Characterization, morphology and thermal properties of ethylene–propylene block copolymers

Zhenhua Sun*, Fusheng Yu and Yuchen Qi
Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, Jilin, China
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Characterization, morphology and thermal properties of commercial ethylene–propylene block copolymers have been studied by ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy, differential scanning calorimetry (d.s.c.), dynamic mechanical analysis (d.m.a.) and scanning electron microscopy (SEM). The results obtained show that there exists some ethylene–propylene random copolymer in the block copolymers extractable by n-heptane. The possibility of forming PP-b-PE diblock copolymer is questionable on the basis of the effects of residual propene and the chain-transfer reaction in the sequential copolymerization. A difference in the thermal properties between commercial ethylene–propylene block copolymers and PP/PE blends was noticed, which cannot be used to identify PP-b-PE diblock copolymer. The multiphase structure has been confirmed by d.m.a. and SEM, with ethylene–propylene random copolymer and polyethylene forming the domains in the matrix of polypropylene.

(Keywords: ethylene–propylene copolymer; thermal analysis; blends; morphology; polypropylene)

INTRODUCTION

It is known that homopolymer polypropylene shows unsatisfactory impact strength at low temperatures, owing to its relatively high glass transition temperature and its large spherulite dimension. Two means are often used to overcome this shortcoming; one is the production of physical blends of the homopolymer with various types and amount of rubbers, and the other is developing copolymers.

The synthesis of ethylene–propylene block copolymers with Ziegler–Natta catalysts has been widely studied[1,2]. The formation of block structures, however, has been disputed[3–8] and is difficult to be identified as the result of chain-transfer reactions in the subsequent polymerization. No definite evidence has been presented for the formation of true block structure. The evidence to date has been based on the comparison of the properties of the product prepared by a monomer sequential copolymerization technique with those of homopolymer blends[6–11]. Evidence has been presented for the existence of true block structure by comparing the thermal properties of the sequential polymerization products with those of known mechanical blends of comparable compositions[6]. Recently, the morphology of such ethylene–propylene block copolymers has been widely studied by a variety of techniques. These results have confirmed that there exists amorphous ethylene–propylene random copolymer (EPR) in such block copolymers, which is removable by physical means[12–19]. Therefore, using differences between thermal and mechanical behaviour of the presumed ethylene–propylene block copolymers and polypropylene (PP)/polyethylene (PE) blends as evidence for the existence of true block copolymers is questionable, because EPR can act as a compatibilizer in PP/PE blends to enhance mechanical properties and change thermal properties of PP/PE blends[20–24].

The objective of this paper is to study the molecular characteristics, morphology and thermal properties of some commodity ethylene–propylene block copolymers giving particular attention to the relationship between the structure and properties of such copolymers.

EXPERIMENTAL

Samples

Commercially available ethylene–propylene block copolymers supplied by Yanshan Petrochemical Co. were used in this study. Their characteristics are listed in *Table 1*. Blending of PP and PE was carried out with Plasti-Corder Brabender for 10 min at 185°C.

^{13}C n.m.r.

^{13}C n.m.r. spectra were made on a Jeol FX-100 pulsed Fourier transform n.m.r. spectrometer at 120°C with observation frequency at 25 MHz. Samples were prepared as 10–15% (w/v) solutions of polymer in a 50/50 mixture of *o*-dichlorobenzene/deutero-*o*-dichlorobenzene. The pulse interval was 10 s and the pulse angle was 90°, and the number of transients accumulated was more than 4000. The spectra were proton noise decoupled.

Differential scanning calorimetry

Differential scanning calorimetry scans were recorded on a Perkin–Elmer DSC-7 thermal analyser under N_2 atmosphere. A sample weighing 8 ± 1 mg was used. The sample was heated to 200°C and maintained at 200°C for 3 min to eliminate thermal history effects. In the cooling cycle, the sample was cooled from 200 to 50°C under a controlled cooling rate of 10°C min^{-1}. Once the

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* To whom correspondence should be addressed

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Table 1 Characteristics of samples

Samples	Content of ethylene (mol%)	Melt index (g per 10 min)
Copolymer 1	18.2	16
Copolymer 2	18.4	12.5
Copolymer 3	19.2	10
Copolymer 4	19.6	21
Copolymer 5	21.2	1.4
Copolymer 6	24.2	15
iPP	–	10
HDPE	–	0.9

sample had reached 50°C, it was kept at this temperature for 3 min and the melting behaviour was recorded by heating the sample from 50 to 200°C under the programmed rate of 10°C min^{-1}.

Dynamic mechanical analysis

Specimens for d.m.a. were thin films which were compression moulded at 200°C and air quenched. The specimens, approximately 35 mm long and 4 mm wide with a nominal thickness between 0.10 mm and 0.20 mm were examined on a direct-reading viscoelastometer (Rheovibron DDV-II-EA) operating at 3.5 Hz and a heating rate of 3°C min^{-1}.

Microscopy

Scanning electron micrographs of the samples were obtained on a Jeol-JXA-840 microscope. Notched impact specimens of the block copolymers were frozen in liquid nitrogen for 1 h, placed in a frame and quickly fractured in the impact mode. Fractured surfaces were etched in xylene at room temperature for 8 h.

RESULTS AND DISCUSSION

Molecular characterization of sequence distribution

The ^{13}C n.m.r. spectrum of an ethylene–propylene block copolymer is given in *Figure 1*, and the terminology used in the analysis is that of Carman *et al.*[25], where S, T and P refer respectively to secondary (methylene), tertiary (methine), and primary (methyl) carbons. The Greek subscripts refer to the distance of a given carbon atom from the neighbouring methine carbon atom bearing a methyl group. The assignment of ^{13}C resonance lines are made on the basis of Cheng's work[26].

Thus, the ^{13}C n.m.r. spectrum of an ethylene–propylene block copolymer should have four major peaks representing the CH_3 ($P_{\beta\beta}$), CH ($T_{\beta\beta}$), CH_2 ($S_{\alpha\alpha}$) carbons from the polypropylene segments and the CH_2 ($S_{\delta\delta}$) carbons from the polyethylene segments. As seen in *Figure 1*, not only resonance peaks of $P_{\beta\beta}$, $T_{\beta\beta}$, $S_{\alpha\alpha}$ and $S_{\delta\delta}$, but also resonance peaks of $S_{\alpha\gamma}$, $S_{\alpha\delta}$, $S_{\beta\delta}$, $S_{\gamma\delta}$ exist in the spectrum. This indicates that some amount of ethylene–propylene junctions exist in the ethylene–propylene block copolymers. The result suggests that there is no inverted propylene sequences in block copolymers. The propylene content P′ and ethylene content E′ are given by:

$$P' = S_{\alpha\alpha} + \tfrac{1}{2}(S_{\alpha\gamma} + S_{\alpha\delta})$$

$$E' = \tfrac{1}{2}[S_{\delta\delta} + S_{\beta\delta} + S_{\alpha\gamma} + \tfrac{1}{2}(S_{\gamma\delta} + S_{\beta\delta} + S_{\alpha\delta})]$$

and the following equations were used to determine the monomer sequence distribution of ethylene–propylene block copolymers:

$$\begin{aligned}
P &= P'/(P' + E') \\
E &= E'/(P' + E') \\
PP &= S_{\alpha\alpha}/(P' + E') \\
PE &= (S_{\alpha\gamma} + S_{\alpha\delta})/(P' + E') \\
EE &= \tfrac{1}{2}(S_{\beta\delta} + S_{\delta\delta} + \tfrac{1}{2}S_{\gamma\delta})/(P' + E') \\
PPP &= P \times T_{\beta\beta}/(T_{\beta\beta} + T_{\beta\delta} + T_{\delta\delta}) \\
PPE &= P \times T_{\beta\delta}/(T_{\beta\beta} + T_{\beta\delta} + T_{\delta\delta}) \\
EPE &= P \times T_{\delta\delta}/(T_{\beta\beta} + T_{\beta\delta} + T_{\delta\delta}) \\
EEE &= \tfrac{1}{2}(S_{\delta\delta} + \tfrac{1}{2}S_{\gamma\delta})/(P' + E') \\
EEP &= S_{\alpha\delta}/(P' + E') \\
PEP &= \tfrac{1}{2}S_{\alpha\gamma}/(P' + E')
\end{aligned}$$

Owing to the overlapping of $S_{\gamma\gamma}$ and $T_{\beta\delta}$, the following relationship was used to resolve the two peaks:

$$S_{\gamma\gamma} = \tfrac{1}{2}(S_{\beta\delta} - S_{\gamma\delta})$$

The sequence information of six samples of the block copolymer is listed in *Table 2*. It is clear that there exist in the block copolymers not only sequences of PP, PPP, EE, EEE that represent the polypropylene and polyethylene segments, respectively, but also PE, PEP, EPE, PPE and EEP originating from ethylene–propylene random copolymer segments.

From the mechanism of Ziegler–Natta catalysed reaction, the presence of EPR may be due to a chain-transfer mechanism and the existing residual propylene monomer during the transition from propylene monomer feedstock to ethylene monomer.

Considering the mean lifetime of the growing polymer chains, the chain-transfer mechanism, and the residual propylene monomer in the polymerization process, the ethylene–propylene block copolymers may be a mixture of PP, polypropylene-b-(ethylene-propylene tapered block), random EPR, and PE.

In order to characterize components of the block copolymers, pellets were pressed into 0.04–0.08 mm thick

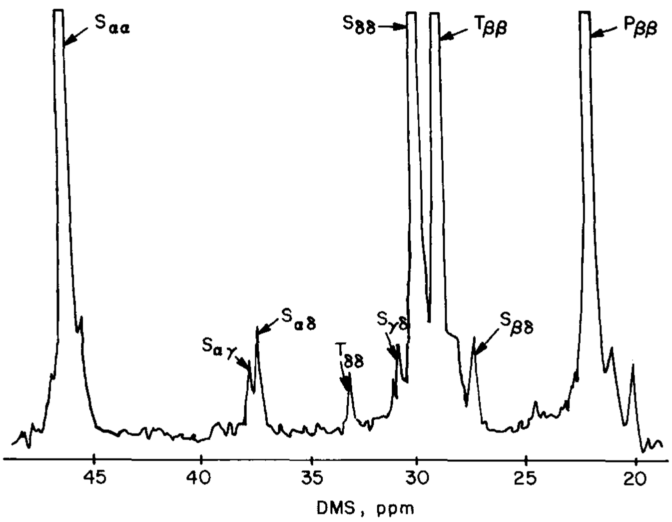

Figure 1 Typical ^{13}C n.m.r. spectrum of an ethylene–propylene block copolymer

Table 2 Mole fraction of n-ad distributions of block copolymers

Sample	P	E	PP	PE	EE	PPP	PPE	EPE	EEE	EEP	PEP
Copolymer 1	81.8	18.2	80.4	2.8	16.7	79.4	1.3	1.1	15.7	1.6	0.6
Copolymer 2	81.6	18.4	79.3	4.7	15.9	78.7	2.0	1.0	14.4	2.3	1.2
Copolymer 3	80.8	19.2	78.8	3.9	17.2	78.3	1.4	1.0	15.8	2.2	0.9
Copolymer 4	80.4	19.6	78.9	2.9	18.3	78.8	1.1	0.8	17.5	1.8	0.6
Copolymer 5	78.8	21.2	77.2	3.1	19.9	74.6	3.7	0.5	19.5	1.7	0.7
Copolymer 6	75.8	24.2	73.3	5.1	21.6	73.1	1.3	1.3	20.3	2.8	1.2

Table 3 Weight percentage of extraction in block copolymers

Sample	Content of extraction (wt%)
Copolymer 1	5.9
Copolymer 2	3.9
Copolymer 3	4.4
Copolymer 4	4.1
Copolymer 6	5.6

films in a hydraulic press at about 200°C for 3 min, and fractionation occurred by extraction of the films by refluxing n-heptane in a Soxhlet apparatus for 48 h. The weight percentage of extractions are listed in *Table 3*, showing that 4–6 wt% of the block copolymers can be extracted by n-heptane. The molecular characteristic of the extracted fraction was determined by ^{13}C n.m.r., and the results obtained are listed in *Table 4*.

From the above results, it can be concluded that a large amount of the ethylene–propylene random copolymer exists in the ethylene–propylene block copolymers. *Table 5* shows that the content of ethylene and ethylene–propylene random copolymer sequence is greatly reduced after extraction, but the ethylene–propylene random copolymer sequence cannot be removed completely due to the following factors: the thickness of films, the limited solubility of EPR with long ethylene or propylene sequence in n-heptane, the interfacial penetration between EPR and PP and PE, and the possible existence of some amount of PP-b′-(ethylene–propylene tapered block) block copolymer.

Thermal properties

The difference in thermal properties between block copolymers and PP/PE blends has been studied widely[6–9]. Ke[7,8] and Barrall[9] have found that two melting peaks existed in both block copolymers and PP/PE blends, and two crystalline peaks in block copolymers but only one in blends. However, by studying the effect of thermal history and cooling rate on the crystalline behaviour of blends, Wang[6] found two crystalline peaks in blends at low cooling rate and in samples annealed above the melting temperature of PP. Meanwhile, he found that the melting temperature and the heat of fusion of PP and PE in block copolymers is a few degrees lower than that in blends, and the presence of true block structure in the block copolymers is inferred. Our studies on six block copolymers show that two crystalline peaks are present in five block copolymer samples but only one in sample 5, and two melting peaks were observed for all samples (*Figures 2* and *3*).

The relation between T_m(PE) (melting temperature of

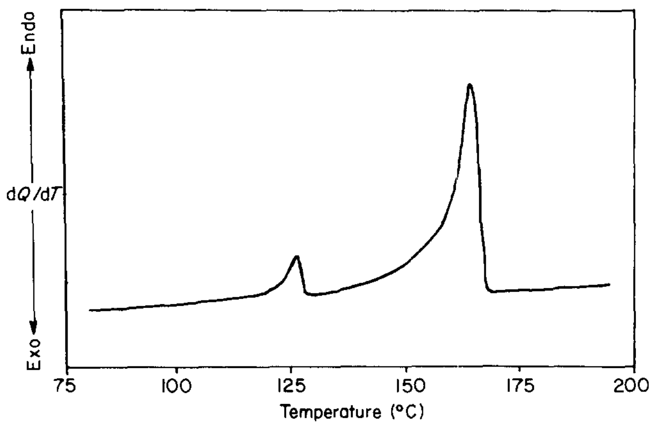

Figure 2 Melting behaviour of copolymer 6

Table 4 Mole fraction of n-ad distributions of n-heptane-soluble fractions from block copolymers

Sample	P	E	PP	PE	EE	PPP	PPE	EPE	EEE	EEP	PEP
Copolymer 1	41.1	58.9	31.7	18.8	49.4	31.1	4.3	5.8	42.9	12.4	3.2
Copolymer 2	47.7	52.3	34.8	21.1	39.4	34.8	8.9	5.9	31.7	15.3	5.2
Copolymer 4	45.5	54.5	33.3	24.2	41.5	27.3	12.5	5.5	34.0	11.6	6.3
Copolymer 6	39.8	60.2	29.5	20.6	49.6	25.7	10.6	3.5	41.8	14.7	3.0

Table 5 Mole fraction of n-ad distributions of n-heptane-insoluble fractions from block copolymers

Sample	P	E	PP	PE	EE	PPP	PPE	EPE	EEE	EEP	PEP
Copolymer 1	87.0	13.0	86.0	2.0	12.2	85.3	0.9	0.7	11.9	1.2	0.4
Copolymer 2	83.0	17.0	81.6	2.6	15.1	81.0	1.2	0.8	13.1	1.6	0.5
Copolymer 4	83.4	16.6	82.4	2.0	14.4	80.6	1.9	0.4	12.3	1.3	0.3
Copolymer 6	84.5	15.5	83.7	1.8	14.4	81.5	2.2	0.9	13.5	0.9	0.3

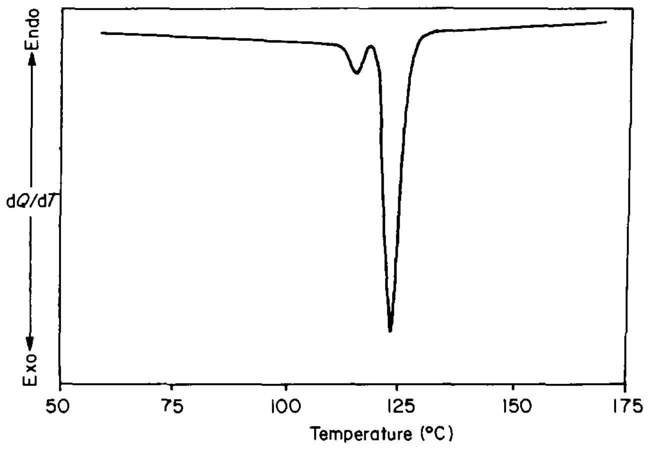

Figure 3 Crystallization behaviour of copolymer 6

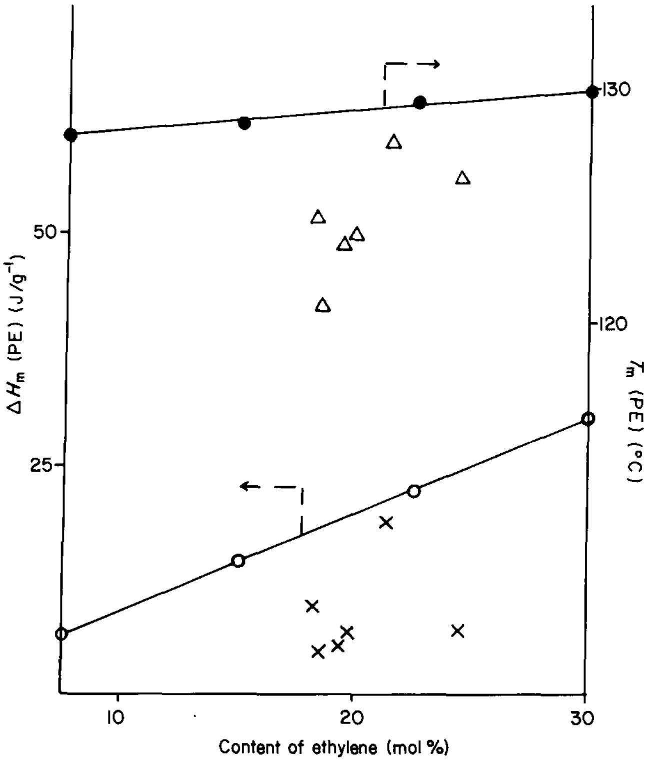

Figure 4 Relationship between T_m(PE) and ΔH_m(PE) and the content of PE. ○, ΔH_m(PE) of blends; ●, T_m(PE) of blends; ×, ΔH_m(PE) of block copolymers; Δ, T_m(PE) of block copolymers

PE) and ΔH_m(PE) (heating fusion of PE) with the content of PE in block copolymers and blends is shown in *Figure 4*. The results show that T_m(PE) and ΔH_m(PE) of blends increase linearly with the content of PE, but no clear correlations of T_m(PE) and ΔH_m(PE) with the content of PE exist in block copolymers. Furthermore, the values of T_m(PE) and ΔH_m(PE) of block copolymers is much lower than that of the blends with the same content of PE. Wang used these phenomena as evidence for the formation of PP-b-PE true block structure, explained in terms of restricted block movement due to covalent bond between blocks that affect the crystallization processes in block copolymers. However, the authors ignored the random copolymerization of ethylene with residual propylene in the sequential copolymerization process. When considered, this random copolymerization could bring many defects to the polyethylene chains, thus, the depression of T_m(PE) and ΔH_m(PE) is not necessarily evidence for true block structure in block copolymers.

The relation between T_m(PP) (melting temperature of PP) and ΔH_m(PP) (heating fusion of PP) with content of PP in block copolymers and blends is shown in *Figure 5*. Not much depression of T_m(PP) and ΔH_m(PP) of block copolymers is found compared with those of the blends having the same content of PP.

By comparing the thermal properties of block copolymers before and after extraction with n-heptane, we found that solvent extraction has a marked effect on the thermal properties of block copolymers, especially on the crystalline behaviour (see *Table 6*).

From the data in *Table 6*, it can be found that the crystalline peak temperature of PE(T_c(PE)) increases and the crystalline peak temperature of PP(T_c(PP)) decreases after extraction. This is due to the substances that act as

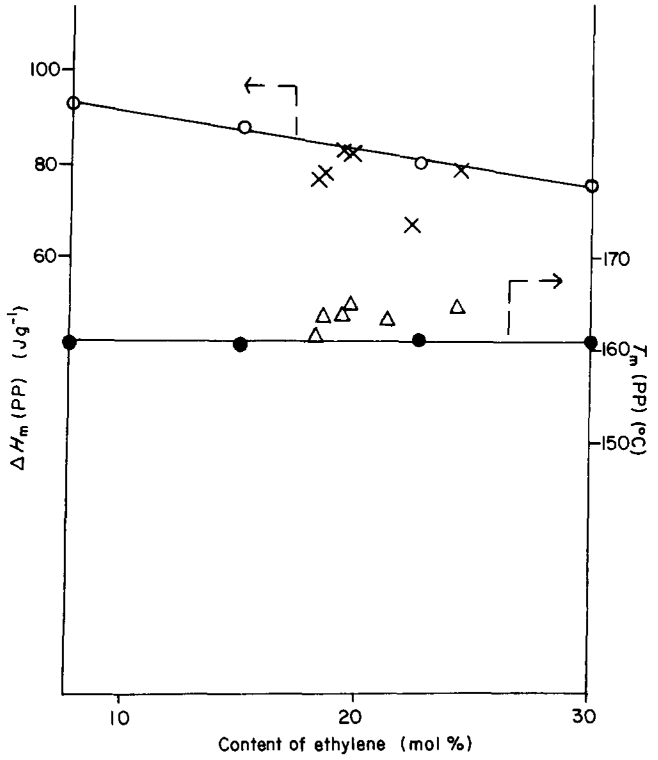

Figure 5 Relationship between T_m(PP) and ΔH_m(PP) and the content of PP. ○, ΔH_m(PP) of blends; ●, T_m(PP) of blends; ×, ΔH_m(PP) of block copolymers; Δ, T_m(PP) of block copolymers

Table 6 Crystallization temperature of block copolymers

Sample		T_c (PP) (°C)	T_c (PE) (°C)	Number of peak(s)
Copolymer 1	Original	116.1	111.1	2
	Extracted	114.3	114.3	1
Copolymer 2	Original	118.8	105.3	2
	Extracted	118.3	107.1	2
Copolymer 3	Original	117.0	112.2	2
	Extracted	114.7	114.7	1
Copolymer 4	Original	119.3	111.8	2
	Extracted	117.3	113.2	2
Copolymer 5		115.2	115.2	1
Copolymer 6	Original	122.7	114.5	2
	Extracted	122.4	115.3	2

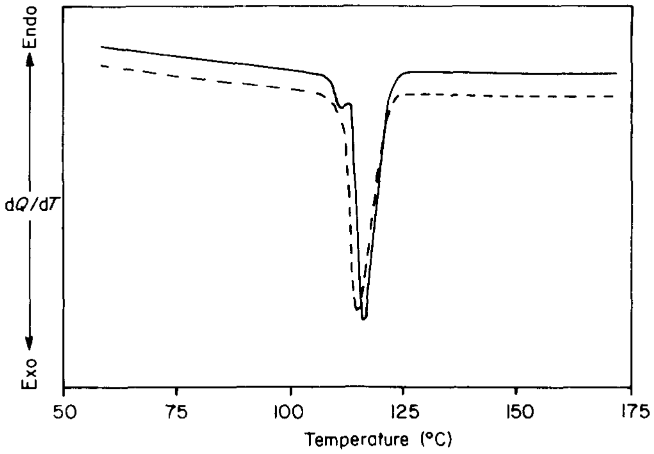

Figure 6 Crystallization behaviour of copolymer 1 before (———) and after (– – –) n-heptane extraction

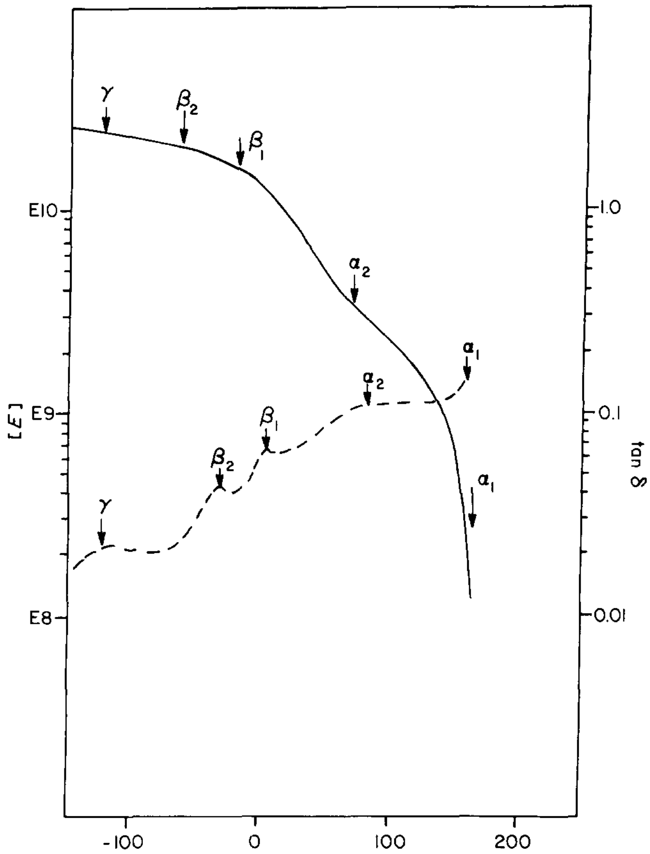

Figure 7 Dynamic mechanical properties of copolymer 5. ———, $[E]$; – – –, tan δ

nucleating agents for PP and EPR and also hinder the crystallization of PE being removed by extraction. Therefore, the extraction makes the two crystalline peaks of PP and PE shift closer together and even become one. The crystalline behaviour of sample 1 is shown in *Figure 6*. After extraction, the two crystalline peaks become one. This indicates that one or two crystalline peaks in block copolymers has no relation to the true block structure.

Morphology

Dynamic mechanical analysis and SEM are effective methods to reveal the morphology of the multi-phase structure of polymer alloys. In *Figure 7*, the five transitions denoted as α_1, α_2, β_1, β_2 and γ reveal the multi-phase feature of the block copolymers. The α_1, α_2, β_1 and γ transitions are related to different mechanisms of molecular motion of PP and PE[27], but the β_2 transition, at $-50°C$ to $-30°C$, is the glass transition of EPR in block copolymers. These results also imply the existence of ethylene–propylene random copolymer segments in block copolymers.

From the fractographs of the surfaces of the brittle fractured samples (*Figure 8*), the two-phase structure could be clearly seen indicating the immiscibility of PE,

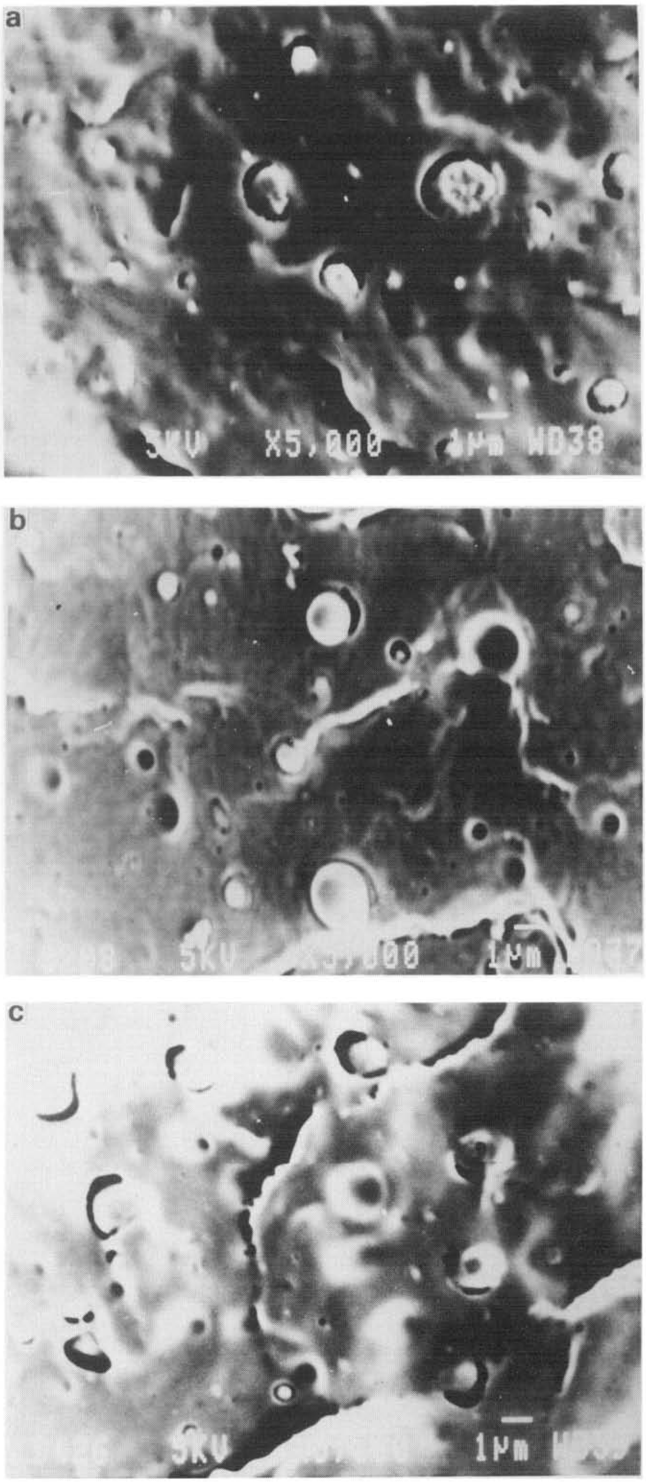

Figure 8 Scanning electron micrographs of block copolymers. Copolymer: (a) 3, (b) 4, (c) 5

EPR with PP. Considering the effects of EPR on crystalline behaviour of PE, the dispersed phases should be composed of PE and EPR.

CONCLUSIONS

From the results above, it can be concluded that:

1. the residual propylene and chain-transfer reaction of the Ziegler–Natta catalyst lead to the formation of EPR during a two-step copolymerization process, and the EPR has a large influence on the properties of block copolymers;
2. the thermal properties of block copolymers differ from those of PP/PE blends, but no certain evidence can be drawn from the comparison of them to support the formation of true block structure, and
3. the two-phase structure has been revealed in block copolymers, with PE combining with EPR to form the dispersed domains in a PP matrix.

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