

# Functionalized Polypropylene Prepared by Melt Free Radical Grafting of Low Volatile Oxazoline and Its Potential in Compatibilization of PP/PBT Blends

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## SYNOPSIS

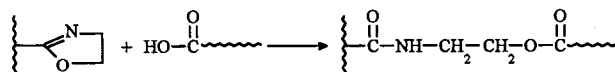
This article concerns the functionalization of polypropylene (PP) with oxazoline functionality by melt free radical grafting along with a low degree of degradation of PP in a batch mixer. A low volatile oxazoline, ricinoloxazoline maleinate (OXA), was used as the monomer. The grafting yield of OXA ranged from about 0.5 phr up to 1.5 phr (grams per 100 grams of PP) when its initial concentration and that of the peroxide ranged from 1.5 to 6.0 phr and 0.1 to 0.7 phr, respectively. The corresponding conversion of OXA to grafted OXA ranged from about 15 to 50%. Addition of styrene (St) as the comonomer did not enhance the grafting yield of OXA but markedly reduced the PP degradation. Also, little homo- and/or copolymers of OXA and/or St were found in the grafting system. This agrees with our finding that OXA and St did not copolymerize easily. The potential of using an OXA modified PP (PP-*g*-OXA) as the compatibilizer precursor in PP/PBT blends was examined as well. The presence of PP-*g*-OXA reduced the particle size of the dispersed phase (PBT) along with improved cohesion between the PP and PBT phases. This is consistent with a model kinetic study, which showed that the reaction between oxazoline and carboxylic functionalities was very fast. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The search for new and interesting polymeric materials with complementary properties has recently intensified. A relatively easy and cost-effective way to produce new combination of properties is blending. However, most blends achieved by melt mixing are immiscible and thus exhibit poor properties. Therefore, compatibilization is needed to obtain a blend with desired properties. A common way to improve the compatibility between two immiscible polymers is to add preformed block or graft copolymers.

Graft copolymers of polyolefins are widely used as compatibilizers in the blends of polyolefins with engineering plastics such as polyamides and polyesters. Graft copolymers are produced by the melt free radical grafting of monomers onto the polyolefin chains. The most commonly employed monomers are maleic and itaconic anhydrides and vinyl and acrylic monomers containing reactive functional groups.

The oxazoline functionality is also interesting owing to its reactivity towards a carboxylic group to form an esteramide, as shown below:



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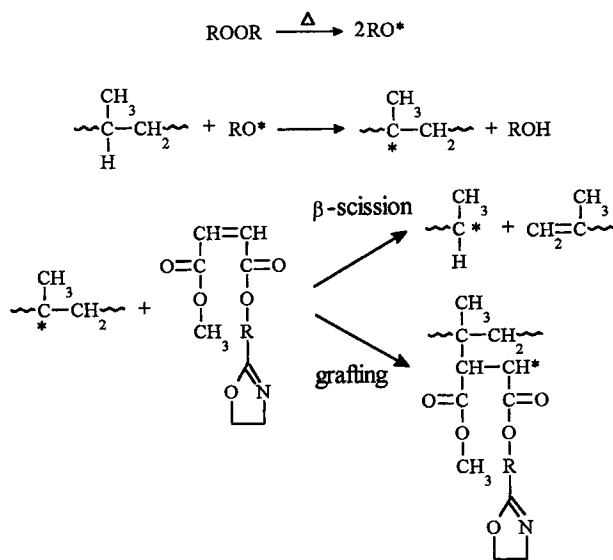
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This reactivity should be useful for the compatibilization of blends of which one polymer component contains a carboxylic group. The oxazoline group can also react with other functional groups

such as amine, phenol, and mercaptan. An overview of the reactions and preparation of different oxazolines can be found in the literature.<sup>1</sup>

In fact, the oxazoline functionality has already been employed in compatibilization studies. For example, a copolymer of styrene and vinyloxazoline has been used in the reactive blending of PS with PE bearing carboxylic groups and with NBR.<sup>2-5</sup> PP functionalized with 2-isopropenyl-2-oxazoline has been used as a compatibilizer precursor in PP/NBR<sup>6,7</sup> and in PP/PC<sup>8</sup> blends.

This article describes how to graft oxazoline onto PP by melt free radical grafting and examines the efficiency of using such functionalized PP as a compatibilizer precursor for PP/PBT blends. The oxazoline monomer used here is ricinoloxazoline maleinate (OXA), which was earlier used for functionalizing polyethylene (PE)<sup>9,10</sup> and poly(*n*-butylacrylate).<sup>11</sup> The overall free radical grafting scheme of the OXA onto PP is depicted below:



Of course, the above free radical grafting scheme should be completed with homopolymerization of the monomer, various termination, and transfer processes along with other possible reactions.

As shown in the overall grafting scheme, PP is prone to chain degradation by  $\beta$ -scission when free radicals are present. Our previous studies showed that addition of styrene (St) as a comonomer not only allowed to increase greatly the grafting yield of maleic anhydride (MAH)<sup>12</sup> and glycidyl methacrylate (GMA)<sup>13-15</sup> but also to reduce PP degradation. Basically, in the case of MAH, its double bond is highly activated by the formation of a charge transfer complex (CTC).<sup>16</sup> In the case of GMA, the basic

concept is that addition of a comonomer should be beneficial if this comonomer can react with PP tertiary radicals much faster than GMA and the resulting radicals can readily copolymerize with GMA leading to grafted GMA moieties. In this case, GMA is not grafted directly into PP but via this comonomer. Obviously this concept is more general and works only when the comonomer is capable of doing two things: it reacts with a PP macroradical rapidly and the resulting radical copolymerizes with GMA easily. St is an ideal comonomer because it has a greater reactivity towards PP macroradicals than GMA. Also, its corresponding radical is more stable than a GMA radical and copolymerizes easily with GMA leading to grafted GMA moieties.

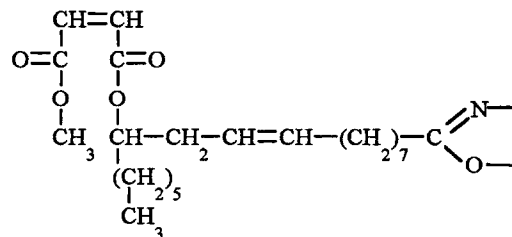
In this article the effect of St addition on the grafting yield of the OXA and the degradation of PP will be examined. Possible homo- and/or copolymerization of the OXA and/or St will also be discussed.

## EXPERIMENTAL

### Materials

The polypropylene (Himont, Valtec CL101D, MFI = 0.3 g/10 min) was a random copolymer of propylene and ethylene (6–12 wt %), supplied in the form of small porous pellets capable of absorbing liquid monomers. The number and weight average molecular weights of the PP were 141,000 and 654,000 g/mol, respectively. The poly(butylene terephthalate) (PBT) used in the blending experiments was Arnite T08-200 from DSM-Akzo ( $\bar{M}_n$  = 28000 g/mol,  $\bar{M}_w$  = 65,000 g/mol). The concentrations of the terminal groups were [—COOH] = 0.040 eq/kg and [—OH] = 0.032 eq/kg.

The monomer containing the oxazoline group was ricinoloxazoline maleinate (OXA) supplied by Henkel KGaA (grade: Loxamid V-EP 8515). Its chemical structure is presented below:



This monomer is in liquid form and exhibits very low volatility (bp > 250°C at 0.1 mbar). Styrene was used as a comonomer (Aldrich, purity 99%). The

peroxide was 1,3-bis(*tert*-butylperoxy-isopropyl)benzene, supplied by Akzo (Perk-14, purity 90%). The estimated half-lifetime at the melt grafting temperatures (206–212°C) was about 17 to 11 s, respectively.

### Grafting and Blending Procedure

The melt free radical grafting was carried out in a melt mixer (Haake Rheomix 600, 50 cm<sup>3</sup>) equipped with two counterrotating sigma rotors. The rotor speed was 64 rpm and the set temperature 200°C. Depending on the viscous dissipation, the actual melt temperature ranged from 206 to 212°C. Before the materials were charged to the mixer, the monomers and peroxide were allowed to absorb into small porous PP pellets for about 15 min. The initial concentration of the OXA varied between 1.5 and 6.0 phr, that of St between 0.36 and 1.44 phr, and that of the peroxide between 0.1 and 0.7 phr. To allow the comparison of the steady state torque, a given amount of PP was charged to the mixer for all experiments. The grafting time was typically 15 min after startup, and in some experiments 2 and 4 min. After 15 min of mixing, samples were taken from the mixer and cooled immediately in liquid nitrogen.

The blending procedure (blends of functionalized PP with PBT) was similar to the grafting procedure except that the set temperature of the mixer was 250°C (actual melt temperatures 256–258°C).

### Purification of Samples and Determination of Grafting Yield

The functionalized PP samples were purified by dissolving them in boiling xylene and then, by precipitating them either in acetone or in methanol. Acetone could precipitate only the unmodified and modified PP [i.e., PP, PP-*g*-OXA, PP-*g*-St, and PP-*g*-(OXA-*co*-St)], while the methanol precipitated not only the unmodified and modified PP but also the possible nongrafted homo- and copolymers of OXA and St [i.e., P(OXA), PS, P(OXA-*co*-St)]. By this procedure any homo- and copolymer of OXA and St was separated and the real grafting yield could be determined.

The grafting yield was determined by FTIR (Nicolet SX60) from thin (100–150 mm) compression molded films of the purified PP samples. The peak at 2722 cm<sup>-1</sup> representing the skeleton of the PP chain was chosen as the reference. The peak at 1671 cm<sup>-1</sup> was attributed to a complex mode involving C—N stretching and oxazoline ring bending, and was treated as a characteristic peak of the grafted

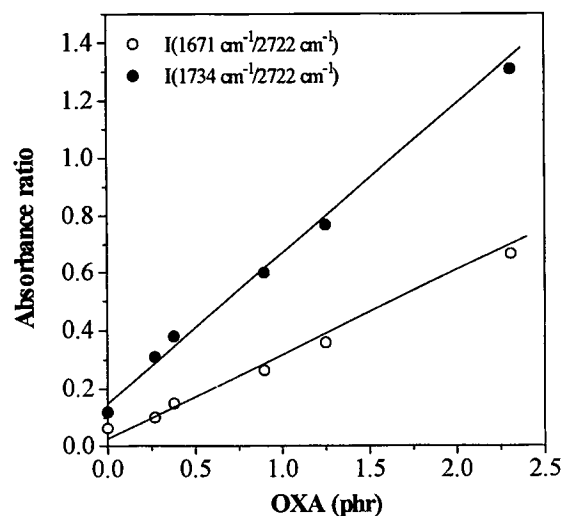
OXA. Another strong peak at 1734 cm<sup>-1</sup> (resulting from the ester group in OXA) was also treated as a characteristic peak of OXA to verify the results. The peak at 700 cm<sup>-1</sup> was chosen as the characteristic peak of grafted St. Calibration curves (Fig. 1) were made using samples containing known concentrations of OXA based on elemental analysis. Grafting yields were then calculated from the ratios of the intensities of the characteristic absorbance peaks. The IR calibration curve established elsewhere<sup>13</sup> was used to determine St grafting yields.

### Determination of Molecular Weights

The number and weight average molecular weights of the functionalized polypropylenes were determined by gel permeation chromatography (Waters 150-C ALC/GPC, equipped with three Waters Styragel columns: 10<sup>3</sup>, 10<sup>4</sup>, and 10<sup>5</sup> Å in series) at 140°C with a flow rate of 1 mL/min. The solvent was 1,2,4-trichlorobenzene.

### Characterization of Blend Morphology

The morphology of the melt mixed functionalized PP/PBT blends was analyzed with a scanning electron microscope (SEM, JEOL JXA-840A). The samples were prepared by fracturing them after liquid nitrogen cooling. Before scanning, the fractured surface was coated with a 15 nm layer of gold.



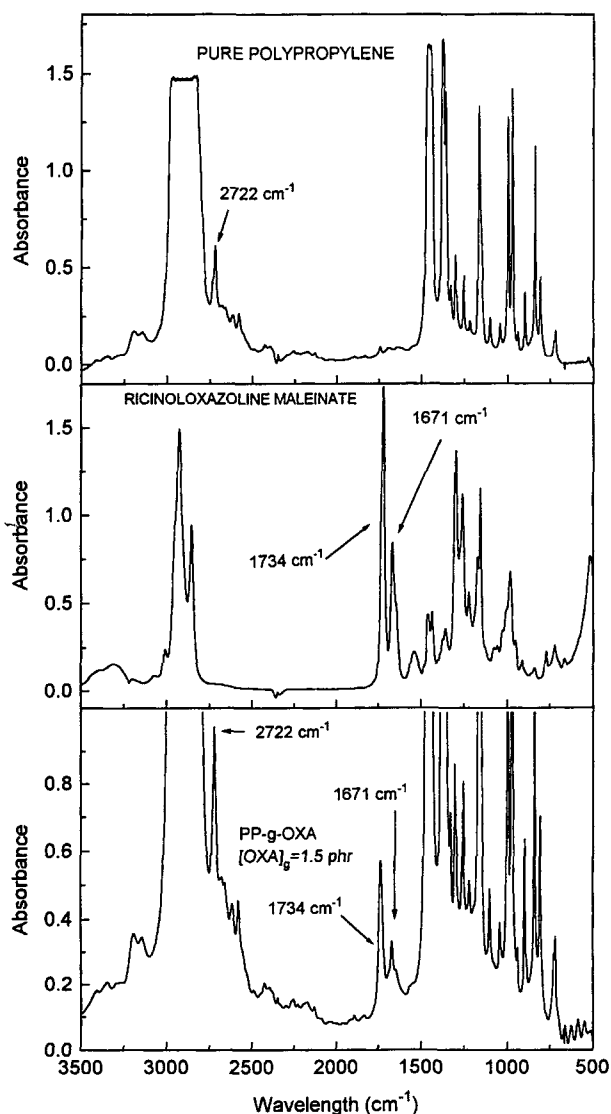
**Figure 1** Calibration curves for the determination of the content of OXA by FTIR.

## RESULTS AND DISCUSSION

### Functionalization of PP

The IR spectra of the pure PP, pure OXA, and a typical PP-*g*-OXA are shown in Figure 2. In the case of the PP-*g*-OXA, a peak appears at  $1671\text{ cm}^{-1}$ , which is characteristic of the oxazoline ring. The amount of grafted OXA could be calculated from the ratio of the intensities of the absorbance peaks at  $1671$  and  $2722\text{ cm}^{-1}$  by using the earlier established calibration curve (Fig. 1).

The compositions of different grafting experiments and the corresponding grafting yields of the monomers are set out in Table I.



**Figure 2** FTIR spectra of pure polypropylene (top), ricinoloxazoline maleinate (middle), and PP-*g*-OXA (bottom,  $[\text{OXA}]_g = 1.5$  phr).

The grafting yield of OXA onto PP varied from about 0.5 to 1.5 phr, while that of St ranged from 0.2 to 0.5 phr, depending on the concentrations of the monomers and peroxide at feed. Thus, the conversion of OXA monomer to grafted OXA ranged from about 15 to 50%. The lowest conversion of OXA was obtained at high initial concentration of OXA and low peroxide concentration.

### Effect of Initial Peroxide Concentration on the Grafting Yield

The effect of the initial peroxide concentration on the grafting yield of OXA and the comonomer St are illustrated in Figure 3. As expected, the higher the initial peroxide concentration, the higher the grafting yields of OXA and St. For example, when the initial peroxide concentration was increased from 0.1 phr to 0.7 phr, the grafting yield of OXA increased from about 0.5 phr to 1.5 phr (when St was not added). At the same time, the conversion of OXA monomer to grafted OXA increased from 19 to 50%. The conversions of St monomer to grafted St were higher (up to 70%) than those of OXA. Note that without externally added peroxide, no grafting was observed, either for OXA or for St.

It is also shown in Figure 3 that when St was added as comonomer, the grafting yield of OXA did not increase, unlike our earlier studies concerning the melt free radical grafting of glycidyl methacrylate (GMA)<sup>13-15</sup> and maleic anhydride (MAH).<sup>12,16</sup> Instead, the grafting yield of OXA was even decreased as compared to the cases where St was not added. This will be discussed further below.

### Effect of the Initial Concentration of OXA on Its Grafting Yield

The effect of the initial concentration of OXA on its grafting yield is depicted in Figure 4. As the initial concentration of OXA was increased from 1.5 phr to 6.0 phr, its grafting yield increased from about 0.6 to 1.5 phr, while its conversion to grafted OXA decreased from about 40 to 25%. When St was added, lower grafting yields and, thus, lower conversions of OXA were obtained. For a particular application, there must be an optimal initial concentration of OXA corresponding to a best compromise between grafting yield and nonreacted monomer. This could be of vital importance for the OXA used here because of its low volatility. This latter gives rise to greater difficulties of removing nonreacted OXA from the system.

**Table I** Compositions of the Grafting Experiments

Exp. No.	[OXA] <sub>i</sub> (phr)	[St] <sub>i</sub> (phr)	[ROOR] <sub>i</sub> (phr)	[OXA] <sub>g</sub> (phr)	[OXA] <sub>t</sub> (phr)	Grafting efficiency <sup>a</sup>	[St] <sub>g</sub> (phr)	Conv. <sup>b</sup> (%)	Torque <sup>c</sup> (Nm)
1	0	0	0	—	—	—	—	—	13.7
2	3.0	0	0	0	2.31	0	—	0	11.8
3	1.5	0	0.3	0.61	0.87	2.4	—	41	1.4
4	1.5	0.36	0.3	0.58	0.80	2.6	0.25	39	2.2
5	3.0	0	0.3	1.05	1.95	1.2	—	35	1.7
6	3.0	0.36	0.3	0.87	1.83	0.9	0.25	29	2.7
7	3.0	0.72	0.3	0.70	1.66	0.7	0.34	23	3.1
8	3.0	1.08	0.3	0.72	1.88	0.6	0.51	24	4.6
9	3.0	0	0.1	0.56	1.84	0.4	—	19	5.4
10	3.0	0	0.7	1.51	2.01	3.0	—	50	0.3
11	3.0	0.72	0.1	0.46	1.80	0.3	0.22	15	6.3
12	3.0	0.72	0.7	1.35	1.93	2.3	0.43	45	1.0
13	6.0	0	0.3	1.47	3.52	0.7	—	25	2.6
14	6.0	1.44	0.3	1.02	3.47	0.4	0.46	17	4.3
15	0	0.36	0.3	—	—	—	0.27	—	2.2
16	0	0.72	0.3	—	—	—	0.44	—	3.1
17	0	1.08	0.3	—	—	—	0.65	—	5.6

Concentrations are expressed in grams per hundred grams of polypropylene (phr).

<sup>a</sup> The grafting efficiency is defined as the ratio of concentration of grafted OXA to residual OXA,  $[OXA]_g/[OXA]_t$ .

<sup>b</sup> The conversion of OXA monomer to grafted OXA.

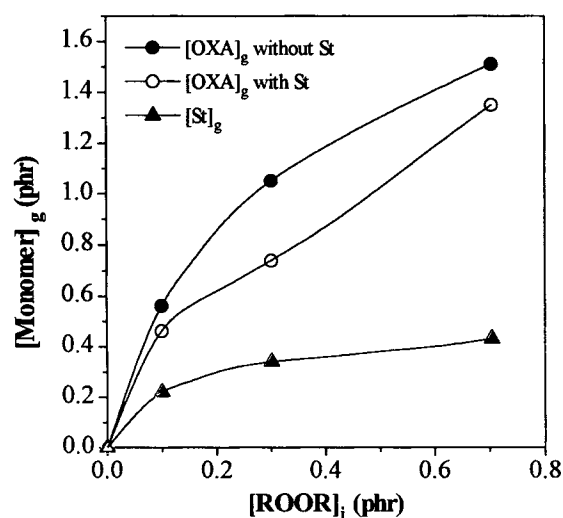
<sup>c</sup> The value of torque after 15 min of mixing.

### Effect of the Initial Concentration of St on the Grafting Yield

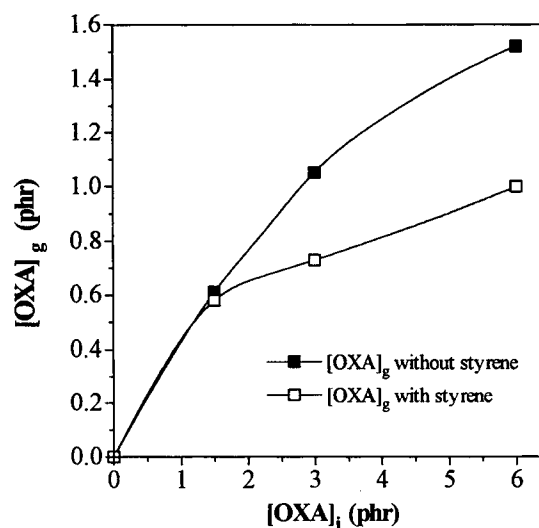
Different initial concentrations of St were used to quantify its effect on the grafting efficiency. As shown in Figure 5, for a given concentration of OXA, increasing the concentration ratio  $[St]_i/[OXA]_i$  from 0 to 1.5 mol/mol decreased the grafting yield of OXA

from about 1.0 phr to 0.7 phr. At the same time the grafting yield of St was increased to 0.5 phr (1.08 phr at feed).

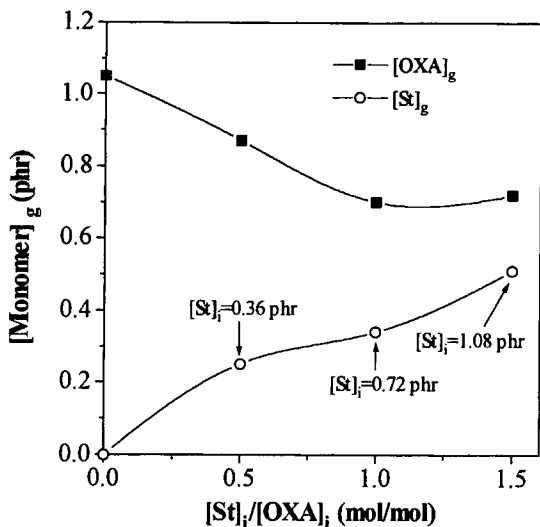
St alone was also grafted onto PP (Experiments 15–17 in Table I). As shown in Figure 6, the grafting yield of St was higher when OXA was not added. Combining the results shown in Figures 4 and 6 al-



**Figure 3** Effect of the initial peroxide concentration on the grafting yields of OXA and St.  $[OXA]_i = 3.0$  phr,  $[St]_i = 0.72$  phr (if St added).



**Figure 4** Effect of the initial concentration of OXA on the grafting yield of OXA.  $[ROOR]_i = 0.3$  phr,  $[St]_i = 0.72$  phr (if St added).



**Figure 5** Effect of the molar ratio of St and OXA on the grafting yield of the monomers.  $[OXA]_i = 3.0$  phr,  $[ROOR]_i = 0.3$  phr.

lows us to conclude that the presence of each monomer (OXA and St) adversely affects the grafting yield of the other.

After all, the negative effect of adding St on the grafting yield of OXA can be explained. As stated earlier, the concept of using a comonomer works only when the following two conditions are satisfied: the reactivity of the comonomer towards PP macroradicals must be greater than the monomer (OXA) and the resulting radical must copolymerize readily with the monomer leading to grafted monomer moieties. In the case of OXA and St, separate polymerization experiments showed that the second condition was not fully satisfied.

In fact, we carried out polymerization reactions in solution (solvent: xylene) at 70°C for 8 h with 1 wt % of azobisisobutyronitrile (AIBN) used as an initiator. Five different monomer compositions of OXA/St by weight were (co)polymerized: 100/0, 75/25, 50/50, 25/75, and 0/100. The (co)polymers were precipitated in methanol. Results showed that the OXA did not homopolymerize at all under the above conditions. On the other hand, St homopolymerized readily, as expected. In the copolymerization experiments, only high amounts of St (50 and 75 wt %) led to copolymers. Furthermore, the conversions were low and the molecular weights of the copolymers were small. The composition of OXA/St = 75/25, which is close to that of the grafting compositions did not yield any homopolymer or copolymer. The fact that OXA and St do not copolymerize easily is surely the main factor that is responsible for the

negative effect of adding St on the grafting yield of OXA.

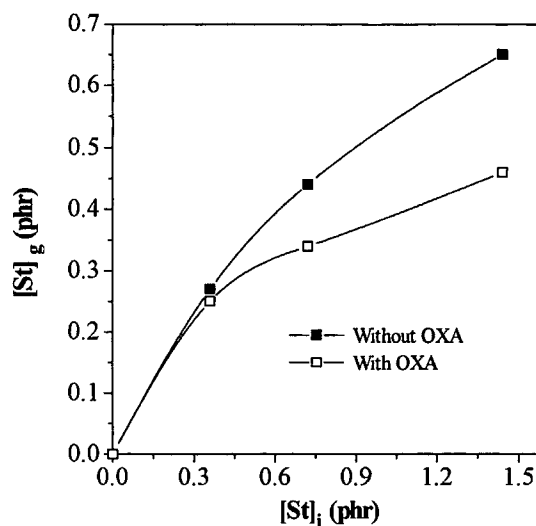
The copolymers generated from the OXA/St compositions of 50/50 and 25/75 were found to be readily soluble in acetone but not at all in methanol. We also found that the grafting yields of OXA and St measured from the samples precipitated in methanol and acetone were virtually the same for all grafting experiments. In fact, as shown by our previous work (see Fig. 2 in Ref. 14), the homopolymerization of St is very weak at low initial concentration of St ( $< 2$  phr). Thus, styrene is much more easily grafted onto PP than homopolymerized in the conditions applied in this study. This fact, together with the copolymerization experiments shown above, suggests that nonreacted OXA and St were primarily in the form of monomers.

### Rate of Grafting Reactions

It was estimated by taking samples after 2 and 4 min of mixing. As shown in Figure 7, the reaction is very fast: about 75% of the ultimate grafting yield is reached within 2 min of mixing. The grafting reaction is almost over within 4 min of mixing. The very fast grafting rate is primarily governed by the half-life of the peroxide under the actual processing conditions.<sup>16</sup>

### Molecular Weight of Functionalized PPs

The changes in molecular weight during the grafting reactions are presented in Figure 8. As expected, the



**Figure 6** Grafting yield of St as a function of its initial concentration.  $[ROOR]_i = 0.3$  phr,  $[St]_i/[OXA]_i = 1.0$  mol/mol (if OXA added).

molecular weight decreased dramatically with increasing peroxide concentration. Moreover, the molecular weight distribution ( $\bar{M}_w/\bar{M}_n$ ) became narrower with increased degradation. For example, when the  $\bar{M}_w$  dropped from 250,800 to 88,600 g/mol, the molecular weight distribution decreased from 3.6 to 2.3. Addition of St as a comonomer reduced PP degradation.

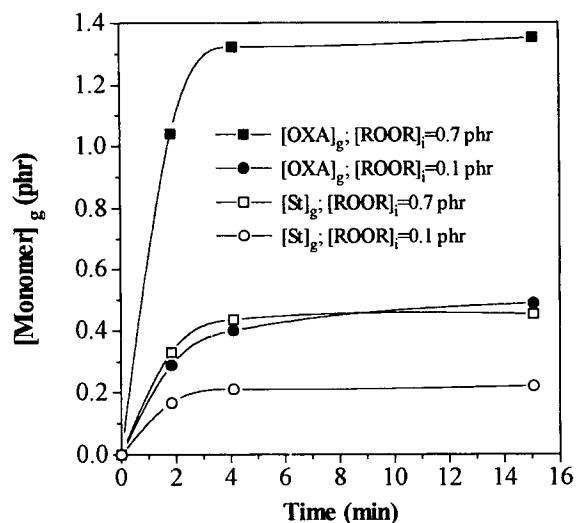
### Compatibilization of PP and PBT Blends

Blends of functionalized PP with PBT were prepared to examine the compatibilization efficiency of the PP-g-OXA. The blend compositions are shown in Table II. The ratio of the amount of the carboxylic group to the amount of the oxazoline group was varied by changing the proportion of the functionalized PP. The viscosity ratio of the blend components ( $\eta_{PBT}/\eta_{PP}$ ) under the actual blending conditions ( $T \approx 260^\circ\text{C}$ , shear rate  $\approx 240\text{ s}^{-1}$ ) was 0.6 measured by capillary rheometer (Rosand RH7-2).

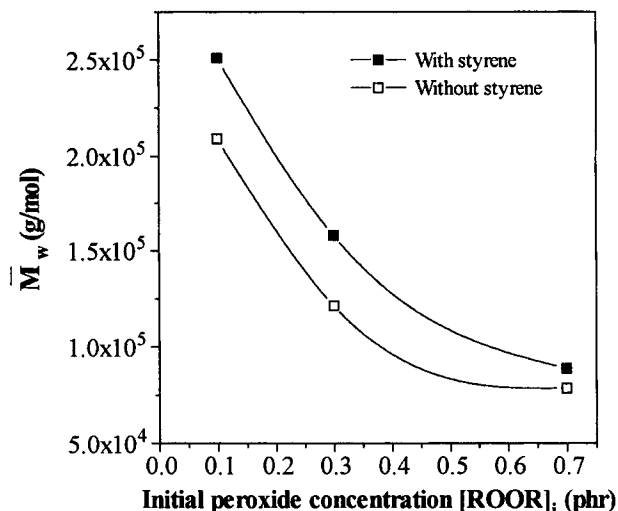
The morphology of the blends was characterized by SEM. As shown in Figure 9, the particle size of the dispersed phase (PBT) was reduced from 2–5  $\mu\text{m}$  to 0.5–1  $\mu\text{m}$  when the functionalized PP was added. Also, the phase boundaries became less clear when a PP-g-OXA was added to the blend. This is typical of compatibilized blends with improved phase cohesion.

### Kinetics of the Reaction between Oxazoline and Carboxylic Groups

To better characterize the reaction between oxazoline and carboxylic groups, a model system was cho-

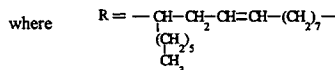
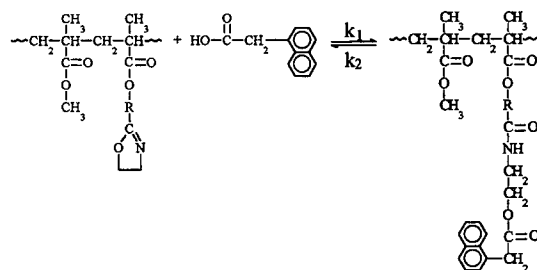


**Figure 7** Grafting yield of OXA as a function of mixing time.  $[\text{OXA}]_i = 3.0\text{ phr}$ ,  $[\text{St}]_i = 0.72\text{ phr}$ ,  $[\text{St}]_i/[\text{OXA}]_i = 1.0\text{ mol/mol}$ .



**Figure 8** Weight average molecular weight (measured by GPC) of functionalized PP as a function of the initial peroxide concentration.  $[\text{OXA}]_i = 3.0\text{ phr}$ ,  $[\text{St}]_i = 0.72\text{ phr}$  (if St added).

sen. It consisted of a laboratory-made copolymer of methyl methacrylate (93.7 wt %) and ricinoloaxolinemethacrylate (6.3 wt %), and of 1-naphthylacetic acid (NA, powder form, melting temp.  $130^\circ\text{C}$ ). The reaction scheme can be written as follows:



The reaction was performed in a Haake Rheomix 600 melt mixer (50  $\text{cm}^3$ ) at four temperatures (165, 175, 185, and  $195^\circ\text{C}$ ) for 50 min at a rotation speed of 64 rpm. The initial concentration of the reactive groups was  $[\text{carboxylic}]_i/[\text{oxazoline}]_i = 1.6\text{ mol/mol}$ . Samples were taken at intervals of 10 min (first sampling at 3 min). The purified samples dissolved in chloroform were analyzed by UV spectrometer (Shimadzu UV2101PC) to detect the conversion of the acid as a function of time. The acid (NA) could easily be detected at 293 nm. The conversion of the acid as a function of time is presented in Figure 10. The equilibrium constants  $K_e$  (in Table III) were calculated on the basis of the conversion data.

**Table II** Compositions of PP/PBT Blends

Blend	Pure PP (wt %)	Functionalized PP (wt %)	PBT (wt %)	[—COOH]/[—OXA] <sup>c</sup> (mol/mol)
Blend 1	70	0	30	—
Blend 2	60	10 <sup>a</sup>	30	5.0
Blend 3	60	10 <sup>b</sup>	30	5.0
Blend 4	0	70 <sup>b</sup>	30	0.7

Blends were prepared in a batch mixer at 250°C.

<sup>a</sup> Functionalized PP contained only PP-*g*-OXA, free of residual OXA; [OXA]<sub>g</sub> = 1.05 phr.

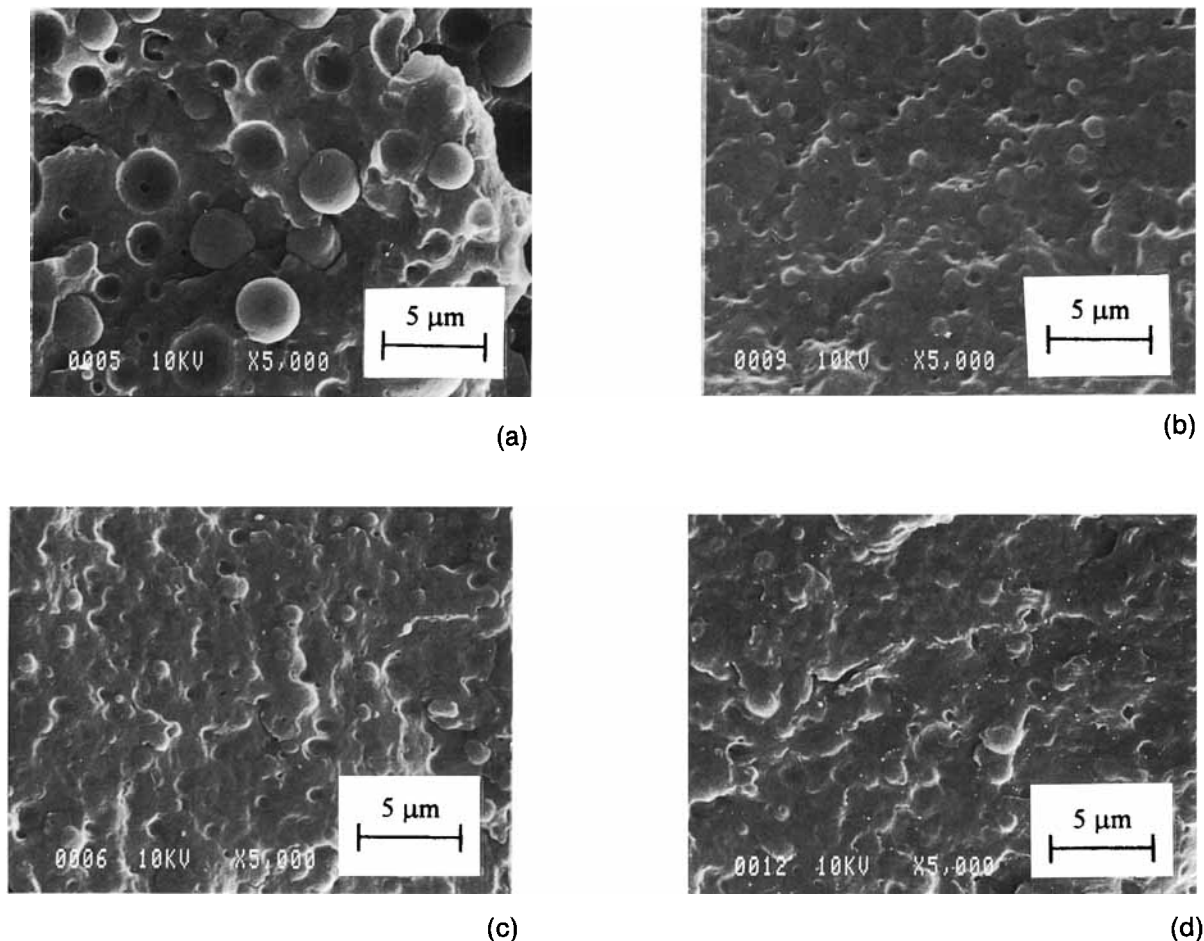
<sup>b</sup> Functionalized PP contained PP-*g*-OXA and residual OXA; [OXA]<sub>g</sub> = 1.05 phr, [OXA]<sub>r</sub> = 0.9 phr.

<sup>c</sup> The ratio of the amount of carboxylic groups in the PBT to that of oxazoline groups in the functionalized PP.

This kinetic study showed that the reaction between oxazoline and carboxylic acid is very fast, at least under those conditions. The equilibrium of conversion was achieved within 3 to 5 min. Sur-

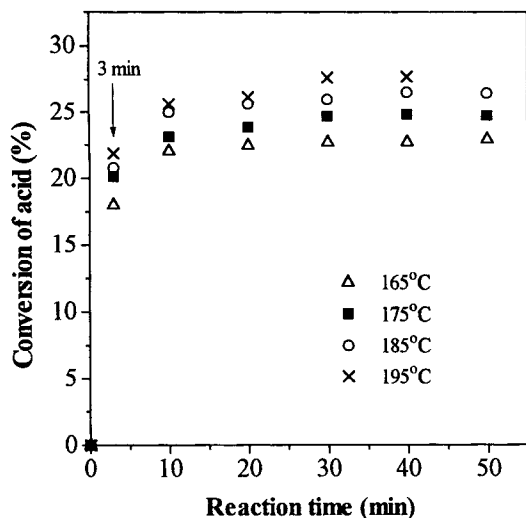
prisingly, the conversions were limited to about 25% (theoretical maximum achievable: 63%).

To confirm this result obtained by UV spectroscopy, measurements were also carried out with



**Figure 9** SEM micrographs of fracture surface of (a) Blend 1 = PP/PBT (70/30), (b) Blend 2 = PP/PP-*g*-OXA purified/PBT (60/10/30), (c) Blend 3 = PP/PP-*g*-OXA non-purified/PBT (60/10/30), and (d) Blend 4 = PP-*g*-OXA/PBT (70/30). Blend numbers refer to Table II.





**Figure 10** Conversion of acid as a function of time. [Carboxylic]<sub>i</sub>/[oxazoline]<sub>i</sub> = 1.6 mol/mol.

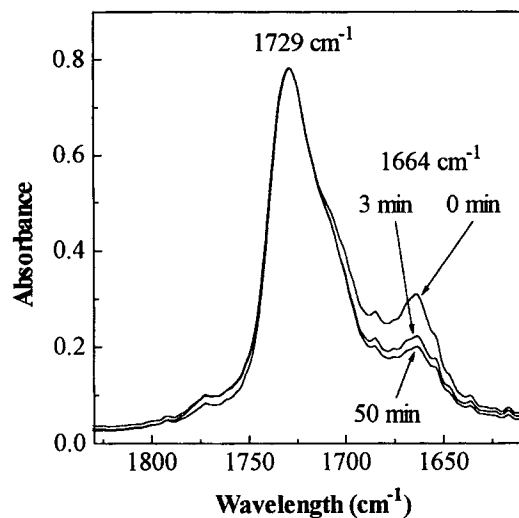
FTIR spectrometer. The FTIR spectra of the copolymer of methyl methacrylate and ricinloxazolinemethacrylate before (0 min) and after 3 and 50 min of the reaction with 1-naphthylacetic acid at 185°C are depicted in Figure 11. The peak at 1729 cm<sup>-1</sup> resulting from the ester group was treated as a reference peak because the peak did not change during the reaction. The peak at 1664 cm<sup>-1</sup> was attributed to the oxazoline ring, of which the concentration decreased as a function of reaction time. The conversions were calculated from the ratios of the intensities of the absorbances at 1664 cm<sup>-1</sup> and 1729 cm<sup>-1</sup>.

The conversions calculated on the basis of these FTIR spectra were virtually identical to the conversions obtained from the UV measurements. For example, the equilibrium conversion at 185°C measured with UV and FTIR was 27 and 25%, respectively.

**Table III** The Equilibrium Constants ( $K_e$ ) and Conversions at Equilibrium ( $X_e$ ) at Different Temperatures of the Reaction between Oxazoline and Carboxylic Groups

Temperature (°C)	$K_e = (l/mol)$	$X_e$ (%)
165	4.2	23
175	4.9	25
185	5.6	27
195	6.2	28

[Carboxylic]<sub>i</sub>/[oxazoline]<sub>i</sub> = 1.6 mol/mol.



**Figure 11** FTIR spectra of a copolymer of methyl methacrylate (93.7 wt %) and ricinloxazoline methacrylate (6.3 wt %) after different reaction times with 1-naphthylacetic acid at 185°C. The conversions of the acid were calculated from the ratios of the intensities of the absorbances at 1664 cm<sup>-1</sup> and 1729 cm<sup>-1</sup>.

## CONCLUSIONS

This article has described the melt free radical grafting behavior of a low volatile oxazoline, ricinloxazoline maleinate (OXA), onto polypropylene (PP) in a batch mixer and the efficiency of using such functionalized PP as a compatibilizer precursor for PP/PBT blends. The findings of our study can be summarized as follows: (1) grafting yield of OXA up to 1.5 phr was obtained. The conversion of the OXA monomer to grafted OXA ranged from about 15 to 50%, depending on the initial concentrations of the monomer and peroxide. (2) Addition of St as a comonomer did not enhance the grafting yield of OXA because both monomers do not copolymerize easily. This also agrees with the finding that non-grafted OXA and/or St were in the form of monomers. (3) The use of oxazoline modified PP (PP-g-OXA) as a compatibilizer precursor in a PP/PBT blend resulted in a clear reduction in the particle size of the dispersed phase (PBT) along with improved cohesion between the phases. (4) The significant compatibilization efficiency of PP-g-OXA was further sustained by the fact that the reaction between oxazoline and carboxylic groups was fast.

## SYMBOLS

[x] concentration of x (phr, mol)  
phr grams per hundred grams of PP

I	intensity of infrared absorption
$k_1, k_2$	reaction rate constants (mol/cm <sup>3</sup> )/s
$K_e$	equilibrium constant ( $k_1/k_2$ )
$\bar{M}_n$	number average molecular weight (g/mol)
$\bar{M}_w$	weight average molecular weight (g/mol)
$X_e$	conversion at equilibrium (%)
AIBN	azobisisobutyronitrile
FTIR	Fourier transform infra-red spectroscopy
GMA	glycidyl methacrylate
GPC	gel permeation chromatography
MAH	maleic anhydride
NA	1-naphthylacetic acid
NBR	nitrile butadiene rubber
OXA	ricinoloxazoline maleinate
PBT	poly(butylene terephthalate)
PE	polyethylene
POXA	poly(ricinoloxazoline maleinate)
P(OXA-co-St)	copolymer of ricinoloxazoline maleinate and styrene
PP	polypropylene
PP-g-OXA	PP grafted with OXA
PP-g-St	PP grafted with styrene
PS	polystyrene
SEM	scanning electron microscope
St	styrene

### Subscripts

e	equilibrium
g	grafted
i	initial, at feed

r	residual
t	total (amount)

### REFERENCES

1. J. A. Frump, *Chem. Rev.*, **71**, 483 (1971).
2. W. E. Baker and M. Saleem, *Polym. Eng. Sci.*, **27**, 1634 (1987).
3. W. E. Baker and M. Saleem, *Polymer*, **28**, 2057 (1987).
4. M. W. Fowler and W. E. Baker, *Polym. Eng. Sci.*, **28**, 1427 (1988).
5. M. Saleem and W. E. Baker, *J. Appl. Polym. Sci.*, **39**, 655 (1990).
6. N. C. Liu, H. W. Xie, and W. E. Baker, *Polymer*, **34**, 4680 (1993).
7. N. C. Liu and W. E. Baker, *Polymer*, **35**, 988 (1994).
8. Y. Fujita, T. Sezume, K. Kitano, K. Narukawa, T. Mikami, T. Kawamura, S. Sato, T. Nishio, T. Yokoi, and T. Nomura, EP 308179 A2 (1989).
9. P. Birnbrich, H. Fischer, J.-D. Klamann, and B. Wegemund, *Kunststoffe*, **83**, 885 (1993).
10. P. Birnbrich, H. Fischer, L. Schieferstein, R. Tenhaef, and J.-D. Klamann, DE 4209283, (1993).
11. T. Vainio, H. Jukarainen, and J. Seppälä, *J. Appl. Polym. Sci.*, to appear.
12. J.-J. Flat, Doctorate dissertation, Université Louis Pasteur, Strasbourg, France (1991).
13. Y.-J. Sun, Doctorate dissertation, Université Louis Pasteur, Strasbourg, France (1994).
14. Y.-J. Sun, G.-H. Hu, and M. Lambla, *Angew. Makromol. Chem.*, **229**, 1 (1995).
15. Y.-J. Sun, G.-H. Hu, and M. Lambla, *J. Appl. Polym. Sci.*, **57**, 1043 (1995).
16. G.-H. Hu, J.-J. Flat, and M. Lambla, in *Reactive Modifiers for Polymers*, to appear.

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