The structure of propylene–ethylene sequential copolymers

Po-Len Yeh, Arthur W. Birley and Derek A. Hemsley
Institute of Polymer Technology, Loughborough University of Technology,
Loughborough, Leicestershire LE11 3TU, UK

(*Received 23 November 1984*)

Polypropylene is frequently modified by incorporating ethylene during polymerization or by blending with ethylene polymers or copolymers. Such ethylene-containing systems exhibit a very characteristic texture of small particles (globules) superposed on the spherulitic crystallinity of the polypropylene. The nature and occurrence of these particles have been investigated. The conclusion reached is that they contain ethylene polymers, both crystalline and amorphous, and that they can exist in a quiescent melt.

(Keywords: ethylene-modified polypropylene; propylene copolymers; polypropylene copolymers; propylene–ethylene sequential copolymers; globular texture)

INTRODUCTION

In a research programme investigating the relationships between processing, structure and properties of car coolant reservoir tanks, manufactured by extrusion blow moulding of propylene–ethylene sequential copolymers, the texture of the inner and outer surfaces was closely examined. The inner surface showed 'globular' particles on a very coarse spherulitic texture (see *Figure 1*), resulting from the slow cooling to which the inner surface of the tank of considerable wall thickness had been subjected (Propathene HSE 110). This morphology is associated with the 'speckled' appearance of many sequential copolymers, e.g. ethylene on propylene, which has been reported in the literature[1]. This morphology is not seen in homopolymer.

In proof tests on car coolant reservoir tanks, and in service, cracks developed at the inner wall, under the combined effects of pressure, time, temperature and an active environment, ethylene glycol. The last appears to be mildly aggressive towards propylene polymers. It is not known whether the globules contribute or are neutral in the initiation and propagation of these cracks; this is sufficient reason for finding out more concerning:

(a) their nature.
(b) conditions for their occurrence,
(c) conditions for their growth,
(d) the effect of globules on significant properties, and
(e) methods of destroying globular texture.

EXPERIMENTAL

A variety of microscopical techniques has been employed during this programme, including common light, polarised light, differential interference contrast and scanning electron methods. Additionally, other methods of structural analysis have been utilised as appropriate; included were infra-red spectroscopy, differential scanning calorimetry (d.s.c.) and dynamic mechanical thermal analysis. The sample and specimen preparation required to make optimum use of the techniques listed in the previous paragraph involved the following.

Blends were made by tumble-mixing granules of the components, thereafter homogenizing the blend by two passes through a single screw extruder at a temperature of 200–210°C.

A 'freely crystallized surface' technique was developed to study the incidence of globular texture in modified polypropylene. The sample was prepared by placing a compression moulded plaque, 4 mm thick, in an aluminium foil container, heating at 230°C for 20 min, then conditioning for 60 min at 125°C. The thermal treatment was carried out under nitrogen, and the 'free surface' so generated was sputter coated with gold for subsequent examination in a Cambridge Stereoscan S2A scanning electron microscope.

Surfaces of mouldings were also prepared for examination by s.e.m. by sputter coating with gold, the coating being carried out in such a way as to avoid overheating the sample.

Sections for examination by common or polarized light microscopy were cut on a Leitz sledge microtome with a freshly prepared glass knife.

Sections for differential interference contrast microscopy were required to be of lower thickness and were prepared using a LKB Ultratome.

A melt pressing procedure was followed for selected sections to eliminate features which might have arisen from the microtoming technique. 3 μm sections were cut from compression moulded plaques and placed on a microscope slide with a cover slip. The assembly was heated on a hot plate at 200°C for 8 min and then transferred to a Mettler microscope hot stage at 125°C for 1 h.

Solvent etching was achieved by treatment with xylene either *cold*, by digesting the sample at 20°C for 24 h, or *hot*, by exposing the sample to xylene at 130°C for 10 s.

RESULTS AND DISCUSSION

Globular texture has been found in a large number of sequential copolymers, ethylene on propylene, made by diluent or gas phase processes (see Appendix), and in

0032–3861/85/081155–07$03.00

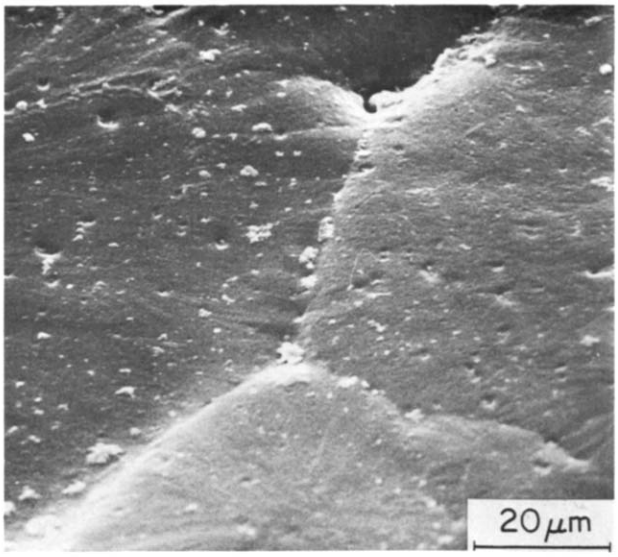

Figure 1 SEM micrograph of inner surface of car coolant reservoir tank in Propathene HSE 110. (Sequential copolymer, ethylene on propylene)

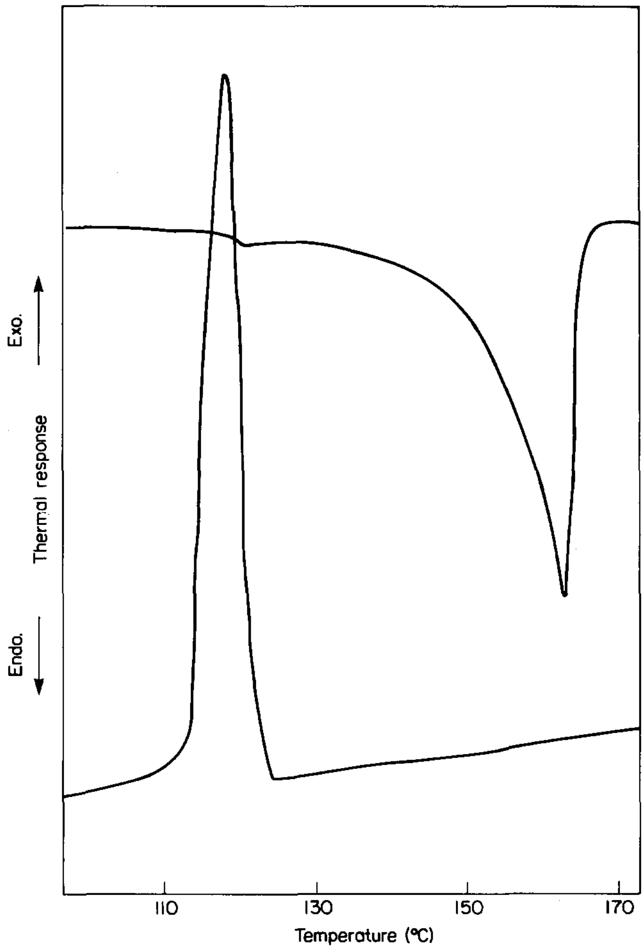

Figure 2 D.s.c. scan of sequential copolymer, ethylene on propylene, showing distinct melting peak of the polyethylene phase. (Propathene HSE 110)

blends of a propylene homopolymer (Profax 6824) with high density polyethylene (Unifos 0905) and with ethylene/propylene copolymer rubber (Intolan 170A). It has *not* been observed in extensive examination of propylene homopolymers from two manufacturers (Profax 6824 and Propathene GWM 22), or in a somewhat less detailed investigation of polypropylene (Profax 6824) blended with linear low density polyethylene (LLDPE—'Dowlex' 2045). The occurrence of globules is most likely in slow-cooled samples, and is encountered only rarely in samples quench-cooled from the melt.

A variety of characterization methods has been employed in this work to assist in elucidating the nature of the globules. Differential scanning calorimetry (d.s.c.), scans on many samples of ethylene-modified polypropylene have confirmed the presence of a crystalline polyethylene phase, see *Figure 2*, and since all such materials can be induced to show globular texture, whilst propylene homopolymer is never associated with globules, the simplest interpretation is that the globules are of crystalline polyethylene, incompatible with the polypropylene. Slow cooling the samples, a condition which is known to favour the development tof the globular texture, increases

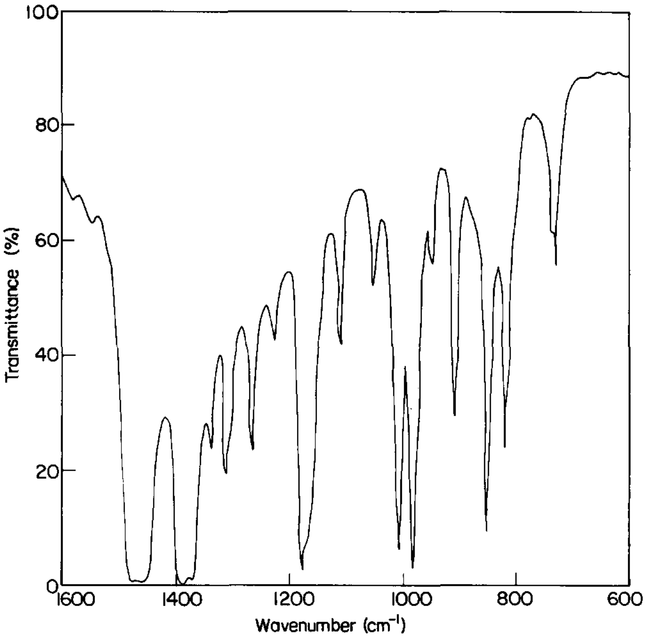

Figure 3 Infra-red spectrum of sequential copolymer, ethylene on propylene, at 25°C. (Propathene HSE 110)

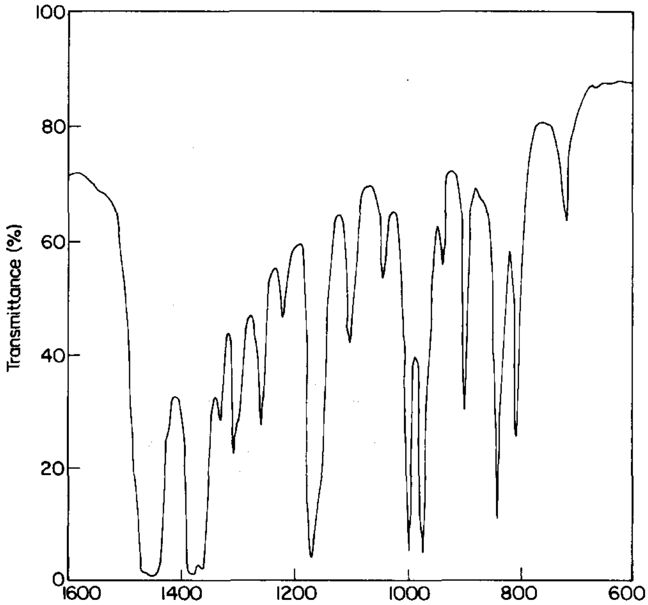

Figure 4 Infra-red spectrum at 25°C of propylene homopolymer blended with ethylene/propylene rubber

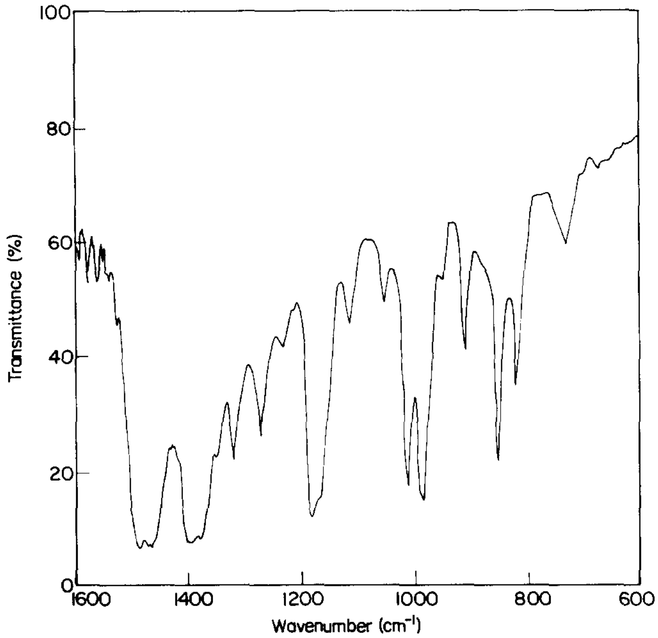

Figure 5 Infra-red spectrum of sequential copolymer, ethylene on propylene, scanned at 145°C. (Propathene HSE 110)

the magnitude of the polyethylene fusion peak disproportionately, strengthening the thesis of a link between globules and polyethylene crystallinity.

Further comment on the state of the polyethylene in sequential copolymers, ethylene on propylene, can be made by an analysis of infra-red scans made at ambient temperature, when the doublet at 720–740 cm^{-1} indicates the presence of crystalline polyethylene in the sequential copolymer, see *Figure 3*. By contrast, the infra-red spectrum of the polypropylene–ethylene/propylene rubber blend has only a singlet absorbance at 720 cm^{-1} (*Figure 4*), similar in character to the singlet absorbances shown by systems involving crystalline polyethylene if scanned at 145°C, above the melting point for crystalline PE[2], see *Figure 5*. However, the PP–E/P rubber blend shows globular texture, suggesting that the globules might be a segregated rubber phase.

Dynamic mechanical thermal analysis was carried out in a nitrogen atmosphere, over a temperature range of −160 to +170°C with a Polymer Laboratories instrument, operating at a frequency of 1 Hz. The mechanical loss spectra, illustrated in *Figure 6*, provide the following information.

(a) For propylene homopolymer at 0°C there are rising losses, associated with amorphous propylene homopolymer. (The peak is at 8°C is not reached in *Figure 6*).

(b) Two loss peaks are seen for the PP blend with E/P rubber, the rising losses at 0°C, characteristic of amorphous PP, and at −42°C, which must represent T_g for the ethylene/propylene rubber.

(c) The PP–high density polyethylene (HDPE) blend also shows two loss peaks, rising losses at 0°C (amorphous PP) and at −110°C, which is characteristic for amorphous polyethylene.

(d) Examination of the loss spectrum for a typical sequential copolymer reveals three loss processes: rising losses at 0°C, associated with PP; at −50°C, (E/P) rubber); and at −115°C (a small peak for amorphous PE). This leads to the surprising conclusion that a sequential copolymer has two crystalline phases and three amorphous phases. This information confuses rather than clarifies the nature of the globules.

Further direct observations on the globules

Thin sections of homopolymer and sequential copolymer samples with well defined spherulites were viewed between crossed polars on a Riechert microscope with a Mettler hot stage. At room temperature, comparable spherulitic texture was observed, with no globules visible in either sample. The stage was heated at 10°C min^{-1} and, as the temperature of the copolymer approached 120°C, the spherulites became less visible and black droplets, globular particles, became apparent. This is shown in *Figure 7a* (room temperature) and *Figure 7b* (125°C). On further heating, the light intensity faded rapidly between 150 and 160°C and extinguished completely at 160–164°C. No globules were observed for the homopolymer throughout the temperature range. The reason for the globular particles being visible at 125°C, but not at room temperature, is attributed to the phase change, with corresponding changes in density and refractive index, as the crystalline polyethylene melts. The temperature associated with this phase change, 125°C, is in good agreement with the melting temperature of the crystalline polyethylene phase recorded in the d.s.c. results. These findings, together with the observation that the globules are not obtained with homopolymer, indicate that the

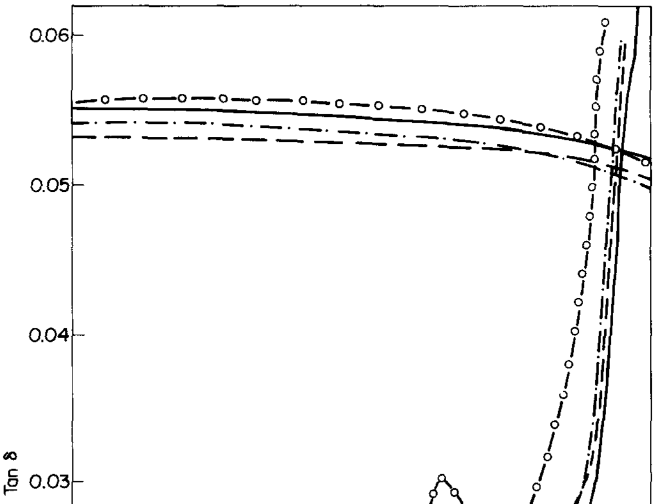

Figure 6 Mechanical loss vs. temperature curves: (– – –): propylene homopolymer, Propathene GWM 22; (–·–): propylene homopolymer blended with E/P rubber; (———): propylene homopolymer blended with HDPE; (–○–): sequential copolymer, ethylene on propylene, (Propathene HSE 110)

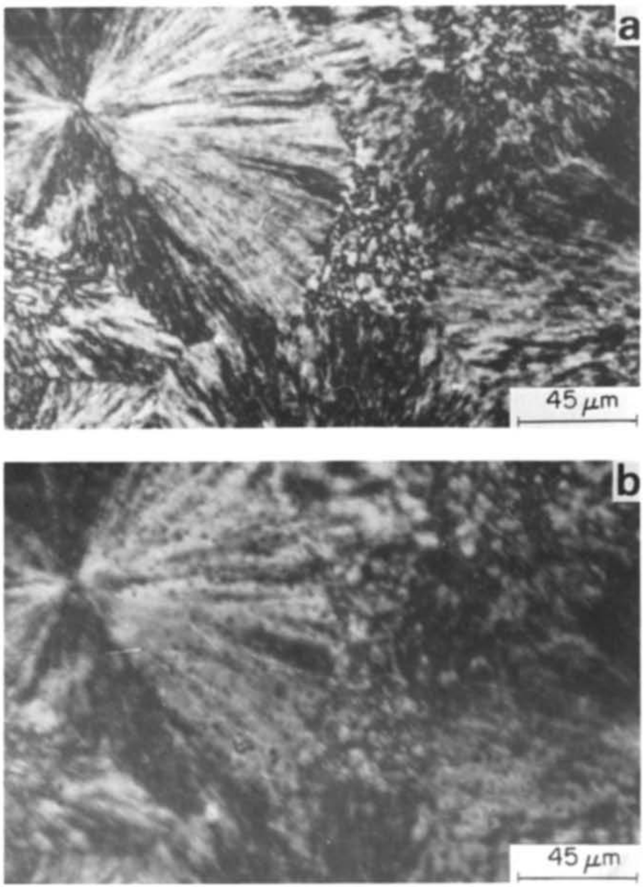

Figure 7 Section of sequential copolymer, viewed between crossed polars. (a) at 21°C; (b) at 125°C

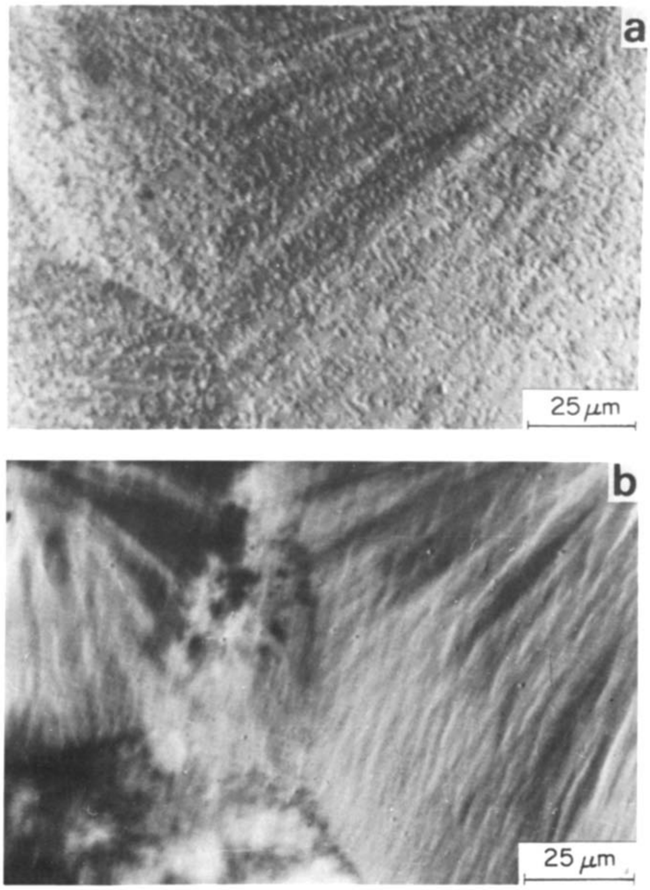

Figure 9 Melt pressed samples from thin sections viewed by d.i.c. microscopy: (a) sequential copolymer; (b) homopolymer

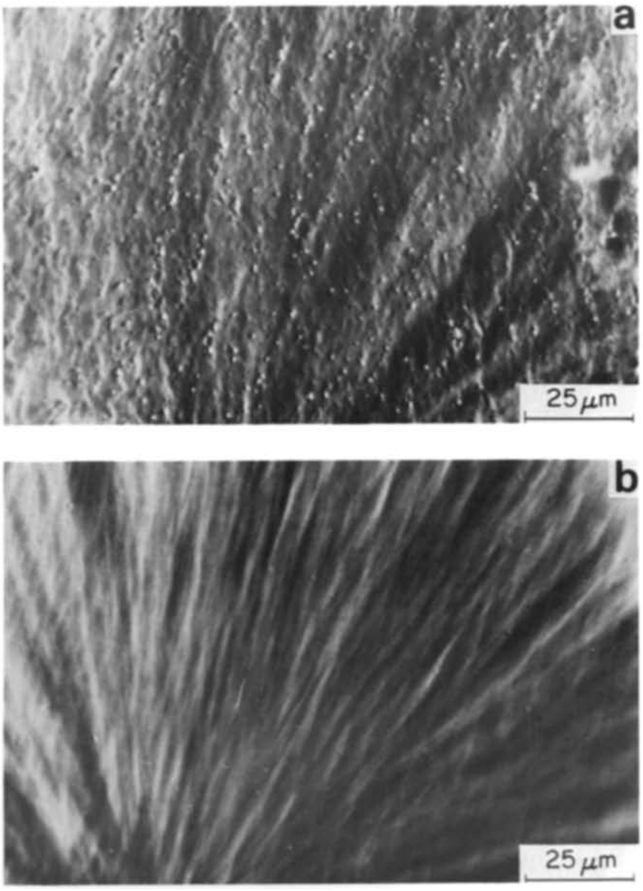

Figure 8 3 μm sections from compression moulded plaques, viewed in differential interference contrast mode. (a) sequential copolymer, (b) homopolymer

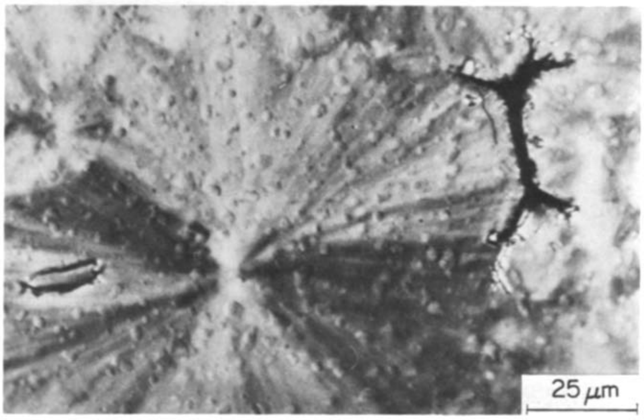

Figure 10 Melt pressed samples from thin sections of PP–HDPE blend, viewed in differential interference contrast mode

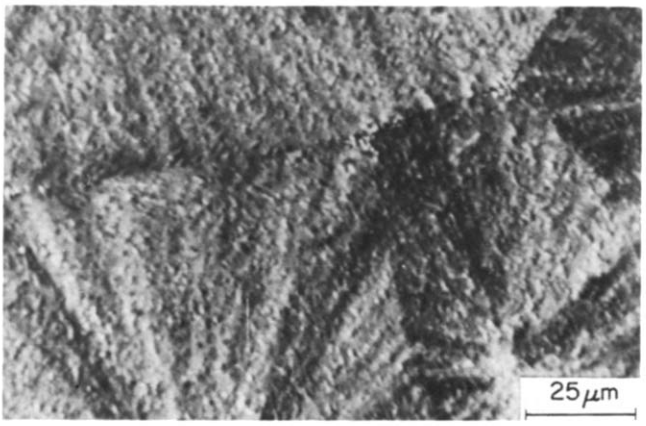

Figure 11 Melt pressed samples from thin sections of PP–E/P rubber blend, viewed in differential interference contrast mode

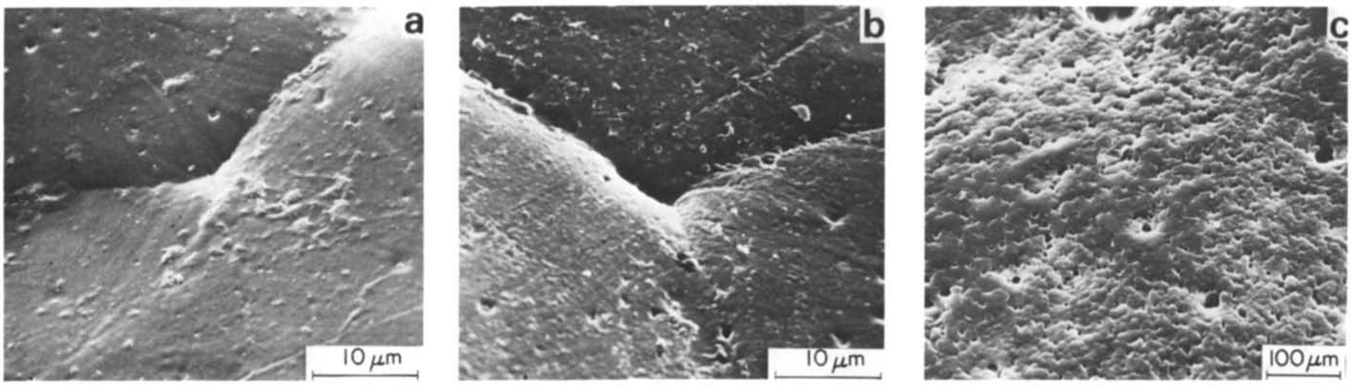

Figure 12 S.e.m. micrographs of inner surface of car coolant reservoir tank: (a) treated for 24 h with xylene at 20°C; (b) same sequential copolymer before xylene treatment; (c) surface of slow cooled compression moulding of sequential copolymer after 10 s xylene treatment at 130°C

globular particles probably contain crystalline polyethylene. A further factor contributing to the appearance of the globules at high temperatures is that the masking due to the highly birefringent polypropylene texture is also reduced.

To confirm that the appearance of the globules at high temperature was related to the melting of crystalline PE, two blends, PP–HDPE and PP–E/P rubber, were examined as a function of temperature on the hot stage microscope. For the PP–HDPE blend, it was observed that 'blurred' globules were visible even at room temperature; these transformed into the distinct black droplets as the temperature approached 135°C, the melting point of HDPE. Although the 'blurred' globules were also visible at room temperature for the PP–E/P rubber blend, they did not undergo any further change throughout the temperature range studied. It is well known that HDPE and E/P rubber appear as droplets in blends with PP[3,4], leading us to the tentative conclusion that the globules in sequential copolymers contain both crystalline PE and amorphous E/P copolymer.

The difficulty in distinguishing globular particles at room temperature has been noted above. To overcome this, a differential interference contrast microscope, which is sensitive to very small changes in refractive index, was employed. 3 μm sections, cut with a glass knife from slow cooled compression moulded plaques, were viewed in a d.i.c. system. In *Figure 8a*, the inhomogeneities of the globular inclusions are clearly visible in the bulk of the spherulites, the dimensions of the globules being in the range 0.5 to 4 μm. There is no corresponding phase separation in *Figure 8b*, which is for homopolymer. Examination of the thin sections of the sequential copolymers in common light revealed that some of the globules were still clearly visible, casting some doubt on the interpretation reached previously and indicating that the globules are, in fact, voids. To eliminate this possible consequence of the microtoming technique, the microstructure of melt pressed samples was examined. As shown in *Figure 9a* and *b*, the appearance of the globules is identical with that in the microtomed sections, although it must be admitted that the cutting might introduce some voids. Melt pressed specimens of PP–HDPE blend and PP–E/P rubber blend were also examined by d.i.c. microscopy, *Figures 10* and *11* respectively. Globular particles were observed in both systems, whilst closer examination revealed that the globules are larger and more clearly defined for the HDPE blend, compared with the

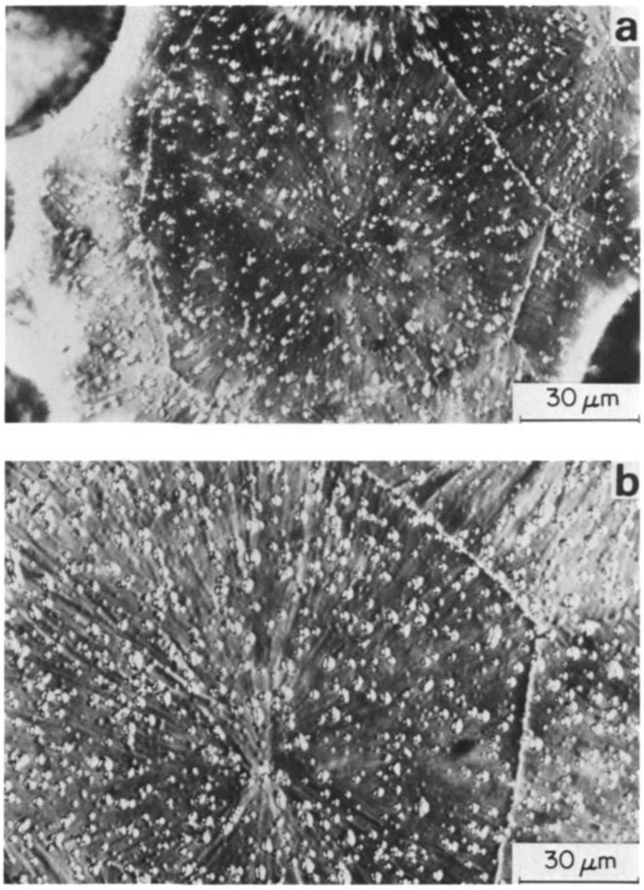

Figure 13 Melt pressed samples from thin sections of sequential copolymer, examined by d.i.c. microscopy: (a) specimen 2 min at 230°C, followed by 60 min at 125°C; (b) conditions same as (a) except for 10 min at 230°C

Table 1 Thermal treatment and globular particle statistics

	Melting conditions		Cooling conditions		Globular particles	
Sample	Temperature (°C)	Time (min)	Temperature (°C)	Time (min)	Average size (μm)	Number in 50 μm × 50 μm
1	230	2	125	60	3	211
2	230	10	125	60	4	165
3	230	10	90	60	2	184
4	230	10	25	60	1.5	182

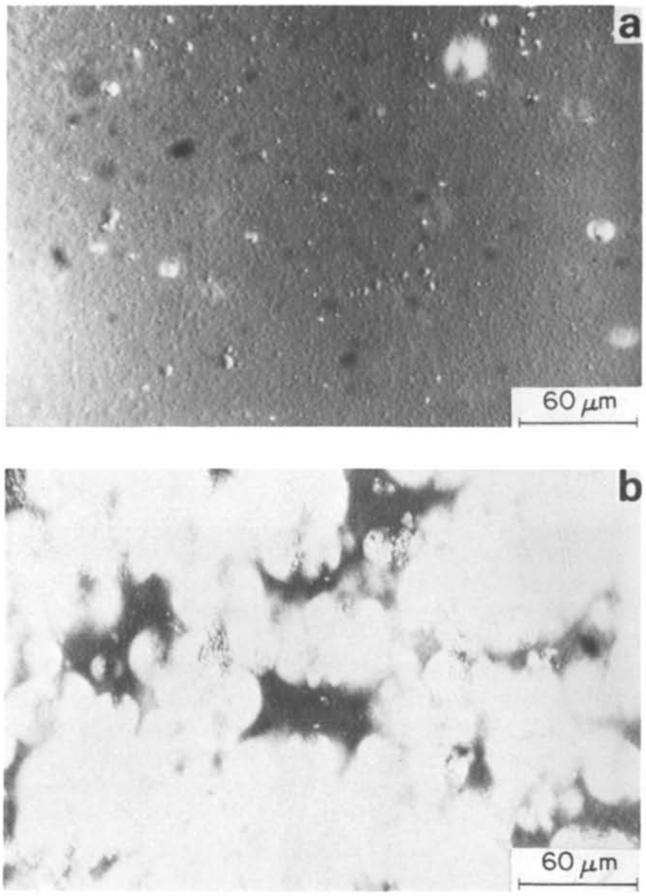

Figure 14 (a) Melt pressing of sequential copolymer at 230°C, showing globules in the melt; (b) the same, with polymer starting to crystallize

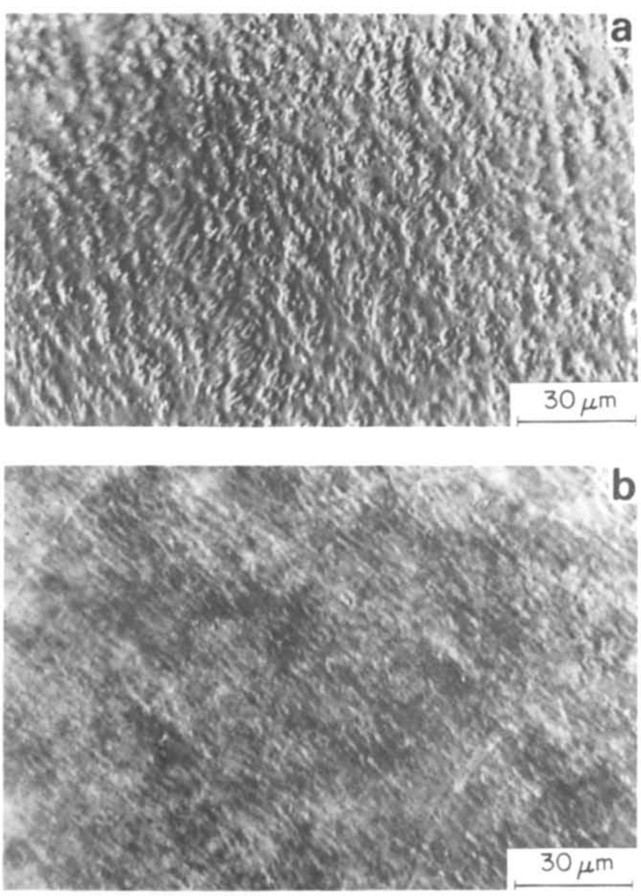

Figure 15 Effect of cooling conditions on globule size: (a) compression moulding maintained at 125°C for 60 min; (b) compression moulding quench cooled from the melt

E/P rubber blend and with the sequential copolymers. This could be associated with the poor compatibility of the HDPE in the PP matrix: Wenig *et al.*[4] reported that PE domains in a PP–HDPE blend grow by coalescence of the droplets.

The nature of the globular particles in sequential copolymers was also investigated by s.e.m. examination of solvent-etched, free surface samples; xylene was chosen as an appropriate solvent. The validity of the technique was examined by observing the effect on E/P rubber (Intolan 170A) and on crystalline HDPE (Unifos 0905) of immersion in xylene for 24 h at room temperature. The rubber dissolved completely, whilst the HDPE was unaffected. Having established the method, sequential copolymers were examined, the samples being obtained from the inside surface of blow moulded tanks, where well defined spherulites and globules had already been found, *Figure 1*. Because of the need for gold coating of the surface prior to s.e.m. examination, it is not possible to examine the same sample before and after etching, so two adjacent samples from the same moulding were compared; one sample was solvent etched for 24 h, whilst the other was untreated. *Figures 12a* and *b* are micrographs of unetched, and etched samples, and show broadly similar texture; however, the number and average size of the globules seem to be decreased by the solvent treatment. Nevertheless, their continued existence following the solvent treatment confirms that they contain crystalline material, but the reduction in number and size suggests that rubber constituent in the globules has been dissolved by the xylene. Further etching was carried out at 130°C for 10 s: *Figure 12c* shows that the globular particles are no longer visible on the surface of the sequential copolymer after this further treatment, which dissolves crystalline PE.

Having determined the likely composition of the globular particles, it is important to know how they form, and what is the effect on them of thermal history. This was investigated using the melt pressing technique, with various thermal treatments imposed, given in *Table 1*, the specimens being subsequently examined by d.i.c. microscopy.

Samples 2, 3 and 4 in *Table 1* show that the size of the globules increases as the crystallization temperature increases; thus sample 2 has the largest globules. The same sample also has the smallest number of particles, suggesting that some coalescence of smaller particles has taken place. The effect of melt history can be determined by comparing samples 1 and 2; *Figures 13a* and *13b* are d.i.c. micrographs of these samples, respectively. From these and *Table 1* it can be seen that the sample with the longer melting time has globules of greater size, but they are fewer in number. This is presumably a commentary on the incompatibility of PP and PE in the melt, the ethylene-rich regions tending to aggregate and form bigger droplets with increasing time in the melt. These results indicate that the number of globules, and their size, depend not only on the cooling conditions, but on how long the melt state has been quiescent. This is likely to be variable in commercial processing.

Having observed the effects of melt history and cooling conditions on the globular texture, one may question when and where do the globules form? To attempt to

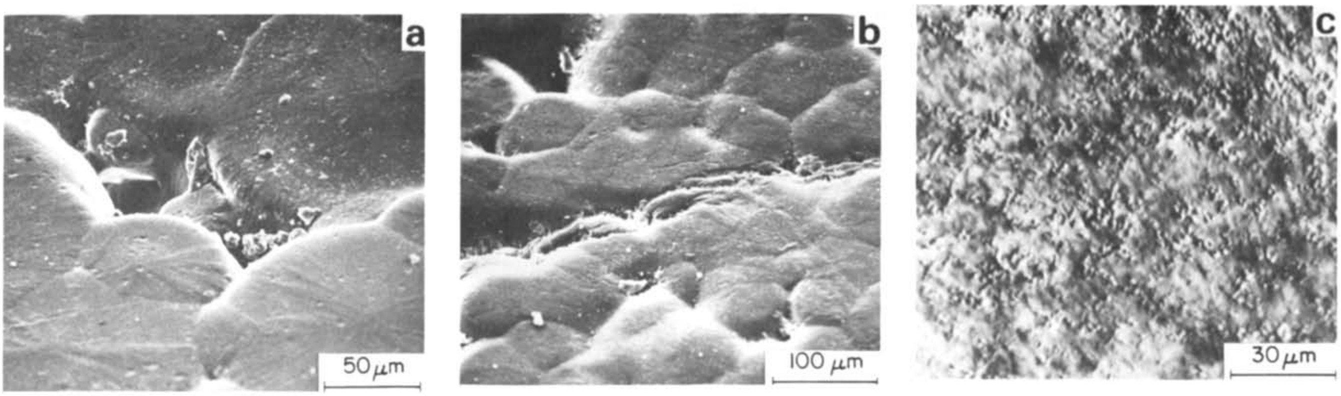

Figure 16 Inner surface of car coolant reservoir tank in sequential copolymer, showing large PP spherulites, ethylene polymer globules and interspherulitic cracks. (a) S.e.m. micrograph, prior to test. (b) S.e.m. micrograph, after proof test. (c) D.i.c. examination

answer this question, a melt pressed sample of sequential copolymer was melted on a hot plate at 230°C and then transferred to the d.i.c. microscope, and observations made as the polymer cooled. *Figure 14a* shows the globules in the molten state, and *Figure 14b* shows the molten polymer starting to crystallize. It is obvious that the globules already existed in the melt before the crystallization process started, refuting the proposal by some workers that the globules result from the exclusion of the ethylene-rich polymer from the crystallizing PP matrix[5]. The average size of the droplets in the melt is less than that observed in samples 1 and 2 in *Table 1*, indicating that some growth has taken place for the latter samples.

The appearance of globular texture has been compared for compression moulded samples of sequential copolymer, one of which was crystallized isothermally at 125°C for 1 h, and the other quench cooled from the melt originally at 230°C. *Figures 15a* and *15b*, respectively, show globule sizes of 4–7 μm for the former, and 0.5–1 μm for the latter.

Examination of many coolant reservoir tanks manufactures by extrusion blow moudling in sequential copolymer reveals that the comparatively slow cooling of the inner surface results in a proliferation of globules, and the growth of PP spherulites of very large size, 150–300 μm. There is also evidence that the globules mainly reside in the regions between the spherulites (see *Figures 16a–c*); further, they consist of ethylene polymers which melt in the temperature region imposed in the proof test. It is already known that PP of coarse texture is prone to interspherulitic cracking, a situation which is aggravated in the case of the coolant tanks by the internal pressure and the aggressive environment. The globules are thus located in a very vulnerable part of the texture, but whether they act as 'crack-stoppers', or are favoured areas for attack by the ethylene glycol (antifreeze) solution is still not known.

ACKNOWLEDGEMENT

Po-Len Yeh was supported for part of this programme by the Polymer Engineering Directorate of the Science and Engineering Research Council and by R. B. Blowmoulders Ltd.

REFERENCES

1 See, for example, Heggs, T. G. in 'Block Copolymers' Ch. 8 (Ed. D. C. Allport and W. H. Janes), Applied Science Publishers, London, 1973; also Kojima, M. *J. Macromol. Sci.-Phys.* 1981, **B19**, 523; and: Ramsteiner, F., Konig, G., Heckmann, W. and Gruber, W. *Polymer* 1983, **24**, 365
2 Ng, P. C., Yeh, P.-L., Gilbert, M. and Birley, A. W. *Polymer* 1984, **25** (*Commun.*), 250
3 Thamm, R. C. *Rubber Chem. Tech.* 1977, **50**, 25
4 Wenig, W. *et al. Colloid Polym. Sci.* 1980, **258**, 1009
5 Prentice, P. *Polymer* 1982, **23**, 1189

APPENDIX 1

Summary of polymers examined.
Homopolymers—polypropylene

Profax 6824 (Hercules Powder) MFI (230/2.16) 0.3
Propathene GWM 22 (ICI) MFI (230/2.16) 4.0

—polyethylene (used in blends)

Unifos 0905 (high density; Unifos Kemi AB) MFI (190/2.16) 0.13

Dowlex 2945 (linear low density; Dow Chemical) MFI (190/2.16) 1.2

Sequential copolymers (ethylene on propylene)

Profax 7824 (Hercules Powder) MFI (230/2.16) 0.39
Profax 7631 (Hercules Powder) MFI (230/2.16) 2.0
Propathene HSE 110 (ICI). Many development polymers examined, including those made by gas phase reaction and diluent processes. MFI (230/2.16) 0.38–0.72

Random copolymer (ethylene and propylene)

Intolan 170A (ISR); E/P ratio 57/43