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0032-3861/98/$ - see front matter

Synthesis and characterization of isotactic polystyrene-b-poly(ethylene-*co*-propylene)

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A variety of isotactic polystyrene-b-poly(ethylene-co-propylene) diblock copolymers were synthesized directly by using $TiCl_4/MgCl_2/Al(i\text{-}Bu)_3$ catalyst system modified by rare earth compound of $NdCl_x(OR)_y$ which was developed in our laboratory. The influence of temperature, catalyst and cocatalyst concentration, prepolymerization time and monomer feed ratio on the copolymerization were investigated and optimized. After successive extracting the copolymerization products with suitable solvents, the isolated block copolymer (about 20–30 wt.% content in total), which is soluble in boiling butanone or chloroform was characterized in detail by ^{13}C n.m.r. spectroscopy, gel-permeation chromatography (g.p.c), differential scanning calorimetry (d.s.c), X-ray diffraction, transmission electron micrographs (TEM), etc., which showed that this kind of copolymer containing isotactic polystyrene segments was semi-crystalline diblock copolymer with special microphase separation structure. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: isotactic polystyrene-b-poly(ethylene-*co*-propylene); synthesis; characterization)

INTRODUCTION

Copolymerization of styrene and olefins by a conventional Ziegler–Natta catalyst have been reported by several authors since 1964[1–5]. Ziegler–Natta catalytic methods are commonly used throughout the polymer industry, especially for the production of ethylene, propylene and their copolymers. However, for a vinyl aromatic comonomer, such as styrene, the polymerization activity is low, such that an styrene/olefin copolymer usually has low yield or small content of styrene units. In addition, conventional Ziegler–Natta catalysts consist of multiple active species which differ in the oxidation states of their transition metals, stereospecificity, etc., therefore, many reported copolymers in the previous literature are actually mixtures of large amounts of homopolymers and some copolymers with polymer chains of varying length.

More recently, we have developed a highly active catalyst system modified by a rare earth compound of $NdCl_x(OR)_y$. Studies show that this catalyst system has high yield, high catalytic efficiency and high isotacticity for the homopolymerization of styrene[6]. Moreover, it also has comparatively stable oxidation state and longer active lifetime, which has been used successfully for the copolymerizations (both random and block) of styrene with ethylene[7,8], styrene with propylene[9,10] and styrene with butene[11]. In this paper, the same catalyst system will be used for the ternary diblock copolymerization of styrene with ethylene and propylene. We present the details of both the synthesis and the structural characterization of isotactic polystyrene-b-poly(ethylene-co-propylene) [iPS-b-Poly(E-*co*-P)] copolymers.

EXPERIMENTAL

Catalyst preparation

The catalyst system was mainly composed of $TiCl_4/MgCl_2/NdCl_x(OR)_y/Al(i\text{-}Bu)_3$, and the procedures of preparation were carried out according to the method described previously[12].

Copolymerization

The polymerization was conducted in a 250 ml glass reactor equipped with a mechanical agitator. purified anhydrous toluene (80 ml) and freshly distilled styrene (20 ml) were charged into the reactor. The catalyst was activated by triisobutylaluminium $[Al(i\text{-}Bu)_3]$ in another flask for 5 min under N_2 atmosphere. The prepolymerization of styrene was initiated by introducing the activated catalyst into the polymerization reactor at definite temperature with vigorous stirring. After 5–30 min, the gaseous monomer mixture (ethylene and propylene) was fed on demand to start block copolymerization, and the pressure was kept at 115 kPa. The total polymerization reaction was conducted for 2 h and terminated by adding a dilute hydrochloric acid solution in ethanol. The polymerization product was washed with excess ethanol and dried at 50°C in vacuum. The binary diblock copolymer of isotactic polystyrene block isotactic polypropylene (iPS-b-iPP), the random copolymer of poly(ethylene-co-propylene), and the homopolymers of isotactic polystyrene (iPS), isotactic polypropylene (iPP) were also prepared with the same catalyst and under the same conditions.

Measurements

The composition of the polymerization product was determined by measuring the volume of the consumed

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ethylene and propylene. The crude polymer was fractionated by successive extraction with boiling butanone, boiling heptane and 55°C chloroform. ^{13}C n.m.r. spectra of the block copolymers (20 g/100 ml in chloroform) were recorded at 55°C using a JEOL FX-90Q spectrometer operating at 22.5 MHz. The molecular weights of block copolymers were measured with a Waters GPC-244 using polystyrene standards. Chloroform was used as solvent. Differential scanning calorimetry thermograms were obtained on a Perkin-Elmer DSC 7 at scanning rates of 10°C/min. The X-ray diffraction curves were made with a Regahu D/max-3A Diffraction (Cu Kα). Transmission electron microscopy (TEM) studies were carried out on a JEOL JEM-100CX/II instrument. The samples were stained with RuO_4 vapor for 1 h.

RESULTS AND DISCUSSION

Copolymerization

Experiments had shown that the $TiCl_4$ catalyst modified by $NdCl_x(OR)_y$ had much higher activity for the homopolymerization and copolymerization of styrene and α-olefins than many other conventional Ziegler–Natta catalysts[6,7]. The Nd → Cl → Ti bridge may increase the density of electron cloud of titanium, weaken the Ti–C bond, and consequently increase the ability of coordination reaction for the active species. Moreover, $NdCl_x(OR)_y$ in the catalyst system seems to play a role of a promoter for enhancing the activity of styrene. It is possible that a weak action of the f electrons of Nd in the active centres with the π electrons of styrene attracts and activates styrene molecules. Thus, copolymers with higher styrene unit and isotacticity can be made easily by the present catalyst system.

The influence of temperature on the block copolymerization is shown in *Figure 1*. The catalytic efficiency has a maximum value of 1.62 kg-P/g Ti at 65°C. Temperature below 65°C is not favourable for the polymerization of styrene because of its large space hindrance and high activation energy. Higher temperature is good for increasing the polymerization rate constant, k_p, but it also increases the probability of chain transfer reaction, and lowers the solubility of gaseous monomers in solvent.

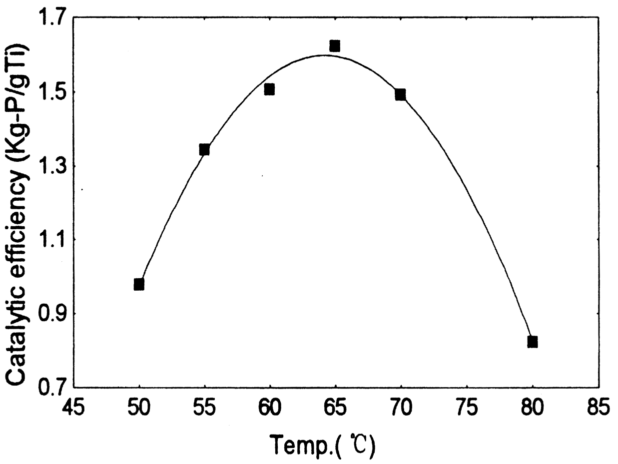


Figure 1 Effect of temperature on copolymerization of styrene with propylene/ethylene. Copolymerization conditions: [Ti] = 1.5–1.6 mmol/l; prepolymerization time of styrene, 10 min; comonomer feed ratio, [P]:[E] = 90:10 (mol/mol); [Al/Ti] = 20 (mol/mol); solvent, toluene; pressure, 115 kPa

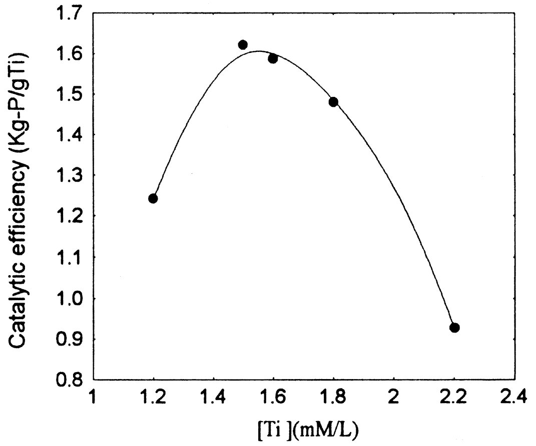


Figure 2 Effect of catalyst concentration on copolymerization of styrene with propylene/ethylene. Copolymerization conditions: prepolymerization time of styrene, 10 min; comonomer feed ratio, [P]:[E] = 90:10 (mol/mol); [Al/Ti] = 20 (mol/mol); temp., 65°C; solvent, toluene; pressure, 115 kPa

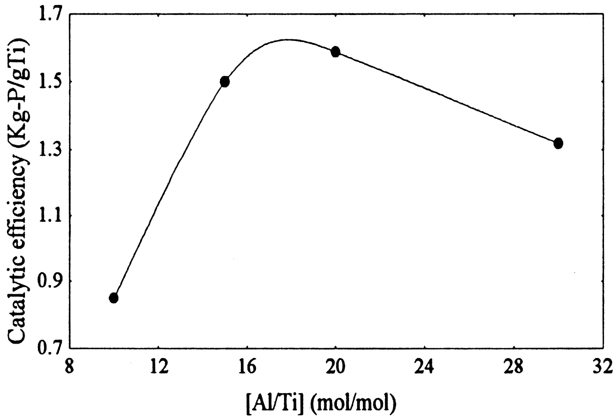


Figure 3 Effect of Al/Ti ratio on copolymerization of styrene with propylene/ethylene. Copolymerization conditions: [Ti] = 1.5–1.6 mmol/l; prepolymerization time of styrene, 10 min; comonomer feed ratio, [P]:[E] = 90:10 (mol/mol); temp., 65°C; solvent, toluene; pressure, 115 kPa

Figure 2 gives out the effect of catalyst concentration on the catalytic efficiency of block copolymerization. The catalyst yield increases with decreasing catalyst concentration. The peak value of yield is at the titanium concentration of 1.5–1.6 mM/l. This phenomenon occurs frequently in many Ziegler-type polymerizations.

Triisobutylaluminium [$Al(i-Bu)_3$] plays an important role in the copolymerization process. Apart from being used as cocatalyst to activate the titanium catalyst and monomers, it can help to consume the trace impurity that may be in the reactor, such as water, oxygen, etc. In addition, $Al(iBu)_3$ is also one of the major chain transfer agents in the polymerization system. Thus, one can see from *Figure 3* that there is an optimum $Al(i-Bu)_3$ concentration, i.e. [Al/Ti] = 15 (mol/mol) for the present block copolymerization to get good yield.

The results of the block copolymerization of styrene with ethylene/propylene carried out by changing the prepolymerization time of styrene and the feed ratio of gaseous monomers are summarized in *Table 1*. It is evident that by extending the prepolymerization time of styrene, the content of iPS segment in copolymerization product increases at the expense of catalytic efficiency. This is because the $TiCl_4$ catalyst system has much higher activity for the polymerization of α-olefins than for styrene monomer. The

Table 1 Effect of prepolymerization time and monomer feed ratio on catalytic efficiency and composition of copolymerization products

Run	Monomer feed ratio [P]:[E] (mol.%)	Styrene prepolymerization time (min)	Efficiency (kg-P/g Ti)	Composition of products (wt.%) [St]:[P]:[E]
D_{-5}	100:0	5	1.21	57:43:0
D_{-10}	100:0	10	1.07	67:33:0
D_{-15}	100:0	15	0.97	74:26:0
D_{-20}	100:0	20	0.78	86:14:0
D_{-30}	100:0	30	0.72	93:7:0
$T_{90\text{-}5}$	90:10	5	1.86	48:48:4
$T_{90\text{-}10}$	90:10	10	1.62	60:37:3
$T_{90\text{-}20}$	90:10	20	1.22	71:27:2
$T_{90\text{-}30}$	90:10	30	0.93	85:14:1
$T_{80\text{-}5}$	80:20	5	2.30	30:60:10
$T_{80\text{-}10}$	80:20	10	2.00	45:47:8
$T_{80\text{-}20}$	80:20	20	1.56	61:34:5
$T_{80\text{-}30}$	80:20	30	1.18	70:26:4
$T_{80\text{-}40}$	80:20	40	0.95	86:12:2
$T_{66\text{-}10}$	66:33	10	2.16	41:44:15
$T_{66\text{-}20}$	66:33	20	1.78	56:33:11
$T_{66\text{-}30}$	66:33	30	1.33	69:23:8
$T_{66\text{-}40}$	66:33	40	1.02	80:15:5

Polymerization conditions: [Ti] = 1.5–1.6 mmol/l; [Al/Ti] = 20 (mol/mol); [St] = 20 g/100 ml; total polymerization time, 2 h; temperature, 65°C; pressure, 115 kPa; solvent: toluene.

Table 2 Results of fractionation of the polymerization products

Run	Boiling butanone soluble fraction (12 h; wt.%)	Boiling heptane soluble fraction (12 h; wt.%)	55°C chloroform soluble fraction (4 h; wt.%)	Remnant fraction (wt.%)	Total (wt.%)
iPS	5.6	0	6.3	87.8	99.7
iPP	0	4.2	1.1	94.5	99.8
E/P[a]	6.0	78.7	0.2	16.0	99.9
Blend[b]	5.2	38.4	3.8	51.9	99.3
D^{c}_{-10}	23.3	9.3	16.1	50.7	99.4
$T^{d}_{80\text{-}100}$	23.8	12.6	14.9	48.2	99.5
$T_{80\text{-}30}$	16.1	7.4	10.8	64.8	99.1

[a] E/P represents the copolymer of Poly(E-co-P) ([E]:[P] = 20:80 mol/mol)
[b] Blend of iPS/(E/P) (50:50 in wt.%)
[c] Binary block copolymerization products from *Table 1*: [St]:[P] = 67:33 (wt.%)
[d] Ternary diblock copolymerization products from *Table 1*:$T_{80\text{-}10}$, [St]:[P]:[E] = 45:47:8 (wt.%); $T_{80\text{-}30}$: [St]:[P]:[E] = 70:26:4 (wt.%)

catalytic efficiency also increases with increasing the monomer feed ratio of [E]/[P]. For the addition of ethylene unit greatly improve the external environment of active species.

Fractionation and characterization

The Ziegler-type catalysts, even highly isospecific ones, contain multiple active species, resulting in production of not only copolymers but appreciable amounts of homopolymers. Therefore, fractionation for the crude product is necessary to determine the structure of block copolymers. Solvent extraction is one of the efficient methods for fractionation of polymers. The results of successive extraction for the crude copolymerization product with boiling butanone, boiling heptane and 55°C chloroform are given in *Table 2*. For comparison, the extraction was also done for iPS, iPP, the random copolymer of poly(ethylene-co-propylene) and the polyblend of iPS with poly(ethylene-co-propylene) under the same conditions.

It can be seen from *Table 2* that the solubility of the block copolymerization products are different from that of iPS and its polyblend with poly(ethylene-*co*-propylene). Their higher solubility in boiling butanone and chloroform indicate that the block copolymers are mainly distributed in these two fractions. In addition, i.r. studies show that there is still a smaller part of the copolymer which has a long poly(ethylene-co-propylene) segment, and a short iPS segment exists in boiling heptane-soluble fraction. The insoluble residues are those homopolymers of iPS, iPP. etc. with high crystallinity. Apart from block copolymers with lower isotacticity and smaller molecular weight, the butanone-soluble fraction also contains small amounts of atactic polystyrene and some other impurities. By cooling the solution down to 0°C, the block copolymers which have relatively lower solubility in butanone at room temperature can be easily separated from others (see *Figure 4*). The total content of block copolymers in the crude products is about 20–40 wt.%, which differs from copolymerization conditions.

Figure 5 shows the ^{13}C n.m.r. spectra of iPS-b-Poly(E-*co*-P) separated from boiling butanone and chloroform soluble parts, and the spectra of iPS-b-iPP are also given for comparison. The copolymer obtained from the butanone fraction displays multi-peaks at around 146 ppm, which shows that the isotacticity of the polystyrene segment in this copolymer is low. Some expected chemical shifts of monomer sequence distributions that are found in ^{13}C n.m.r. and calculated according to Randall and co-workers[13,14] are listed in *Table 3*.

The molecular weight of the block copolymers are given in *Figure 6*. Broadening in polydispersity might be caused by the multiplicity of active species which differ in propagating rate constants (k_p) as reported in the literature[15]. The molecular weight distribution curve for the

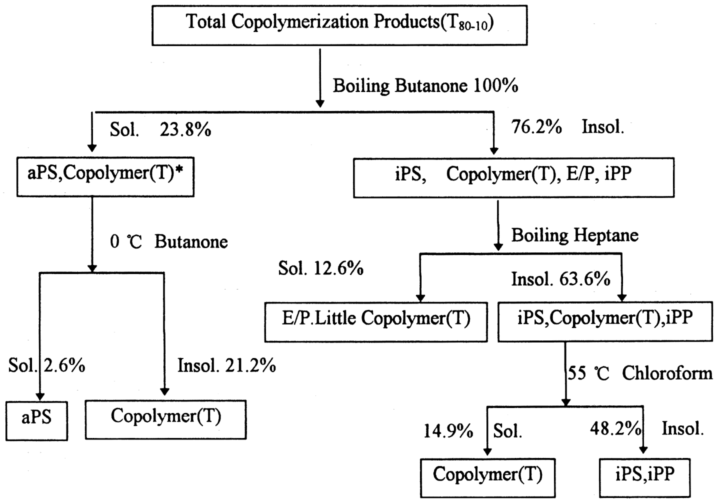
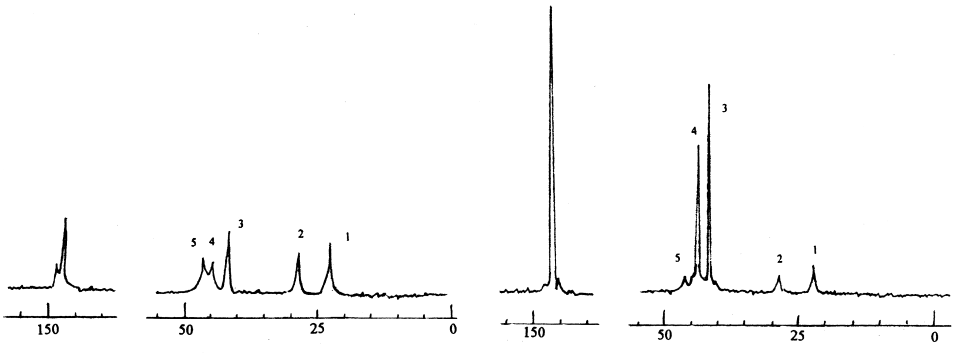
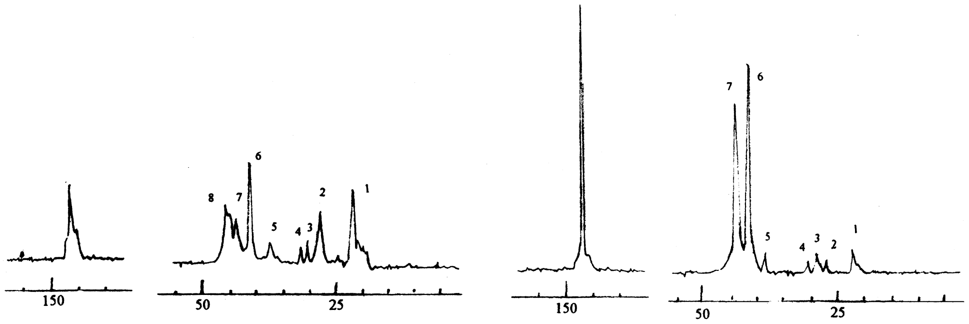


Figure 4 Schedule of solvent extraction fractionation of the copolymerization products (*). Copolymer (T) represents the pure iPS-b-Poly(E/P) block copolymer



(a) Copolymer in Butanone Fraction (b) Copolymer in Chloroform Fraction

(1) iPS-b-iPP (D_{-10})



(a) Copolymer in Butanone Fraction (b) Copolymer in Chloroform Fraction

(2) iPS-b-Poly(E-co-P) (T_{80-10})

Figure 5 ^{13}C n.m.r. spectra of the block copolymers

copolymer shows a unimodal shape, indicating that it does not contain homopolymers.

The thermal and crystalline properties of block copolymers are analysed by d.s.c (*Figure 7*). It can be seen that two endothermic peaks appear in the curve of the iPS-b-iPP copolymer, which may be attributed to the fusion of iPS and iPP segments, respectively, while the copolymer of iPS-b-Poly(E-*co*-P) displays only one peak of iPS. The crystallinity of iPP segment is greatly affected by the insertion of ethylene unit. This indicates that these block copolymers contain long segments of iPS and iPP or random copolymerization chains of Poly(E-*co*-P). Both melting point (T_m) and heat of fusion (ΔH_f) for the copolymers are found to be lower than those for iPS and iPP homopolymers. This conclusion is consistent with the results of X-ray diffraction, as shown in *Figure 8*. Two kinds of diffraction peaks appear in the curve of the iPS-b-iPP copolymer, which corresponds to the crystals of the iPS (i.e. $2\theta = 14.0$, 16.2, 18.1, 21.5°, etc.) and iPP (α-crystal, i.e. $2\theta = 13.9$, 16.7, 18.4, 20.9, 21.7°, etc.) segments, respectively. The

Table 3 Peak assignments of ^{13}C n.m.r. spectra

	Carbon type	Chemical shift (δ, ppm)			Peak no.
		Calculated	Observed (a)	Observed (b)	
D^a_{10} sequence					
SSS	$S_{\alpha\alpha}$	41.2	41.3	41.0	3
	$T_{\beta\beta}$	43.7	43.8	43.3	4
PPP	$S_{\alpha\alpha}$	44.3	44.1	44.5	5
	$T_{\beta\beta}$	26.9	28.0	27.1	2
	CH_3	20.3	22.2	21.7	1
$T^b_{80\text{-}10}$ sequence					
SSS	$S_{\alpha\alpha}$	41.2	40.6	41.0	6
	$T_{\beta\beta}$	43.7	43.4	43.3	7
PPP	$S_{\alpha\alpha}$	44.3	44.9	—	8
	$T_{\beta\beta}$	26.9	27.1	27.0	2
	CH_3	20.3	21.3	21.7	1
PPE	$T_{\beta\delta}$	29.3	29.4	29.4	3
EPE	$T_{\delta\delta}$	31.7	31.0	30.9	4
PEP	$S_{\alpha\delta}$	37.4	37.1	37.8	5
PPE	$S_{\alpha\delta}$	37.1	37.1	37.8	5

S, styrene unit; P, propylene unit; E, ethylene unit

[a] [D_{-10}] from *Table 2*

[b] [$T_{80\text{-}10}$] from *Table 2*

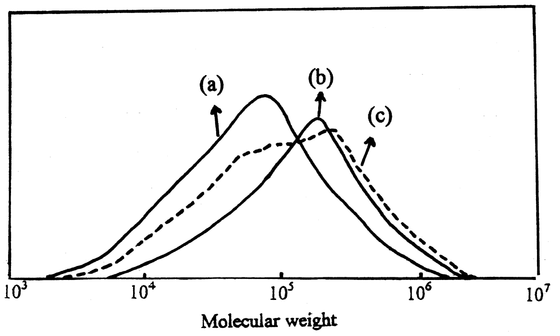


Figure 6 G.p.c. curves of the block copolymers ($T_{80\text{-}10}$). (a) Copolymer in butanone fraction: M_n = 89 000, M_w = 780 000, M_w/M_n = 8.8. (b) Copolymer in chloroform fraction: M_n = 210 000, M_w = 1 600 000, M_w/M_n = 7.6. (c) Crude copolymerization product

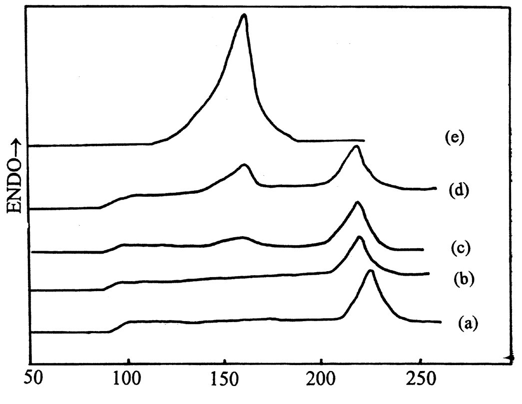


Figure 7 D.s.c. thermograms of iPS, iPP and the block copolymers. (a) iPS; (b) $T_{80\text{-}10}$ [St]:[P]:[E] = 45:47:8 (wt%); (c) $T_{90\text{-}10}$ [St]:[P]:[E] = 60:37:3 (wt%); (d) D_{-10} [St]:[P] = 67:33 (wt%); (e) iPP

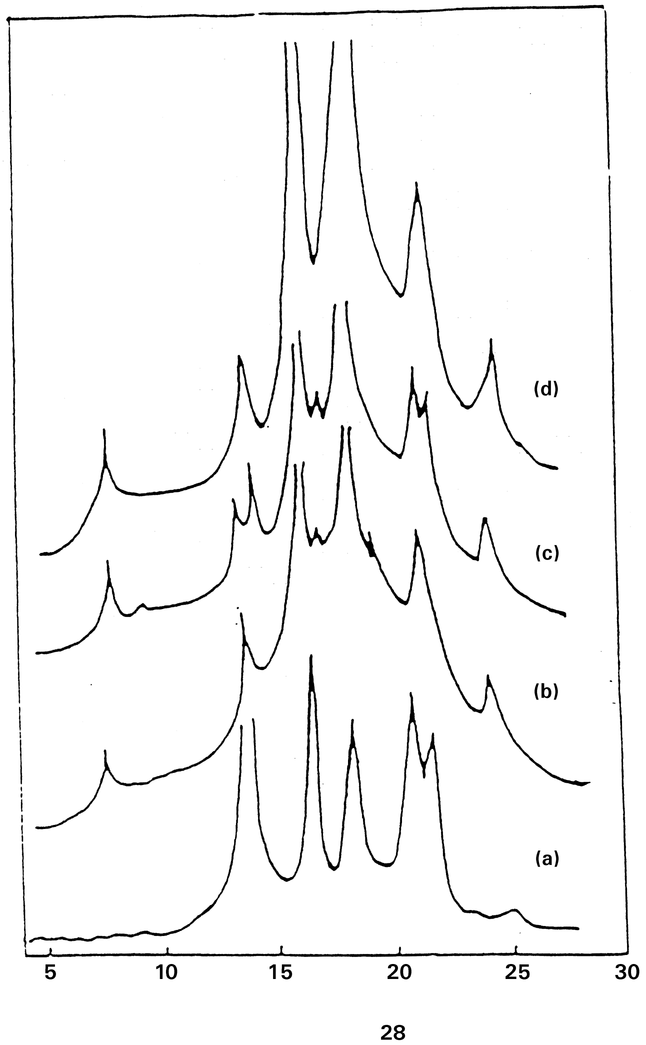


Figure 8 X-ray diffraction diagrams of iPS, iPP and the block copolymers. (a) iPP; (b) $T_{80\text{-}10}$ [St]:[P]:[E] = 45:47:8 (wt%); (c) D_{-10} [St];[P] = 67:33 (wt%); (d) iPS

iPS-b-Poly(E-co-P) copolymer shows only one kind of crystal diffraction of iPS, and the area of amorphous phase is increased obviously in comparison with the iPS-b-iPP copolymer.

TEM is perhaps the most direct way to prove block copolymer structure owing to the unique microphase separation exhibited by such materials. *Figure 9* shows the TEM photos of iPS-b-Poly(E-*co*-P) copolymers of various compositions. It is clear that the size of microphase of iPS-b-Poly(E-*co*-P) (about 10 nm) is much smaller than that of the usual polyblend system, and the phase distribution is uniform.

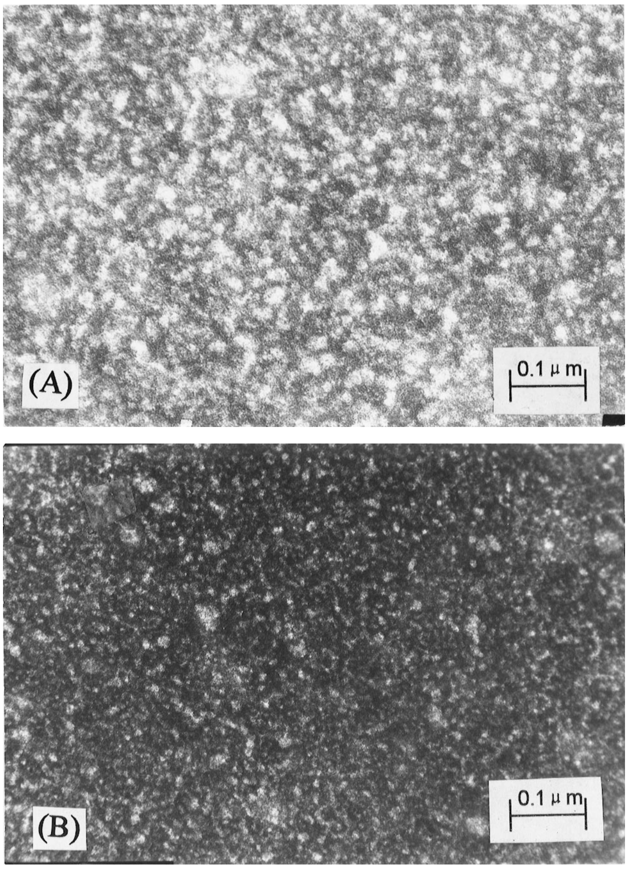


Figure 9 TEM micrograph of iPS-b-Poly(E-*co*-P) copolymers obtained by solvent extraction (A) [St] = 47.5 mol% (B) [St] = 86.5 mol%

CONCLUSION

In conclusion, judging from the difference in the melting point, g.p.c. results and the solubility between the block copolymer and homopolymers, it may be said that the present copolymer is not a mixture of copolymer and homopolymers, but is essentially a block copolymer with the structure of iPS-b-Poly(E-*co*-P). Studies show that this kind of block copolymer has long segments of iPS and poly(ethylene-co propylene), and the iPS segment could crystallize separately.

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