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Polypropylene-*graft*-Polycaprolactone: Synthesis and Applications in Polymer Blends

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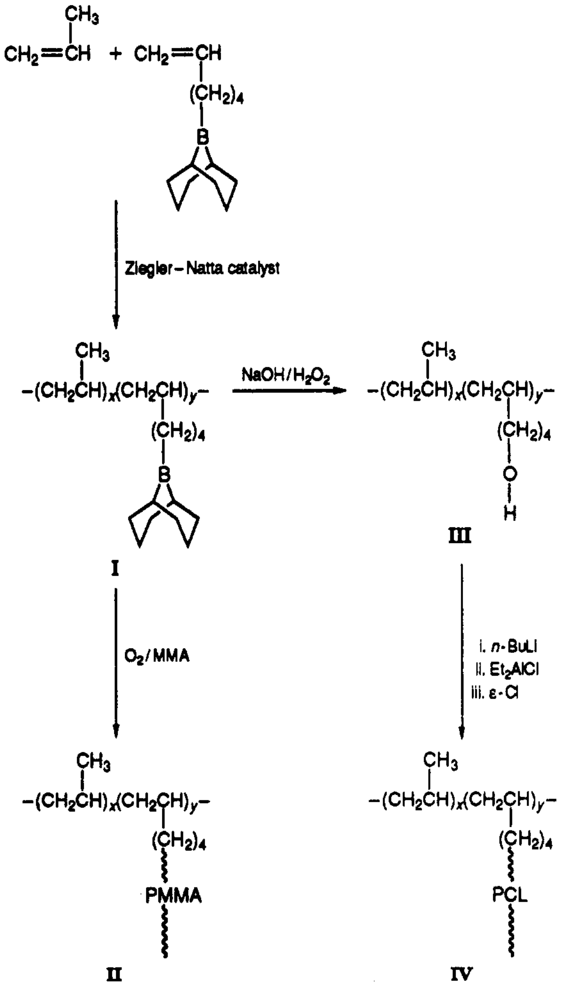
ABSTRACT: This paper describes a new graft copolymer, polypropylene-*graft*-polycaprolactone (PP-*g*-PCL), which is an effective compatibilizer for PP blends with many engineering plastics, such as polycarbonate (PC) and poly(vinyl chloride) (PVC). The chemistry in the preparation of this graft copolymer involves hydroxylated PP, containing primary or secondary alcohol groups, and the anionic ring opening polymerization of ϵ-caprolactone (ϵ-CL). Despite the heterogeneous reaction conditions, the molecular structures of PP-*g*-PCL copolymers can be controlled by OH content, ϵ-CL concentration, and reaction time. In the bulk, the individual PP and PCL segments in the graft copolymers are crystallized into two separate phases with high crystallinities. The microscopy studies reveal the effectiveness of PP-*g*-PCL in the polymer blends by reducing the phase sizes and improving the dispersion of the minor component in the PP matrix.

Introduction

The area of incompatible blends is identified as the one area with significant growth potential and providing the greatest scientific and technological challenge. The key to meeting this challenge is the concerted effort in three areas, i.e. thermodynamics, processing, and new compatibilizers.[1] Traditionally, PP forms very poor blends with other polymers because it has no chemical functionalities. Without any specific interactions PP is unlikely to form miscible blends or even to adhere to other polymers. On the other hand, polycaprolactone (PCL) forms truly miscible blends with numerous polymers and possesses considerable interaction with many more. For example, PCL forms miscible blends with PC, PET, PVC, $PVCl_2$, SAN, nitrocellulose, and chlorinated PE to name a only few.[2] Therefore, PP grafted with PCL would potentially be an extremely useful compatibilizer for many different polypropylene blend combinations.

In the literature there are several examples of PP blended with polyesters. Typically when PP is blended with the liquid crystalline polyester (LCP), the mechanical strength in the machine direction is improved due to fiberlike LCP phases in the flow direction. Since very little interaction exists between phases, the transverse properties are not improved. By addition of some maleic anhydride modified PP in the melt blending of PP and a proprietary Vectra LC polyester, both directions were significantly improved, including impact and tensile strength.[3] The anhydride groups on PP react with the polyester in situ to form a graft compatibilizer. Blends of PP and PET have likewise been improved by the addition of acrylic acid modified PP.[4] The blend of these two commodity polymers showed some improvement in yield stress indicative of better interfacial adhesion.

The use of graft copolymers as emulsifiers and interfacial compatibilizers[5–7] is an established technique to improve polymer interaction and mophology in polymer blends. Unfortunately, only very few PP graft copolymers have been reported, most of them without detailed molecular structure information. In the previous paper, we have described a new method[8] to prepare PP-*g*-PMMA graft copolymers (II) by using borane-containing polypropylene (I) and free radical graft-from reaction as shown in eq 1.



(1)

Borane-containing polypropylene (**I**) acts as a polymeric free radical source to initiate the graft-from polymerization of methyl methacrylate. This chemistry can be applied to most free radically polymerizable monomers to form a series of PP graft copolymers with a PP backbone and several free radically prepared polymers bonded to the side chains.

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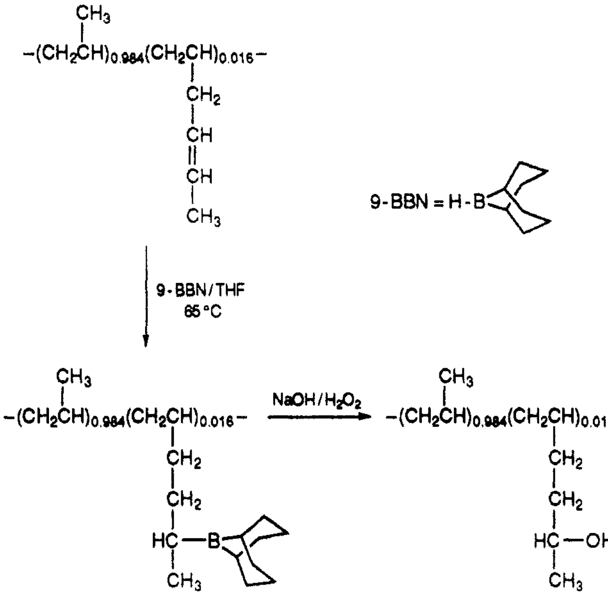
Results and Discussion

In this paper, we introduce another type of PP graft copolymer (IV) which contains a PP backbone and condensation polymers on the side chains. The chemistry is based on hydroxylated polypropylene (PP-OH) and the anionic ring opening reaction of ε-caprolactone (ε-CL). Both direct[9] and postpolymerizations[10] were used to prepare PP-OH. The direct process shown in eq 1 involves the combination of Ziegler–Natta catalysis and borane chemistry and the subsequent oxidation reaction. The postreaction is based on the hydroboration of an unsaturated PP, i.e. poly(propylene-*co*-1,4-hexadiene), as shown in eq 2. Both hydroxylated PP **III** and **III′** have high crystallinity, T_m about 150–160 °C, and high molecular weight, M_v approximately 150000–200000 g/mol as determined from the viscosity in decalin at 135 °C. The graft-from reaction was initiated by an aluminum alkoxide formed on the PP hydroxy groups. Two different methods were used to generate the Al alkoxide groups on the polymer as shown in eq 3.



(2)

III′

$$\mathrm{PP\text{-}OH} \xrightarrow{\mathrm{AlEt_3}} \mathrm{PP\text{-}O\text{-}AlEt_2}$$

or

$$\mathrm{PP\text{-}OH} \xrightarrow{\mathrm{BuLi}} \mathrm{PP\text{-}OLi} \xrightarrow{\mathrm{AlEt_2Cl}} \mathrm{PP\text{-}O\text{-}AlEt_2} \qquad (3)$$

Attempts were made evaluating the first process, reacting $AlEt_3$ with the OH groups. When formation of homo-PCL was observed a second method was investigated. The lithium alkoxide was used to react with Et_2AlCl. Some decrease in the amount of ungrafted PCL was noted. It is interesting to note that both metalation and graft-from reactions were carried out using suspension conditions with the PP fine particles slightly swollen in the toluene. Amorphous regions should be completely soluble in toluene, but the crystalline domains would be unaffected. Being a defect in the PP helix, the hexenol units would preferentially be in the amorphous domain and hopefully more accessible to reaction.

Molecular Structure of Graft Copolymers. The ring opening reaction was carried out at room temperature by the insertion and ring opening of ε-CL into the Al–O bond.[11] The driving force for the polymerization is the release of mild ring strain in the seven-membered cyclic ester monomer. The thermodynamic change in energy from acyclic to polymer is ΔG_p = −12.8 kJ/mol. In all the reactions the polymer was separated into acetone soluble and insoluble fractions in a Soxhlet extractor using hot acetone. This method was proven an effective separation technique for isolating the PCL from a solution cast blend of i-PP and PCL homopolymers. Hot acetone is capable of dissolving atactic or low molecular weight PP, but the catalyst employed produces very little atactic PP. It might be supposed that PP-*g*-PCL with a high percentage of PCL might get pulled into acetone. However, ^{1}H NMR analysis of the acetone extract from even the highest PCL containing grafts showed only PCL peaks with no discernible PP peaks. The acetone-insoluble fraction is soluble in xylene at elevated temperature. Figure 1 shows the ^{1}H NMR spectra of three acetone-insoluble samples in *o*-xylene-d_{10} at 120 °C. The chemical shifts at 4.1 ppm and 2.3 ppm correspond to methylene groups (CH_2O) and ($CH_2C{=}O$) respectively in PCL. The chemical shifts at 1.9, 1.6, and 1.1 ppm correspond to methine, methylene, and methyl groups in polypropylene. The quantitative analysis of copolymer composition was calculated by the ratio of two integrated intensities between δ = 4.1 ppm and δ = 2.0 to 1.0 ppm and the number of protons both chemical shifts represent. Parts a, b, and c of Figure 1 indicate 17, 33, and 57 wt% of PCL respectively in PP-*g*-PCL copolymers. High concentrations of PCL can be incorporated in the side chains of polypropylene despite the heterogeneous reaction conditions. The detailed experimental results and reaction conditions are summarized in Table 1. Runs i through iv all started with the same PP-OH copolymer (**III**) containing approximately 1.4% hexenol monomer units. Runs i, ii, and iii were exactly the same except for the amount of ε-CL in the

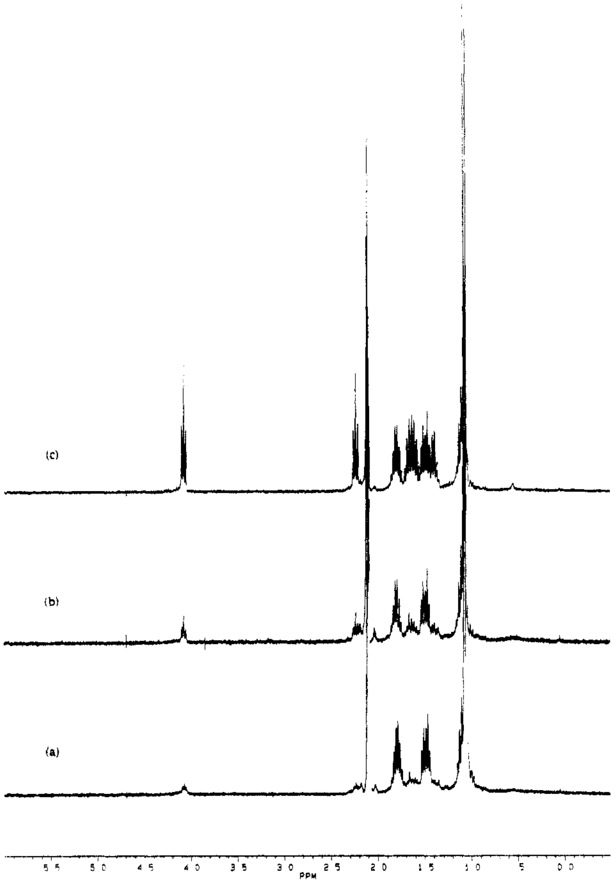


Figure 1. ^{1}H NMR spectra of PP-*g*-PCL graft copolymers, containing (a) 17, (b) 33, and (c) 57 wt % of PCL.

Table 1. A Summary of PP-*g*-PCL Copolymers and Reaction Conditions

run	amt of PP-OAlEt$_2$, g	amt of ϵ-CL, g	reaction time (h)	acetone soluble, g	acetone insoluble, g	wt % ϵ-CL in graft[a]
i	2.0	2.169	24	0.366	2.252	16.8
ii	2.0	4.299	24	0.430	2.763	32.9
iii	2.0	8.243	24	2.581	3.922	56.8
iv	2.0	4.571	60	2.102	4.120	59.5
v	2.0[b]	6.525	24	1.387	3.603	45.4

[a] Determined by ^{1}H NMR. [b] From unsaturated PP-hexadiene.

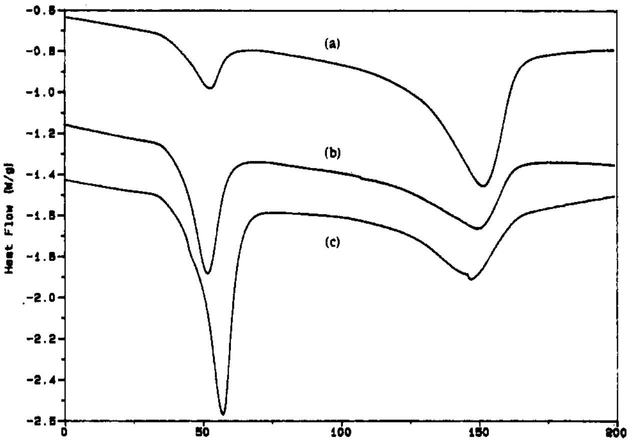


Figure 2. DSC curves comparison between three PP-*g*-PMMA copolymers, containing (a) 17 (b) 33, and (c) 57 wt % of PCL.

feed. The weight percent PCL in the resulting graft copolymer increased linearly with increasing ϵ-CL in the feed. The relatively long reaction time can be explained by the heterogeneous reaction conditions. The diffusion of ϵ-CL into the PP matrix would be the rate limiting step for the reaction. In fact, runs ii and iv differ in the reaction time of 24 and 60 h, but resulted in copolymers with 33 and 59 wt % PCL, respectively. The amount of homo-PCL produced, i.e. the acetone-soluble fraction, also increased with ϵ-CL feed. Any residual aluminum alkyl not covalently bound to the polymer could easily initiate the homopolymerization of ϵ-CL. Excess aluminum alkyl associated with the bound Al–O may not be completely washed out by the nonpolar solvents.

Run v started with commercial grade propylene and 1,4-hexadiene copolymer containing approximately 1.6% unsaturated monomer units. The polymer was hydroborated with 9-BBN or BH$_3$ and oxidized to give functional PP (**III′**) with the secondary alcohols on either the 4 or 5 position of the hexadiene branch. This polymer differed slightly in molecular weight, tacticity, and comonomer concentration from the directly copolymerized PP-OH (**III**). The secondary alcohol can also be converted to the secondary aluminum alkoxide which is approved to be an active initiator in the graft-from reaction of ϵ-CL.

Thermal Analysis. The graft copolymers were analyzed by DSC at a heating rate of 20 °C a minute to determine the crystalline melting behavior. Figure 2 shows the DSC curves of three PP-*g*-PCL copolymers containing 17, 33, and 57 wt % of PCL. All samples were given the same thermal treatment by heating in a Mettler hot stage of 180 °C for 15 min before cooling quiescently. Two distinctive crystalline structures are formed in all graft copolymers. It is clear that the high melting peak at about 150 °C is due to the polypropylene segments in the backbone and the low temperature one at about 50–60 °C is due to the PCL segments in the side chains. Both phases are clearly separated. A slight increase in the melting point of PCL with the increase of the PCL content may indicate an increase in the molecular weight. Table 2 compares the T_m's, ΔH's, and the relative percent crystallinities of several graft copolymers. For comparison, the starting material PP-OH (**III**) and PCL homopolymer (M_n of 45 600 g/mol and a PD of 1.89) were studied under identical thermal treatment. The peak melting points and the heats of fusion (in J/g from the curve area) for the respective PCL and PP peaks were evaluated for all PP-*g*-PCL samples with various PCL contents. The term "percent crystallinity" is used to denote the amount of crystallinity a particular graft has compared to a similar ungrafted polymer. For example the graft copolymer with 32.9 wt % of PCL, would be evaluated in terms of the PCL peak and the PP peak compared to each respective homopolymer. The associated PCL crystallinity would be calculated by the ΔH_{graft} divided by the $\Delta H_{\text{homo-PCL}}$ and the weight percentage of PCL actually in the graft.

$$\text{(PCL)\% X-stal} = (19.97\ \text{J/g})\ (100\%)/(71.79\ \text{J/g})\ (32.9\ \text{wt \% PCL}) = 84\%$$

Table 2 reveals some trends in the graft copolymers' crystalline morphologies. As the weight percent of PCL in the graft copolymer increases, so does the corresponding ΔH value. Since the number of hydroxy groups in the backbone is the same, then the number of grafts per chain is constant. Therefore, the increase PCL content reflects only increasing PCL graft length. Increasing the molecular weight of PCL increases its crystallinity as demonstrated by increasing the ϵ-CL segments on the graft copolymers. Likewise, the increase in the PCL melting points can be explained by the increasing graft lengths. The propylene segment lengths remain constant, since the amount of graft sites are constant. However, the increasing side chain (graft) length of the PCL should cause some change. If increasing the PCL length forces greater phase separation, then the PP would be more distorted and lower in T_m and ΔH. However, the crystallization of the PCL may have little effect on the PP crystallinity, since upon cooling the PP is already crystallized well before the PCL crystallization begins. The phase separated PCL melt may cause PP nucleation at the interface resulting in more nucleation.

Evaluation of the T_g's is the standard method to examine the level of polymer mixing. Unfortunately, DSC did not result in any clear T_g data for the graft copolymers. The glass transitions of the highly crystalline polymers were broad and very low in intensity with no obvious changes observable.

Microscopy Investigation. In the PP-*g*-PMMA cases,[8] the morphologies of the graft copolymers were examined by polarized optical microscopy. Unfortunately, the PP and PCL phases are both highly crystalline at room temperature and their spherulitic phases are difficult to distinguish by optical microscopy. Using a hot stage with the microscope to view the graft copolymer at the temperatures, above T_m of PCL and below T_c (crystallization temperature) of PP, proved to be more conclusive. Thin films of the 70/30 PP/PCL homopolymer blend and a PP-*g*-PCL graft sample were cooled from the melt at 200 to 100 °C over 2 h to crystallize the PP component. At

Table 2. A Summary of DSC Results of PP-*g*-PCL Graft Copolymers

wt % ϵ-CL	PCL mp (°C)	PCL Δ*H* (J/g)	PCL % X-stal[a]	PP mp (°C)	PP Δ*H* (J/g)	PP % X-stal[a]
100	59.84	71.79	100			
16.8	52.15	8.50	71	151.27	54.20	101
32.9	51.59	19.97	84	149.42	30.54	71
56.8	57.19	40.05	98	147.05	33.32	120
59.5	57.91	40.36	94	160.55	36.14	139
45.4[b]	58.45	31.21	95	150.59	43.02	87
30.0[c]	59.57	22.35	104	161.48	42.88	95
0				158.89	64.21	100

[a] Percent crystallinity used as relative to parent homopolymer. % X-stall = $(\Delta H_{\mathrm{Graft}})(100)/(\Delta H_{\mathrm{Polymer}})$(wt % polymer in graft). [b] Graft copolymer from unsaturated PP with ΔH = 90.4 J/g and T_{m} = 154 °C. [c] Blend of two homopolymers, 70/30 PP/PCL.

100 °C the PCL domains were in the melt, while the PP phase was highly crystalline. The homopolymer blend only displayed large, normal-looking PP spherulites, while the graft copolymer displayed smaller, less defect spherulites. Neither sample exhibited more than one visible phase. The films were then quenched from 100 to −198 °C by immersion in liquid N_2. In the 70/30 PP/PCL homopolymer blend, small PCL crystallites formed around and on top of the PP spherulites as seen in Figure 3a. The PP-*g*-PCL graft copolymer in Figure 3b shows only small, slightly distorted spherulites.

SEM operating with secondary electron imaging was used to observe the surface topography of cold fractured film edges. The films were cryrofractured in liquid N_2 to obtain an undistorted view representitve of the bulk material. Figure 4 shows the micrographs of 70/30 PP/PCL homopolymer blend and PP-*g*-PCL copolymer with similar composition. In the homopolymer blend, the polymers are grossly phase separated as can be seen by the minor component PCL which exhibits nonuniform, poorly dispersed domains and voids at the fracture surface as shown in Figure 4a. This ball and socket topography is indicative of poor interfacial adhesion between the PP and PCL domains and represents PCL domains that are pulled out of the PP matrix. Such pull out indicates that no stress transfer takes place between phases during fracture. The graft copolymer shows a totally different result in Figure 4b. The material exhibits flat mesalike regions similar to pure PP. No distinct PCL phases are observable indicating that fracture occurred through both phases or that the PCL phase is too small to be observed.

PP/PCL Polymer Blends. It is interesting to examine the compatibility of PP-*g*-PCL copolymer in PP and PCL homopolymer blends. A blend comprised of a 70/30/10 weight ratio of PP, PCL, and graft copolymer, PP-*g*-PCL with 57 wt % PCL, was prepared and observed under the polarized optical microscope and the SEM. Figure 3c shows the polarized optical micrograph of the 70/30/10 blend which was dissolved in chlorobenzene and cast on a glass slide. The pattern is clearly different from that of the homopolymer blend shown in Figure 3a and is similar to that of graft copolymer in Figure 3b. Overall, the crystalline structure is visible with spherulitic shape. The spherulites are radially symmetric around a central nucleating site and are slightly larger and distorted compared to either typical PP or PCL spherulites.

Thicker films were prepared for SEM analysis. The polymers were blended in chlorobenzene and precipitated into hexane. The samples were dried under vacuum to remove residual solvent at room temperature, since elevated temperatures would anneal the PCL component. Upon blending PP and PCl with the emulsifier PP-*g*-PCL a drastic change in the morphology occurs. The compatibilized blend shown in Figure 5a no longer displays the distinct PCL globules. Rather, a flat mesalike fracture surface is observed similar to that seen on a fractured PP or PP-*g*-PCL surfaces as shown in Figure 4b. The addition of the graft copolymer to the blend increased the interfacial adhesion between the domains as seen by the mode of

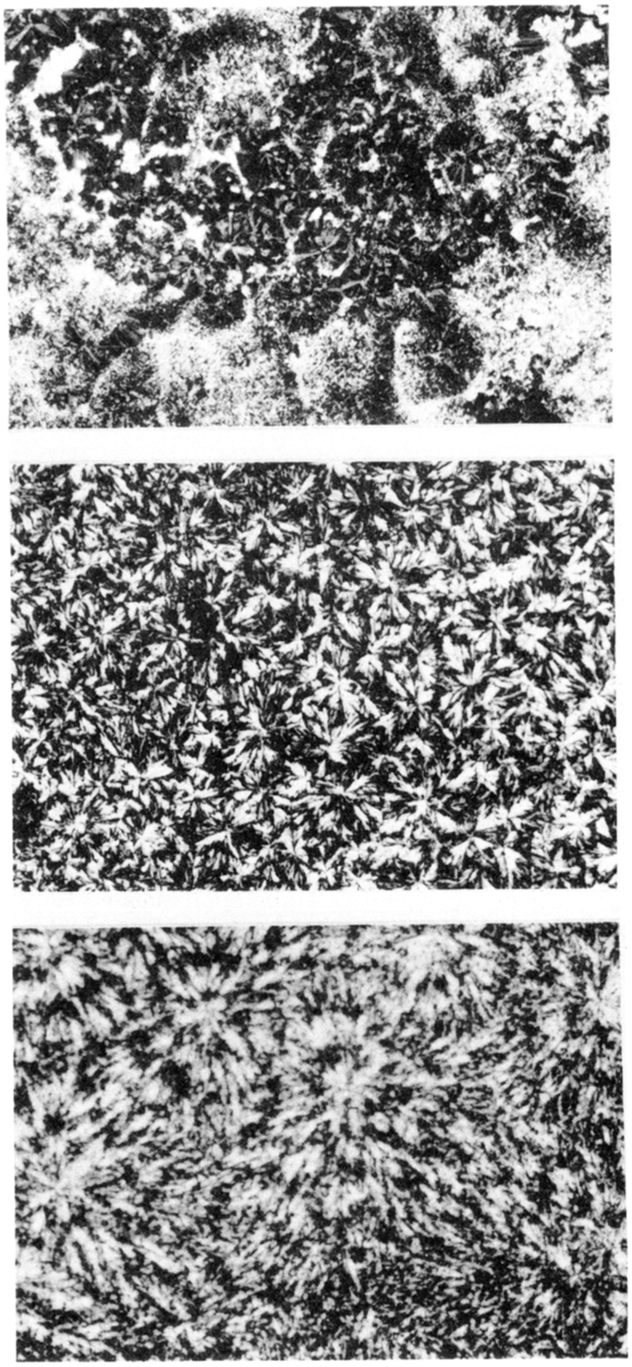


Figure 3. Optical micrographs of polymer blends: (a, top) two homopolymer blends with i-PP/PCL = 70/30; (b, middle) PP-*g*-PCL graft copolymer; (c, bottom) two homopolymers with PP-*g*-PCL, i-PP/PP-*g*-PCL/PCL = 70/10/30 (100×).

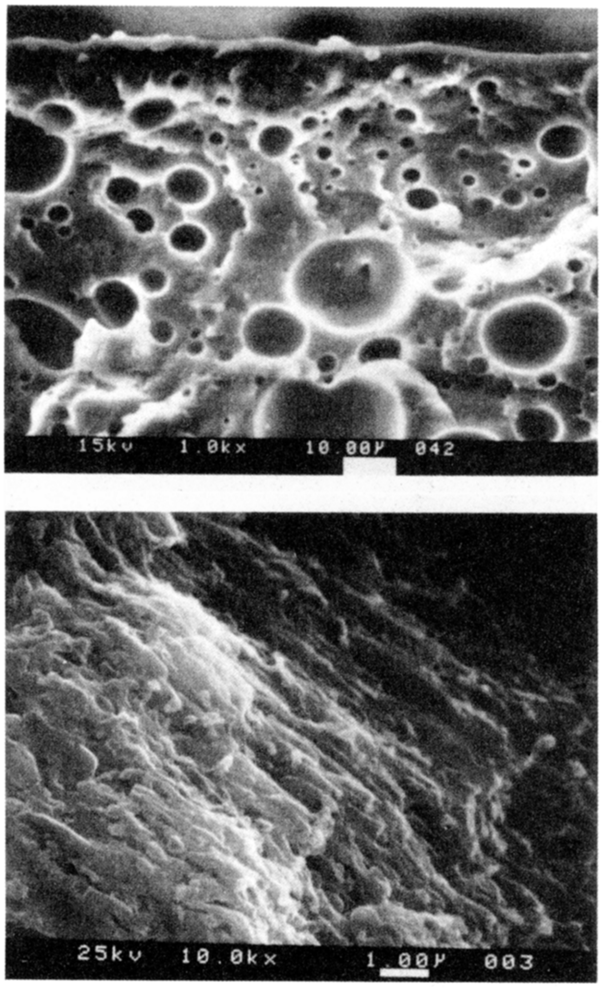


Figure 4. SEM micrographs of (a, top) two homopolymer blends with i-PP/PCL = 70/30 (1000×) and (b, bottom) PP-*g*-PCL graft copolymer (10000×).

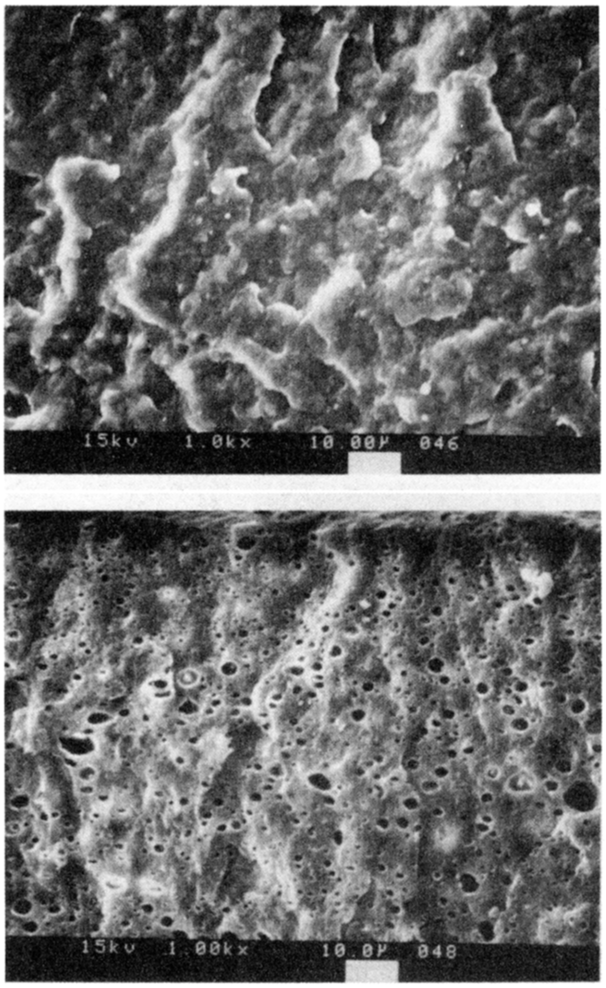


Figure 5. SEM micrographs of (a, top) two homopolymers with PP-*g*-PCL, i-PP/PP-*g*-PCL/PCL = 70/10/30 and (1000×) (b, bottom) the blend after etching to remove PCL (1000×).

fracture. Instead of pulling out, leaving the "ball and socket" formations, as seen in the unmodified blend in Figure 4a, both the PP and PCL phases fractured showing that they are mechanically tied. Ideally, the interface is bridged by the graft copolymer extending into both phases tying them by a covalent bond. To estimate the new PCL domain size, the fractured samples were reduced with BH_3 and hydrolyzed to selectively etch the PCL before OsO_4 staining.[12] Figure 5b shows the micrograph with much smaller, more dispersed voids that represent the missing etched PCL domains.

PP/PC and PP/PVC Blends. It would be extremely advantageous if inexpensive, commodity PP could be effectively compatibilized in blends with the more costly engineering resin polycarbonate. Bisphenol-A polycarbonate (PC) has excellent high and low temperature physical properties even up to 140 °C. Polycarbonate has a T_g of 148 °C and a T_m of 240 °C, although it is usually amorphous.[13] Using PP as the matrix material with a compatibilized polycarbonate dispersed phase could greatly improve the mechanical properties creating a toughened plastic.

Since PCL and polycarbonate (PC) form a miscible blend[14] the graft copolymer PP-*g*-PCL should behave as an emulsifier for PP and PC blends. Blends of polypropylene and polycarbonate, with M_n of 24 800 g/mol and a PD of 2.2 by GPC, were mixed in chlorobenzene solution. Optical microscope samples were solution cast directly from chlorobenzene solution onto a glass slide and heated in a hot stage for 10 min at 200 °C and allowed to cool quiescently. A 70/30 blend of PP/PC observed by polarized optical microscopy in Figure 6a shows gross phase separation of the spherulitic PP and the amorphous PP phases. The PC phases vary widely in both size and shape due to the lack of interaction with the PP matrix. A blend containing 70/30/10 of PP/PC/PP-*g*-PCL, where the graft contains 57 wt % PCL, was used to evaluate the effect of the polymeric compatiblizer on the blend's morphology. Figure 6b shows the micrograph of the compatibilized blend. Only small distorted spherulites are observed and only a few very small distinct PC phases can be found. The PP-*g*-PCL is clearly proven to be an effective compatibilizer for PP and PC blends.

A similar PP-*g*-PCL compatibility study for PP and PVC blends was also investigated by optical microscopy. It is also known that polycaprolactone forms miscible blends with poly(vinyl chloride).[15] Polypropylene and PVC (M_n = 91 000 g/mol and PD = 1.8) in a 70/30 weight ratio were dissolved in chlorobenzene and solution cast onto glass slides. Likewise, a 30/70/10 blend of PP, PVC, and PP-*g*-PCL copolymer was prepared. The homopolymer blend displays gross phase separation of the isotropic, amorphous PVC and the birefringent PP spherulites as shown in Figure 7a. Addition of the PP-*g*-PCL copolymer clearly changes the morphology of polymer blend, as shown in Figure 7b, by reducing the PVC domain size and having a finer dispersion within the PP matrix. Also the mode of PP nucleation has changed, as evidenced by the change in sperulite size, shape, and quantity. The compatibilization of PP with either rigid PVC or plasticized PVC

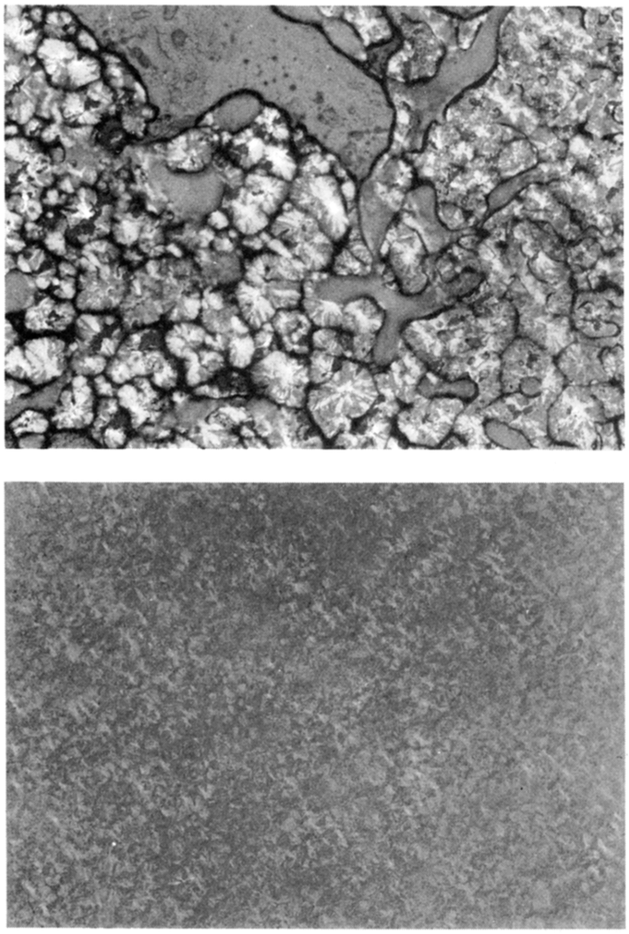


Figure 6. Optical micrographs of (a, top) two homopolymer blends with i-PP/PC = 70/30 and (b, bottom) two homopolymers with PP-*g*-PCL, i-PP/PP-*g*-PCL/PC = 70/10/30 (100×).

should exhibit interesting mechanical properties. The detailed mechanical properties of polymer blends are currently under study.

Experimental Details

Instrumentation and Materials. All ^{1}H NMR were run on a Bruker AM 300 instrument either in benzene-d_6 at room temperature or in *o*-xylene-d_{10} at 130 °C. Peaks were referenced to TMS for room temperature or hexamethyldisiloxane for high temperature analysis. DSC analysis were run on a DuPont Instruments DSC-2910 with Thermal Analyst-2000 controller. Samples were prepared in aluminum sample pans, heated in a Mettler hot stage to 180 °C for 15 min, and allowed to cool quiescently unless otherwise stated. Viscosity measurements were taken using a cone/plate rotational Brookfield Digital Viscometer, Model DVII. The viscosity of polymer solutions in decahydranaphthalene (decalin) inhibited with BHT was determined at 135 °C. The alcohol-containing copolymers were esterified before measuring their viscosity.

In the optical microscopy studies, the samples were observed and photographed with an Olympus BH2 microscope under cross polarizers mounted with a 35-mm C-35A-4 camera and an Olympus AD Systems exposure control unit. The samples were prepared by casting thin films onto glass microscope slides and covering with a cover slip. The PP based polymers were usually cast from dilute solution of hot xylene or chlorobenzene. Scanning electron microscopy was used to view some of the polymer films with a Topcon International Scientific Instruments ISI-SX-40 using secondary electron imaging. SEM samples were prepared from films cryofractured in liquid N_2. Some samples were etched by reduction of the surface with $BH_3{\cdot}S(CH_3)_2$ complex and hydrolysis prior to staining with OsO_4 vapor.[12] Samples were mounted on an aluminum stub and carbon coated to form a conductive coating.

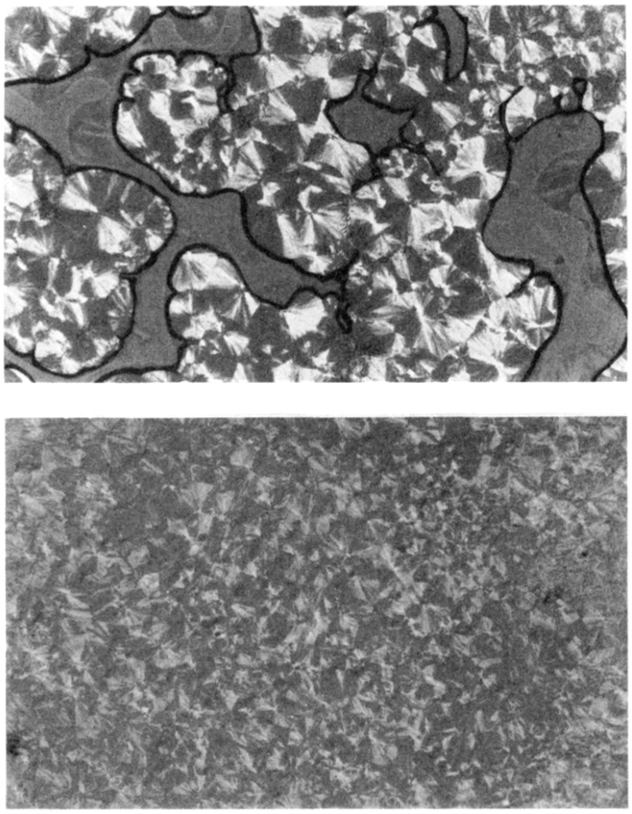


Figure 7. Optical micrographs of (a, top) two homopolymer blends with i-PP/PVC = 70/30 and (b, bottom) two homopolymers with PP-*g*-PCL, i-PP/PP-*g*-PCL/PVC = 70/10/30 (100×).

All O_2 and moisture sensitive manipulations were carried out inside of an argon-filled Vacuum Atmosphere drybox. HPLC grade hexane, tetrahydrofuran, and toluene were deoxygenated by argon sparge before refluxing for 48 h and then distilling from their respective green or purple sodium anthracide solution under argon. 2-Propanol was refluxed in CaH_2 before distilling under argon. All three solvents were stored in the drybox. $Al(Et)_3$, $(Et)_2AlCl$, and *n*-BuLi (Aldrich) were used as received.

Synthesis of PP-*g*-PCL. Both hydroxylated PP, poly(propylene-*co*-hexen-6-ol)[9] and poly(propylene-*co*-hexen-5-ol),[10] were prepared by methods described in our previous papers. In a metalation reaction, a PP copolymer (M_v of 183 000 g/mol) containing 1.4 mol % hexenol units was ground to fine powder and dried under vacuum at 50 °C. The hydroxy-containing PP was placed in a slurry of dry toluene in a drybox and then metalated with excess *n*-butyllithium to form the lithium alkoxide. The polymer was stirred for 12 h before it was isolated by filtration and repeatedly washed and filtered in toluene followed by the same procedure in hexane. The powdery solid was placed in a slurry of fresh toluene and reacted with a 3 molar equiv of diethylaluminum chloride for 12 h to form the PP–aluminum alkoxide. Again, the polymer was isolated by repeated filtering and washing in toluene followed by hexane.

The cyclic ester ϵ-caprolactone (Aldrich Chemical) was purified by drying over calcium hydride and distilling under reduced pressure. In the drybox, 4.3 g of caprolactone was added to a slurry of 2.00 g of $PP{-}OAlEt_2$ in 35 mL of toluene. The reaction was stirred at room temperature for 24 h, at which time the reaction was terminated by the addition of MeOH. The polymer was isolated by precipitating into acidified MeOH. The polymer mass was extracted with hot acetone in a Soxhlet apparatus under N_2 for 48 h to remove any ϵ-CL homopolymer, which is soluble in acetone. After isolation of both fractions, 0.43 g of acetone-soluble lactone homopolymer and 2.76 g of acetone-insoluble polymer were obtained.

Polymer Blending. All the blends were prepared in solution to obtain molecular level mixing. The PP was first dissolved in refluxing chlorobenzene inhibited with BHT and kept under a N_2 blanket to prevent oxidation. The PP-*g*-PCL and the more polar polymer (PVC, PCL, or PC) were then slowly added to the hot solution. After the polymer mixture had formed a clear, homogeneous solution, the blend was precipitated into cold hexane. The blend was dried under vacuum before being melt pressed to form a film.

Conclusion

The major goal of this research is the development of a new graft copolymer, PP-*g*-PCL, for improving the compatibility of PP in many polymer blends. The combination of the hydroxylated PP polymers and anionic ring opening polymerization of ϵ-CL was demonstrated to be an useful route in preparing PP-*g*-PCL copolymers with controllable compositions and molecular structures. The OH content controls the graft density, while the ϵ-CL concentration and reaction time determined the graft length. In the bulk, the individual PP and PCL segments in the copolymers form two separate highly crystalline phases. The PP-*g*-PCL copolymers were shown to be good compatibilizers for PP blends with PCL, PC, and PVC, as evidenced by the minor component's reduced phase sizes and improved dispersion in the PP matrix.

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