consequent reduction of the enthalpy change associated with the low-temperature thermal effect. Therefore, we postulated that a judicious choice of the extraction conditions could lead to a polymer sample displaying no low-temperature thermal effect. Experiments confirmed this expectation. Several solvents and procedures were tested, but the best results were obtained by crystallizing the polymer from a heptane solution. These results are illustrated by the d.s.c. traces shown in *Figure 1*. In order to avoid any effect of the previous thermal history of the samples these were first melted and the cooling and the rerun heating traces were registered. In *Figure 1a* the d.s.c. traces of the crude polymerization product are shown. Two strong endotherms are observed in the heating trace at ~327 and

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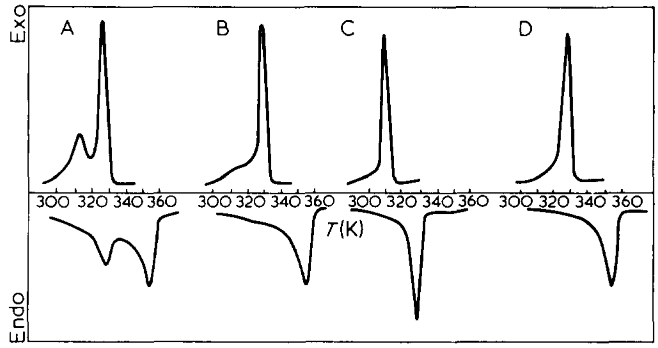

Figure 1 D.s.c. traces (cooling and rerun heating) of poly(octadecylethylene) samples: A, crude polymerization product; B, product of the crystallization of the crude material from 5% w/v heptane solution; C, polymer recovered from the mother liquor of the crystallization; D, same as B, after recrystallization from 2% w/v heptane solution. Scanning speed 16 K min^{-1}

353K; two corresponding exotherms at ~313 and 327 K are present in the cooling trace. By dissolving 10 g of the crude polymer in 200 ml hot heptane and crystallizing at room temperature, two fractions of material were recovered as described in the experimental section: ~6.5 g of crystallized polymer showing the d.s.c. traces of *Figure 1b*, and ~3.5 g of material recovered from the heptane solution which displayed the traces of *Figure 1c*. The latter polymer is composed exclusively of low-melting material, whereas the crystallized polymer just displays a weak shoulder in the low-temperature region of the d.s.c. scans. A subsequent crystallization of 5 g of this polymer from a 2% w/v solution in heptane leads to a crystallized material (~4 g) showing the d.s.c. traces of *Figure 1d* with single melting and crystallization peaks at 354 and 328 K, respectively.

The data illustrated in *Figure 1* demonstrate unambiguously that an appropriate solvent treatment of isotactic poly(octadecylethylene) leads to a complete separation of the material melting at 327 K: unless the crystallized polymer is quenched from the melt (see below), the relevant d.s.c. traces show no indication of low-temperature thermal effect.

The rerun heating traces presented in *Figure 2* illustrate the results obtained with toluene as crystallization medium. Toluene was first used by Holland-Moritz *et al.*[2] and by Trafara *et al.*[4] to develop the Type I crystalline form[7] of higher isotactic poly(alkylethylene)s, but no data on the extraction power of this solvent were provided. A sample of crude poly(octadecylethylene) was treated in a Kumagawa apparatus with boiling ethyl ether as described in the experimental section. The d.s.c. trace of the residue is presented in *Figure 2*, curve A. Evaulation of the peak areas indicates that this sample contains roughly 30% of the low-melting phase. 10 g of this sample was dissolved in 200 ml hot toluene and the solution left at room temperature for 8 h. About 7 g of polymer crystallized: the relevant d.s.c. trace is shown in *Figure 2*, curve B. Curve C is the trace of the polymer left in solution. A comparison of curves A, B and C shows that the crystallization from toluene causes a rough separation of the two phases. In fact, an appreciable reduction of the low-temperature peak area is observed for the crystallized polymer. However, a considerable amount of high-melting material remains in solution. A successive crystallization of the polymer from 2% w/v toluene solution leads to a sample showing the d.s.c. trace presented in *Figure 2*, curve D. Only a low-temperature shoulder is present in this trace. The data of *Figure 2* indicate that an appreciable fractionation of poly(octadecylethylene) can be obtained by crystallization from toluene solution, although the selectivity of this solvent is far lower than that of heptane.

First-run heating d.s.c. traces as well as X-ray diffraction patterns show that the polymers crystallized from either heptane or toluene have the Type I crystalline structure.

The first heating trace of a polymer sample crystallized once from toluene presents a highly asymmetric endothermic peak with a long tail on the low temperature side (*Figure 3*, curve A). No resolved low-temperature endotherm can be observed in this trace, though the sample contains a measurable amount of low-melting material. However annealing this sample at 327 K for 2 h leads to a profound change of the shape of the trace (*Figure 3*, curve B). The low-temperature tail almost disappears whereas the thermal effect at 327 K becomes clearly visible. In addition, a pronounced shoulder at ~342 K appears on the low-temperature side of the melting peak. An X-ray diffraction diagram of this sample indicates that the annealing treatment has not changed the Type I crystalline structure, the reflexes at 4.45, 4.19 and 3.8 Å being only slightly sharper than those of the unannealed sample. The traces of *Figure 3* show that annealing leads to a recrystallization of the poorly crystallized material which is present in the polymer as obtained from the toluene treatment and which gives rise to the low-temperature tail of the trace. In order to investigate in detail the effect of different annealing conditions on the shape of the d.s.c. heating scans of poly(octadecylethylene) having the Type I structure, several samples of this polymer, after double

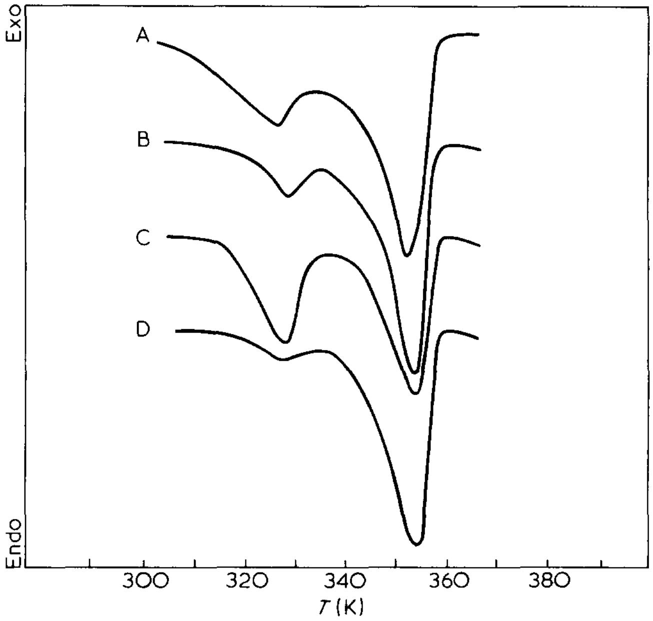

Figure 2 Rerun heating d.s.c. scans of poly(octadecylethylene) samples: A, residue of the Kumagawa extraction of the crude polymerization product with Et_2O; B, same as A after crystallization from 5% w/v toluene solution; C, polymer recovered from the mother liquor of the crystallization; D, same as B, after recrystallization from 2% w/v toluene solution. Scanning speed 16 K min^{-1}

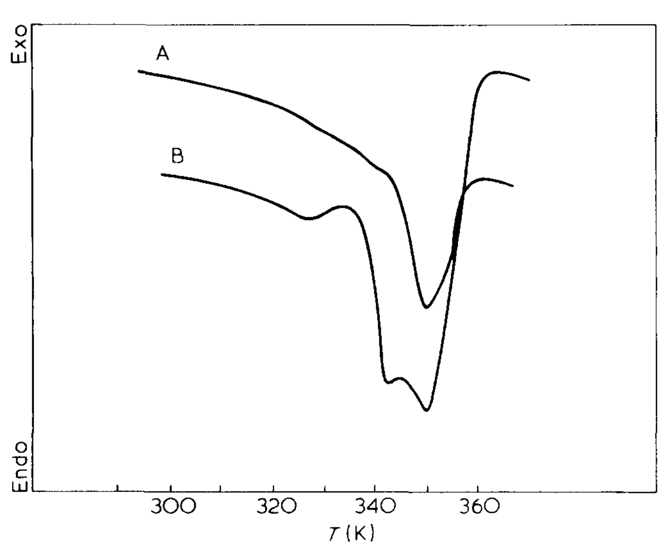

Figure 3 First-run heating d.s.c. scans of poly(octadecylethylene) samples: A, polymer crystallized from 5% w/v toluene solution (*Figure 2B*); B, same as A after annealing 2 h at 327 K. Scanning speed 16 K min^{-1}

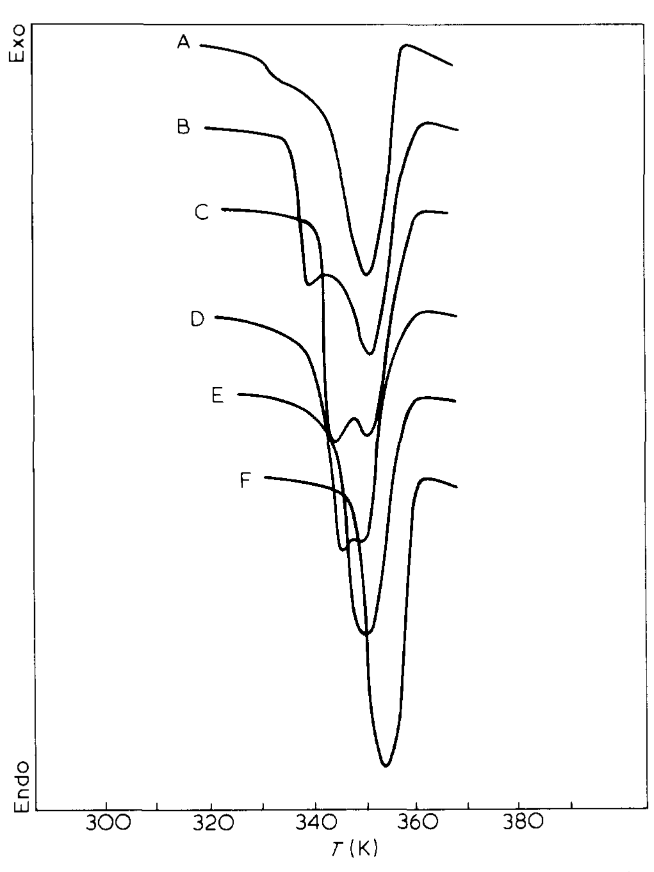

Figure 4 First-run heating d.s.c. scans of poly(octadecylethylene) samples: A, polymer recrystallized from 2% w/v heptane solution (*Figure 1D*). Samples of A annealed at: B, 325 K for 2 h; C, 330 K for 2 h; D, 338.5 K for 2 h; E, 341.5 K for 3 h; F, 348 K for 3 h. Scanning speed 16 K min^{-1}

crystallization from heptane and complete removal of the low-melting material, were annealed at different temperatures. The first-run heating d.s.c. traces of these samples are presented in *Figure 4*. Curve A is the trace of a sample as received from the heptane crystallization. The melting peak is very asymmetric and very similar to that of the polymer crystallized from toluene (*Figure 3*, curve A). Annealing temperatures below about 342 K cause the recrystallization of the polymer responsible for the low-temperature tail of the melting peak. A shoulder appears on the latter peak at a temperature steadily approaching that (349 K) of melting of the Type I structure. Finally, as a result of annealing at 341.5 K, a single melting peak is observed (*Figure 4*, curve E). X-ray diffraction indicated that no qualitative change of the Type I structure takes place as result of annealing at temperatures up to 342 K. The sharpest X-ray pattern is found for the sample annealed at 341.5 K. This suggests that the material giving rise to the shoulders at temperatures between about 335 and 345 K, depending on the annealing conditions, (curves B, C and D) must have a crystalline structure of the Type I, though perhaps less perfect than that of the polymer melting at 349 K.

As already indicated by Turner Jones[7], annealing at a temperature close to the melting point of the Type I structure causes a complete reorganization of the crystals and leads to the more stable Type II crystalline form. This is proved by the d.s.c. trace of *Figure 4*, curve f, as well as by X-ray analysis.

A solid-state reorganization of the less perfect crystals with resulting narrower distribution of crystallite sizes has been observed not only with polymer in the Type I modification but also with polymer crystallized in the hexagonal form. It is known that quenching from the melt

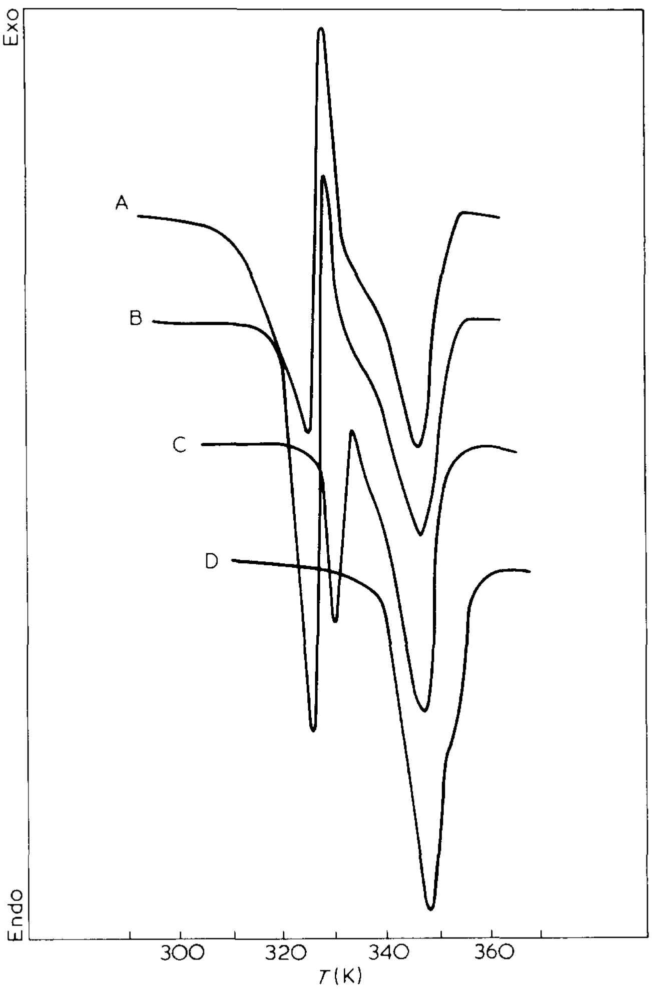

Figure 5 First-run heating d.s.c. scans of poly(octadecylethylene) samples: A, polymer recrystallized from 2% w/v heptane solution (*Figure 1D*), quenched from the melt in liquid N_2. Samples of A annealed at: B, 316 K for 2 h; C, 328 K for 2 h; D, 341 K for 4 h

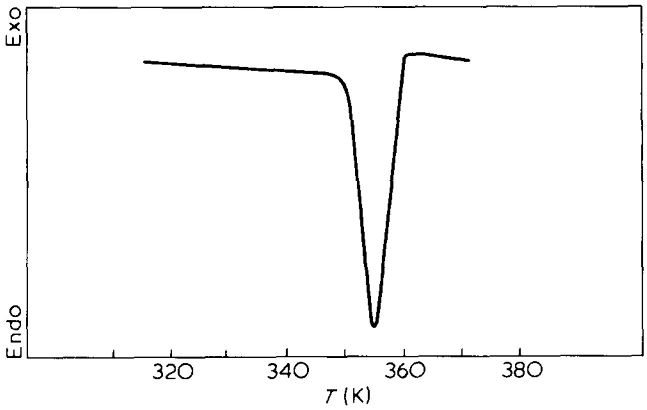

Figure 6 First-run heating d.s.c. scan of a fibre of poly(octadecylethylene) recrystallized from 2% w/v heptane solution (*Figure 1d*), annealed under tension at 346 K for 6 days in ethanol

makes isotactic poly(octadecylethylene) crystallize in a hexagonal structure similar to that formed by atactic polymer[5]. The d.s.c. trace of such a polymer sample is shown in *Figure 5*, curve A. The crystalline phase formed on quenching shows a highly asymmetric endothermic peak at ~325 K. A fast recrystallization follows, as indicated by the exotherm at 328 K, which leads to the Type I structure. This latter melts at 348 K. If a quenched sample is annealed at a sufficiently low temperature (316 K) the only effect is a pronounced reorganization of the low-melting phase. A much sharper and more symmetric low-temperature peak is observed (*Figure 5*, curve B), whereas the shape of the exotherm and of the subsequent endotherm are not altered appreciably. An increase of the annealing temperature causes a more or less pronounced transformation of the hexagonal structure into the Type I structure. Both the low-temperature endotherm and the exotherm decrease in intensity and finally disappear completely (*Figure 5*, curves C and D). A quenched sample of poly(octadecylethylene) shows, after annealing at 341 K, a d.s.c. trace typical of the Type I structure, although a shoulder on the high-temperature side of the melting peak indicates that a small fraction of the material has attained the Type II crystal form.

We will finally mention that a narrower distribution of crystallite sizes can be achieved also by annealing polymers crystallized in the Type II structure. The best results were obtained by immersing for 6 days a fibre of material, held under tension, in ethanol at 346 K. The d.s.c. trace obtained after such a treatment is shown in *Figure 6*. A comparison with the trace of *Figure 1d* shows that a much more symmetric endothermic peak is obtained as result of annealing under tension.

CONCLUSIONS

The data described in this note demonstrate that isotactic poly(octadecylethylene) displays d.s.c. traces with single melting and crystallization peaks, provided that convenient purification procedures are used to remove completely the low-melting, probably atactic material. Moreover, highly symmetric peaks, indicating narrow distribution of crystallite sizes can be obtained for any of the crystalline structures formed by this polymer, by adopting appropriate annealing conditions.

REFERENCES

1 Aubrey, D. W., Barnatt, A. *J. Polym. Sci., Part A-2* 1968, **6**, 241
2 Holland-Moritz, K., Sausen, E. and Hummel, D. O. *Colloid Polym. Sci.* 1976, **254**, 976
3 Trafara, G., Koch, R., Blum, K. and Hummel, D. *Makromol. Chem.* 1976, **177**, 1089
4 Trafara, G., Koch, R. and Sausen, E. *Makromol. Chem.* 1978, **179**, 1837
5 Magagnini, P. L., Andruzzi, F. and Benetti, G. F. *Macromolecules* 1980, **13**, 12
6 Trafara, G. *Makromol. Chem.* 1980, **181**, 969
7 Turner Jones, A. *Makromol. Chem.* 1964, **71**, 1