

The Effect of TIBA on Metallocene/MAO Catalyzed Synthesis of Propylene Oxazoline Copolymers and Their Use in Reactive Blending

Atila Kaya, Gisela Pompe, Ulrich Schulze, Brigitte Voit, Jürgen Pionteck

Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany

Received 16 July 2001; accepted 4 March 2002

ABSTRACT: Oxazoline-functionalized polypropylenes were synthesized by using the *rac*-Et[1-Ind]₂ZrCl₂/MAO catalyst system. The used comonomers were 2-(9-decene-1-yl)-1,3-oxazoline (R-Ox1), 2-(9-decene-1-yl)-4,4-dimethyl-1,3-oxazoline (R-Ox2), and 2-(4-(10-undecene-1-oxy)phenyl)-1,3-oxazoline (R-Ox3). The oxazolines reduce the catalyst activity in the order R-Ox3 > R-Ox1 > R-Ox2. By the addition of triisobutylaluminum (TIBA), the catalyst poisoning is reduced and is most pronounced in the R-Ox1- and R-Ox2-containing systems. The oxazoline-containing copolymers were melt blended with carboxylic acid end-functionalized

polystyrene (PS-COOH) at 200°C. Strong changes in the morphology of the reactive blends compared to the nonreactive blends, especially the cocontinuous morphology in a poly(propylene-co-R-Ox3)/PS-COOH blend, indicate the usefulness of the modified copolymers in the reactive blending processes. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2174–2181, 2002

Key words: oxazoline; metallocene catalysts; functionalization of polymers; propylene copolymer; reactive processing

INTRODUCTION

The absence of reactive groups in polyolefins limits their use in some applications. Therefore, introducing functional groups into the polyolefins is of growing interest. In this way, the adhesion, dyeability, permeability, and printability of the polymer can be improved. Furthermore, functional groups offer sites for initiating a graft copolymerization, allowing compatibilization with other polymers.¹

There are different methods used to introduce the functional groups into the polyolefins. The most widespread method is free-radical-induced grafting. The main disadvantage of this method is chain degradation and crosslinking.^{2–5} Other methods of synthesizing polyolefins with functional groups include the following: functionalization of terminal olefin group of the polymer⁶; functionalization of the olefinic groups of the diene copolymers^{7,8}; direct copolymerization of borane comonomers by using Ziegler–Natta and metallocene catalysts which can then be readily functionalized under mild conditions^{9,10}; copolymerization of olefins with *p*-methylstyrene copolymers; and subsequent replacement of methyl protons at phenyl ring by halogenation, oxidation, and metalation.

^{11–13} These methods, however, have their disadvantages, such as expensive additional chemical treatment.

Another interesting and attractive way of producing functional polyolefins is the direct copolymerization with functional group containing comonomers using metallocene catalysts. Functional groups, however, poison the catalyst, and as a result, the polymerization cannot proceed. Introducing long spacers between the polar and the olefinic group in the comonomer,^{14,15} introducing steric hindrance for the functional groups,^{16–18} and introducing protecting agents for polar groups, which can be removed easily,^{19–21} offer some possibilities for the reduction of catalyst poisoning.

Catalysts based on Ni(II) and Pd(II) complexes can tolerate Lewis basicity and are therefore interesting. With such catalysts, polyethylene could be synthesized even in water.²² However, until now, by using these catalysts, only amorphous polypropylene could be synthesized.^{23–25}

Blending polyolefins with engineering plastics offers an interesting route to materials with new property combinations. Most polymer blends, however, are thermodynamically immiscible and compatibilization is necessary to obtain the desired properties.²⁶ In the last few years, reactive compatibilization became very popular. In this process, the polymers to be blended have to possess the suitable functional groups. During the blending process, the functional groups of the blended polymers react with each other, creating in

Correspondence to: J. Pionteck.

Contract grant sponsor: Deutsche Forschungsgemeinschaft.

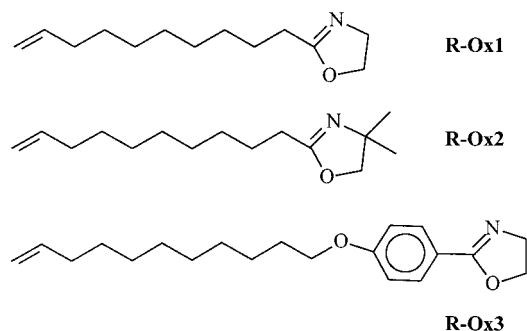


Figure 1 The structures of the comonomers: 2-(9-decene-1-yl)-1,3-oxazoline (R-Ox1), 2-(9-decene-1-yl)-4,4-dimethyl-1,3-oxazoline (R-Ox2), 2-(4-(10-undecene-1-oxy)phenyl)-1,3-oxazoline (R-Ox3).

this manner copolymer structures *in situ*. These copolymers can act as compatibilizers, reducing the interfacial tension, stabilizing the morphologies, and improving the phase adhesion.

The direct synthesis of propylene oxazoline copolymers using metallocene catalysts is described in our earlier works.^{27,28} In this article, we study the influence of TIBA as a protecting agent for polar groups on the copolymerization of propylene with oxazoline comonomers by using the *rac*-Et[1-Ind]₂ZrCl₂/MAO catalyst system. The comonomers were 2-(9-decene-1-yl)-1,3-oxazoline (R-Ox1), 2-(9-decene-1-yl)-4,4-dimethyl-1,3-oxazoline (R-Ox2), and 2-(4-(10-undecene-1-oxy)phenyl)-1,3-oxazoline (R-Ox3) (Fig. 1). The copolymers containing these functional groups were then blended with carboxylic acid end-functionalized polystyrene (PS-COOH) and characterized by using various methods.

EXPERIMENTAL

Materials

Toluene (Fluka, p.a., <0.03 wt % water content) was dried by refluxing over Na/K alloy and finally distilled under argon atmosphere; 2.8 grade propylene was purchased from Riessner-Gase and purified by passing through 3 Å molecular sieves followed by R3-11 copper oxide catalysts (BASF). *rac*-Et[1-Ind]₂ZrCl₂ (Witco) was used as received. Methylaluminoxane (MAO, M = 900 g/mol) solution was obtained from Witco. After passing the solution through a ceramic filter under argon atmosphere, the MAO was crystallized as a white powder by distilling off the solvent (toluene) under vacuum. Triisobutylaluminum (TIBA; Witco) was used as received. The syntheses of the oxazoline comonomers,^{27,28} polypropylene (PP, synthesized at 50°C)²⁸ and PS-COOH^{29,30} (functionality 62%), are described elsewhere.

Synthesis of the copolymers

Polymerizations were carried out in a 1-L glass autoclave (Büchi) equipped with a stirrer, manometer,

thermocouple, and heating and cooling units. The propylene consumption was monitored by a press-flow gas controller (Büchi). The temperature, speed of stirrer, pressure, instantaneous gas flow, and total gas consumption were monitored and recorded as a function of time. The stirring speed, polymerization temperature, and total pressure were held constant at 800 rpm, 30°C, and 3 bar, respectively.

Under argon atmosphere, the reactor was first charged with toluene, cocatalyst (MAO), comonomer, and TIBA. The total solution volume was 220 mL. Thereafter, it was loaded three times with propylene to 3 bar total pressure and expanded to atmospheric pressure while stirring. Then, the solution was saturated with propylene at 30°C and 3 bar total pressure. Finally, the polymerization was initiated by injecting the catalyst solution into the reactor.

The Al (MAO)-to-Zr molar ratio was 5000 ($\pm 2\%$). Catalyst concentrations were 2.96×10^{-5} mol/L and 11.8 mmol/L, respectively (Table I). When the polymerization rate decreased significantly, the polymerization was terminated by careful injection of acetone (strong exothermic reaction with TIBA) into the reaction system. The reaction solution was then precipitated by using an excess of acetone and the precipitate was filtered off. The filter cake was extracted three times with hot xylene. Then, the combined xylene fractions were precipitated at room temperature in acetone, filtered off, washed again with acetone, and dried in vacuum at 70°C for 1 day.

Blending

The blends were prepared in a corotating twin-screw microcompounder (DACA Instruments; capacity, 4.5 cm³). Four grams of the polymer mixture [66.7 wt % polyolefin (sum of homo- and copolymer), and 33.3 wt % PS-COOH] were fed to the system. Screw speed, blend temperature, and mixing time were kept constant at 100 rpm, 200°C, and 5 min, respectively.

Characterizations of polymers and blends

The polymers were characterized by using ¹H-NMR, FTIR, DSC, SEC, TGA (for the ash content of the polymer), and elemental analysis. The remaining filter cake (inorganic phase) of the raw product was pyrolyzed by using a Pyrolysator Pyroprobe 2000.^{27,28} For the characterization of the blends, only FTIR and DSC could be used because the blends were not good solutes even at elevated temperatures. The thermal properties such as the melting heat ΔH_f (2.0 heat), melting peak temperature T_m (2.0 heat), the extrapolated onset temperature of the crystallization $T_{c,o'}$, and $\Delta T_c (=T_{c,o} - T_{c,m'}$, whereas $T_{c,m}$ is the crystallization peak tem-

TABLE I
 Copolymerizations with TIBA { $c_{\text{cat.}} = 2.96 \times 10^{-5}$ mol/l, $c_{\text{comon.}} = 11.8$ mmol/l, A1 (in MAO)/Zr = 5000, A1(in MAO)/comonomer = 12/7}, and without TIBA { $c_{\text{cat.}} = 1.6 \times 10^{-5}$ mol/l, $c_{\text{comon.}} = 7.4$ mmol/l, A1(in MAO)/Zr = 10000, A1(in MAO)/comonomer = 21.6}.^{27,28} (Activities Were Calculated for 2.0 g Propylene Consumption)

Copolymer	TIBA [mmol/l]	Polymer recovered [%]	Activity [kg PP/(mol h)]	Oxazoline in polymer ^a (¹ H-NMR elemental analysis) [mol %]	M_n (¹ H-NMR GPC) [g/mol]	M_w/M_n	ΔH_f [J/g]	T_m [°C]	Ash content [wt %]
R-Ox1	33 ^b	94	443	0.40 (48)	11,000	2.0	81.4	134.7	0.5
				0.5	16,200				
R-Ox2	33	93	482	0.39 (100)	14,200	1.9	80.6	134.7	0.0
				0.3	20,700				
R-Ox3	48	88	247	0.40 (78)	14,900	2.5	78.5	132.8	0.0
				0.4	15,900				
R-Ox1	—	77	136	0.49	12,300	1.5	87.5	133.5	2.0
				0.4	18,000				
R-Ox2	—	74	170	0.61	9100	1.8	84.8	136.2	4.0
				0.6	8400				
R-Ox3	—	90	115	0.52	8400	1.9	83.9	131.4	0.0
				0.5	13,000				

^a The values in parentheses give the percentage of the closed oxazoline ring in the copolymer.

^b At this polymerization condition, no polymerization was observed as no TIBA was added.

perature) were taken for the characterization of the polymers and blends.

The melt rheology of the polymers and blends (η) were investigated with an ARES rheometer (Rheometrics Inc.) in oscillation mode. The frequency sweeps were performed at 200°C under nitrogen atmosphere by using a parallel plate geometry (diameter = 25 mm). The frequency range was between 0.1 and 100 rad/s.

The blend morphologies were characterized with a LEO 435 VP scanning electron microscope (SEM, Leo Elektronenmikroskopie GmbH). The samples were cryofractured in liquid nitrogen, etched with tetrahydrofuran (THF), washed with ethanol, and finally washed with acetone. After drying, the samples were coated with a thin layer of gold and measured.

RESULTS AND DISCUSSION

Copolymerizations

In our earlier works, we presented the results of copolymerizations of propylene with oxazoline comonomers by using the metallocene/MAO catalyst system.^{27,28} There, MAO was used as a protecting agent. Although Al (in MAO)-to-Zr ratios were very high (10,000), the catalyst activities were rather low. This was due to the oxazoline groups, which poisoned the catalyst strongly, and MAO was not a good protecting agent for them. To improve the protecting efficiency, TIBA was added to the reaction system, and the results are presented here.

The structures of the oxazoline comonomers, the polymerization conditions, and the properties of the

resulting polymers are given in Figure 1 and Table I, respectively. The TIBA-to-heteroatom ratio was selected to be 1.4 ($\pm 2\%$) (mol TIBA)/(mol heteroatom in the comonomer). For comparison, the conditions and the results of the polymerizations *without* TIBA^{27,28} were also added to Table I. After terminating the reactions with acetone, the resulting very sticky raw products situated on the reactor glass wall were placed into a 2-L beaker, dissolved in hot xylene, and filtered off. Pyrolysis of the remaining inorganic filter cake indicated polymer residue in it. The comonomer incorporation ratios were around 0.4 mol %. The oxazoline rings of some copolymers, however, were opened partially. Especially the R-Ox1 containing copolymer was sensitive to ring opening side reactions, and up to 52% of the oxazoline rings were transferred to the ring-opened structures. This may be a result of fast and extreme exothermic reaction of TIBA with acetone in the termination step. Ash content of the resulting polymer is nearly zero, and polymer recovery is relatively high. Polymer recovery is directly proportional to the (amount of synthesized polymer)/(amount of added MAO) ratio. As this ratio becomes higher, the polymer recovery after filtration also becomes higher, which is a result of less interaction of functional polymer with the inorganic residue in the raw product. The lower polydispersities in the case of *without* TIBA must also be a result of the purification method through filtration. The adhesion of high molecular polar copolymer chains to the inorganic aluminum-rich phase must be higher than the low molecular copolymer chains so that the low molecular chains are able to extract easily, resulting in relatively lower

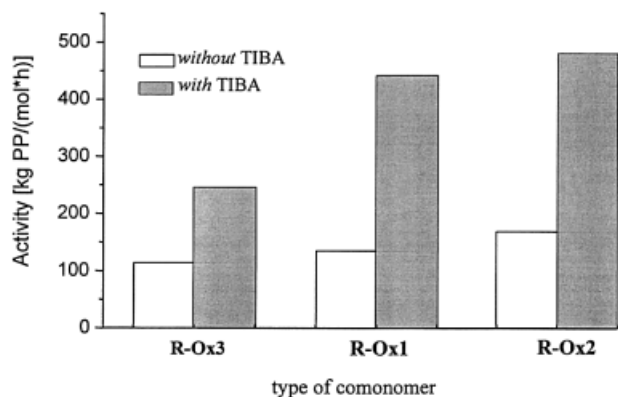


Figure 2 A comparison of catalyst activities of various oxazoline comonomers *with* and *without* TIBA calculated for 2.0 g propylene consumption (see Table I).

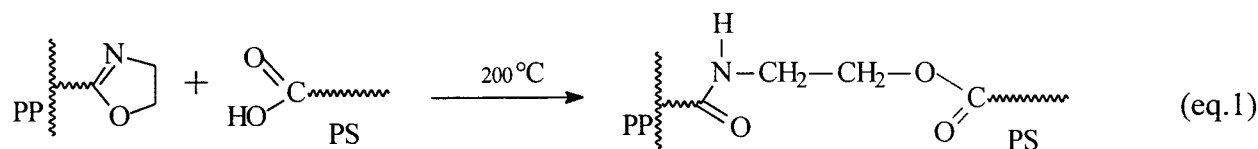
polydispersities. Even though in the case of *with* TIBA the comonomer incorporation ratios are lower than in case of *without* TIBA, the differences are rather low, and these differences may be the result of higher polymerization rates of copolymerizations *with* TIBA.

An important result of this study was the reduction in catalyst deactivation through oxazolines by the addition of TIBA. A comparison between the copolymerizations with TIBA and without TIBA shows that the catalyst poisoning through the oxazolines was reduced strongly by the addition of TIBA (Table I and Fig. 2). No polymerization was observed at the same polymerization conditions as *with* TIBA, when no TIBA was added to the reaction system. This indicates the protecting efficiency of TIBA. Although Al (in MAO)-to-Zr (5000), and Al (in MAO)-to-comonomer

(12.7), ratios in the case of copolymerizations with TIBA are much lower than that of without TIBA (10,000 and 21.6, respectively), the catalyst activities with TIBA are two to three times higher than those of without TIBA. Between TIBA and heteroatoms of the comonomers, partial chemical complex must have been formed which acts as protecting agent in the polar group of the comonomer. Addition of acetone in the termination step of the polymerization destroys this complex, resulting in functional groups without any TIBA. In both cases (with TIBA and without TIBA), the catalyst activities for R-Ox2 are the highest, and for R-Ox3 are the lowest, as expected. Because the two methyl groups in 4,4-position of R-Ox2 act as steric hindrance, an additional reduction in catalyst poisoning (deactivation) takes place, which leads to the highest catalyst activity. Compared to the other two comonomers, R-Ox3 has one extra oxygen atom which deactivates the catalyst additionally. Furthermore, the resonance stability of the phenoxy moiety in the 2-position of the oxazoline group increases the Lewis basicity of the nitrogen toward the cationic active catalyst species, which results in the another additional catalyst poisoning property of R-Ox3.

Blending

To examine the compatibilization effect of the oxazoline containing the polypropylene copolymers, the copolymers were blended with PS-COOH at 200°C. The 2-oxazolines are known to undergo ring-opening addition reactions with carboxylic acids to produce amido-ester bonds, as shown in eq. (1)³¹:



The properties of the polymers used are listed in Table II. The M_n , T_m , and η values of the polypropylenes

used do not differ much from each other. Therefore, a subsequent difference in blends cannot be a result of

TABLE II
Properties of the Polymers Used in the Blends

Polymer	M_n (GPC) [g/mol]	Reactive group in polymer ^a [mol%]	$T_{c,o}$ [°C]	ΔT_c [K]	T_m [°C]	ΔH_f [J/g]	η^b [Pa s]
PP	18,600	0	101.6	5.6	132	78.6	0.7
PS-COOH	28,300	0.23	—	—	—	—	21.7
PP-co-Ox1a	16,200	0.10	101.6	4.1	133.6	79.2	1.8
PP-co-Ox1b	14,500	0.40	102.2	4.2	132.7	72.2	n.d. ^c
PP-co-Ox2	20,700	0.39	100.0	6.2	134.7	78.4	0.9
PP-co-Ox3	15,900	0.31	100.9	5.0	132.8	76.0	0.2

^a In the case of oxazolines, it is the closed oxazoline ring.

^b At 200°C and 100 rad/s.

^c n.d., not determined (but approximated to be around 1.8).

TABLE III
Blend Properties

Blend no.	Polymer composition	Polymer ratio [wt. %]	Reactive group ratio ^a	$T_{c,o}$ [°C]	ΔT_c [K]	T_m [°C]	ΔH_f [J/g]	η^b [Pa s]
1	PP/PS-COOH	66.7/33.3	0	100.5	5.4	131.5	56.1	1.4
2	PP-co-Ox1a/PS-COOH	66.7/33.3	1.5	103.0	5.0	134.2	53.2	8.6
3	PP-co-Ox1b/PS-COOH	66.7/33.3	6.8	103.3	5.1	133.6	50.1	17.2
4	PP-co-Ox2/PS-COOH	66.7/33.3	4.5	101.6	5.4	134.6	54.6	3.2
5	PP/PP-co-Ox3/PS-COOH	0.0/66.7/33.3	4.8	110.0	7.4	134.1	50.4	61.5
6	PP/PP-co-Ox3/PS-COOH	41.7/25.0/33.3	1.8	106.0	5.8	133.2	52.4	14.0
7	PP/PP-co-Ox3/PS-COOH	60.0/6.7/33.3	0.5	103.9	5.0	131.9	52.5	3.2

^a In [mol Ox_i/mol COOH].

^b At 200°C and 100 rad/s.

the structural differences of the polypropylenes, but a result of a chemical reaction between the components.

The preparation conditions and properties of the blends are listed in Table III. In all cases, **PP** was the matrix phase, and **PS** was the dispersed phase. To compare the reactive blends with the nonreactive one, a blend of **PS-COOH** with **PP** was also prepared (blend no. 1). In the case of poly(propylene-co-2-(9-decene-1-yl)-1,3-oxazoline) (**PP-co-Ox1**), blends with different oxazoline contents (0.10 and 0.40 mol %, **PP-co-Ox1a**, and **PP-co-Ox1b**, respectively, Table II) were prepared (blend nos. 2 and 3). To investigate the effect of type of oxazoline group on the blends, poly(propylene-co-2-(9-decene-1-yl)-4,4-dimethyl-1,3-oxazoline) (**PP-co-Ox2**) (blend no. 4) and poly(propylene-co-2-(4-(10-undecene-1-oxy)phenyl)-1,3-oxazoline) (**PP-co-Ox3**) (blend no. 5) were also blended with **PS-COOH**.

Compared to the nonreactive **PP/PS-COOH** blend (blend no. 1), the differences in thermal properties ($T_{c,o}$, ΔT_c , and ΔH_f) and in melt rheology (η) of **PP-co-Ox3/PS-COOH** blend (blend no. 5) are relatively high even though its reactive group ratio (Ox/COOH) is not the highest and the viscosity ratio between the dispersed phase to matrix phase is very unfavorable for the fine dispersion.²⁹ These differences are very low for the **PP-co-Ox2/PS-COOH** blend (blend no. 4), although its reactive group ratio does not differ much from the **PP-co-Ox3/PS-COOH** blend. In the case of the **PP-co-Ox1/PS-COOH** blend, with the increase of oxazoline content of the copolymer (blend nos. 2 and 3, respectively), $T_{c,o}$, ΔT_c , and η values show increasing tendency, whereas the T_m and ΔT_f values have decreasing tendency. Because the crystallization rate is inversely proportional to the ΔT_c , and according to this, the **PP-co-Ox3/PS-COOH** blend has the lowest crystallization rate and the highest $T_{c,o}$ value, it can be concluded that **PP-co-Ox3/PS-COOH** has higher nucleating efficiency.

In Figure 3, the SEM images of the reactive blends with different types of oxazoline copolymers, and in the case of **PP-co-Ox1**, different oxazoline contents,

are given. Blend of the copolymer having methyl groups at 4,4-position in the oxazoline ring (**PP-co-Ox2**) has bigger **PS** spheres than the other blends (blend no. 4). The SEM images of the blends with **PP-co-Ox1a** and **PP-co-Ox1b** show that compared to the former one the size of the dispersed phase (**PS**) is reduced (blend nos. 2 and 3), and with the increase of oxazoline content (**PP-co-Ox1b**), it was much smaller. The **PP-co-Ox3/PS-COOH** blend shows a significant change in morphology from dispersed to a cocontinuous type (blend no. 5), which is an indication of a better interaction between the blend components and must also be the reason for the rather high blend melt viscosity.

According to the results given above, it can be concluded that the compatibilization efficiency in the **PP-co-Ox3/PS-COOH** blend is the highest. This can be due to the increased nucleophilicity of the nitrogen atom in the oxazoline ring, which is a result of the resonance stability of the phenoxy moiety in the 2-position of the oxazoline group, as discussed in the former section (copolymerizations). The carboxylic acid of **PS-COOH** can protonate the nucleophilic nitrogen atom easily, which leads to increased reactivity of the oxazoline ring toward the ring-opening reaction, forming a covalent bond between the components. In the case of the **PP-co-Ox2/PS-COOH** blend, however, the compatibilization efficiency is lowest because this oxazoline ring is substituted in the 4-position with two methyl groups, and as stated in refs.³² and ³³, the reactivity toward the ring-opening reaction is decreased strongly with the substituents in 4- and 5-positions in the oxazoline ring.

Normalized FTIR spectra (section) of the pure **PP-co-Ox3** and the **PP-co-Ox3/PS-COOH** blend (blend no. 5) are given in Figure 4. The skeleton of the polypropylene chain at 2722 cm⁻¹ was taken as specified in ref.² The peak at 1653 cm⁻¹ corresponds to C=N stretching and oxazoline ring bending. A comparison of the spectra shows a decreased oxazoline-to-polypropylene ratio, and an increased ester (at 1721 cm⁻¹)-to-polypropylene ratio in the case of the blend.

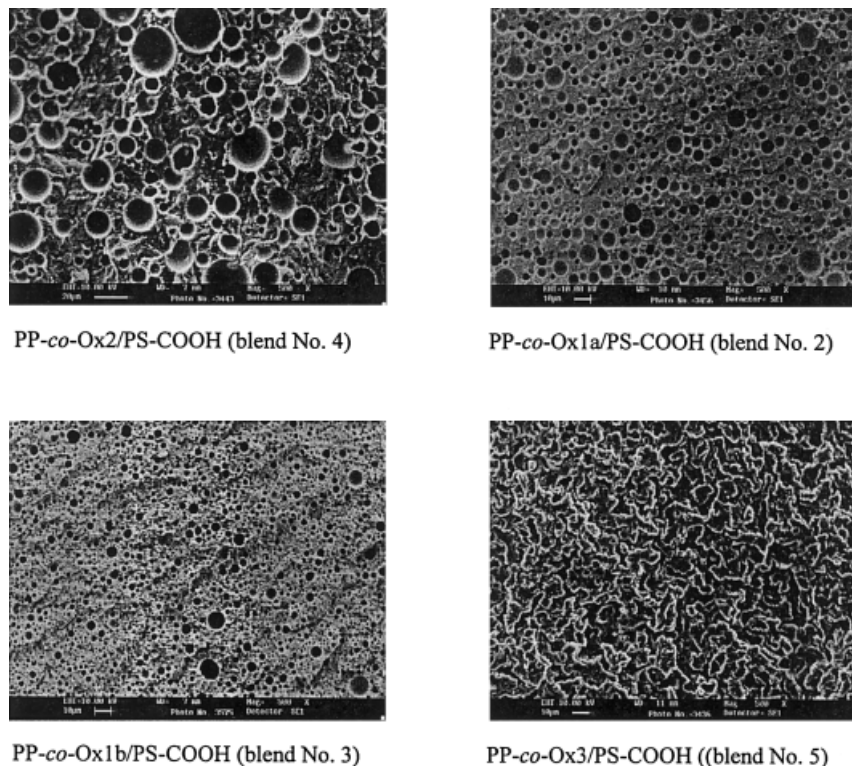


Figure 3 SEM images of PP-*co*-Ox_{*i*}/PS-COOH blends (66.7/33.3). The nonreactive blend (blend no. 1) is given in Figure 5 (frame size 233 × 187 μm).

This means that a reaction between oxazoline and the carboxylic acid group at the given blend conditions took place according to eq. (1), and in this way, the compatibility between **PP** and **PS** could effectively be increased. References ² and ³⁴ give the oxazoline peak between 1671 and 1664 cm⁻¹, and the ester peak at 1729 cm⁻¹. These differences compared to our measurements may result from the different types of oxazolines.

To examine the compatibilization efficiency as a function of reactive group ratio, a couple of ternary

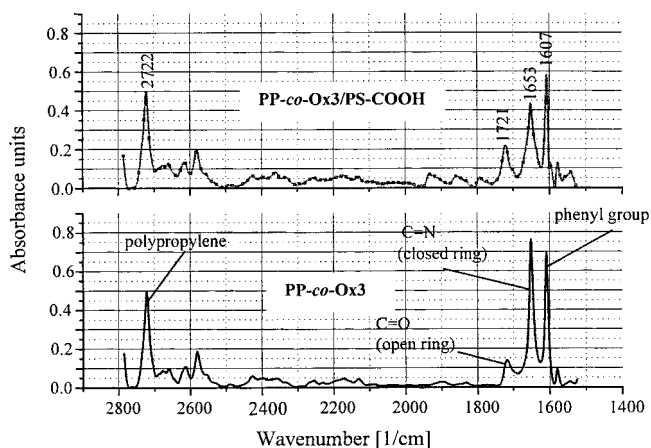


Figure 4 Normalized FTIR spectra (section) of PP-*co*-Ox3 and PP-*co*-Ox3/PS-COOH blend.

blends were prepared by holding the total weight of the blend mixture, and the weight ratio (wt %) of **PS-COOH** constant but by varying the concentration of **PP-*co*-Ox3** by addition of **PP** (blend nos. 6 and 7). The SEM images of these blends are given in Figure 5. Also, the SEM image of the nonreactive **PP/PS-COOH** blend is given there. With the increase of the reactive group ratio (from 0 to 4.8 molOx/molCOOH), the size of the dispersed phase decreases (blend nos. 1, 7, 6), finally reaching a cocontinuous morphology (blend no. 5, **PS** phase change from big spheres to one continuous sphere). Their other properties are listed in Table III. According to the table, the melting heat ΔH_f also decreases with the increase of the reactive group ratio. The $T_{c,o}$, ΔT_c , T_m , and η values, however, are increasing along with the reactive group ratio. To have a visual impression, the melt viscosities η of these blends are also plotted in the frequency range from 0.1 to 100 rad/s and given in Figure 6. The figure shows a decrease in the melt viscosities of the reactive blends with the increase of the frequency, whereas the melt viscosity of the blend with the higher reactive group ratio (blend no. 5) remains always higher.

CONCLUSION

Compared to the copolymerizations without TIBA, the rates of the copolymerizations of propylene with ox-

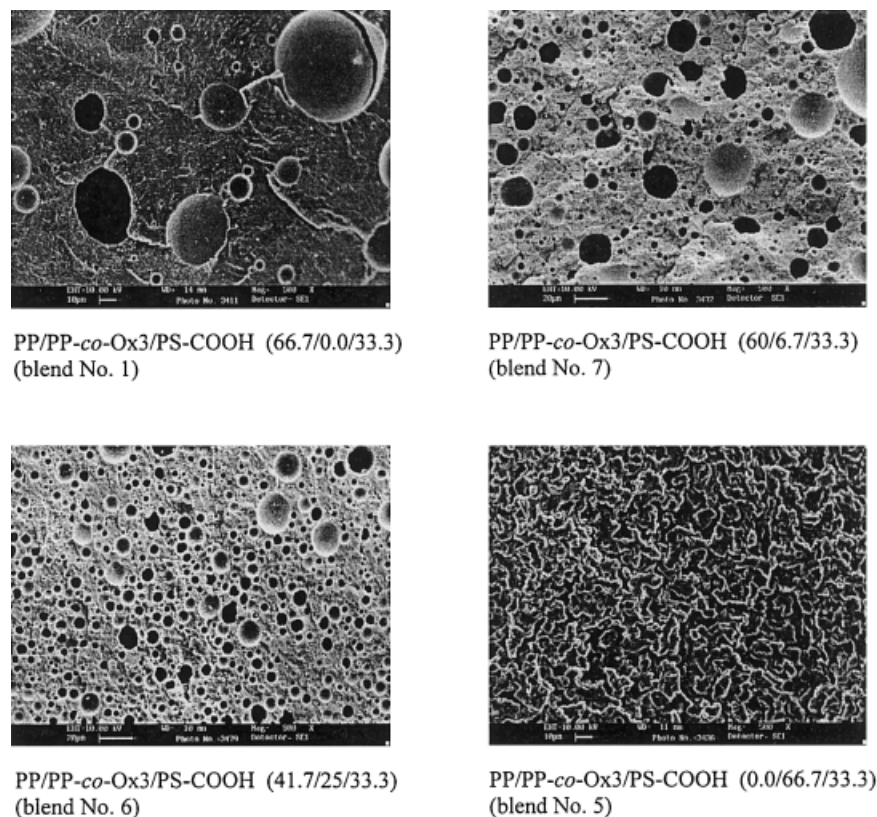


Figure 5 SEM images of PP/PP-*co*-Ox3/PS-COOH blends (frame size $233 \times 187 \mu\text{m}$).

azoline comonomers results in an approximately two- to threefold increase by adding TIBA to the reaction system even with the half of Al (in MAO)-to-Zr ratio and almost half of Al (in MAO)-to-comonomer ratio. To investigate their compatibilization efficiency, co-

polymers with different oxazoline groups were reactive blended with carboxylic-terminated polystyrene. The copolymer with the oxazoline group containing phenoxy moiety in it (R-Ox3) showed the highest compatibilization efficiency. A decrease in oxazoline-to-

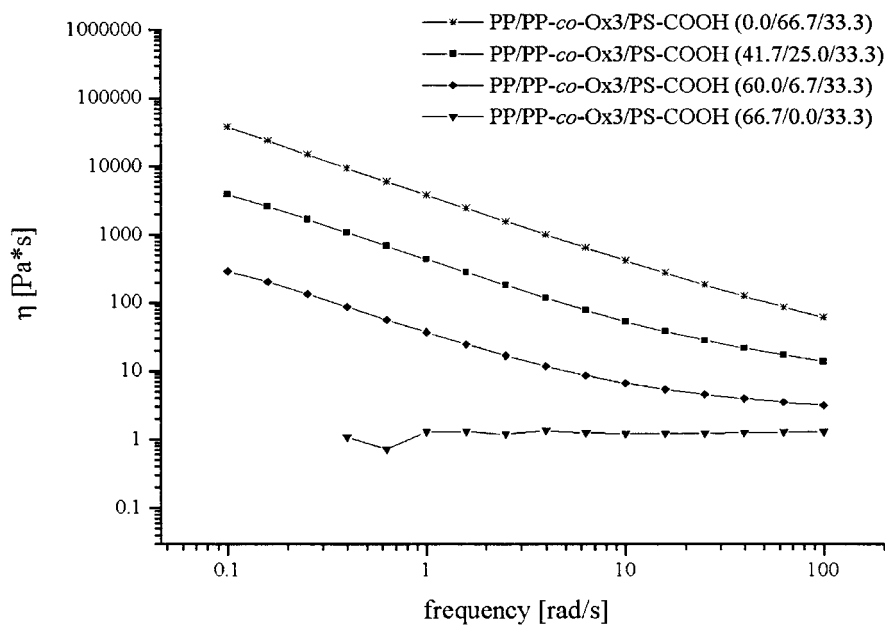


Figure 6 Melt viscosities of PP/PP-*co*-Ox3/PS-COOH blends.

polypropylene ratio; size of PS spheres and melting heat; and an increase in melt viscosity, melting temperature, and onset temperature of the crystallization indicate a reaction between the oxazoline group of the copolymer and the carboxylic group of the polystyrene, resulting in an amide- and an ester-covalent bond.

The authors are indebted to Prof. Dr. W. Kaminsky for helpful discussions, Dr. L. Jakisch for synthesis of comonomers, Dr. H. Komber for $^1\text{H-NMR}$ analysis, Dr. W. Jenschke for the supporting process controlling software, D. Voigt for SEC analysis, G. Adam for FTIR analysis, to K. Eckstein for melt viscosity measurements, H. Kunath for preparation of the blends, and R. Schulze for elemental analysis. The authors are grateful for the support of this work by the Deutsche Forschungsgemeinschaft (Collaborative Research Center 287).

References

- Aaltonen, P.; Löfgren, B. *Macromolecules* 1995, 28, 5353.
- Vainio, T.; Hu, G.-H.; Lambla, M.; Seppälä, J. V. *J Appl Polym Sci* 1996, 61, 843.
- Mierau, U. Ph.D. Thesis; Technische Universität, Dresden, 1994.
- Lui, B.; Chung, T. C. *Macromolecules* 1999, 32, 2525.
- Borsig, E.; Capla, M.; Fiedlerova, A.; Lazar, M. *Polym Commun* 1990, 31, 193.
- Mülhaupt, R.; Duschek, T.; Fischer, D.; Setz, S. *Polym Adv Technol* 1993, 4, 439.
- Kim, I.; Shin, Y. S.; Lee, J. K. *J Polym Sci, Part A: Polym Chem* 2000, 38, 1590.
- Chung, T. C.; Lu, H. L.; Li, C. L. *Polym Int* 1995, 37, 197.
- Chung, T. C. *J Inorg Organomet Polym* 1991, 1, 37.
- Chung, T. C.; Rhubright, D. *Macromolecules* 1993, 26, 3019.
- Lu, H. L.; Hong, S.; Chung, T. C. *J Polym Sci, Part A: Polym Chem* 1999, 37, 2795.
- Chung, T. C. *Polym Prepr* 1998, 39, 218.
- Chung, T. C.; Lu, H. L.; Janvikul, W.; Ding, R. D. *Polym Mater Sci Eng* 1997, 76, 248.
- Aaltonen, P.; Löfgren, B. *Eur Polym J* 1997, 33, 1187.
- Hakala, K.; Löfgren, B.; Helaja, T. *Eur Polym J* 1998, 34, 1093.
- Mustonen, I.; Hukka, T.; Pakkanen, T. *Macromol Rapid Commun* 2000, 21, 1286.
- Wilén, C. E.; Näsman, J. H. *Macromolecules* 1994, 27, 4051.
- Stehling, U. M.; Stein, K. M.; Fischer, D.; Waymouth, R. M. *Macromolecules* 1999, 32, 14.
- Goretzki, R.; Fink, G. *Macromol Rapid Commun* 1999, 200, 881.
- Marques, M. M.; Correia, S. G.; Ascenso, R. J.; Ribeiro, A. F. G.; Gomes, P. T.; Dias, A. R.; Foster, P.; Rausch, M. D.; Chien, J. C. W. *J Polym Sci, Part A: Polym Chem* 1999, 37, 2457.
- Radhakrishnan, K.; Sivaram, S. *Macromol Rapid Commun* 1998, 19, 581.
- Held, A.; Mecking, S. *Chem Eur J* 2000, 6, 4623.
- Heinemann, J.; Mülhaupt, R.; Brinkmann, P.; Luinstra, G. *Macromol Chem Phys* 1999, 200, 384.
- Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* 2000, 287, 460.
- Correia, S. G.; Marques, M. M.; Ascenso, R. J.; Ribeiro, A. F. G.; Gomes, P. T.; Dias, A. R.; Blais, M.; Rausch, M. D.; Chien, J. C. W. *J Polym Sci, Part A: Polym Chem* 1999, 37, 2471.
- Piğłowski, J.; Gancarz, I.; Wlazlak, M. *Polymer* 2000, 41, 3671.
- Kaya, A.; Jakisch, L.; Komber, H.; Pompe, G.; Pionteck, J.; Voit, B.; Schulze, U. *Macromol Rapid Commun* 2000, 21, 1267.
- Kaya, A.; Jakisch, L.; Komber, H.; Voigt, D.; Pionteck, J.; Voit, B.; Schulze, U. *Macromol Rapid Commun* 2001, 22, 972.
- Pötschke, P.; Malz, H.; Pionteck, J. *Macromol Symp* 2000, 149, 231.
- Malz, H. Synthesis of End-Functionalized Polystyrenes and Polypropylenes; Ph.D. Thesis, Technische Universität, Dresden, 1999.
- Fry, E. M. *J Org Chem* 1950, 15, 802.
- Nishikubo, T.; Tokairin, A.; Takahashi, M.; Nosaka, W.; Iizawa, T. *J Polym Sci, Part A: Polym Chem* 1985, 23, 1805.
- Nishikubo, T.; Tokairin, A.; Torikai, S.; Iizawa, T. *Macromol Chem* 1985, 186, 675.
- Wörner, C.; Rösch, J.; Höhn, A.; Mülhaupt, R. *Polym Bull* 1996, 36, 303.