Graft Copolymerization of *p*-Acryloyloxybenzoic Acid and *p*-Methacryloyloxybenzoic Acid onto Isotactic Polypropylene and Their Thermal Properties: Part I

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ABSTRACT: The polymerization and grafting of the monomers *p*-acryloyloxybenzoic acid and *p*-methacryloyloxybenzoic acid were studied. Poly(acryloyloxybenzoic acid) was obtained by γ-radiation-induced solution polymerization and bulk melt polymerization initiated by dicumyl peroxide. Poly(methacryloyloxybenzoic acid) could be obtained only by bulk melt polymerization. The graft copolymerization of the monomers onto isotactic polypropylene was carried out in bulk. The maximum grafting was reached in shorter times at higher temperatures, and it also increased with the concentration of the monomers in the reaction medium. The thermal and crystallization behavior of the graft copolymers was studied with differential scanning calorimetry and wide-angle X-ray diffrac-

tion. The graft copolymerization of *p*-acryloyloxybenzoic acid did not have any influence on the formation of both α forms (monoclinic) of polypropylene, whereas *p*-methacryloyloxybenzoic acid led to the α_2 form. The β-crystalline modification (hexagonal) formed in poly(acryloyloxybenzoic acid)-*g*-polypropylene products at 185°C and at higher grafting temperatures and also in the second run of differential scanning calorimetry studies after fast cooling. The β form was not observed in graft copolymers of poly(methacryloyloxybenzoic acid). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 414–422, 2008

Key words: crystallization; differential scanning calorimetry; graft copolymers; thermal properties; WAXS

INTRODUCTION

The modification of polymers by copolymerization or grafting via increased intermolecular interactions and possible crosslinking of the macromolecules produces some desirable properties without a dramatic change in the architecture of the polymer backbone. This, therefore, gives rise to commercial importance for polymer applications.

A popular approach in the last decade has been combining thermotropic liquid-crystalline polymers (LCPs) and thermoplastics (TPs) in a blend to achieve favorable properties.[1–5] It has been reported that LCPs, exhibiting very high mechanical properties with their stiff molecular backbones,[6] can easily orient and retain this orientation for up to several minutes in the melt state.[7,8] In TPs reinforced by LCPs, LCP fibrils are formed by the use of appropriate processing conditions, and finally, these fibrils reinforce the matrix in a manner analogous to that of fiber-reinforced composites.[9] The advantages of these materials are not only properties comparable to those of composites

of short fibers or whiskers but also improved processability and favorable dispersion of the reinforcing phase. However, the poor interfacial adhesion between the dispersed LCP phase and the TP matrix phase is the most important shortcoming mentioned in many works.[9–13] Several other factors affecting the ability of LCPs to reinforce TPs have been already studied by many workers,[9–15] and O'Donnel and Baird[9] gave an in-depth review of those factors.

Isotactic polypropylene (PP), exhibiting several morphologies affecting its overall performance, ease of processing, recyclability, ability to be modified, and so forth, crystallizes in at least three different crystalline modifications: α (monoclinic), β (hexagonal), and γ (triclinic).[16,17] The α form is the most important, stable, and conventional form and also the most extensively studied primary crystalline phase. It can be easily obtained by crystallization from the melt or from solution.[18] The β form, usually present in commercial PP at low levels, can be obtained by the rapid quenching of highly isotactic PP to temperatures between 100 and 130°C.[17] This is favored by slow growth rates, high-temperature gradients, and large degrees of superheating in the melt in the use of zone solidification.[19] Preferential formation of either of crystal forms α and β has been observed with the use of a selective nucleating agent.[20] The γ form has been observed only in low-molecular-

weight isotactic PP, depending on both the length of the molecule and the particular crystallization conditions employed,[21] such as crystals obtained at a pressure higher than 200 MPa.[22,23] On the other hand, the α and γ forms may coexist in the crystals.[24]

The vinyl monomer p-methacryloyloxybenzoic acid (MBA) was polymerized by free-radical initiation by Blumstein and coworkers.[25–27] The organization of the monomer within a mesophase solvent had a considerable influence on the kinetics of polymerization, molecular weight, and also microtacticity of the polymer.[25,26] When polymerized in bulk, the polymer displayed pronounced crystallinity.[27] The crystallinity and order in atactic poly(acryloyloxybenzoic acid) (PABA) and poly(methacryloyloxybenzoic acid) (PMBA) were studied in the later work of Blumstein et al.[28] These polymers, PABA and PMBA, were obtained by the heating of the corresponding monomers at or above the melting points of the monomers and by solution polymerization in dimethylformamide. Two crystal forms have been reported for PABA;[28] one of these (form I) with a higher degree of crystallinity has a monoclinic structure, and the other (form II) has been identified as smectic. For form I, bulk polymerization by heating on a hot stage leads to an isotropic p-acryloyloxybenzoic acid (ABA) melt, which forms a mobile, nematic schlieren texture, out of which spherulites grow as the polymerization to PABA progresses. The development of spherulite structures is more pronounced for PABA than for PMBA.

The macromolecule of PABA with its more flexible backbone can form a three-dimensional lattice more easily than the PMBA macromolecule, which is crowded by the presence of α-methyl groups along its backbone. The crystallinity and organization of side groups that develop beyond the formation of a long-range lamellar (smectic) order in these atactic polymers are endowed with hydrogen-bonded benzoic acid moieties.[28]

The phase transitions of PABA were studied by Menczel and Wunderlich.[29] It has been reported that PABA may exhibit, beside the reported smectic form,[28] another highly mobile mesophase state that is probably nematic. It is produced by the melting of crystal forms I and II or out of amorphous PABA above the glass transition.

Furthermore, the polymerization of ABA was investigated to resolve questions such as the nucleation of the mesophase and transformation of the mesophase into a solid by the parallel use of optical microscopy and quantitative thermal analysis by Menczel et al.[30] The search led, however, to the discovery of a much more complicated reaction instead of simple vinyl polymerization. It is assumed that the observed mesophase is not connected to ABA or PABA. The polymer is not involved in mesophase formation but seems to cause solidification of the spherulites, schlieren texture, and isomorphous material. After the melting of ABA, which leads to an isotropic phase, acidolysis produces acrylic acid and oligomers of poly(p-oxybenzoate), and these oligomers are the root of the mesophase formation. The polymerization of ABA without oligoester formation gives no intermediate mesophase.

As far as we know, there exists only one study on blends of PABA and PMBA with a TP material. The thermal behavior of PABA/nylon 6 (PA6) blends was investigated by Sainath et al.[31] The melting point of PA6 was depressed with increasing PABA content, and it was suggested by wide-angle X-ray analysis that the crystallinity of PA6 decreased with increasing PABA content.

In this part of our work, we present the polymerization of ABA and MBA and the extent of the graft copolymerization of these monomers onto isotactic PP. The polymers PABA and PMBA and the graft copolymers were analyzed with differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) to determine the effect of the graft copolymerization of ABA and MBA onto PP on the thermal and crystallization behavior of the coproducts.

EXPERIMENTAL

Materials

Granular isotactic PP (coded as MH 418), a product of Petkim (Turkish Petrochemical Industry, Izmir, Turkey), was used to prepare powder PP via dissolution in boiling xylene, which was followed by precipitation by ethanol at room temperature. The powder PP was subjected to 10 kGy of γ irradiation (a Co-60 γ-radiation source at a dose rate of 0.001 kGy; Gammacell 200, Atomic Energy Co. Canada, Ltd., Ottawa, Canada) in an open atmosphere to create active sites, such as peroxy (—COOH) groups. This irradiated powder polypropylene (irr-PP) was used in the graft copolymerization experiments. Therefore, the grafting process carried out in this work must be regarded as grafting on a radiation-peroxidized polymer.

The monomers, ABA and MBA, were synthesized by the condensation of corresponding acid chlorides with p-hydroxybenzoic acid in an alkaline medium as described by Blumstein and Kitagawa.[25] NMR spectra of both monomers are presented in Figure 1(a,b). The yield was 58 wt % with ABA, for which the reported yield, 75%,[31] could not be reached, and the yield was 50 wt % with MBA, in good agreement with the literature.[25]

Polymerization and thermally induced graft copolymerization of ABA and MBA onto PP

There are only few reports about the polymerization of the monomers by which the polymers PABA and
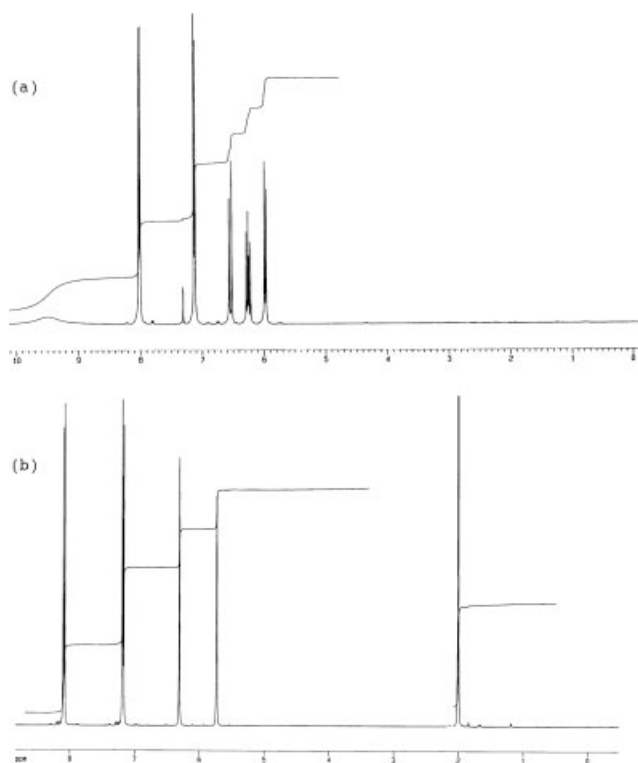
Figure 1 ^{1}H-NMR spectra of (a) ABA and (b) MBA.

PMBA were obtained by solution and bulk melt polymerization.[25–28] Because the aim was to produce graft copolymers of these monomers on irr-PP, the polymerization of the monomers was studied with several techniques. These experiments were carried out to determine the most efficient and successful way of grafting of both monomers.

PABA was obtained as follows:

1. γ-Irradiation-induced polymerization was carried out in a methanol and dimethyl sulfoxide solution of ABA *in vacuo*. The maximum conversion was 87.3%, and this conversion was reached at an early irradiation dose (5 kGy). In air and in the solid state, no polymer was obtained even at high doses.
2. Solution polymerization was performed in a dimethylformamide solution of ABA (10%) containing 1.5% (with respect to the weight of ABA) benzoyl peroxide, which was sealed in a glass tube *in vacuo* and then heated to 90°C (constant temperature) for 40 min. The polymer yield was measured above 81%.
3. The bulk polymerization of ABA was carried out in the presence of dicumyl peroxide (DCP; 2% with respect to the weight of the monomer) *in vacuo* at a constant temperature (200°C) for 40 min. The polymer yield was above 95%.

PMBA was obtained only by bulk melt polymerization. The monomer was heated to 190°C, the temperature being kept constant for 3 h, as reported in the literature.[28] The other methods ended with low yields, usually less than 5%, or without any polymer.

The graft copolymerization experiments were then carried as follows: a mixture (via the mechanical mixing of the powders of irr-PP and the monomers) of the polymer irr-PP and the monomer (ABA or MBA) was heated to the desired temperatures (170, 185, and 202°C), and the temperature was kept constant for certain reaction times (10, 15, 20, 30, 40, and 50 min) *in vacuo*. The amount of grafting was determined gravimetrically from the weight differences after several extensive washings of the graft coproducts by methanol and then by dimethyl sulfoxide to remove unreacted monomers and also ungrafted homopolymers of these monomers, respectively. The results were expressed as percentages of the grafted polymer by weight in the products.

Characterizations of the products

Thermal analyses of the monomers and products were carried out with a TA DSC 910S differential scanning calorimeter (New Castle, DE) under a nitrogen atmosphere at a heating rate of 20°C/min, and the sample size varied between 5 and 10 mg. A cycle of heating, cooling, and heating was carried out for the samples. The cooling after the standard initial heating was done either slowly (2°C/min) or fast (20°C/min). The second run of heating was the same as the first heating run. The results presented in thermograms of the first runs are usually averages of two or three measurements.

The X-ray diffraction patterns of irr-PP, PABA-*g*-PP, and PMBA-*g*-PP samples were obtained with a Rigaku D-MAX 2000 powder diffractometer (Tokyo, Japan) in Ankara University Central Research Labs. They were monochromator-resolved when Cu Kα radiation was employed. The profiles were measured by a scintillation counter system with a 0.5° receiving slit with a step scanning method (0.02° steps every 1 s).

RESULTS AND DISCUSSION

Graft copolymerization of ABA and MBA onto irr-PP

The dependence of the content of PABA and PMBA grafting on the reaction temperature and reaction time was examined at a constant concentration of the monomers (ABA and MBA) in the reaction medium (50/50 mixture of ABA and irr-PP by weight percentage). The extent of grafting of ABA reached a maximum value in a shorter time with increasing temperature: in 30 min at 170°C but in 15 min at 202°C (Fig. 2). The maximum amount of PMBA grafting was achieved in 40 min at 170°C, in 20 min at
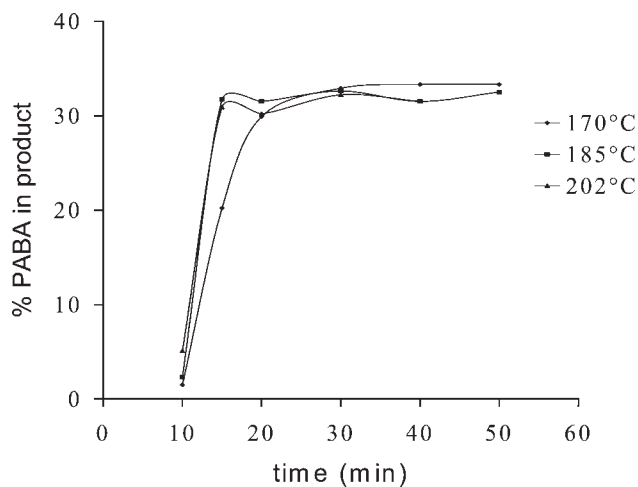
Figure 2 Dependence of the content of PABA grafted onto IPP on the reaction temperature and time.

Figure 4 Dependence of the content of PABA grafted onto IPP on the concentration of ABA in the reaction mixture.

185°C, and in 15 min at 202°C (Fig. 3). There were almost no changes in the degree of grafting in either case for longer times. This indicates that the graft copolymerization reaction proceeded very quickly and reached a plateau value within very short times. The amount of grafting at high temperatures (185 and 202°C) reached the maximum (average of 31.9% in PABA and 24.3% in PMBA) at early times of the reactions. It is important to note that 185°C and higher temperatures are well above the melting point of PP. The molten PP, having higher chain mobility, induced faster grafting in a shorter time than the grafting process at a lower temperature (170°C). Therefore, regarding a controlled degree of grafting, one can prefer an experiment at a low temperature (170°C) that is a little above the melting point of PP (163°C).

The graft copolymerization was also carried out in the presence of DCP at 170°C for a 40-min reaction time. The extents of grafting of PABA and PMBA
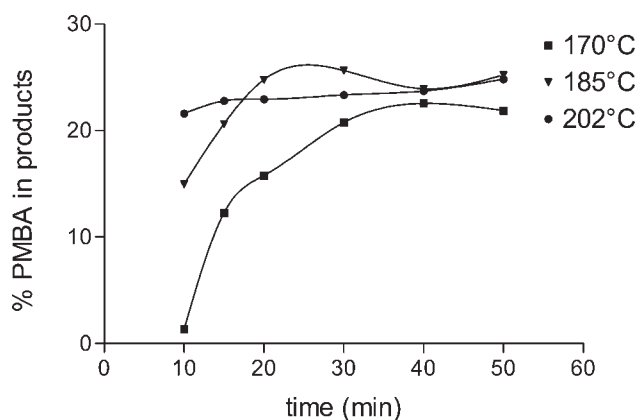
were found to be 23.8 and 20.5%, respectively. The decrease in the grafting extent was due to the direct reactions between the peroxides present in irr-PP and DCP and also the homopolymerization reactions of the monomers, ABA and MBA, initiated by DCP instead of grafting.

The variations of grafting upon changes in the mixing ratio of irr-PP and the monomer (ABA or MBA) were studied at 170°C for a 40-min reaction time (as previously mentioned, the most promising temperature and time for grafting for a 50% mixture). The amount of grafting increased with the concentration of the monomer in the reaction medium (Figs. 4 and 5). Therefore, the grafting extent could also be controlled easily by the mixture composition, temperature, and time. Indeed, for a 40-min reaction time at 170°C, the extent of grafting could be varied from 10 to 60% for PABA and from 12 to 30% for PMBA with the monomer concentration in the irr-

Figure 3 Dependence of the content of PMBA grafted onto IPP on the reaction temperature and time.

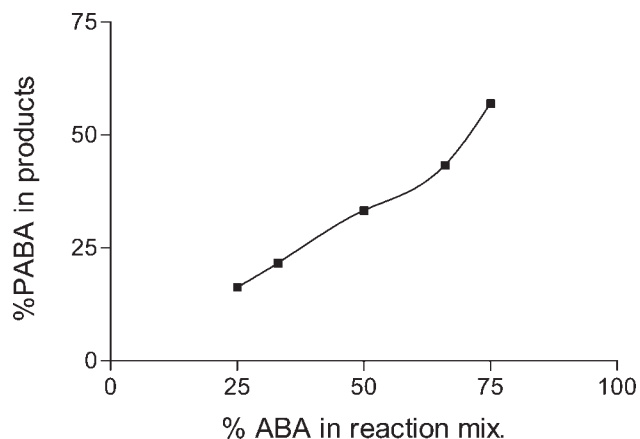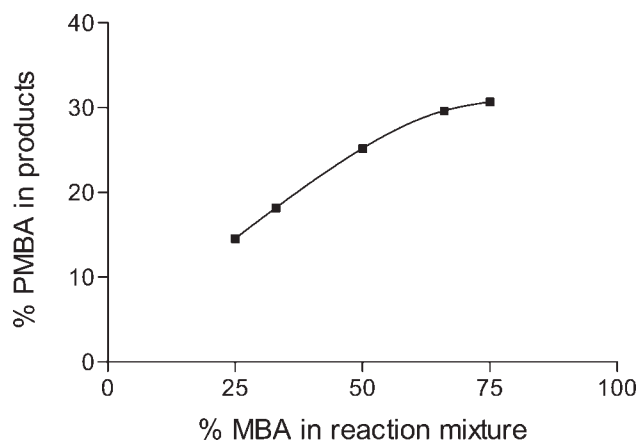**Figure 5** Dependence of the content of PMBA grafted onto IPP on the concentration of MBA in the reaction mixture.

TABLE I
DSC Results for PABA Percentages in Products at the
Reaction Temperature of 170°C After 40 min

ABA in the reaction mixture (%)	25	33	50	66	75
PABA in grafting (%)	16.3	21.9	33.3	39.1	57.0
First run[a]	160.7	159.41	156.8	157.2	157.4
	174.6	174.0			
Second run[b]	132.8	158.7	152.2	156.2	156.9

[a] From 30 to 230°C at 20°C/min and cooling at 2°C/min.
[b] From 30 to 350°C at 20°C/min.

PP/monomer mixtures. Although the extent of grafting was found to reach almost 60% in PABA, a grafting extent above 30% MBA on PP was never attained in these experiments. This could be attributed to the methyl group steric hindrance of MBA, which may restrict the radical polymerization.

Characterization of PABA-*g*-PP and PMBA-*g*-PP by DSC and WAXD

To determine the effect of the graft copolymerization of ABA and MBA onto PP on the thermal and crystallization behavior, the graft coproducts PABA-*g*-PP and PMBA-*g*-PP were analyzed with DSC and WAXD.

The crystalline structure of the α form of PP may show various degrees of disorder in the up and down positioning of the chains as a result of different thermal and mechanical histories of the samples. Two limiting structures were postulated for the α

form: a disordered limiting structure (α_1) and an ordered limiting structure (α_2).[32–34] On the other hand, the formation of the β form (hexagonal) has been shown through rapid quenching,[17] zone solidification,[19] and crystallization in a temperature gradient,[35] as mentioned before. It has been reported that the α form is thermodynamically more stable and that β-type crystals transform into the α form by a melting and recrystallization process.[17]

The isotactic PP used in these graft copolymerization experiments was basically in the α form (monoclinic, presumably α_1), as determined by WAXD experiments, which showed five reflections at spacings of 6.33, 5.26, 4.79, 4.23, and 4.08 Å with a melting point of 162.8°C. This agrees well with other works.[16–18] In the graft coproducts, the melting of the α_1 modification was observed in all products, whereas the melting of the α_2 form was detected in the samples obtained at 170°C as double melting accompanied by the α_1 form. The β form appeared in PABA-*g*-PP samples produced at 185°C and at higher temperatures and in the second run of DSC studies performed with fast cooling (20°C/min) after the first heating.

The first heating cycle of PABA-*g*-PP samples showed double-melting peaks corresponding to the two limiting structures of the α form in products composed of 16.3, 21.9, and 28.9% PABA and obtained at 170°C (Tables I and II). The first melting peak at about 160°C corresponded to the disordered limiting structure, the α_1 form, whereas the second melting peak at a higher temperature, around 174°C, arose from the ordered limiting structure, the α_2 form. Analogous double-melting behavior of the α

TABLE II
DSC Results for PABA Percentages in Products

Reaction time	10 min	15 min	20 min	30 min	40 min	50 min
Grafting (%) at 170°C	1.5	20.2	28.9	32.9	33.3	33.3
First run[a]	162.5	168.5	160.0	157.8	158.1	157.9
			172.2			
Second run A[b]	158.45	144.4	144.2	144.7	146.2	146.1
		158.0	156.1	156.9	158.2	157.9
Second run B[c]	161.1	154.9	150.9	155.8	152.2	150.2
Grafting (%) at 185°C	2.3	31.7	31.5	32.6	31.9	32.5
First run[a]	151.1	147.6	147.7	146.9	148.0	147.8
	162.6	159.2	158.5	158.8	159.6	159.6
Second run A	158.9	146.6	146.1	146.5	147.0	146.3
		159.1	158.8	158.6	159.2	158.5
Second run B[c]	161.2	156.7	153.5	155.9	150.5	136.4
Grafting (%) at 202°C	5.1	30.9	30.2	32.2	31.5	
First run[a]	164.9	148.0	147.7	146.9	148.0	
		160.0	159.7	159.6	160.2	
Second run A[b]	158.2	146.9	146.9	146.7	147.2	
		159.2	159.5	159.0	160.2	
Second run B[c]	154.7	145.2	156.5	140.1	147.4	

[a] From 30 to 230°C at a 20°C/min heating rate and then fast cooling at 20°C/min and slow cooling at 2°C/min.
[b] From 30 to 350°C at a heating rate of 20°C/min.
[c] From 30 to 350°C at a heating rate of 20°C/min.

form has also been described in several studies.[32–34] Figure 6 shows thermograms displaying the melting peaks of these α forms [Fig. 6(a)] and the peaks corresponding to the melting of the β form (ca. 148°C) with the α form [Fig. 6(b–d)]. The occurrence of α forms was also confirmed by WAXD as only the X-ray diffraction pattern of the α form was observed despite the occurrence of double-melting peaks in the thermograms of the products. The X-ray spectra of the α form and the β form accompanying it are shown in Figure 7.

In grafting processes at temperatures higher than 170°C with reaction times longer than 10 min, the formation of the β form was observed in all PABA-g-PP coproducts in the first run of DSC studies mixed with the α form. The formation of a β-type crystal appearance was also reported previously.[17,22] It was detected as a reflection of 5.59 Å from WAXD studies [Fig. 7(b)]. The product obtained at 185°C with a reaction time of 10 min containing a very low percentage of PABA (2.3%) also showed melting corresponding to the β form. However, this appeared as a very weak shoulder at 151°C attached to the melting peak of α. When the reaction time was increased to 15 and 30 min, the shoulder corresponding to the β form became more distinct and noticeable, and the melting points were observed between 147 and 148°C, as shown in Figure 6(b,c). The β form was observed as separate peaks in the
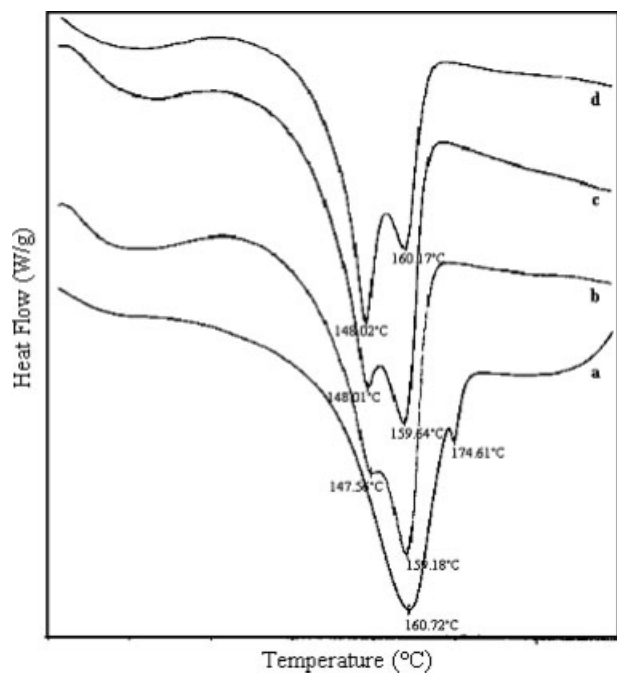

Figure 7 X-ray spectra of PABA-g-PP produced at (a) 170°C with a reaction time of 40 min (16.3% PABA) and (b) 202°C with a reaction time of 30 min (32.2% PABA).

products of 40- and 50-min reaction times, and the corresponding melting points were observed around 148°C. The melting of β-form PP at 148°C and that of α-form PP at 160°C were also shown at a heating rate of 20°C/min.[36,37]

The higher melting peaks in the region of 167°C are described as melting for the α spherulite. As the reaction time increased to 40 and 50 min, β-form crystals seemed to become more regular and ordered. In the products obtained at 202°C, which were similar to those obtained at 185°C, the β form was observed in all products except for the products of a 10-min reaction time, for which only an α form was detected at 165°C for low-grafting PABA (5.1%). The melting peaks corresponding to the β form were more distinguishable and prominent with respect to those of samples produced at 185°C [Fig. 6(c,d)]. It may be concluded that as the reaction temperature increased from 185 to 202°C, the formation of β-form crystals increased.

In the second runs after fast cooling of 20°C/min, the formation of the β form was observed in all PABA-g-PP samples [Fig. 8(a–c)], except for products of a 10-min reaction time that contained less grafted PABA. The product obtained at 170°C with a reaction time of 10 min (1.5% PABA) had only an α_1-form single melting peak at 158°C, although for the remaining products obtained at 170°C, the α form was observed between 156 and 158°C (Table II). The β form also appeared in the grafted polymers obtained with a 15-min reaction time as a shoulder at 144°C on the endotherm with the α form. The formation of the β form depended on the reaction time

Figure 6 DSC thermograms of PABA-g-PP produced at (a) 170°C with a reaction time of 40 min (16.3% PABA), (b) 185°C with a reaction time of 15 min (31.7% PABA), (c) 185°C with a reaction time of 40 min (31.9% PABA), and (d) 202°C with a reaction time of 40 min (31.5% PABA).
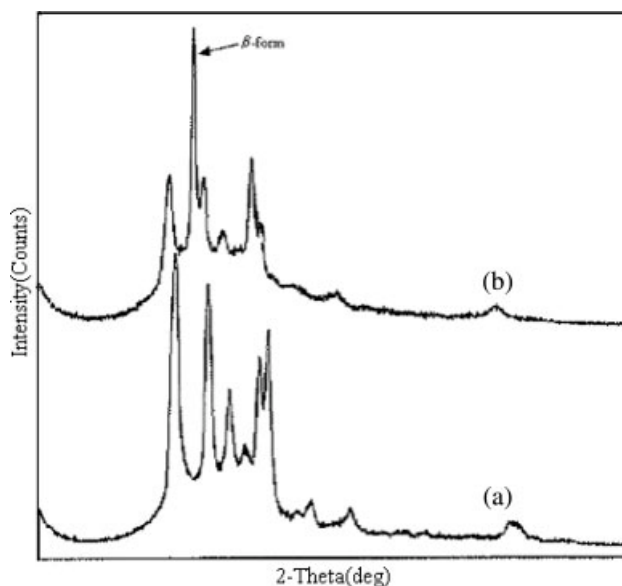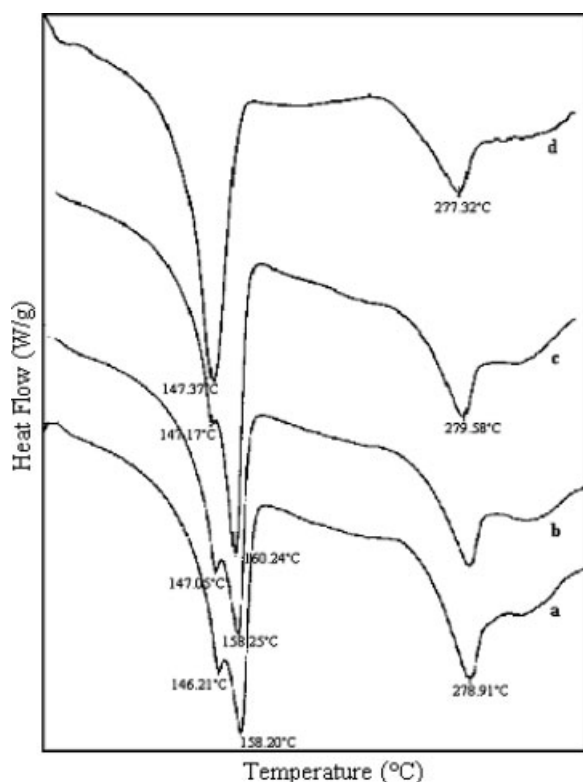
Figure 8 Second-run DSC thermograms of PABA-*g*-PP produced with a reaction time of 40 min at (a) 170 (33.3% PABA), (b) 185 (31.9% PABA), and (c) 202°C (31.5% PABA) after cooling at a rate of 20°C/min and (d) 202°C (31.5% PABA) after cooling at a rate of 2°C/min.

for the product of a 10-min reaction time at 185°C disappeared, probably because of the transformation into the α form. As the reaction time increased from 15 min, the β form appeared between 146 and 147°C more sharply with respect to those in the first runs. The melting points of the α form, like those in the first runs, were always seen between 158 and 159°C. At a reaction temperature of 202°C, a β form was observed similar to that found in the products of 185°C. The formation of the β crystalline form was still present nearly as a shoulder near the melting peak of the α form in the second runs, although they were detected as separate peaks in the first runs [Figs. 6(d) and 8(c)].

When cooling was performed at a slower rate, 2°C/min, after the first heating cycle there was no evidence corresponding to the formation of the β form in any of the products in the second heating. The second-run DSC thermogram of a PABA-*g*-PP sample produced at 202°C after slow cooling (2°C/min) is shown in Figure 8(d). Furthermore, the melting points that belonged to the melting of the α form were found to be very improper and devious in these second runs in comparison with those cooled at a faster rate (20°C/min). They were detected at lower temperatures ranging from 138.1 to 156.8°C, with the exception of the 170 and 185°C products of a 10-min reaction time with a very low percentage of PABA, which were very close to the melting point of pure PP (Table II). The β form is known to be produced by the very rapid quenching of molten samples to below 130°C.[17] The β form was formed predominantly because the rate of nucleation and/or growth of the α form was inherently slower than that in the other PPs examined, as mentioned previously. Therefore, it may also be concluded that when fast cooling was performed at a rate of 20°C/min, the formation of the β form became predomi-

in a fashion similar to that observed in the first-run DSC studies of 185°C products. For longer reaction times (20 min or more), a separate peak was seen at about 146°C, although there was no considerable difference in the PABA percentages between 30- and 40-min reaction times (32.9% and 33.3%, respectively). However, the β form detected in the first run

TABLE III
DSC Results for PMBA Percentages in Products

Reaction time	10 min	15 min	20 min	30 min	40 min	50 min
Grafting (%) at 170°C	3.8	10.2	16.7	18.8	19.8	17.9
First run[a]	149.0	163.1	162.7	161.4	151.0	170.7
	163.8		174.4	173.9	162.0	
					175.1	
Second run[b]	161.5	133.0	147.1	150.7	149.5	143.6
		152.8				
Grafting (%) at 185°C	12.3	19.7	24.6	24.4	24.6	24.2
First run[a]	143.2	161.2	161.6	149.0	161.2	161.1
	162.8			162.5		
Second run[b]	150.0	142.8	156.9	154.1	156.5	157.7
Grafting (%) at 202°C	22.6	23.9	24.1	25.4	24.3	27.0
First run[a]	151.7	161.1	160.5	161.5	161.2	159.9
	161.6					
Second run[b]	157.6	133.0	155.4	153.6	142.8	149.3

[a] From 30 to 230°C at 20°C/min and cooling at 2°C/min.
[b] From 30 to 350°C at 20°C/min.

nant with respect to the α form. A more stable α form was, therefore, formed with slow cooling at a rate of 2°C/min, but it depended on the extent of grafting. Nevertheless, despite this slow cooling, the α-form crystal did not develop perfectly and faultlessly; therefore, the melting peaks were apparently rather improper because of the higher extent of grafting.

Regarding the PMBA-g-PP samples, a double-melting peak corresponding to the two crystalline forms of the α form was observed in the products obtained at 170°C (Tables III and IV) in the first heating. Moreover, after a certain reaction time, the probable melting peaks of the α_1 form were observed between 161 and 163°C. The other melting points, presumably corresponding to the α_2 form, were observed between 171 and 175°C. Although the α_2 form was observed either as a weak shoulder or small peak in thermograms of PABA-g-PP, here it was detected as a major and sharp peak next to the melting endotherm of the α_1 form in a 30-min reaction time in some of the PMBA-g-PP samples [Fig. 9(a)]. Furthermore, the single melting point of a 50-min product, 171°C, presumably belonged to the α_2 form [Fig. 9(b)]. The melting points at 149 and around 151°C, in products of all reaction temperatures, which were observed as a very weak shoulder on the α melting, may be attributed to the melting of the β form. However, no characteristic peak of the β form could be detected in the X-ray spectra of those samples other than the diffraction peaks of the α form [Fig. 10(a)]. Weak diffraction peaks of the β form might be overlapped with the reflections of the α form. The other melting points due to the melting of the α-crystalline form were observed between 160 and 163°C.

There was no considerable difference in the melting point of the 170°C product containing a very low percentage of PMBA (3.8%) in the second runs after slow cooling at a rate of 2°C/min. In the other products obtained at all temperatures, large depressions were observed in the melting points with improper variations, and they were perceived between 133 and 158°C. For example, the melting peak at 133.0°C of
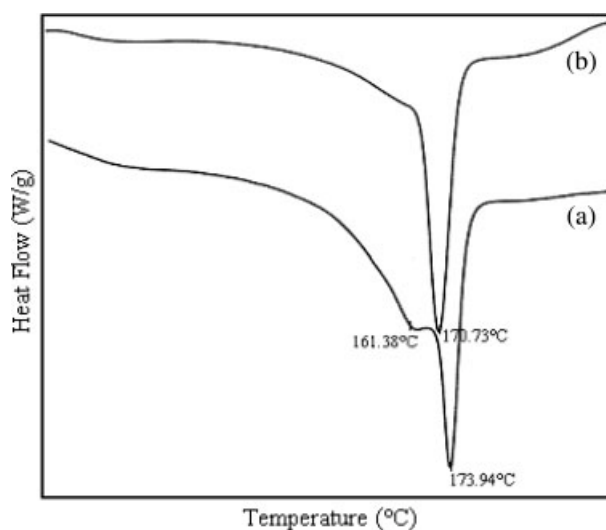

Figure 9 DSC thermograms of PMBA-g-PP produced at 170°C with reaction times of (a) 30 (18.8% PMBA) and (b) 50 min (17.9% PMBA).

the 15-min product of 170°C (Table III) was detected as a very weak shoulder on the melting endotherm of the α form. X-ray analysis showed that these melting points obviously also corresponded to the α form [Fig. 10(b)]. Any characteristic peak corresponding to the formation of the β form could not be detected on the X-ray spectra. The fast cooling (20°C/min) on the crystallization of PP after the first run of DSC did not show any reflection of the β form in PMBA-g-PP in X-ray analysis; however, we have observed β modification in the case of PABA-g-PP.

To obtain further clarification for the effect of graft copolymerization, that is, the presence of PABA or PMBA, on the formation of the α and β forms, virgin PP samples were heated to 170, 185, and 202°C, with
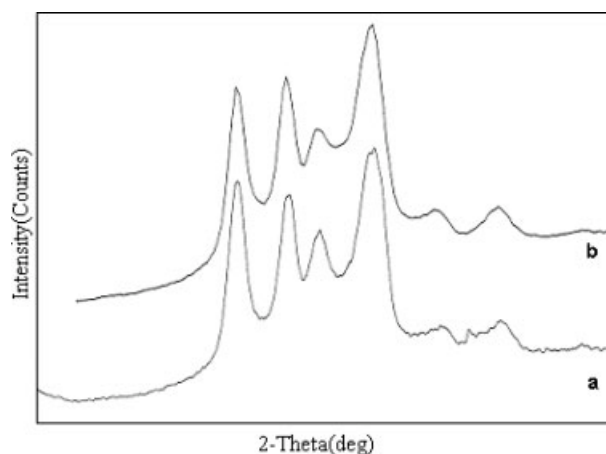
TABLE IV
DSC Results for PMBA Percentages in Products

MBA in the reaction mixture (%)	25	33	50	66	75
Grafting (%)	14.6	18.2	19.8	29.6	30.7
First run[a]	162.5	162.2	151.0	160.6	160.3
		175.1	162.0		174.8
			175.1		
Second run[b]	153.8	153.2	149.5	150.4	150.7

[a] From 30 to 230°C at 20°C/min and cooling at 2°C/min.
[b] From 30 to 350°C at 20°C/min.

Figure 10 X-ray spectra of PMBA-g-PP produced with a reaction time of 40 min at (a) 170 (19.8% PMBA) and (b) 202°C (heated to 230°C and cooled to room temperature at 2°C/min; 23.8% PMBA).

the temperature kept constant for 30 min *in vacuo*, as graft copolymerization experiments were carried out. A double melting of 165 and 176°C was also observed in virgin PP that was kept in the melt state at 170°C for 30 min. These melting points can apparently be attributed to the α_1- and α_2-crystalline forms. In the experiments at 185 and 202°C, melting was detected at 159 and 161°C, respectively; obviously, the α_1 form was found, but there was no β.

Finally, the crystalline melting of grafting polymer PABA was observed between 275 and 287°C in all graft coproducts (Fig. 8). PABA was indexed to a monoclinic unit cell by Blumstein et al.[28] One of the reflections reported at the spacing of 4.47 Å, corresponding to the monoclinic cell, was also observed in the X-ray spectrum of the graft coproducts (Fig. 7). However, the other diffraction peaks noted, 3.71 and 3.08 Å, overlapped with the peaks of PP, and it could hardly be stated that these diffraction peaks arose from either PP or PABA units. A loose and weak melting point of PMBA was observed between 274 and 286°C for the graft coproducts, and this was not very conclusive in comparison with the PABA-*g*-PP samples. The smectic structure of PMBA was reported by Blumstein and Kitagawa[25] with the reflection at the spacing of 4.44 Å in WAXD. No reflection peak was detected on the X-ray spectra corresponding to the smectic structure in these PMBA-*g*-PP products, again because of a possible overlapping with the reflections of the α form (Fig. 10).

CONCLUSIONS

The best way of grafting either of these monomers can be achieved at a lower temperature (170°C) and with control of the mixture ratio of the matrix polymer. Because of the presence of the methyl group in MBA, high grafting degrees should not be expected. We could state that the crystallization of PP units in both α_1 and α_2 forms in the graft copolymer was not affected by the presence of grafting units of PABA, but the presence of PABA caused the formation of the β form in the graft coproducts obtained at 185°C and at higher temperatures. PABA also led to the formation of the β form in the second run of DSC studies when fast cooling was performed at a rate of 20°C/min. The presence of PMBA, however, led to the predominant formation of the α_2 form in some of the graft products obtained at 170°C. At higher temperatures, the crystallization of PP units in both α_1 and α_2 modifications in the graft form were found to be not affected by the presence of grafting units

of PMBA. In addition, in comparison with the graft copolymer PABA-*g*-PP, PMBA did not have any influence on the crystallization of PP during the high-temperature grafting process leading to the formation of the β form.

References

1. Done, D.; Sukhadia, A. M.; Datta, A.; Baird, D. G. Soc Plast Eng Tech Pap 1990, 48, 1857.
2. Datta, A.; Sukhadia, A. M.; Desouza, J. P.; Baird, D. G. Soc Plast Eng Tech Pap 1991, 49, 913.
3. Federici, C.; Attalla, G.; Chapoy, L. Eur. Pat. A2:0 340 655 (1989).
4. Yongcheng, Y.; La Mantia, F. P.; Valenza, A.; Citta, V.; Pedretti, U.; Roggero, A. Eur Polym J 1991, 27, 723.
5. Tjong, S. C.; Liu, S. L.; Li, R. K. Y. J Mater Sci 1996, 31, 479.
6. Barham, P. J.; Keller, A. J. J Mater Sci 1985, 20, 2281.
7. Done, D.; Baird, D. G. Polym Eng Sci 1987, 27, 816.
8. Done, D.; Baird, D. G. Polym Eng Sci 1990, 30, 989.
9. O'Donnel, H. J.; Baird, D. G. Polymer 1995, 36, 3113.
10. He, J.; Liu, J. J Appl Polym Sci 1998, 67, 2141.
11. Datta, A.; Chen, H. H.; Baird, D. G. Polymer 1993, 34, 759.
12. Datta, A.; Baird, D. G. Polymer 1995, 36, 505.
13. Kozlowski, M.; Mantia, F. P. L. J Appl Polym Sci 1997, 66, 969.
14. Ide, Y.; Ophir, Z. Polym Eng Sci 1983, 23, 261.
15. Kohli, A.; Chung, N.; Weiss, R. A. Polym Eng Sci 1989, 29, 573.
16. Natta, G.; Corradini, P. Nuovo Cimento Suppl 1960, 15, 9.
17. Jones, A. T.; Aizlewood, J. M.; Beckett, D. R. Makromol Chem 1964, 75, 134.
18. Napolitano, R.; Prozzi, B.; Varriale, V. J Polym Sci Part B: Polym Phys 1990, 28, 139.
19. Lovinger, A. J.; Chua, O. J.; Gryte, C. C. J Polym Sci Polym Phys Ed 1977, 15, 641.
20. Leugering, V. H. J Makromol Chem 1967, 109, 204.
21. Morrow, D. R.; Newman, B. A. J Appl Phys 1968, 39, 4944.
22. Baer, E.; Kardos, J. L. J Polym Sci Part A: Gen Pap 1965, 3, 2827.
23. Nakafuku, C. Polymer 1981, 22, 1673.
24. Kojima, M. J Polym Sci Part A-2: Polym Phys 1968, 6, 1255.
25. Blumstein, A.; Kitagawa, N. Mol Cryst Liq Cryst 1971, 12, 215.
26. Blumstein, A.; Billard, J.; Blumstein, R. Mol Cryst Liq Cryst 1974, 25, 83.
27. Blumstein, A.; Blumstein, R. B.; Clough, S. B.; Hsu, E. C. Macromolecules 1975, 8, 73.
28. Blumstein, A.; Blumstein, R. B.; Clough, S. B.; Patel, L.; Hsu, E. C. Macromolecules 1976, 9, 243.
29. Menczel, J.; Wunderlich, B. Polymer 1981, 22, 778.
30. Menczel, J.; Walsh, J. P.; Wunderlich, B. J Polym Sci Polym Phys Ed 1981, 19, 837.
31. Sainath, A. V. S.; Inoue, T.; Yonetaka, K.; Koyama, K. Polymer 2001, 42, 9859.
32. Guerra, G.; Petraccone, V.; Corradini, P.; De Rosa, C.; Napolitano, R.; Pirazzi, B. J Polym Sci Polym Phys Ed 1984, 22, 1029.
33. International Tables for X-Ray Crystallography; Kynoch: Birmingham, England, 1952; Vol. I.
34. Pae, K. D.; Sauer, J. A. J Appl Polym Sci 1968, 12, 1901.
35. Asano, T.; Fujiwara, Y.; Yoshida, T. Polym J 1979, 11, 383.
36. Karger-Kocsis, J. Polypropylene 1: Structure, Blends and Composites; Chapman & Hall: London, 1995; p 37.
37. Jacoby, P.; Bersted, B. H.; Kissel, W. J.; Smith, C. E. J Polym Sci Part B: Polym Phys 1986, 24, 461.