Synthesis of PP–LCP Graft Copolymers and Their Compatibilizing Activity for PP/LCP Blends

P. L. MAGAGNINI,[1] M. PRACELLA,[1] L. I. MINKOVA,[2] TS. MITEVA,[2] D. SEK,[3] J. GROBELNY,[3] F. P. LA MANTIA,[4] R. SCAFFARO[4]

[1] Department of Chemical Engineering, University of Pisa, via Diotisalvi 2, 56126 Pisa, Italy

[2] Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

[3] Institute of Polymer Chemistry, Polish Academy of Sciences, 34 M. Curie str., 41-800 Zabrze, Poland

[4] Department of Chemical Engineering, University of Palermo, viale delle Scienze, 90128 Palermo, Italy

Received 2 May 1997; accepted 18 October 1997

ABSTRACT: The aim of this work was the synthesis of new graft copolymers consisting of polypropylene (PP) backbones and liquid crystalline polymer (LCP) branches, to be used as compatibilizing agents for PP/LCP blends. The PP-*g*-LCP copolymers have been prepared by polycondensation of the monomers of a semiflexible liquid crystalline polyester (SBH 1 : 1 : 2), that is, sebacic acid (S), 4,4′-dihydroxybiphenyl (B), and 4-hydroxybenzoic acid (H) in the mole ratio of 1 : 1 : 2, carried out in the presence of appropriate amounts of a commercial acrylic-acid-functionalized polypropylene (PPAA). The polycondensation products, referred to as COPP50 and COPP70, having a calculated PPAA concentration of 50 and 70 wt %, respectively, have been fractionated with boiling toluene and xylene, and the soluble and insoluble fractions have been characterized by Fourier transform infrared and nuclear magnetic resonance spectroscopy, scanning electron microscopy (SEM), differential scanning calorimetry, and X-ray diffraction. All analytical characterizations have concordantly shown that the products are formed by intricate mixtures of unreacted PPAA and SBH together with PP-*g*-SBH copolymers of different composition. Exploratory experiments carried out by adding small amounts of COPP50 or COPP70 into binary mixtures of isotactic polypropylene (iPP) and SBH while blending have demonstrated that this practice leads to an appreciable improvement of the dispersion of the minor LCP phase, as well as to an increase of the crystallization rate of iPP. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 391–403, 1998

Key words: functionalized polypropylene; liquid crystalline polymer (LCP); copolymers; polypropylene–LCP blends; compatibilization

INTRODUCTION

Compatibilization with appropriate additives is needed very often to improve the adhesion and enhance the properties of incompatible polymer blends. This requirement is particularly pressing for blends of polyolefins with liquid crystalline polymers (LCPs). Indeed, LCPs are aromatic copolyesters with relatively high chain stiffness and polarity and display poor interfacial adhesion to hydrocarbon polymers such as polyethylene (PE) and polypropylene (PP). As a consequence of this, the well-known reinforcing effect generally obtained by the *in situ* addition of LCPs into flexible polymers[1,2] is very poor (if any) when PE or PP are used as the blend matrix.

Correspondence to: P. L. Magagnini.

Journal of Applied Polymer Science, Vol. 69, 391–403 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/020391-13

Reinforcement of PP with several LCPs has been attempted by Baird and coworkers[3,4] and by others.[5–7] However, in the absence of appropriate compatibilizers, the blends, though exhibiting some modulus improvement, have been found to possess similar, or even lower, tensile strength as neat PP. For this reason, recent investigations have dealt with the preparation and the characterization of PP/LCP blends containing different commercially available compatibilizers, such as maleic-anhydride-grafted PP (PP-*g*-MA)[8–10] or an ethylene-based reactive terpolymer.[11] The use of the latter additives has been shown to improve the phase dispersion and the interfacial adhesion, but the enhancement of tensile modulus, tensile strength, and surface finish was generally modest.[8–10] Their effect has been attributed to polar interactions between the components rather than to chemical reactions of the compatibilizer functionalities with the LCP bonds.

Miller and coworkers[12–14] have used an acrylic-acid-functionalized PP (PPAA) and a PPAA-based graft copolymer for the compatibilization of PP/LCP blends and have observed an improvement of the tensile properties, the thermal stability, and the crystallinity of the fibers produced therefrom. Also, in this case, the enhancement of the properties has been attributed to the promotion of specific polar interactions between the blend components.

An ethylene–glycidyl methacrylate copolymer (EGMA),[15] and a terpolymer of ethylene, ethyl acrylate, and glycidyl methacrylate (EEAGMA)[16] have also been investigated as reactive compatibilizers for PP/LCP blends. The reaction between the epoxy groups of the compatibilizers and the LCP end groups has been found to lower the dimensions of the LCP domains and to improve the impact strength.[15,16] However, this positive effect has been shown to be accompanied by a substantial reduction of the PP degree crystallinity and of the tensile modulus.[15]

It is well known that, among compatibilizing agents, block or graft copolymers made up of segments whose chemical structure and solubility parameters are similar to those of the polymers being blended appear best suited to the scope.[17] These compatibilizers can migrate to the interphase and reduce the interfacial energy between matrix and dispersed phase, thus causing a reduction of the minor phase dimensions and a stabilization of polymer blend morphology. The *ad hoc* synthesis of compatibilizing copolymers containing the monomer units of the polymers being blended has been considered recently by some of us. Blends of PE with a semiflexible LCP (SBH), synthesized from sebacic acid (S), 4,4′-dihydroxybiphenyl (B), and 4-hydroxybenzoic acid (H), in the mole ratio of 1 : 1 : 2, as described before,[18,19] have been compatibilized with new PE-*g*-SBH copolymers purposely synthesized either by the melt polycondensation of the LCP monomers carried out in the presence of a PE sample containing free carboxyl functionalities[20] or by reactive blending of the same functionalized PE with preformed SBH.[21] A comparison of the morphology and of the rheological and mechanical properties of the ternary blends containing a small amount of the copolymers with those of reference blends, either without or with a conventional compatibilizer (maleic-anhydride-grafted PE), demonstrated that the PE-*g*-SBH copolymers do in fact improve the interfacial adhesion both in the melt and in the solid state.[22] A similar approach had also been followed[23] for the compatibilization of blends of poly(ethylene terephthalate) (PET) with SBH, and it was found that the addition of small amounts of *ad hoc* synthesized PET–SBH copolymers gave rise to significant improvements of both tensile strength and elongation at break.

The successful fabrication of PE-*g*-SBH copolymers from a fairly low molar mass PE containing reactive carboxylic groups, by the polycondensation[20] and the reactive blending[21] procedures, prompted us to apply the same techniques to the production of similar graft copolymers from functionalized polyolefins of higher molar mass. Actually, copolymers with long backbones and significant spacing between the grafts are expected to be best suited in view of a reduction of the interfacial tension in incompatible polymer blends.[24] In this work, a commercially available sample of acrylic-acid-grafted PP (Polybond 1001) of fairly high molar mass was used as the substrate for the synthesis of PP-*g*-SBH copolymers by the *in situ* melt polycondensation of the SBH monomers. Two products, refereed to as COPP50 and COPP70, where the figures denote the nominal mass percent concentration of PPAA, were synthesized. The two products and their soluble and insoluble fractions, obtained by extraction with boiling toluene and xylene, were characterized by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). The compatibilizing activity of the products was then preliminarily evaluated by adding them into blends of isotactic PP (iPP)

and SBH and checking their effect on the morphology and the thermal properties of the blends.

EXPERIMENTAL

Materials

IPP was a commercial pelletized material, Moplen F30S, produced by Himont, Ferrara, Italy. PPAA was a commercial pelletized sample of acrylic-acid-grafted PP (Polybond 1001) by BP Chemical International, England. This polymer has a weight-average molar mass of about 100,000 and contains 6% w/w of acrylic acid branches. This corresponds approximately to 0.7 mmols of carboxylic groups per gram.

Sebacic acid (S), 4,4′-dihydroxybiphenyl (B), and 4-hydroxybenzoic acid (H) were supplied by Merck, Schuchardt, and Aldrich (Milano, Italy) and were used without further purification. The hydroxylated monomers B and H were acetylated and purified by crystallization before being used for the polymer synthesis.[25,26] The LCP was a laboratory sample of SBH 1 : 1 : 2 (LCP1B/024) kindly supplied by Eniricerche S.p.A., Milan. This copolyester was synthesized from S, B, and H, in the mole ratio of 1 : 1 : 2, as described elsewhere.[18,19] The sequence distribution was shown to be random by NMR analysis.[26] The inherent viscosity of SBH, measured in pentafluorophenol at 60°C with a concentration of 0.1 g/dL, was 1.20 dL/g.

All materials were accurately dried in a vacuum oven at 100°C before being used for the copolyester synthesis or the blends preparation.

Techniques

PP-g-SBH Compatibilizer Synthesis

PPAA was reduced to a fine powder, either by grinding under liquid nitrogen or by precipitation into methanol from a hot toluene solution (approximately 100 mL/g) and then dried in a vacuum oven and dry blended with the solid SBH monomers. The composition of the mixtures was calculated in such a way as to obtain graft copolymers containing 50 or 70% w/w PPAA, respectively, for the synthesis of COPP50 and COPP70. The amount of S was reduced, with respect to that employed for the synthesis of neat SBH, in order to have equivalent concentrations of acetoxyl and carboxyl groups in the feed, including those contained in the PPAA. Thus, for the synthesis of, for example, COPP50, the following amounts of raw materials were weighed: PPAA, 20.0 g; S, 5.41 g; B, 9.17 g; H, 12.16 g. A minute amount of sodium acetate was added as a catalyst. The powdered monomers and the catalyst were accurately blended with the powdered PPAA, and the mixture was fed to the reactor. The latter was a round-bottomed cylindrical flask of approximately 400-mL capacity, equipped with a stainless steel stirrer, nitrogen inlet, and vacuum outlet. After feeding the mixture, the reactor was closed and flushed with dry nitrogen. Vacuum was than applied for approximately 10 min, at room temperature, and nitrogen was again admitted after closing the vacuum outlet. These operations were repeated three times to achieve complete oxygen removal, and a nitrogen atmosphere was finally left in the reactor.

The reactor was then immersed in a salt bath preheated to 230°C, and stirring was started with a rate of about 60 rpm. After ~ 1 h, the temperature was raised to 240°C, and this led to a reduction of the viscosity of the mass and to the progressive evolution of acetic acid vapors that were condensed in a trap cooled with liquid nitrogen. The high temperatures normally employed for the synthesis of liquid crystalline polyesters (up to 280–300°C) may cause decarboxylation of PPAA, thus preventing grafting. For this reason, the reaction temperature was kept to fairly low values (230–240°C) during the first reaction stage so as to allow acidolysis to take place before, or at least concurrently with, decarboxylation.

After 1 more hour, the evolution of acetic acid had practically ceased, and the temperature was then gradually raised to 260°C. During this period, the reaction mixture had the appearance of a macroscopically homogeneous, white, opaque paste of increasing viscosity. The temperature was kept at about 260°C for 1.5–2 h and was then gradually raised to 280°C. The pressure was concurrently lowered gradually to about 10 Pa to complete the evolution of low-molar-mass materials, and these conditions were maintained for ~ 30 min, until no more vapor evolution was noticed and the product was highly viscous. The reactor was then opened under nitrogen blanket, and the polymer was extracted while hot with a stainless steel spoon. After cooling, the product was milled and extracted with boiling acetone to remove all low-molar-mass materials still present.

Blends Preparation

Mechanical blends of PPAA and SBH containing 50 and 70% w/w PPAA, referred to herein as

MIXP50 and MIXP70, respectively, were prepared in a Brabender apparatus at 245°C and 50 rpm with a blending time of 10 min. Binary and ternary blends of iPP, SBH, and COPP, if any, were also prepared with the same technique. The w/w ratio of PP to SBH was held constant at 90/10 or 80/20; these blends were compatibilized by the addition of 0, 2.5, 5, and 10 w% COPP50 or COPP70. The addition of, for example, 10 w% COPP50 to the 80/20 iPP/SBH blend led to a ternary iPP/COPP50/SBH blend having the 75/10/15 w/w/w composition.

Characterization Techniques

The products of the polycondensation reactions, COPP50 and COPP70, and the binary blends with the same calculated composition, MIXP50 and MIXP70, were fractionated by solvent extraction, using Kumagawa devices. A small amount (3–5 g) of the samples was placed in a thimble and extracted with about 250 mL of refluxing toluene for 24–25 h. At the end of this period, the solution was isolated, cooled, and poured into excess methanol. The precipitated polymer was then filtered, dried, and weighed. The insoluble fraction in the extraction thimble was dried, weighed, and extracted once more with boiling xylene by the same procedure.

Infrared spectra of PPAA, SBH, MIXP50, MIXP70, COPP50, COPP70, and their fractions were recorded on a Perkin–Elmer FTIR 1600 apparatus. Thin films of the samples were obtained by hot molding.

High-resolution solid-state ^{13}C-NMR measurements were performed at 20°C on Varian VXR 300 spectrometer operating at the ^{1}H resonance frequency of 300 MHz and the ^{13}C resonance frequency of 75 MHz. Hartmann–Hahn spin lock crosspolarization (CP) along with dipolar decoupling (DD) and magic angle sample spinning were used to obtain ^{13}C spectra from the solid state. The sample spinning at magic angle was carried out at 4000–5000 Hz in a Doty Scientific Co. (Columbia, SC) solids NMR probe. Powder specimens of about 200 mg were pressed into Macor rotors with Kel-F end caps. For all materials studied, 500–1000 scans were accumulated with 3–10 s delay between pulse sequence repetitions. Chemical shifts relative to tetramethylsilane (TMS) were determined from the aromatic carbons line (132.1 ppm) of hexamethylbenzene (HMB) standard. Spin lattice relaxation times for protons, T_1^H, were obtained at 20°C from 180°-τ-90° pulse sequence followed by simultaneous 0.5 ms ^{13}C and ^{1}H spin lock, and then acquisition of the ^{13}C magnetization with ^{1}H 50 kHz decoupling.

The thermal behavior of polymers was monitored by DSC using a Perkin–Elmer DSC-4 apparatus. Scanning rates of 10°C/min were normally used.

Wide-angle X-ray scattering (WAXS) investigations were carried out at room temperature in a URD diffractometer, using the Ni-filtered CuKα radiation in the reflectance mode.

Morphological investigation was made by SEM, with Jeol T300 and Jeol 550 apparatuses. The SEM micrographs were taken on fracture surfaces produced under liquid nitrogen and coated with gold.

RESULTS AND DISCUSSION

Copolymer Synthesis and Fractionation

The acidolysis reaction illustrating the expected grafting to PPAA is schematically shown in Figure 1. In this scheme, *X* represents any molecule, either monomeric or polymeric, carrying the acetoxyl end group of a *B* or *H* moiety. In principle, the formation of polyester cross bridges linking different PPAA chains might be expected. However, no indication of appreciable crosslinking was observed under the reaction conditions used in this work. The yield of the crude copolymer was about 90% of theory and showed no difference with respect to that obtained for the synthesis of neat SBH.

In order to gain information on the presence of a true graft copolymer molecules in COPP50 and COPP70, these polycondensation products were fractionated with two PP solvents, toluene and xylene, in the order of increasing boiling point.

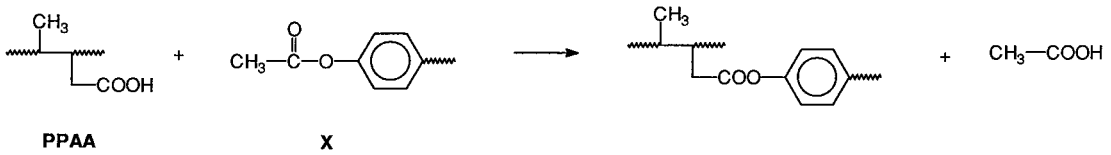

Figure 1 Reaction scheme.

Table I Solvent Fractionation of the Materials

Material	Code	Yields of the Fractions (%)
Acrylic acid grafted PP (Polybond 1001)	PPAA	100.0
soluble in toluene		70.0
soluble in xylene		30.0
Mechanical blend PPAA/SBH 70/30 w/w	MIXP70	100.0
soluble in toluene	STMP70	37.2
soluble in xylene	SXMP70	32.1
insoluble in xylene	RXMP70	30.7
Mechanical blend PPAA/SBH 50/50 w/w	MIXP50	100.0
soluble in toluene	STMP50	25.0
soluble in xylene	SXMP50	25.6
insoluble in xylene	RXMP50	49.4
Copolymer PPAA–SBH 70/30 w/w	COPP70	100.0
soluble in toluene	STCP70	26.5
soluble in xylene	SXCP70	44.3
insoluble in xylene	RXCP70	29.2
Copolymer PPAA–SBH 50/50 w/w	COPP50	100.0
soluble in toluene	STCP50	28.6
soluble in xylene	SXCP50	25.2
insoluble in xylene	RXCP50	46.2

The obtained fractions were compared with those of PPAA/SBH mechanical blends (MIXP50 and MIXP70) of similar composition. The presence of SBH segments in the soluble fractions and that of PP segments in the insoluble fractions would be a sign of the presence of PP-*g*-SBH copolymer. The masses of the different fractions obtained from the COPPs and the MIXPs are presented in Table I. Data regarding extraction experiments of neat PPAA are also included.

The extraction of PPAA with refluxing xylene is fast and can generally be completed in less than 1 hour. On the contrary, that with toluene is a fairly slow process: under the conditions employed in this work, only 24% of the initial amount was dissolved after 4 h of extraction, and this increased to 70% after 24 h (Table I). Moreover, IR and DSC analyses showed that the first fraction consisted of practically pure PP. This indicates that PPAA is actually a mixture of acrylic-acid-grafted PP molecules with varying concentrations of AA grafts and of ungrafted PP chains. The result also shows that the extraction with toluene is faster for neat PP and gets slower as long as the concentration of AA grafts increases.

As far as the solvent fractionation of the mechanical blends is concerned, the data in Table I show that, as it could be expected, the masses of the soluble and insoluble fractions of MIXP50 and MIXP70 correspond closely to the nominal PPAA and SBH contents of these blends. The situation for the fractions of the alleged copolyesters, though showing some deviations with respect to that of the mechanical blends, especially for the toluene and xylene soluble fractions of COPP70, is not such as to be taken as a definite evidence in favor of grafting. In fact, the differences between the masses of the corresponding fractions of the COPPs and the MIXPs are probably within the experimental errors.

Characterization of the Copolymers

The IR spectra of the soluble fractions of MIXP50 and MIXP70 do not display absorption bands ascribable to the SBH component, and the insoluble fractions do not contain bands typical for the PP component. This demonstrates that the adopted fractionation technique grants fairly complete separation of the two phases, in a practically pure form. The 2nd derivatives ratio of the band characteristic for CH_3 groups and that of the aromatic ring vibrations was 0.09 for the residue RXMP50. Interestingly, the spectra of the STMP50 and STMP70 practically coincide with that of pure PP as demonstrated by the absence of the band at 1715 cm^{-1}, typical for free carboxyl groups. This confirms that the extraction with toluene is faster for the ungrafted PP chains of PPAA.

The IR spectra of the fractions of COPP50 (Fig. 2) and COPP70 (not shown) provide no clear evidence indicating the presence of SBH sequences in the toluene soluble fractions. This may be due to the fact that toluene does solve ungrafted PP

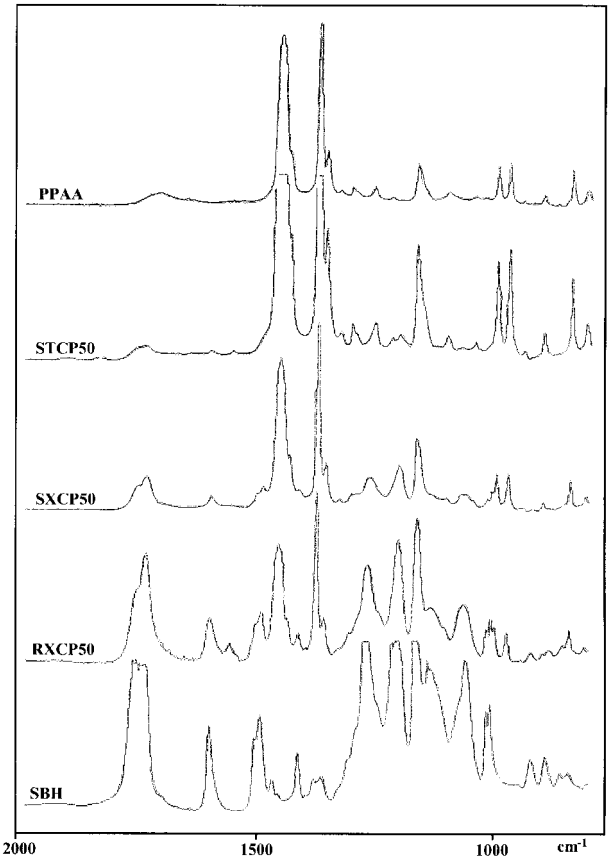

Figure 2 IR spectra of PPAA, SBH, and COPP50 and its fractions.

preferentially and is probably a poor solvent for PP-*g*-SBH copolymers. On the contrary, as the IR spectra of Figure 2 show for the COPP50 fractions, some SBH absorption bands are visible in the spectra of the xylene soluble fractions. This is demonstrated, in particular, by the presence of the bands at 1745, 1600, 1492, 1201, and 1006 cm^{-1}, which are characteristics for the SBH component. It can also be noticed that the band typical for free carboxyl groups at 1715 cm^{-1} is very weak in the IR spectra of these fractions. On the other hand, the spectra of RXCP50 and RXCP70 indicate that a considerable amount of PPAA is present in these fractions, as demonstrated by the intense bands corresponding to the CH_2 and CH_3 groups at 1472, 1460, 1377, 1358, and 973 cm^{-1}. The 2nd derivatives ratio of the band characteristic for the CH_3 groups and that of the aromatic ring vibrations was 2.51 for RXCP50.

It might be argued that the presence of PPAA sequences in the residues of the copolymers fractionation could be ascribed to some crosslinking eventually undergone by PPAA during the polycondensation process. To disprove this hypothesis, RXCP50 and RXCP70 were treated with boiling alcoholic NaOH to hydrolyze the polyester chains, and the toluene solubility of the residues was checked. It was found that these residues dissolve completely in boiling toluene, thus showing that no PP crosslinking had taken place during polycondensation. It may be concluded, therefore, that the IR analysis provides clear evidence indicating that the polycondensation of the SBH monomers carried out in the presence of PPAA has actually led to a substantial yield of PP-*g*-SBH copolymers.

The solid-state ^{13}C-NMR spectra of MIXP70, MIXP50, COPP70, COPP50 and RXCP50 are displayed in Figure 3. The samples exhibit several lines corresponding to their constituents, namely the lines at 44, 26.1, and 21.6 ppm due to CH_2, CH, and CH_3 carbons of PPAA, and the lines at 127.4, 122.8, 34.5, and 31.0 ppm due to the SBH carbons. The values of the proton spin-lattice relaxation time T_1^H, which are indicative of homoge-

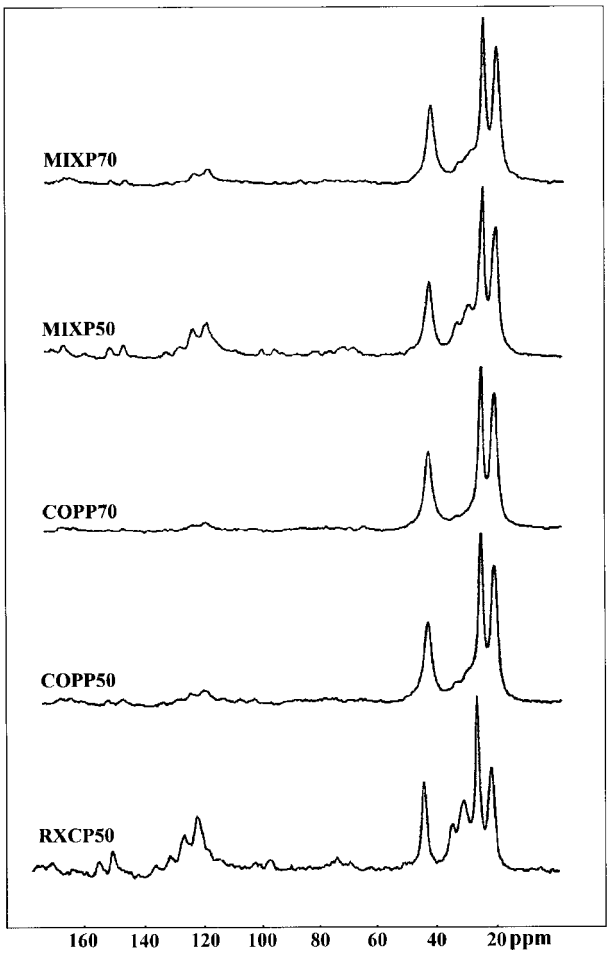

Figure 3 ^{13}C-NMR spectra of MIXP70, MIXP50, COPP70, COPP50, and RXCP50.

Table II Average Values of Proton Spin-Lattice Relaxation Time for the PPAA and SBH Components of Different Materials

Sample	T_1^H (s) (SBH carbons)	T_1^H (s) (PPAA carbons)
PPAA	—	0.9
SBH	0.75	—
MIXP70	1.15	0.95
MIXP50	1.15	0.95
COPP70	0.71	0.92
COPP50	0.31	0.89
RXCP50	0.30	0.79

neity on a 100–200 Å scale, are determined as average T_1^H values, measured from individual carbon resonance lines for SBH and PPAA component respectively, for every sample (Table II).

It can be seen that in MIXP70 and MIXP50, there is an increase of the T_1^H values for the SBH component from 0.75 to 1.15 s, and a slight increase from 0.9 to 0.95 s for the PPAA component. Such relaxation behavior indicates the existence of large, separated domains in the samples, as could be expected for a mechanical blend. This behavior is also indicative of similar changes in the morphology of the two components, as compared to neat SBH and PPAA. As it is clearly seen in Table II, there is a slight decrease of T_1^H for the SBH component of COPP70; whereas for COPP50, the decrease becomes significant (from 0.75 to 0.31 s). The T_1^H values for the PPAA component remain practically unchanged in comparison to that of neat PPAA, and this may be due to the (expected) presence of unreacted PPAA in both COPP70 and COPP50 samples. The observed behavior indicates that the grafting reaction has actually occurred between the two components and that these components are bonded chemically in the copolymers and form separated domains with linear dimensions larger than several hundreds Å.

The NMR spectra of the toluene soluble fractions of COPP70 and COPP50 do not contain absorption bands of the SBH component, whereas an indication of the presence of SBH sequences can be found for the xylene soluble fractions. The insoluble fractions RXCP70 and RXCP50 contain both SBH and PPAA components. For the latter fractions, the T_1^H value of the SBH component decreases strongly from 0.75 to 0.30 s, and that of the PPAA component decreases from 0.9 to 0.79 s. This means that these components are bonded chemically in the insoluble fractions.

Examples of the SEM micrographs taken on the fracture surfaces of bulk samples of MIXP70 and COPP70 are shown in Figure 4. It is clearly seen that MIXP70 [Fig. 4(a)], and MIXP50 as well, is a biphasic material characterized by poor dispersion of the phases and practically no interfacial adhesion. COPP70 [Fig. 4(b)] and COPP50 are also biphasic, but the two phases do adhere strongly to each other. The dispersed phase visible in Figure 4(b) consists of fairly large domains and must be formed, therefore, by ungrafted SBH macromolecules. However, the fact that these droplets have been seriously involved in the fracture process is strong evidence in favor of the presence PP-*g*-SBH copolymer molecules in the interphase. Moreover, a large number of very fine droplets that are absent in the blends can be detected throughout the matrix, though being hardly distinguishable from it. Thus, the observation of the SEM micrographs of the polycondensation products provides evidence that the transesterification reaction

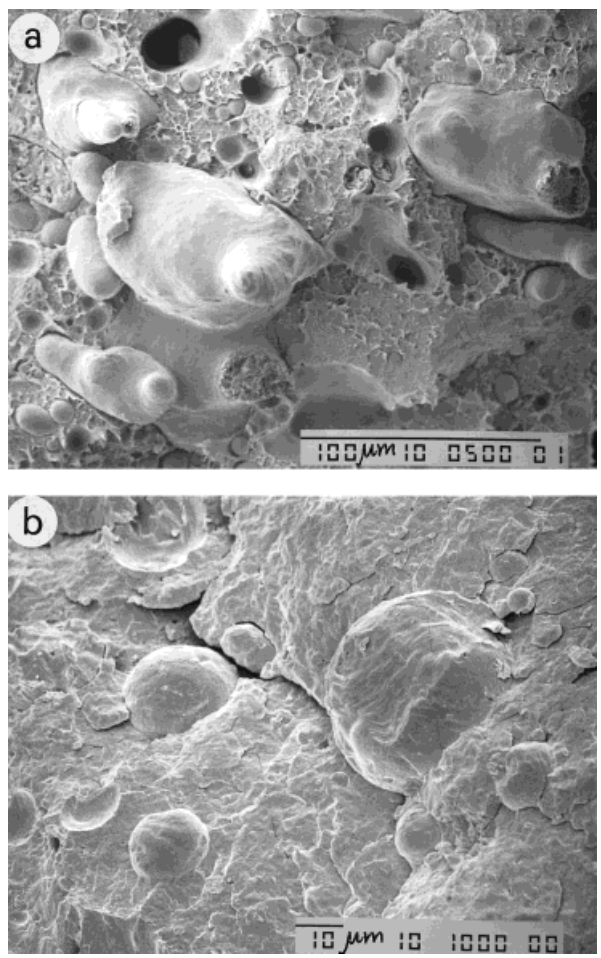

Figure 4 SEM micrographs of the fracture surfaces of (a) MIXP70 and (b) COPP70.

Table III DSC Characteristics of the PPAA Phase of the Different Materials

	1st Cooling		2nd Heating	
Sample	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PPAA	125.3	97.8	163.7	92.6
MIXP50	124.0	48.9	162.5	43.3
STMP50	116.0	91.6	157.7	94.9
SXMP50	123.7	95.8	164.2	98.8
RXMP50	125.2	1.1	164.3	0.8
MIXP70	123.8	65.8	162.0	65.6
STMP70	115.8	92.2	160.2	93.5
SXMP70	123.4	96.5	163.1	97.6
RXMP70	124.3	1.3	164.0	1.2
COPP50	122.4	60.2	161.6	56.5
STCP50	113.6	87.4	155.3	86.6
SXCP50	121.6	91.1	163.0	90.4
RXCP50	122.8	42.7	163.2	38.7
COPP70	124.6	75.7	163.4	77.1
STCP70	114.2	75.7	161.4	73.2
SXCP70	123.8	94.9	164.1	93.5
RXCP70	124.4	61.4	164.5	60.0

involving the carboxylic groups of PPAA and the acetoxyl groups of the SBH monomers has taken place concurrently with the polymerization of the latter. Therefore, the products COPP50 and COPP70 are formed by intricate mixtures of unreacted PPAA, ungrafted SBH, and PP-*g*-SBH copolymers probably containing variable proportions of the two components.

The DSC data regarding the transitions involving the PPAA phase of the blends, the copolymers, and their fractions are collected in Table III. The thermal characterization of the copolymers and the blends provides definite evidence that a complete phase segregation takes place even for the copolymers due to the strong incompatibility of the PP and the SBH chains. It may be observed, in fact, that the temperatures of fusion and crystallization of the PPAA phase are almost unaffected by the presence of the other component in both the blends and the copolymers. The enthalpy changes of the transitions associated with the PPAA phase in the blends (MIXP50 and MIXP70) correspond closely to their composition. For the two copolymers (COPP50 and COPP70), these enthalpy changes correspond to SBH contents ($\sim$ 40 and $\sim$ 17%) appreciably lower than calculated. This apparent discrepancy can be easily accounted for, considering that the yield of the polycondensation of the SBH monomers is certainly lower than 100%. The most important information provided by the DSC analysis concerns the copolymers fractions. The data in Table III demonstrate that substantial amounts of PPAA are retained in the residues of the copolymers (RXCP50 and RXCP70), whereas this is not so for the residues of the blends. As demonstrated by the hydrolysis experiments described before, no PPAA crosslinking has taken place as a result of the high-temperature treatment during the polycondensation. Therefore, the presence of PPAA chains in RXCP50 and RXCP70 must be attributed to the formation of graft copolymers. Finally, the considerably lower crystallization temperature of the PPAA phase of the toluene soluble fractions confirms that the toluene extraction leads to selective solution of the PPAA molecules with few, or none, acrylic acid grafts.

WAXS investigation of samples of the blends (MIXP50 and MIXP70) and of the copolymers (COPP50 and COPP70), as crystallized from the melt, as well as of their soluble and insoluble fractions, as obtained by precipitation from solution, was carried out in order to gain information on the crystalline structure of the products. The diffraction patterns of both the mechanical blends and the transesterification products are characterized by the presence of the reflections typical for both components, namely, the reflections corresponding to the α crystalline modification of iPP and the single reflection at $2\theta = 20.4°$ associated with the parallel packing of the SBH molecules having cylindrical symmetry. No significant variations of the d_{hkl} values are found for the PP phase of the blends and copolymers; analogously, the values for SBH spacings do not show differences for all the samples. These results indicate the absence of interactions in the crystal phase, as well as of cocrystallization phenomena between the components of the blends and the copolymers.

The diffraction patterns of the soluble and insoluble fractions of the copolymer samples depend on composition. As an example, the X-ray diffractograms of COPP50 and its fractions are shown in Figure 5. It is worth noting that the SBH reflection is observable in X-ray diffractograms of xylene soluble fractions of the copolymers. That could mean that the SBH grafts of the copolymers are long enough to form crystalline structure similar to those of the neat LCP.

Concerning the insoluble fractions of the copolymers (RXCP70 and RXCP50), the X-ray diagrams confirm that a PP component is present in these fractions as the backbones of the PP-*g*-SBH copolymer molecules and gives rise to a separate

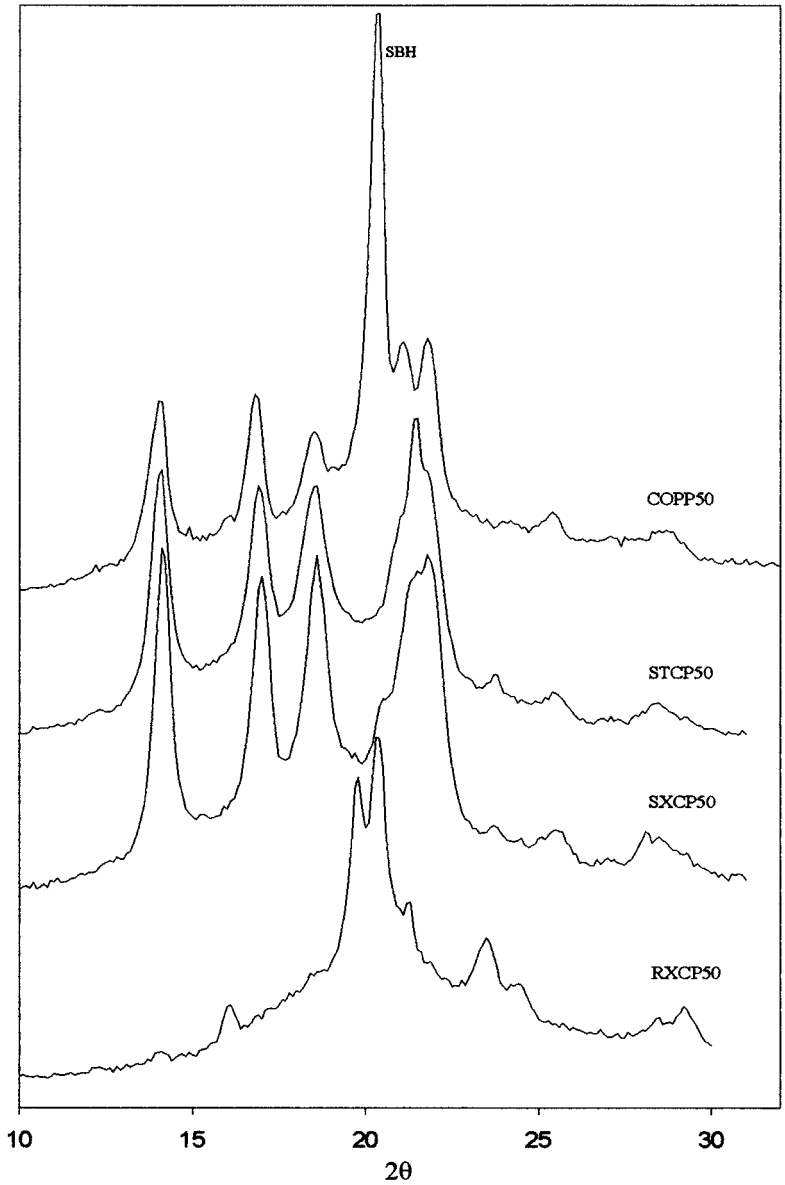

Figure 5 Powder XRD patterns of COPP50 and its fractions.

crystal phase. Interestingly, the PP phase of these residues crystallize mainly in the β and γ crystalline modifications, as is shown in Figure 5 for RXCP50.

From the WAXS investigations, it may be concluded that the PP-*g*-SBH copolymers (COPP50 and COPP70) consist of long PP backbones and SBH grafts of different length. However, both the PP chains and the SBH grafts are long enough to give rise to crystalline structures typical for the neat polymers.

Characterization of iPP/COPP/SBH Blends

The polymeric products prepared by the polycondensation of the SBH monomers in the presence of PPAA have been shown, by several analytical techniques, to be comprised of PP-*g*-SBH copolymer molecules of different composition, mixed with neat PPAA and SBH. The latter polymers give rise to separated phases, whereas the copolymer is supposed to form the interphase, thus granting the system considerable interfacial adhesion. On the other hand, PPAA has been shown by SEM and DSC to be completely miscible with iPP. Thus, the addition of appropriate amounts of COPP50 or COPP70 into iPP can be expected to provide a compatibilized iPP/SBH blend. Moreover, it can be expected that the addition of small amounts of these products into binary iPP/SBH blends can mean an improvement of phase disper-

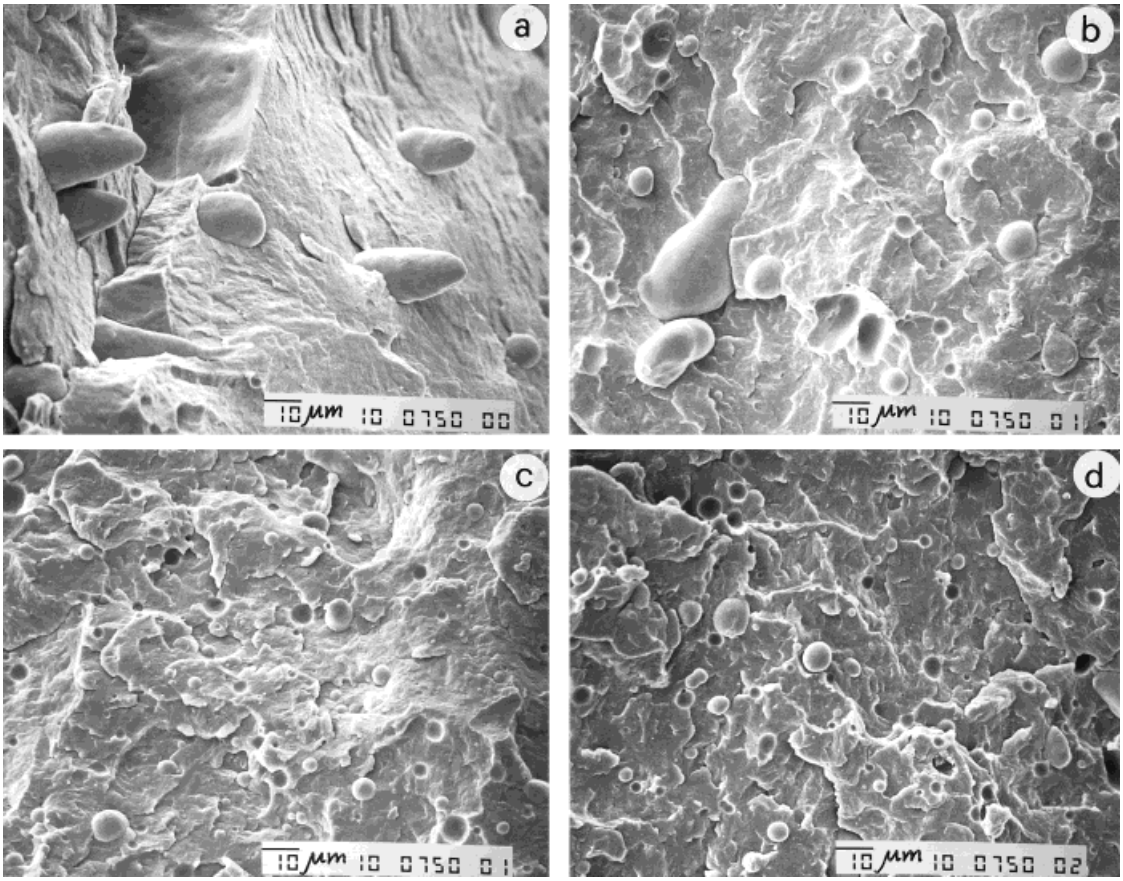

Figure 6 SEM micrographs of the fracture surfaces of (a) 90/10 iPP/SBH blend; (b) the same, with 2.5% COPP70; (c) the same, with 5% COPP50; and (d) the same, with 5% COPP70.

sion and interfacial adhesion. In other words, the products synthesized in this work can be considered either as reinforcing fillers for iPP or as compatibilizing agents for iPP/SBH blends.

The second possibility has been preliminarily tested in this work through a study of the effect played by the addition of different amounts (0, 2.5, 5, or 10%) of COPP50 or COPP70 into iPP/SBH blends on their morphology. The SEM micrographs of the fracture surfaces of bulk samples of 90/10 and 80/20 iPP/SBH blends with different concentrations of COPP50 or COPP70 are shown in Figures 6 and 7, respectively. The uncompatibilized blends are characterized by a dispersed SBH phase appearing as large (20–70 μm) unequal droplets whose smooth surface denounces the complete incompatibility of the two phases. As it is clearly demonstrated by the examples given in Figures 6 and 7, the addition of either COPP leads always to a significantly finer dispersion of the LCP droplets, whereas no clear indication of a substantially improved adhesion can be drawn from the micrographs. The average SBH droplet size is plotted in Figure 8 as a function of the amount of added compatibilizer, for both COPP50 and COPP70. The former copolymer seems to develop its maximum efficiency at a concentration of about 5%, whereas higher concentrations are needed for the latter.

The phase behavior of the ternary iPP/COPP/SBH blends has also been studied by DSC analysis. The results show that the temperature of crystallization T_c of the iPP phase increases strongly when either type of copolymer is added to the binary blend (Fig. 9). The amount of added compatibilizer seems to have a limited effect, if any. The average increase of T_c is of about 10°C and provides an evidence that the LCP dispersed phase has the effect of enhancing the crystallization rate of iPP only when a compatibilizer is present.

CONCLUSIONS

The different analytical techniques employed for the characterization of the polymeric materials produced by the polycondensation of the SBH

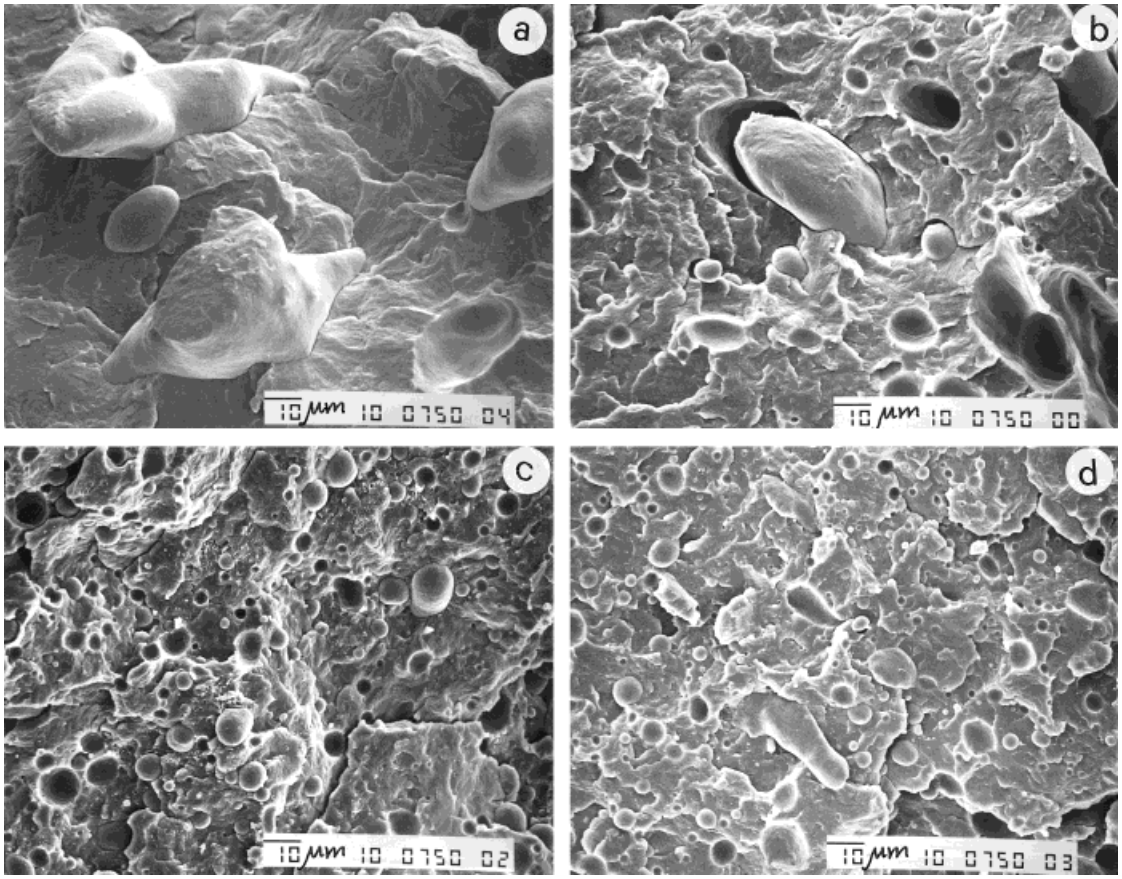

Figure 7 SEM micrographs of the fracture surfaces of (a) 80/20 iPP/SBH blend; (b) the same, with 2.5% COPP50; (c) the same, with 5% COPP50; (d) the same, with 10% COPP50.

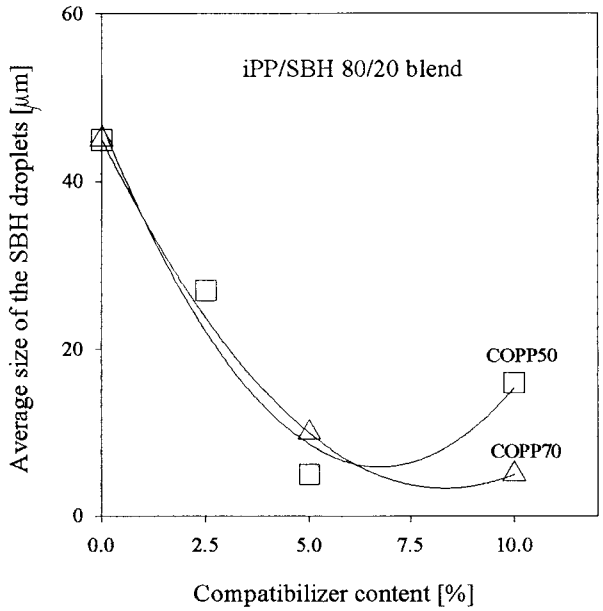

Figure 8 Dependence of the average size of the SBH droplets on the compatibilizer content in a 80/20 iPP/SBH blend.

monomers carried out in the presence of PPAA have concordantly demonstrated that grafting of SBH chains to the functional groups of PPAA has, in fact, taken place to a certain extent. The PP-*g*-SBH copolymers are built up of long PP backbones and SBH grafts of different length. Due to the strong incompatibility of both PP and unreacted PPAA for SBH, the synthesized materials display a distinctly biphasic morphology, and their phase behavior and crystal structure reveal the presence of two hardly interacting crystalline phases. However, SEM investigation has demonstrated very clearly that the two phases of the synthesized products are much more adherent to each other than those of mechanical blends of similar composition. The effect has been attributed to the presence of PP-*g*-SBH in the interphase.

The addition of relatively small amounts of the synthesized materials into binary iPP/SBH blends has been shown to mean a considerable reduction of the dimensions of the SBH droplets and an increase of the iPP crystallization rate, thus providing preliminary evidence of the compatibilizing activity of these products.

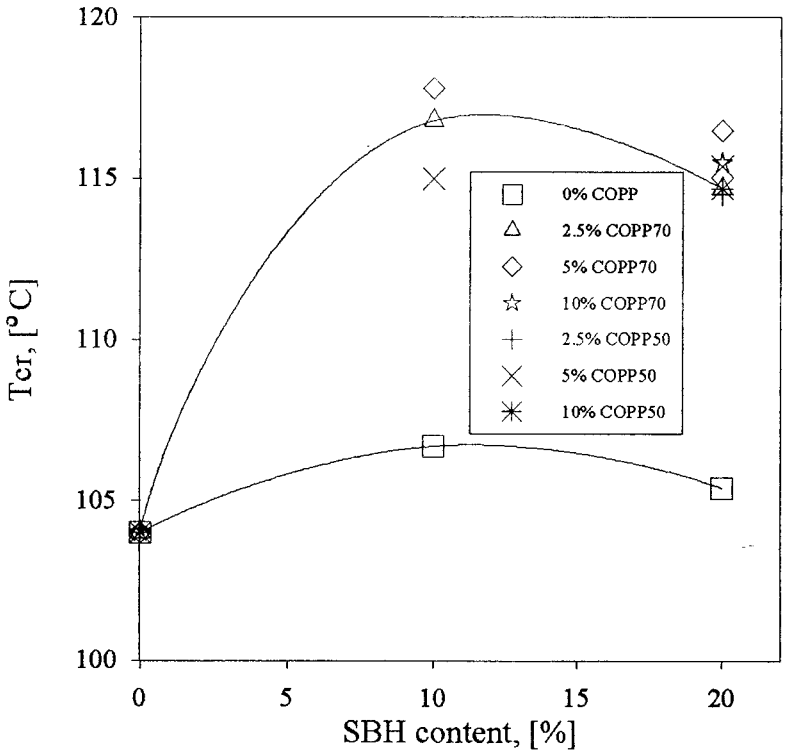

Figure 9 Dependence of the crystallization temperature T_c of the iPP phase on the SBH content for uncompatibilized and compatibilized iPP/SBH blends.

This work was carried out within a Copernicus Program (Contract no. CIPA-CT94-0118) funded by the Commission of the European Communities.

REFERENCES

1. D. Dutta, H. Fruitwala, A. Kohli, and R. A. Weiss, *Polym. Eng. Sci.,* **30,** 1005 (1990).
2. F. P. La Mantia, Ed., *Thermotropic Liquid Crystal Polymer Blends,* Technomic, Lancaster, PA, 1993.
3. D. Done, A. M. Sukhadia, A. Datta, and D. G. Baird, *SPE Tech. Pap.,* **48,** 1857 (1990).
4. A. Datta, A. M. Sukhadia, J. P. Desouza, and D. G. Baird, *SPE Tech. Pap.,* **49,** 913 (1991).
5. C. Federici, G. Attalla, and L. Chapoy, Eur. Pat. 0,340,655 A2 (1989).
6. Y. Yongcheng, F. P. La Mantia, A. Valenza, V. Città, U. Pedretti, and A. Roggero, *Eur. Polym. J.,* **27,** 723 (1991).
7. S. C. Tjong, S. L. Liu, and R. K. Y. Li, *J. Mater. Sci.,* **31,** 479 (1996).
8. A. Datta, H. H. Chen, and D. G. Baird, *Polymer,* **34,** 759 (1993).
9. A. Datta and D. G. Baird, *Polymer,* **36,** 505 (1995).
10. H. J. O'Donnel and D. G. Baird, *Polymer,* **36,** 3113 (1995).
11. M. T. Heino and J. V. Seppala, *J. Appl. Polym. Sci.,* **48,** 1677 (1993).
12. M. M. Miller, D. L. Brydon, J. M. G. Cowie, and R. R. Mather, *Macromol. Rapid. Commun.,* **15,** 857 (1994).
13. M. M. Miller, J. M. G. Cowie, J. G. Tait, D. L. Brydon, and R. R. Mather, *Polymer,* **36,** 3107 (1995).
14. Y. Qin, M. M. Miller, D. L. Brydon, J. M. G. Cowie, R. R. Mather, and R. H. Wardman, in *Liquid Crystalline Polymer Systems, Technological Advances,* A. I. Isayev, T. Kyu, and S. Z. D. Cheng, Eds., American Chemical Society, Washington, DC, 1996, p. 98.
15. Y. P. Chiou, K. C. Chiou, and F. C. Chang, *Polymer,* **37,** 4099 (1996).
16. R. M. Holsti-Miettinen, M. T. Heino, and J. V. Seppälä, *J. Appl. Polym. Sci.,* **57,** 573 (1995).
17. X. Jin and W. Li, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.,* **C35,** 1 (1995).
18. P. L. Magagnini, U. Pedretti, G. Perego, B. Bresci, S. Carrozzino, and A. Roggero, U.S. Pat. 4,833,229 (1989).
19. U. Pedretti, A. Roggero, V. Città, E. Montani, F. P. La Mantia, and P. L. Magagnini, in *Processing and Properties of Liquid Crystalline Polymers and LCP Based Blends,* D. Acierno and F. P. La Mantia, Eds., ChemTec, Toronto, 1993.
20. P. L. Magagnini, M. Paci, L. I. Minkova, Ts. Miteva, D. Sek, J. Grobelny, and B. Kaczmarczyk, *J. Appl. Polym. Sci.,* **60,** 1665 (1996).
21. L. I. Minkova, Ts. Miteva, D. Sek, B. Kaczmarczyk,

P. L. Magagnini, M. Paci, F. P. La Mantia, and R. Scaffaro, *J. Appl. Polym. Sci.,* **62,** 1613 (1996).
22. F. P. La Mantia, R. Scaffaro, P. L. Magagnini, M. Paci, D. Sek, L. I. Minkova, and Ts. Miteva, *Polym. Eng. Sci.,* **37,** 1164 (1997).
23. G. Poli, M. Paci, P. L. Magagnini, R. Scaffaro, and F. P. La Mantia, *Polym. Eng. Sci.,* **36,** 1244 (1996).
24. Y. Lyatskaya, D. Gersappe, N. A. Gross, and A. C. Balazs, *J. Phys. Chem.,* **100,** 1449 (1996).
25. P. L. Magagnini, B. Bresci, M. Paci, A. Roggero, U. Pedretti, and F. P. La Mantia, in *Recent Advances in Chemical Ingeneering,* D. N. Saraf and D. Kunzru, Eds., Tata–McGraw-Hill, New Delhi, 1990, p. 541.
26. F. P. La Mantia, P. L. Magagnini, M. Paci, U. Pedretti, A. Roggero, and A. Valenza, in *Trends in Polymer Science,* Vol. 1, J. Menon, Ed., Research Trends, Trivandrum, India, 1991, p. 9.