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Polymer 41 (2000) 3599–3607

polymer

Synthesis of novel compatibilizers and their application in PP/nylon-66 blends. I. Synthesis and characterization

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Received 20 April 1999; received in revised form 12 July 1999; accepted 9 August 1999

Abstract

A series of novel compatibilizers with different length of oligocaprolactone branch chains, which are capped with one, two or three carboxyl groups at one of these branch chains' extremities, were synthesized by a three-step approach involving: (1) the oligomerization of ϵ-caprolactone initiated by various of hydroxy acids (glycollic acid, DL-malic acid, or citric acid); (2) the reaction of acryloyl chloride with α-hydroxyl-ω-carboxyl (1,2,3)-oligocaprolactone (HCPCL); and (3) the graft copolymerization of α-acryloyl-ω-carboxyl (1,2,3)-oligocaprolactone (ACPCL) with polypropylene.

Effects of various parameters such as monomer ACPCL and initiator benzoyl peroxide concentration, reaction time, and ACPCL kinds on the grafting percentage of ACPCL onto polypropylene (PP) in xylene solution were studied. The grafting of ACPCL onto PP in a laboratorial single screw extruder was also investigated. The maximum extents of grafting achieved in solution and melt were about 10.2 and 12.3%, respectively.

The intermediate products, HCPCL and ACPCL were characterized by acid–base titration, hydroxyl value titration, Fourier transform infrared spectroscopy (FTIR), ^{1}H- and ^{13}C-nuclear magnetic resonance analyses, respectively. The grafting copolymers were also characterized by electrometric titration, FTIR analysis, and differential scanning calorimetric, respectively.

Keywords: ϵ-caprolactone; Hydroxyl acid; Compatibilizer

1. Introduction

Polypropylene (PP) has become the largest and fastest growing plastic because of its versatility, wide applicability, and low cost [1]. However, it is nonpolar, and therefore has poor miscibility in blends and alloys with polar polymers like nylons, polyesters, engineering thermoplastics, and so forth. This restricts its use in several new emerging technologies. Chemical modification of PP through grafting offers an effective means for introducing some desirable properties into the polymer without adverse effecting on the nature of polymer backbone.

Grafting of vinyl monomers on PP was carried out by several workers using various methods and was thoroughly reviewed by Singh [2] and Naqvi and Choudhary [3] Maleic anhydride (MAH) has been shown to an effective modifier to PP in PP/nylons blends and PP/Wood Cellulose composites [4–14]. However, the unreacted MAH in the MAH-g-PP strongly hampers the adhesion of modified PP to polar materials [15,16]. A mixture of alkyl acrylates was used by Canterino [17] for grafting onto PP using benzoyl peroxide initiator. Grafting of acrylic acid and methacrylic acid onto PP in *o*-dichlorobenzene was carried out by Pegoraro et al. [18,19] and Masahiko and Iwata [20] using benzoyl, dicumyl, and *t*-butyl peroxide initiators. PP was grafted with acrylamide, ethylene glycol methacrylate, and membranes of these graft copolymers were prepared by solvent evaporation technique [21]. Ide and Hasegawa [22] and Park and Shin [23] synthesized maleic anhydride-g-PP using benzoyl peroxide in xylene. Kiyotada [24] and Klosiewicz [25] modified PP by grafting bicyclo(2,2,1) hept-5-ene 2,3-dicarboxylic acid anhydride and butyl methacrylate in *o*-chlorobenzene using butyl peroxide as an initiator. Masahiko [26] synthesized 10.5:89.5 *N*-butyl maleimide propylene graft copolymer using chlorobenzene as a solvent and dicumyl peroxide initiator at 125°C.

However, all the above mentioned compatibilizers have the similar structure; that is, their pendent functional groups are very short in length and attached to the polymer backbone directly [as shown in Fig.1(a)]. This unique structure may affect the compatibilizing efficiency due to a steric

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0032-3861/00/$ - see front matter
PII: S0032-3861(99)00582-0

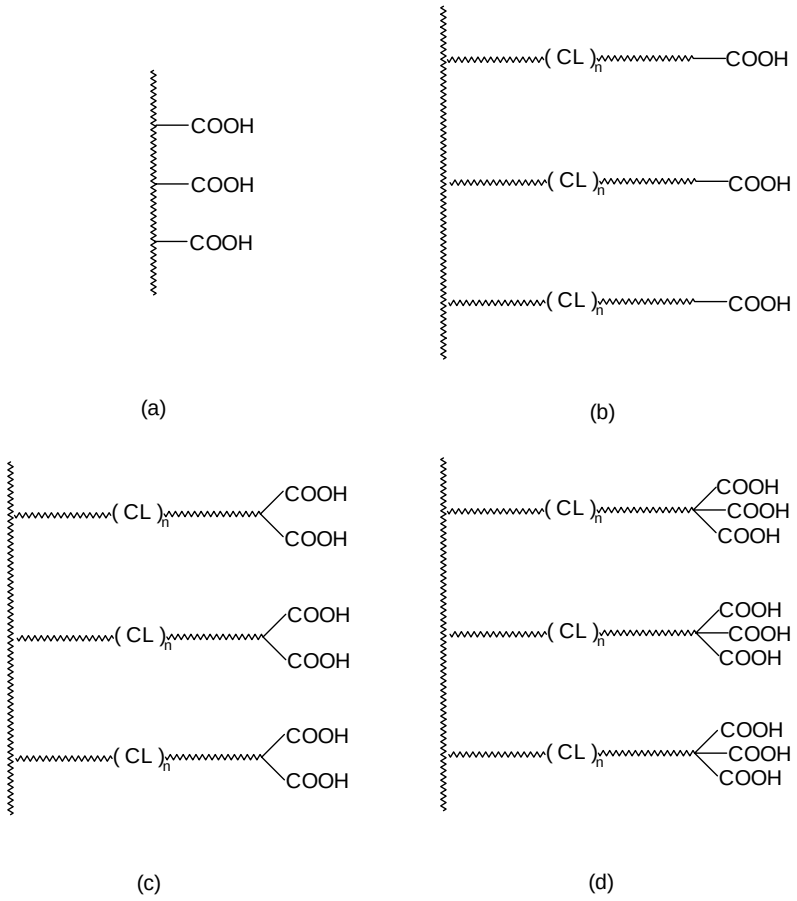
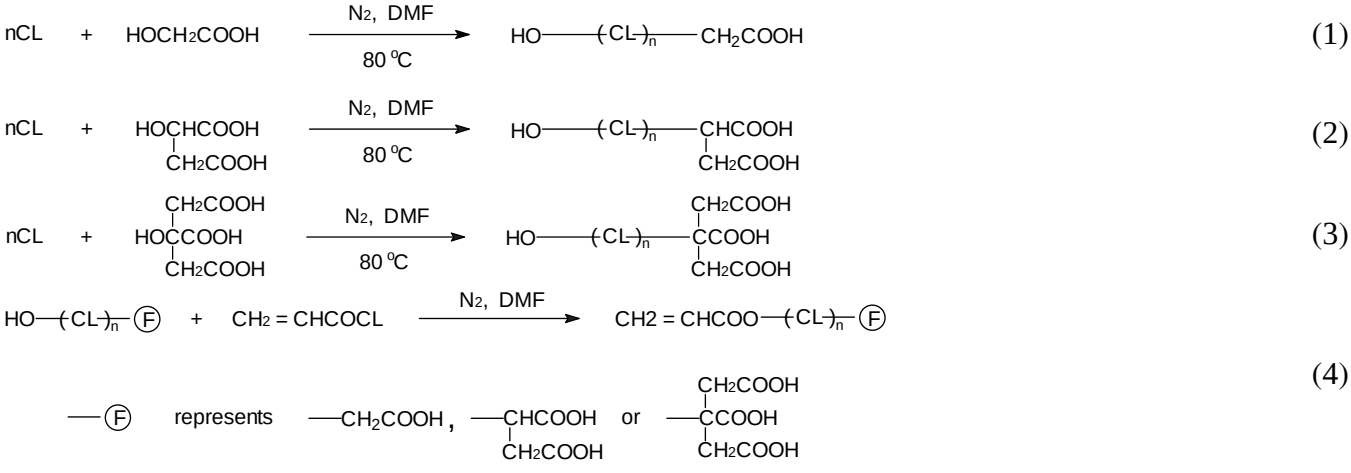


Fig. 1. Schematic models of various compatibilizers.

affect. In this study, a series of α-acryloyl-ω-carboxyl (1,2,3)-oligocaprolactones (ACPCL) will be synthesized by the oligomerization of ϵ-caprolactone which are initiated with glycollic acid, DL-malic acid, or citric acid [see Eqs. (1)–(3)] and the following reaction of acryloyl chloride with α-hydroxyl-ω-carboxyl (1,2,3)-oligocaprolactone (HCPCL) [see Eq. (4)], then used as modifiers to modify the PP. These ACPCLs contain both the double linkages and the carboxyl groups in the molecular structure. The double bonds can graft copolymerize with PP in the presence of initiator, and the carboxyl groups can react with amino groups in nylons; moreover, the oligocaprolactone branch chain has a unique ability to blend with a variety of other polymers over wide composition ranges. So, these ACPCL-grafted PP (ACPCL-g-PP) copolymers [structures as shown in Fig. 1(b)–(c), respectively] are expected to be used as the compatibilizing agents in PP/nylons or PP/polyester blends.



This part was concerned mainly with the oligomerization of ϵ-caprolactone initiated by various hydroxy acids (glycollic acid, DL-malic acid or citric acid) and the graft polymerization of ACPCL onto PP in solution and in a laboratorial single screw extruder. Effects of various parameters such as monomer ACPCL and initiator BPO concentration, reaction time, and ACPCL kinds on percentage grafting in solution were studied. As to the compatibilizing effect of ACPCL-g-PP in PP/nylon-66 blends in terms of inner morphology, thermal properties, crystalline structure, and macroscopic mechanical properties will be described in a forthcomming article (Part II. Application in PP/nylon-66 blends).

2. Experimental

2.1. Materials

ϵ-Caprolactone (Aldrich) was dried over calcium hydride at room temperature for 24 h, then distilled under reduced pressure. Glycollic acid, DL-malic acid, and citric acid were milled and sieved to 100 mesh, then dried in a vacuum oven (60°C) for at least 24 h. Polypropylene [(B900F) from YUKONG Limited, Korea] was used in this work after drying in vacuum at 80°C for 48 h. Benzoyl peroxide (BPO) was used after dissolving it in chloroform and reprecipitating in methanol. *N*,*N*-Dimethyl formamide (DMF) was purified by following the same procedure outlined for ϵ-caprolactone. AR grade xylene, methanol and acetone were used as-received without further purification.

2.2. Measurements

The Fourier transform infrared spectra (FTIR) of ACPCLs and HCPCLs were obtained on a NICOLET 170SX FTIR spectrometer in KBr. FTIR spectra of PP and ACPCL-g-PP were recorded onto a Bruker IFS66V spectrophotometer. A 2% sample xylene solution was filmed in NaCl slide for the measurement. The 500 MHz ^{1}H nuclear magnetic resonance (^{1}H-NMR) spectrum was recorded on a Bruker AM-500 spectrometer. Solution of 50 mg sample in 0.5 ml of deuterated dimethyl sulfoxide (DMSO-d_6) solvent was measured in a 5 mm o.d. sample tube.

The content of carboxyl group of HCPCLs and ACPCLs was measured with the normal acid–base titration (ABT). Titrant and indicator are 0.05 N NaOH alcohol solution and phenolphthalein, respectively. The measurement of the hydroxyl value of HCPCL was performed by the normal hydroxyl value titration (HVT) in which the sample was first treated with maleic anhydride in DMF under nitrogen at 80–100°C so that the new carboxyl group in a number equivalent to the original hydroxyl group was liberated, and then subjected to ABT for determining the total content of the carboxyl group.

The percentage of ACPCL grafted onto PP was determined under nitrogen in a 150 ml four neck round-bottom flask equipped with a basic burette, a ball condenser, a magnetic stirrer, and an electrometric titration outfit (PHS-3D, China).

2.2.1. Measuring procedure

After 2.000 g of the grafted product ACPCL-g-PP was weighed to the bottle, about 75 ml of xylene was added, and then the temperature of a silicone oil bath was increased to 135°C. Once the sample was fully dissolved, the temperature was lowered to 115°C, and then the hot solution was titrated with 0.05 N NaOH *n*-butyl alcohol (b.p. 117.5°C) solution, and the curve of the electropotential of the solution vs. the volume of the titrant obtained. The computation equation of the percentage of ACPCL grafted onto PP which was defined by the value of $W_{ACPCL}/(W_{ACPCL} + PP)$ was as follows:

$$\text{Grafting percentage} = \frac{(V - V_0)20\%}{(V_{20\%} - V_0)} \quad (5)$$

where V_0 is the volume of NaOH *n*-butyl alcohol solution titrated in blank hot solution, $V_{20\%}$ the volume of NaOH *n*-butyl alcohol solution titrated in a mixture of 0.400 g ACPCL with 1.6 g PP in hot xylene for calibration, and V is the volume of NaOH *n*-butyl alcohol solution in the sample solution.

Differential scanning calorimetric (DSC) study was conducted using a Perkin–Elmer thermal analyzer. The analysis was carried out at a constant heating rate of 20°C/min in the temperature range of 300–470 K under nitrogen atmosphere. The relative crystallinity of various samples was obtained by using the following expression:

$$\%\text{Relative crystallinity} = \frac{\Delta H_f}{\Delta H_f^*}100\% \quad (6)$$

where ΔH_f^* is heat of fusion of the crystalline PP and ΔH_f is the heat of fusion of graft copolymer.

2.3. The oligomerization of CL initiated by hydroxyl acids

All polymerizations [as shown in Eqs. (1)–(3), respectively] were performed in a 250 ml Wolff bottle equipped with a ball condenser, a isobaric funnel and a magnetic stirrer, and protected under nitrogen. After the stoichiometric amount of initiator was weighed into the bottle, a proper amount of anhydrous DMF solvent was added. After the initiator hydroxyl acid was completely dissolved in DMF, the temperature of the silicone oil bath was increased to 80°C, and then the monomer CL was slowly dropped from the isobaric funnel into the bottle at a speed of 3 drops/min. After the dropping was finished, the polymerization was kept at 80°C for 6–8 h. At the end of reaction, the product mixture was precipitated twice or more from DMF into water for removing of the unreacted monomer and initiator, and then the sample was filtered and dried under vacuum at 60°C for 24 h.

Table 1
Organization of CL initiated by different kinds and amounts of hydroxyl acids in DMF under N_2 at 80°C (GA: Glycollic acid; MA: DL-Malic acid; CA: Citric acid;

$$M_n = \frac{\text{Carboxyl number of used hydroxyl acid}}{\text{Content of carboxyl group of the oligocaprolactone}}$$

Reaction series	Hydroxyl acids	Mole ratio of hydroxyl acid to CL	HCPCL			
			M_n	Content of hydroxyl group (10^{-3} mol/g)	Content of carboxyl group (10^{-3} mol/g)	Mole ratio of hydroxyl to carboxyl groups
A	GA	1:3	478	2.05	2.09	1:1.02
B	GA	1:4	581	–	1.72	–
C	GA	1:5	699	1.39	1.43	1:1.03
D	MA	1:3	530	1.85	3.77	1:2.04
E	MA	1:4	649	–	3.08	–
F	MA	1:5	781	1.25	2.56	1:2.05
G	CA	1:3	640	1.53	4.69	1:3.06
H	CA	1:4	758	–	3.96	–
I	CA	1:5	901	1.08	3.33	1:3.08

2.4. The reaction of the HCPCL with acryloyl chloride

The reaction [as shown in Eq. (4)] proceeded in DMF solvent under nitrogen protection in a flask with an isobaric funnel, a magnetic stirrer, a ball condenser, and an acid adsorption plant. A proper amount of HCPCL in DMF was added to the bottle, and then a 150% molar excess of the stoichiometric amount of acryloyl chloride was slowly dropped to the bottle; the reaction temperature was controlled at 5–20°C. After the dropping was completed, the reaction was kept at 70°C for 6–8 h, and then a proper amount of water was dropped into the reaction mixture for neutralizing the unused acryloyl chloride. Finally, the product mixture was precipitated twice from DMF into water for removing of the side product acrylic acid, after which the product ACPCL was filtered and dried under vacuum at 60°C for 24 h.

2.5. Grafting of ACPCL onto PP in solution

The solution graft copolymerization was carried out in a 250 ml four neck round-bottom flask equipped with a magnetic stirrer, a ball condenser, a thermometer, and a nitrogen gas inlet. PP (8.0 g), ACPCL (2.0 g) and xylene (200 ml) were added into the flask and heated with agitation at 135°C to homogenize the mixture, followed by the addition of the BPO (0.1 g) at once. The reaction continued for 6 h at 135°C under nitrogen. The reaction mixture was then poured into 750 ml of methanol under vigorous stirring. The precipitated graft copolymer was isolated and washed several times with acetone, and then the Soxhlet was extracted with acetone until no further decrement of the weight of this sample by ther Soxhlet extraction procedure to remove traces of ungrafted APCLA and xylene. Finally, the product was dried first in infrared heat lamp and then under vacuum at 80°C for 24 h.

2.6. Grafting of ACPCL onto PP in an extruder

The melt graft copolymerization was performed in a laboratorial single screw extruder (CSI 194A). A mixture of PP (20.0 g), ACPCL (5.0 g), and BPO (0.25 g) were fed to the extruder with the operating parameters as $L/D = 30$, rotation speed = 40 rpm, rotor temperature = 220°C and head temperature = 230°C. For measuring the graft percentage, the graft copolymer mixture needs to be purified as per the procedure mentioned above.

3. Results and discussion

3.1. Effect of hydroxyl acids on the CL polymerization

We have studied the effect of hydroxyl and carboxyl groups on the opening polymerization of CL in previous papers [27–28]. According to the carboxyl-catalyzed hydroxyl group-initiated polymerization of CL, these hydroxyl acids can initiate the polymerization of CL by the hydroxyl group, whereas the carboxyl groups do not play the initiation role, but can accelerate the hydroxyl-initiated polymerization of CL. On the contrary, to avoid the esterification of the hydroxyl group with the carboxyl group at a high temperature, the polymerization has to be controlled at a moderate temperature. In this paper, all polymerizations were performed at about 80°C.

Table 1 lists the polymerizations of ϵ-caprolactone initiated by different kinds and amounts of hydroxyl-acids (glycollic acid, DL-malic acid, or citric acid) in DMF under nitrogen at 80°C. For the DL-malic acid or citric acid initiated polymerization of CL, Table 1 shows the dependence of the molecular weight of HCPCL on the amount of added hydroxyl-acid initiator. On the contrary, for these hydroxyl-acids initiated polymerization of CL, esterification

Table 2
Reaction of HCPCL with acryloyl chloride in DMF under nitrogen (GA, Glycollic acid; MA, DL-Malic acid; CA, Citric acid)

Reaction series	Hydroxyl acids	Reactants		Products		
		M_n of used HCPCL	Acryloyl chloride (mol% of HCPCL)	Content of carboxyl group of ACPCL (10^{-3} mol/g)	Theoretical M_n of ACPCL	Practical M_n of ACPCL
J	GA	478	150	1.95	532	513
K	GA	581	150	1.60	635	625
L	GA	699	150	1.35	753	740
M	MA	530	150	3.47	584	576
N	MA	649	150	2.87	703	697
O	MA	781	150	2.44	835	820
P	CA	640	150	4.36	694	688
Q	CA	758	150	3.73	812	804
R	CA	901	150	3.18	955	943

between the hydroxyl group and the carboxyl group must be investigated, because esterification will affect the molecular structure of HCPCL. Usually, an intramolecular esterification causes the formation of cyclic oligomers and modifies the chain structure of HCPCL. Both intra and intermolecular esterification will cause an ill-defined molecular structure of HCPCL. In this article, esterification level was also evaluated by comparing the mole ratio of the hydroxyl group to the carboxyl group of HCPCL with that of the hydroxyl acid. It is clear that the hydroxyl group and the carboxyl group are consumed as an equivalent mole number in the esterification. Thus, for the HCPCL which was produced by glycollic acid-, DL-malic acid-, or citric acid-initiated polymerization of CL, while in the absence of esterification, the mole ratio of hydroxyl to carboxyl groups should be equal to that of the hydroxyl acid, that is, 1/1 for glycollic acid, 1/2 for DL-malic acid and 1/3 for citric acid, whereas in the presence of esterification, this mole ratio should be less than that of the hydroxyl acid.

Table 1 also shows the contents of hydroxyl and carboxyl groups measured by ABT and HVT methods. From Table 1, for these hydroxyl acid initiators, the HCPCL have an

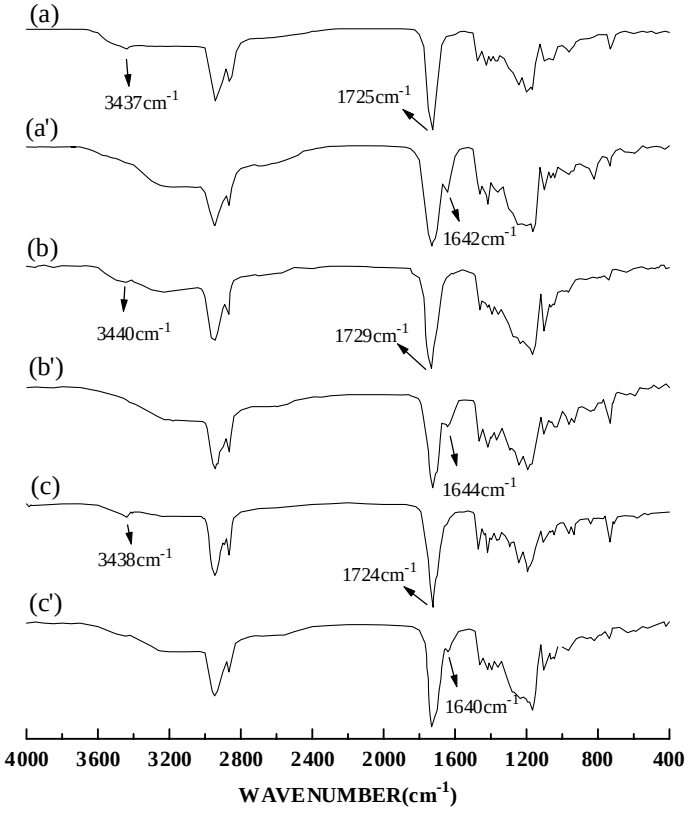


Fig. 2. FTIR spectra of HCPCLs and ACPCLs.

Table 3
500 MHz ^{1}H-NMR chemical shifts δ (ppm relative to internal TMS) of HCPCLs and ACPCLs measured in DMSO-d_6

Chemicals	Chemical shifts (ppm)								
	1	2	3	4	5	6	7	8	9
HO—$CH_2CH_2CH_2CH_2CH_2O)_n$—CH_2COOH	6.1	3.7	1.6	1.3	2.4	2.8	–	–	–
$CH_2=CHCOO$—$(CH_2CH_2CH_2CH_2CH_2O)_n$—$CH_2COOH$	9.8	3.8	1.7	1.3	2.5	3.0	2.0	2.7	–
HO—$(CH_2CH_2CH_2CH_2CH_2O)_n$—$CH(CH_2COOH)_2$	11	3.8	1.7	1.4	2.4	3.2	2.1	–	–
$CH_2=CHCOO$—$(CH_2CH_2CH_2CH_2CH_2O)_n$—$CH(CH_2COOH)_2$	12	3.8	1.8	1.4	2.5	3.2	2.0	2.8	3.0
HO—$(CH_2CH_2CH_2CH_2CH_2O)_n$—$C(CH_2COOH)_3$	10	3.9	1.9	1.5	2.5	3.3	–	–	–
$CH_2=CHCOO$—$(CH_2CH_2CH_2CH_2CH_2O)_n$—$C(CH_2COOH)_3$	13	3.9	1.8	1.5	2.5	3.2	2.1	2.9	–

almost equivalent mole ratio of hydroxyl to carboxyl groups to that of the correspondent hydroxyl acid. So, at a moderate reaction temperature, the esterification reaction can be neglected for these hydroxyl acids-initiated polymerizations of CL.

The reaction results of HCPCLs with acryloyl chloride are shown in Table 2. From Table 2, the practical molecular weights of product ACPCLs which are measured by ABT are almost coincident with the theoretical molecular weights of ACPCLs which are calculated by adding the molecular weight of HCPCL to that of acryloyl chloride and subtracting that of hydrogen chloride, thereby indicating higher reaction efficiencies in reactions of HCPCLs with acryloyl chloride.

3.2. The spectroscopic analysis of ACPCLs and HCPCLs

Fig. 2(a)–(c) is the FTIR spectra of HCPCLs which were produced by the oligomerization of CL initiated with glycollic acid, DL-malic acid, or citric acid, respectively. The biggest peaks at 1725, 1729, and 1724 cm^{-1} belong to the characteristic $\nu_{C=O}$. The small peaks at 3437, 3440, and 3438 cm^{-1} are assigned to the end hydroxyl group stretching vibration. The broad peaks at 3300–2400 cm^{-1} are due to the ν_{O-H} of the end carboxyl groups. The peaks at 1235–1166 cm^{-1} are attributed to the ν_{CO-O-C} stretching vibration. Fig. 2(a′)–(c′) show the FTIR spectrum of ACPCLs which were synthesized by the reactions of HCPCLs with acryloyl chloride. The appearance of $\nu_{C=C}$ stretching vibration peak at 1642, 1644, 1640 cm^{-1} results from the acryloyl groups of ACPCLs, and the disappearance of the −OH peaks at 3437, 3440, and 3438 cm^{-1} also demonstrates that the hydroxyl groups of HCPCLs have been reacted with acryloyl chloride.

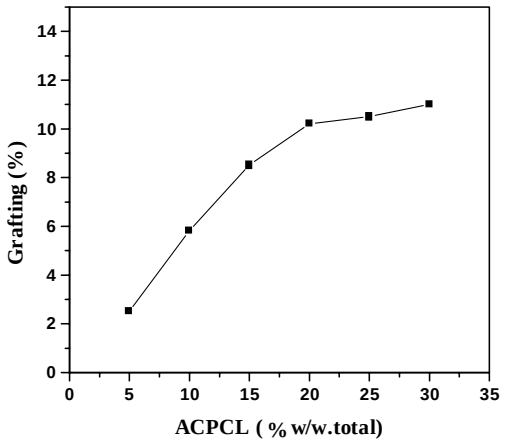


Fig. 3. Effect of ACPCL concentration on grafting percentage. PP + ACPCL(2) = 10.0 g, BPO = 1.5%, T = 135°C, V_{xylene} = 200 ml, t = 8 h.

The end-group analyses of HCPCLs and ACPCLs are also performed by 500 MHz ^{1}H-NMR spectroscopy. The assignments are listed in Table 3.

3.3. Effects of various parameters on the grafting of ACPCL onto PP

In order to optimize the conditions for the grafting of ACPCL onto PP, effects of ACPCL concentration, initiator BPO amount, grafting time, ACPCL kinds, and grafting method on the graft copolymerization were investigated.

3.3.1. Effect of ACPCL concentration

The effect of ACPCL(2) concentration on the grafting percentage was illustrated in Fig. 3. The grafting percentage increases initially with an increase in ACPCL(2) concentration up to 20% of total amount (PP + ACPCL(2)) and then laid off at about 10.2% grafting percentage. This may be because initially the number of ACPCL(2) molecules diffusing through the reaction medium and reaching the free radical sites on the PP backbone govern the grafting extent, whereas at higher concentrations of ACPCL(2), the grafting percentage remains almost constant as the number of free radical sites available on the PP backbone becomes a limiting factor.

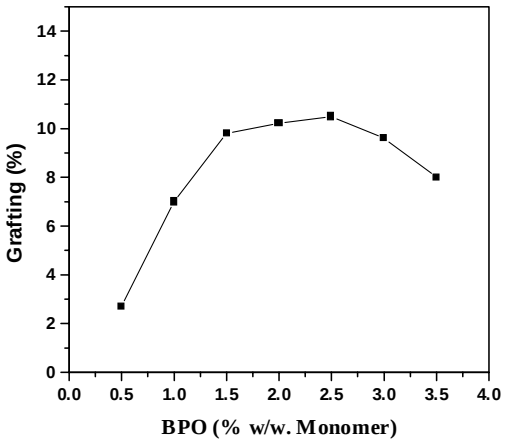


Fig. 4. Effect of initiator BPO concentration on grafting percentage. PP + ACPCL(2) = 10.0 g, ACPCL(2) = 2.0 g, $T = 135$°C, $V_{xylene} = 200$ ml, $t = 8$ h.

3.3.2. Effect of initiator amount

Fig. 4 shows the effect of initiator amount on grafting percentage of ACPCL(2) onto PP. The observed trend is typical for the graft copolymerization reaction occurring vis., chain transfer. The initial increase in the grafting percentage is caused by an increase in concentration of radicals formed through the decomposition of initiator. Thus the higher the concentration of radicals, the higher the chain transfer to polymer backbone and the higher the grafting percentage. Further, an increase in the initiator concentration decreases the average molecular weight of the side chains because of mutual termination reactions. These two opposing tendencies result in the appearance of a maximum.

3.3.3. Effect of grafting time

Fig. 5 illustrates the effect of reaction time on the grafting percentage of ACPCL(2) onto PP. It was observed that the grafting percentage increases initially and then remains constant. With an increase in the reaction time, the radicals will have more time for reaction, after a certain reaction time all the initiator is used up. As a result, no further change in the grafting percentage was observed with an increase in the reaction time.

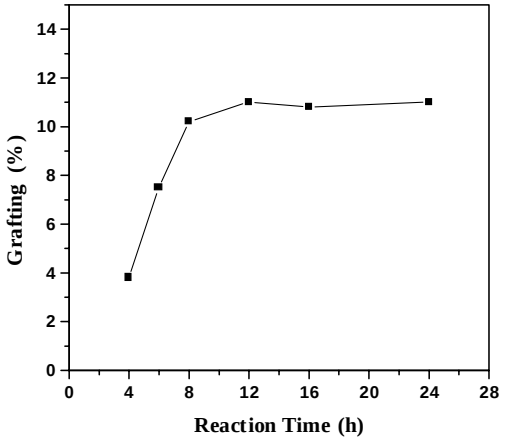


Fig. 5. Effect of reaction time on grafting percentage. PP + ACPCL(2) = 10.0 g, ACPCL(2) = 2.0 g, BPO = 1.5%, $T = 135$°C, $V_{xylene} = 200$ ml.

Table 4
Effect of ACPCL kind on grafting percentage. PP + ACPCL = 10.0 g, ACPCL = 2.0 g, BPO = 1.5%, $T = 135$°C, $V_{xylene} = 200$ ml, $t = 8$ h

ACPCL Kinds	M_n of ACPCL	Grafting percentage (%)
ACPCL (1)	513	10.9
ACPCL (1)	625	10.2
ACPCL (1)	740	9.5
ACPCL (2)	576	10.5
ACPCL (2)	697	9.8
ACPCL (2)	820	9.2
ACPCL (3)	688	9.8
ACPCL (3)	804	9.5
ACPCL (3)	943	9.0

The effect of different kinds and molecular weights of ACPCLs on the graft percentage is shown in Table 4. From Table 4, no obvious difference in the grafting percentage is observed for the three kinds of ACPCLs, whereas there is a slight decrease in the grafting percentage with an increase in the molecular weight for every kind of ACPCL. Table 5 also indicates that the melt grafting has a higher grafting percentage than does the solution grafting.

3.4. FTIR spectra analyses of ACPCL-g-PP

The FTIR spectra of PP and ACPCL-grafted PP (ACPCL-g-PP) are given in Fig. 6(a) and (b). The FTIR spectrum of the band showed at 1724 cm^{-1}, is characteristic of the carbonyl group in the structure of ACPCL. On the contrary, if ACPCL does not graft copolymerize but mixes with the PP, the sample mixture may also present a similar FTIR spectrum. Although the reaction product is purified by the

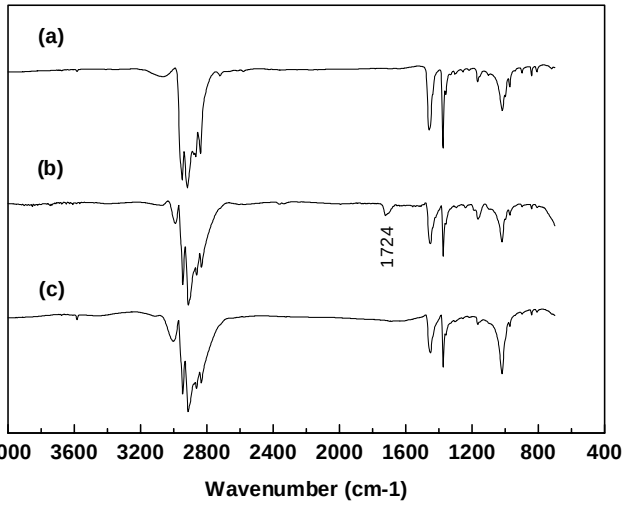


Fig. 6. FTIR spectra of: (a) PP; (b) the mixture of ACPCL(2) with PP in the presence of BPO (after purification by extraction); and (c) the mixture of ACPCL(2) with PP but in the absence of BPO (after purification by extraction).

Table 5
Effect of grafting method on grafting percentage. PP + ACPCL = 10.0 g, ACPCL = 2.0 g, BPO = 2.0%, $T = 135°C$, $V_{xylene} = 200$ ml, $t = 8$ h

ACPCL kinds	M_n of ACPCL	Grafting method	Grafting percentage (%)
ACPCL(1)	625	Solution	10.2
ACPCL(1)	625	Melt	12.3
ACPCL(2)	697	Solution	9.8
ACPCL(2)	697	Melt	11.5
ACPCL(3)	804	Solution	9.5
ACPCL(3)	804	Melt	11.7

method as described in Section 2, the feasibility of this method is not verified. So, a blank experiment in which PP mixed with ACPCL but without addition of initiator BPO was also first carried out under identical reaction conditions and purification method as that of the graft copolymerization process; and then the sample was also subjected to FTIR analysis (as shown in Fig. 6 (c)). Comparing Fig. 6(c) with Fig. 6(a), both FTIR spectra are very similar, and the carbonyl peak at 1724 cm^{-1} cannot be seen. All these facts show that ACPCL has been introduced as a graft, and not a mixture, into the PP.

3.5. DSC analyses of ACPCL-g-PP

A rapid, qualitative assessment of the overall polymer crystallization rate can be made by evaluating the crystallization peak temperature (T_c) upon cooling from the melt. This value, which is indirectly related to the overall crystallization rate, is influenced by factors such as nucleating agents, temperature of the melt, time in the melt, and the molecular weight [29–30]. T_c values measured at a cooling rate of 10°C/min for the PP and for the grafted copolymer ACPCL-g-PPs are listed in Table 6. The crystallization exothermic peaks for PP and ACPCL-g-PPs are at 113.8 and 118.3–125.7°C, respectively, indicating a high crystallization temperature for the grafted samples than for PP. The observed increase in crystallization temperature can be attributed to the ACPCL acting as a nucleating agent. Rybnikar et al. [31] and Sachin et al. [32] also found nucleation due to incorporation of carbonyl group and maleic anhydride in PP. Fig. 7 also schematically shows the effect of the molecular weight of ACPCL on the T_c of ACPCL-g-PP. From Fig. 7, the larger the molecular weight of ACPCL, the higher the T_c. This may be because an increase in the length (molecular weight) of the ACPCL branch chain increases the number of nucleating sites.

The heats of fusion (ΔH_f) from DSC curves of the various grafted samples are also given in Table 6. The percent crystallinity was calculated on the assumption that the heat of fusion of 100% crystalline PP is 50 cal/g [33]. As the heat of fusion is directly proportional to the amount of crystalline PP in the sample, it decreases linearly with an increase in the grafting percentage. An apparent decrease in heat of fusion was due to the decrease in the weight fraction of crystalline PP in ACPCL-g-PP due to an incorporation of ACPCL. Sachin et al. [32] and Mukherjee [34] observed similar trends in the previous study for MAA-g-PP.

4. Conclusions

A series of novel compatibilizers with different lengths of oligocaprolactone branch chains, which are capped with one, two or three carboxyl groups at one of these branch chains' extremities, can be synthesized by a three-step approach involving: (1) the oligomerization of ϵ-caprolactone initiated by various hydroxy acids (glycollic acid, DL-malic acid, or citric acid); (2) the reaction of acryloyl chloride with HCPCL; and (3) the graft copolymerization of ACPCL with PP.

The graft copolymerization of ACPCL with PP is influenced by various parameters such as the monomer (ACPCL)

Table 6
DSC Analysis

Samples	M_n of ACPCL	Carboxyl group (10^{-4} mol/g)	Grafting (%)	T_c (°C)	ΔH_f (cal/g)	Relative crystallinity (%)
PP	–	–	–	113.8	50	100
ACPCL(1)-g-PP	513	2.12	10.9	118.3	19.2	38.4
ACPCL(1)-g-PP	625	1.63	10.2	120.8	18.8	37.7
ACPCL(1)-g-PP	740	1.28	9.5	123.9	18.4	36.9
ACPCL(2)-g-PP	576	3.64	10.5	119.4	18.7	37.4
ACPCL(2)-g-PP	697	2.81	9.8	122.2	18.6	37.1
ACPCL(2)-g-PP	820	2.24	9.2	124.7	18.2	36.5
ACPCL(3)-g-PP	688	4.27	9.8	121.4	18.6	37.2
ACPCL(3)-g-PP	804	3.54	9.5	123.8	18.5	37.0
ACPCL(3)-g-PP	943	2.86	9.0	125.7	18.1	36.2

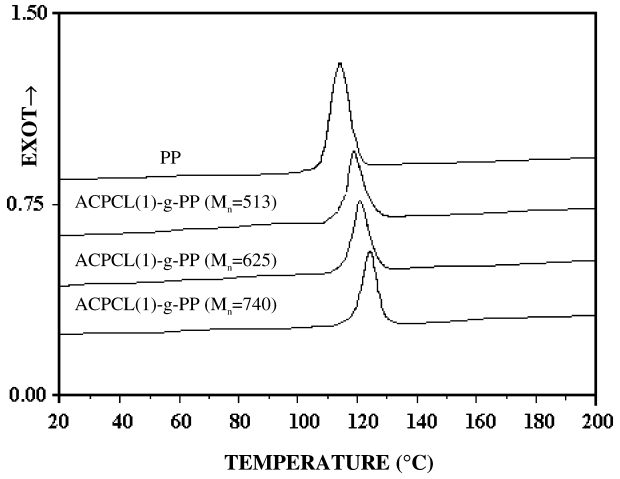


Fig. 7. DSC cooling curves of various ACPCL(1)-g-PP samples.

and the initiator (BPO) concentration, the reaction time, ACPCL molecular weights, and grafting methods. Generally, melt grafting has a higher grafting percentage than does the solution grafting. The maximum extents of grafting achieved in solution and in an extruder were about 10.2, 12.3%, respectively.

The crystallization exothermic peaks for PP and ACPCL-g-PP are at 113.8 and 118.3–125.7°C, respectively, indicating a high crystallization temperature for the grafted samples than for PP. An apparent decrease in the heat of fusion for ACPCL-g-PP in comparison with PP also indicates that ACPCL has graft copolymerized with PP.

Acknowledgements

This research was supported in part by the National Nature Science Foundation of China.

References

[1] Mehta LK, Sunil Kumar, Chauhan GS, Mishra BN. J Appl Polym Sci 1990;41:1171.
[2] Singh RP. Prog Polym Sci 1992;17:251.
[3] Naqvi MK, Choudhary MS. J Mol Sci C: Rev Macromol Chem Phys 1996;36(3):601–29.
[4] Canterino PJ. US Patent, 3 (1964) 162,692.
[5] Rengarajan R, Parameswaran VR, Lee S, Rinaldi PL. Polymer 1990;31:1703.
[6] Chung TC, Rhubright D. Macromolecules 1991;24:970.
[7] Nishio T, Suzuki Y, Kojima K, Kagugo M. J Polym Engng 1991;10:123.
[8] Chen CC, Fontan E, Min K, White J. Polym Engng Sci 1988;28: 69.
[9] Chung HK, Han CD. Polymer blends and composites in multiphase systems, Washinton, DC: American Chemical Society, 1984 chap. 11.
[10] Park SJ, Kim BK, Jeong HM. Eur Polym J 1990;26:131.
[11] Stromvall HE. PhD Thesis, Chalmers University of Technology, Gothenburg, Sweden, 1984.
[12] Kishi H, Yoshika M, Yamanoi A, Shiraishi N. Mokuzai Gakkaishi 1988;34:133.
[13] Takase S, Shiraishi N. J Appl Polym Sci 1989;37:645.
[14] Woodhams RT, Thomas G, Rogers DK. Polym Eng Sci 1984;24:1160.
[15] Bataille P, Ricard L, Sapieha S. Polym Compos 1989;10:103.
[16] Fujiyama M, Wakino T, Wachi H, Tani K. Kobunshi Ronbunshu 1992;49:87.
[17] Fujiyama M, Wakino T, Wachi H, Tani K. Kobunshi Ronbunshu 1992;49:97.
[18] Pegoraro M, Penati A, Natta G. Chim Ind (Milan) 1971;53:235.
[19] Pegoraro M, Penati A. Chem Zvest 1972;26:224.
[20] Masahiko O, Iwata T. Jpn Patent, 7 (1973) 328,092.
[21] Pegoraro M, Penati A. Chim Ind (Milan) 1972;54:505.
[22] Ide F, Hasegawa A. J Appl Polym Sci 1974;18:963.
[23] Park SJ, Shin CH, Kim CK, Kim BK. Polymer (Korea) 1989;13: 347.
[24] Kiyotada N. Jpn. Patent, 7 (1978) 828,940.
[25] Klosiewicz DW. US Patent, 595,726 (1980).
[26] Masahiko O. Jpn. Patent, 7 (1977) 730,546.
[27] Xie DL, Ge HX, Zhang LX, Yang CZ. J Appl Polym Sci 1998;68:205–16.
[28] Xie DL, Hu Y, Shen QD, Yang CZ. J Appl Polym Sci 1999.
[29] Khanna YP, Reimschuessel AC. J Appl Polym Sci 1988;35:2259.
[30] Khanna YP, Reimschuessel AC, Banerjie A, Altman C. Polym Engng Sci 1988;28(24):1600, 1607, 1612.
[31] Rybrinkar F, Pospisil C, Jankar JJ. Mater Sci Letts 1990;9:499.
[32] Sathe SN, Srinivasa Rao GS, Surekha Devi. J Appl Polym Sci 1994;53:239–45.
[33] Martuscelli R, Silvestre C, Abate G. Polymer 1982;23:229.
[34] Mukherjee AK. J Appl Polym Sci 1985;36:3479.