Grafting of Oxazoline Functional Group to Polycaprolactone

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ABSTRACT: A twin-screw extruder was used to graft oxazoline reactive group onto polycaprolactone (PCL) by free radical initiation reaction. A low-volatility oxazoline compound was used to facilitate a high-temperature grafting reaction. The effect of melt temperature, screw speed, and initiator and monomer concentrations on graft content were evaluated. The graft content ranged from 0.7 to 2.6%. Increased melt temperature and reduced screw speed increased the graft content. Molecular weight and molecular weight distribution evaluated with the help of intrinsic viscosity and gel permeation chromatography measurements gave values that were close to that of the unmodified PCL. The oxazoline-grafted polyester gave considerable increase in the tensile force when compared with that of pure PCL. The grafting reaction was confirmed using Fourier transform infrared spectroscopy and nuclear magnetic resonance techniques. A probable reaction mechanism for the grafting reaction is proposed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1947–1955, 1998

Key words: chemical grafting; polycaprolactone; FTIR; proton NMR

INTRODUCTION

Heterocyclic compounds are effective chain extenders for polymers due to their capability of coupling reaction through addition reaction. Oxazoline copolymers can react with a variety of reagents, such as carboxylic acids,[1] making them an effective functional group on polymers for compatibilization reaction. Baker and Saleem[2] reported that melt-blended polystyrene (PS) with oxazoline functionality and polyethylene (PE) with carboxylic acid functionality produced an alloy with better impact strength and tensile properties than ordinary PE–PS blends. Several researchers explored the potential of oxazoline functionality as a compatibilizer for various polymer blends.[3–6]

Our interest in oxazoline functionality originates from the fact that this functionality helps to compatibilize polymer blends through amido–ester linkages. Epoxy compounds, cyclic carboxylic anhydrides, and diisocyanates were used as addition-type chain extenders.[7] But the main disadvantage of these types of compounds is that the reaction often leads to branching, and the bonds formed are thermally viable. We have reported[8] the grafting of cyclic anhydrides (viz., maleic anhydride) to polycaprolactone (PCL) to produce functionality capable of reacting with natural polymers such as starch and protein to make biodegradable polymers. For this purpose we used an oxazoline derivative as a compatibilizing agent to react with carboxylic and/or amino group functionality present in proteins and modified starches. This article deals with the free radical-initiated grafting reaction of ricinoloxazoline maleinate (OXA) to PCL in the presence of dicumyl peroxide (DCP). The grafted polymer can be used as a compatibilizer for the polymer blends. Since

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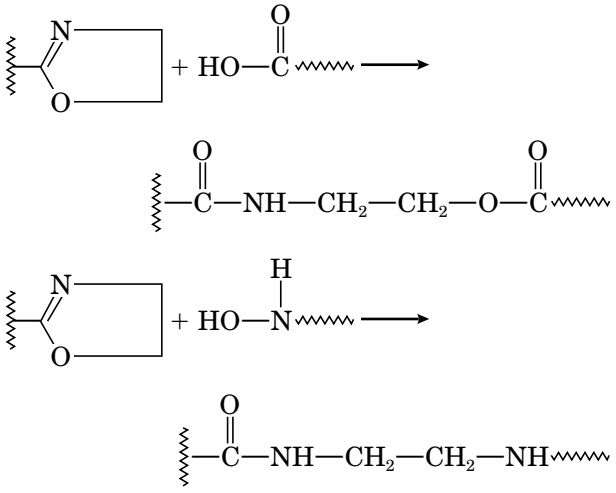
PCL is biodegradable, the grafted polymer was blended with wheat gluten or starch to form fully biodegradable compositions. The carboxyl group in modified starch and amino or carboxylic groups in gluten are capable of reacting with the oxazoline functional group. The reaction between the carboxylic and oxazoline groups will result in an ester–amide linkage and is a fast reaction. The reaction between the amino and carboxylic functional group in proteins and oxazoline can be represented as follows:



The compounds from the above two reactions are a good energy source for microorganisms and will be completely biodegradable in natural environments.

EXPERIMENTAL

Materials

PCL resins 767E and 787 (commercially available as TONE Polymer) were obtained from Union Carbide Chemicals and Plastics Company, Inc. (Bound Brook, NJ). These materials have a melting point of 61°C and melt flow indices of 30 and 4, respectively (at 190°C, ASTM test D1238). These resins were dried in a vacuum oven at 50°C for 24 h prior to use. DCP (98%) was obtained from Aldrich Chemical (Milwaukee, WI). Loxamid VEP-8515 (ricinoloxazoline) was supplied by Henkel KGaA Corporation USA (Ambler, PA). HPLC grade (for viscosity measurements and gel permeation chromatography [GPC]) and analytical grade solvents (for extraction and estimation) were obtained from Fisher Scientific (Pittsburgh, PA).

Grafting Reactions

A laboratory-scale, conical, twin-screw extruder (Rheomex TW-100, Haake Scientific Instruments, Paramus, NJ) with corotating screws was used for the grafting reaction. A detailed experimental procedure can be found elsewhere.[8] The temperature of the first zone was kept at 80°C while the second and third zones were changed to obtain the desired experimental temperature. The screw speed was changed depending upon the experiment and the feed rate was approximately 1.0 kg/h. The extrudate was chopped into small pieces using a pelletizer and compression-molded to produce tensile bars for testing mechanical strength.

Tensile Strength

The samples were compression-molded using Power-Twin compression molding equipment (Owatonna Tool Company, Owatonna, MN) to obtain samples for the tensile test (ASTM test Method D-638). An MTS T5002 tensile testing machine was used to obtain the tensile force and elongation at break. The values were the average of at least five specimens.

Analytical Characterization

In order to estimate the graft content, the sample from the extruder was extracted with xylene for 2–3 h and reprecipitated in methanol. The samples were then vacuum-dried for 24 h at 50°C. Any unreacted monomers will be removed during this step.

Determination of Graft Content

The oxazoline content was determined by modifying the procedure outlined by Inata and Matsumura.[9] A 1-g portion of the extracted sample was taken in a conical flask, 10 mL of 0.009*N* solution of *p*-toluenesulfonic acid in 60/40 (w/w) phenol-tetrachloroethane was added along with 50 mL of xylene, and the mixture was refluxed for 15 min until the polymer was completely dissolved. After cooling, the mixture was titrated against a 0.01*N* solution of sodium hydroxide in benzyl alcohol using 3–4 drops of tropaeolin OO in ethanol as an indicator. A blank titration was also carried out simultaneously and taken into account for calcu-

lation. The exact value was determined from a calibration curve obtained using samples having known oxazoline content.

FTIR and NMR Spectroscopy

Fourier transform infrared (FTIR) spectra were recorded using a Nicolet 550 instrument and were processed using OMNIC version FTIR software. The polymer samples were dissolved in toluene and cast on a KBr disc to obtain a thin film and then dried in a chamber under a nitrogen flow.

Proton nuclear magnetic resonance (NMR) of the samples were recorded using a Varian VXR 300 instrument with a 12.2-μs (90-degree) pulse and an acquisition time of 2.0 s using $CDCl_3$ as reference. Correlation spectroscopy (COSY) was recorded with a single transient per t_1 increment and a 1.29-s relaxation delay (30-min experiment time) with a sweep width of 2441.7 Hz in both dimensions. The samples were dissolved in deuterated chloroform and the spectra were obtained at room temperature.

Intrinsic Viscosity

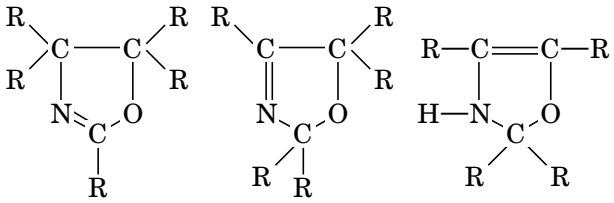
Intrinsic viscosity of the grafted and pure samples were determined in a constant temperature bath (Cannon CT-1000, Cannon Instruments, State College, PA) at 30°C using a Ubbelohde viscometer.

Gel Permeation Chromatography

The molecular weight distribution of the samples was determined using a Waters 150-C ALC/GC with a refractive index detector. A Phenogel (Phenomenex, Torrance, CA) having three columns (300 × 7.8 mm) with 5, 10, and 100 μm particle size was used for separation. HPLC-grade tetrahydrofuran (THF) was used as mobile phase at room temperature with a solvent flow rate of 1 mL/min with 35 bar pressure. The refractive index versus the elution volume was obtained for each sample and correlated to the elution volume versus molecular weight for the PS standard.

RESULTS AND DISCUSSION

Oxazolines are five-membered heterocyclic compounds having one double bond. There are three possible structures for an oxazoline ring, depending upon the position of the double bond. These possible structures are



2-oxazoline 3-oxazoline 4-oxazoline

The 2-oxazoline structure is the most common form. There are different methods of obtaining oxazolines and their derivatives; 2-oxazolines are usually derived from amino alcohols and low-cost carboxylic acids. The oxazoline derivative used in the present study was OXA (Fig. 1)

We selected this particular compound because we needed to preserve the oxazoline ring for later reaction while at the same time a site was needed for grafting onto the polymer chain. The grafting reaction involves the abstraction of hydrogen from the PCL chain combined with the addition of this radical to the double bond in the ricinoloxazoline. The possibility of monomer polymerization, termination reaction, and chain scission reaction were not ruled out during the course of grafting reaction. The graft content of oxazoline varied depending upon the temperature of the reaction and the concentrations of initiator and monomer. A uniform feed of the reaction mixture to the extruder was achieved because oxazoline was in the liquid state.

Effect of Initiator Concentration on Graft Content

DCP was selected as the initiator because a simple one-stage decomposition is obtained when it is subjected to high temperatures. The concentration of DCP was varied from 0.2 to 0.6% while maintaining all other variables constant. As expected, the graft content increased as the initiator

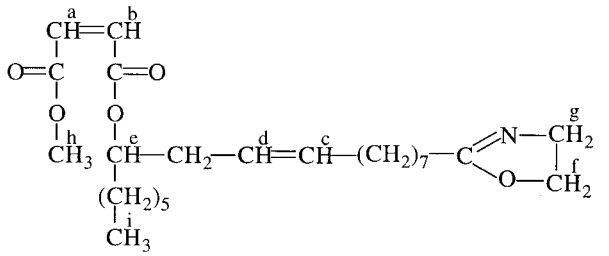


Figure 1 Structure of OXA.

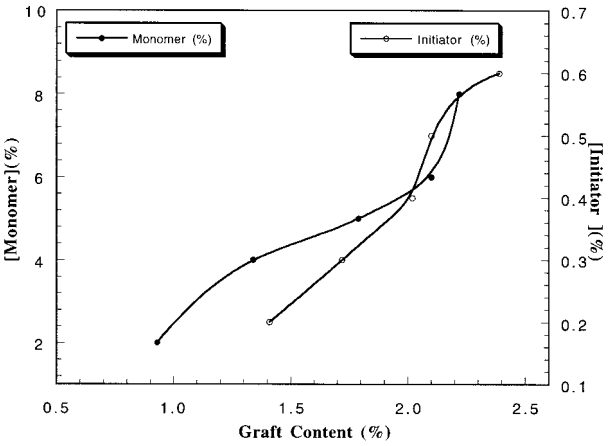


Figure 2 The influence of initiator and monomer concentration on percentage oxazoline grafted at 165°C with a constant concentration oxazoline (6.0%) and at a constant concentration of initiator (0.5%) with a screw speed of 25 rpm.

concentration increased. Figure 2 illustrates the effect of monomer concentration on graft content. Earlier we reported a detailed description of the effect of initiator concentration on the grafting of maleic anhydride to PCL.[8] We found that the grafted oxazoline content increased from 1.4 to 2.0% as the initiator concentration changed from 0.2 to 0.6% at a melt temperature of 165°C and an extruder screw speed of 25 rpm. This increase appeared to be fairly linear. However, there may be an optimum amount of initiator concentration beyond which the oxazoline percentage levels off. The efficiency of grafting reaction is dependent upon the structure, abstraction power, and radical lifetime of the initiator employed. From our previous work with grafting of maleic anhydride to polyesters,[8] we found DCP to be more effective, as compared with benzoyl and lauryl peroxides.

Effect of Monomer Concentration

The effect of oxazoline concentration on the graft content is also shown in Figure 2. The monomer concentration was increased from 2 to 8% while the initiator concentration, melt temperature, and screw speed were kept constant at 0.5%, 165°C, and 25 rpm, respectively. The graft content increased from 0.93 to 2.22%. From these results we observed that the percent of oxazoline grafted decreased considerably when the initial concentration of oxazoline used was increased, even though the graft content showed an increase. Hence we needed an optimum initial concentration of the monomer to obtain maximum conversion. Higher amounts of monomer can lead to homopolymerization as well as difficulties encountered in removing unreacted material from the final product. Addition of comonomers, such as styrene and similar compounds, to the reaction mixture can prevent homopolymerization of the monomer while at the same time reducing the degradation of main chain. Vainio and colleagues[6] discussed the addition of styrene as a comonomer and found that this did not enhance the grafting reaction but markedly reduced the polypropylene degradation. Intrinsic viscosity measurement results showed a slight increase as the graft content increased, but the value was often well above that of pure polymer. This supports the fact that that there is minimal degradation of the polymer chain during the grafting reaction.

Effect of Temperature

Temperature is the discerning factor of any chemical reaction, and this is especially true in the case of grafting reaction. The graft content will depend upon the number of free radicals produced and its mobility and stability. Also, because the reaction was carried out in the extruder, diffusion plays an important role. All these factors are directly related to the reaction temperature. The effect of temperature on graft content is depicted in Figure 3. As the temperature increased from 120 to 180°C, the graft content increased from 0.63 to 2.42%. The graft content increased linearly as the temperature increased from 120 to 165°C and

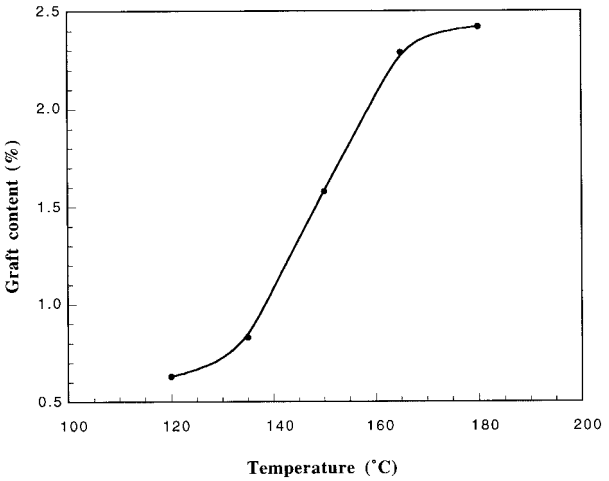


Figure 3 Effect of temperature on percentage of oxazoline grafted at constant concentration of oxazoline (6%) and initiator (0.5%) with a screw speed of 25 rpm.

Table I Summary of Grafting Reactions at Different Temperatures Using a Twin-Screw Extruder

Exp. No.	Temperature (°C)	Graft Content (%)	Conversion[a] (%)	Intrinsic Viscosity (dL/g)	Number Average (M_n)	Weight Average (M_w)
1	120	0.63	10.5	0.7630	87,335	143,710
2	135	0.83	13.8	0.7741	88,723	137,520
3	150	1.58	26.3	0.8278	92,134	154,150
4	165	2.29	38.2	1.0071	104,062	222,339
5	180	2.42	40.3	1.0471	99,741	224,578
6 (767)	165	2.01	33.5	0.5756	71,513	164,628
7 (767)				0.5712	62,301	109,732
8				0.8343	86,545	132,777

Monomer 6%; initiator 0.5%; polymer used: PCL 787, except in Exp. Nos. 6 and 7: PCL 767.
[a] Conversion of initial monomer to grafted monomer concentration.

then attained a stable value near 180°C. Because thermal degradation of polyester is a possibility at higher temperatures, no experiments were conducted at temperatures above 180°C. The M_w/M_n ratios of all these samples were close to that of pure polymer (Table I). However, at temperatures above 165°C, the ratio showed a slight increase as compared with that below 150°C. A possible explanation could be the branching or crosslinking reaction that is generally favored at higher temperatures. The slight lowering of molecular weight corresponds to the fact that branched molecules will tend to appear at the lower elution volume in size exclusion chromatography measurements compared with the linear polymer. If chain scission reaction takes place, small linear molecules will be formed and could be detected as multiple peaks in chromatograph measurements as low molecular weight fractions. The normalized gel permeation chromatogram for pure PCL 787 and the grafted polymer are shown in Figure 4. In the present case there are no multiple peaks in the chromatogram for grafted polymer. As can be seen from the figure, a wider molecular weight distribution was obtained for grafted polymer when compared with the pure polymer. This indicates that the linearity of the polymer chain is disturbed after grafting reaction. Apparently there is only one peak in the chromatogram, indicating there is no chain scission or crosslinking reaction taking place during the grafting reaction. In order to reduce any degradation of the PCL, and to make sure that enough free radical concentration is available for the reaction, the temperature was optimized to 165°C.

Effect of Screw Speed

Screw speed affects the residence time in the extruder and thus plays an important role in the graft content. Experiments were carried out to determine the optimum screw speed for obtaining maximum graft content. The screw speed was changed from 10 to 50 rpm while all other variables were kept constant. The effect of screw speed on graft content is shown in Figure 5. A detailed description of the effect of screw speed on grafting reaction can be found elsewhere.[8] It should be noted that screw speed, along with the length of the extruder, melt temperature, and screw configuration, determine the residence time. The graft content depends on the residence time as well as the half-life period and concentration of initiator used. Independent measurement

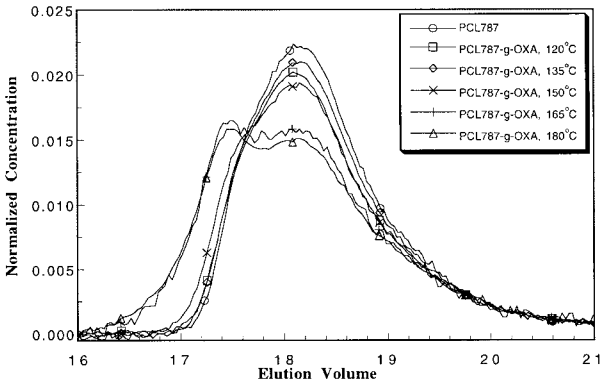


Figure 4 Gel permeation chromatogram of pure and grafted polymers at room temperature with 35 bar pressure using THF as the mobile phase.

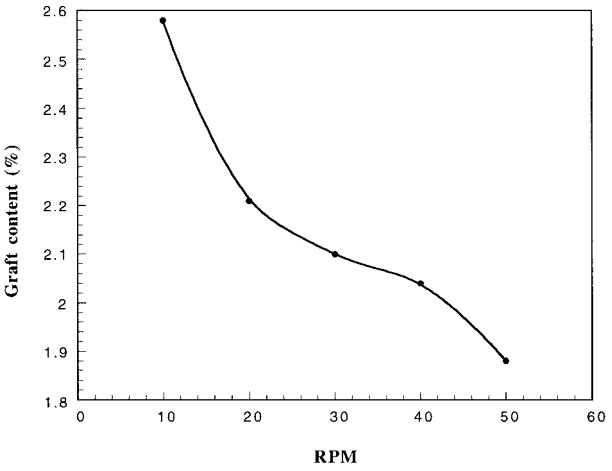


Figure 5 Effect of residence time (rpm) on percentage oxazoline grafted in the extruder at 165°C with constant monomer (6%) and initiator (0.5%) concentrations.

of residence time as a function of screw speed was not attempted in this study.

Mechanical Properties

The samples obtained from the grafting reaction were compression-molded and the tensile strength of pure and grafted polymer are shown in Table II. The tensile strength values were comparable to those of unmodified polymer for PCL 787, although there was a slight decrease in the percent elongation. This is also in agreement with the results of intrinsic viscosity and GPC experiments (Table I), showing there was apparently no degradation of the polymer employed for grafting reaction. For PCL 767, a decrease in tensile strength and elongation was observed but no decrease in intrinsic viscosity values, while a slight increase in molecular weight was seen.

FTIR Spectra

FTIR spectra of the purified grafted PCL showed a new peak at 1670 cm^{-1}, confirming the grafting

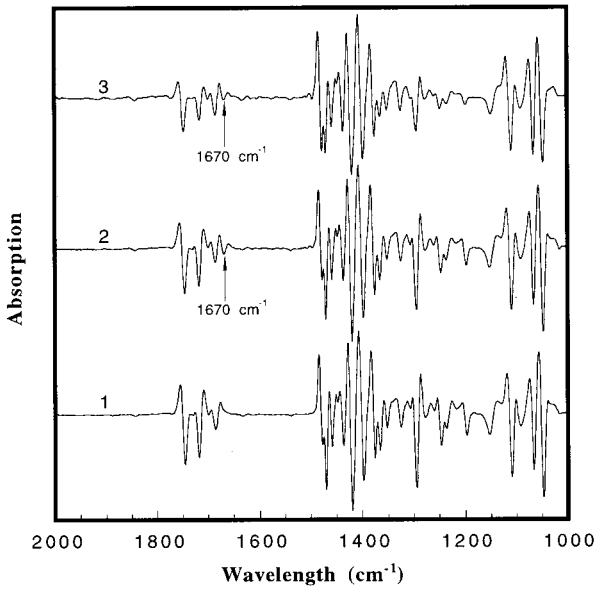


Figure 6 Second derivative FTIR spectra of: (1) unmodified PCL, (2) grafted polymer without extraction with xylene, and (3) spectra of (2) after extraction with xylene.

of oxazoline functional group (Fig. 6). Since the strong carbonyl peak of PCL was masking the weaker signals, identification of peaks was carried out using a second derivative spectrum. In order to reconfirm the grafting reaction, the spectra of physical mixture of oxazoline–PCL without initiator were also recorded separately with and without extraction. The spectra of the physical mixture showed the characteristic peak of an oxazoline ring but this peak disappeared after extraction with xylene (Fig. 7). The characteristic peak of oxazoline was present when the spectra were taken after extraction with xylene for grafted polymer (Fig. 6). This confirms the grafting reaction.

NMR Spectra

The ^{1}H-NMR spectra are shown in Figure 8 for unmodified PCL, OXA, PCL–*g*–OXA, and PCL–

Table II Tensile Strength and Elongation Before Break for Pure and Grafted Polymers for Samples Obtained from Extruder

Exp. No.	PCL (wt %)	PCL–*g*–OXA (wt %)	Tensile Force (N)	Elongation (%)
1	100 (787)		550.0	>850.0
2	100 (767)		650.0	~1000.0
3		100 (787)	685.7	~700.0
4		100 (767)	503.3	~650.0

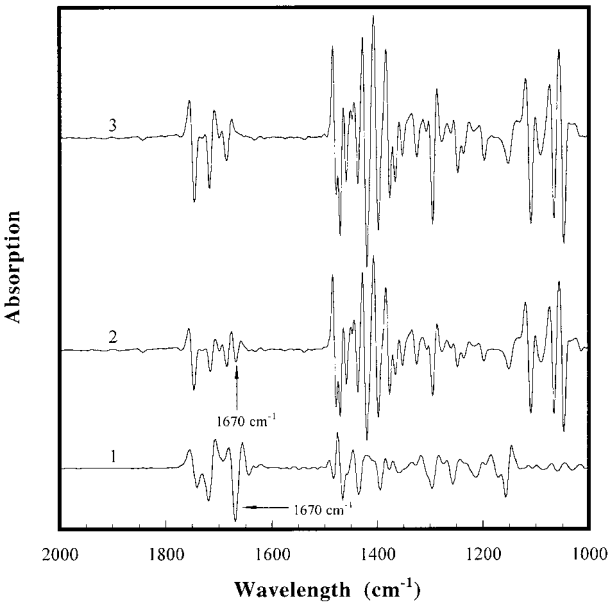


Figure 7 Second derivative FTIR spectra of: (1) oxazoline, (2) mixing product of PCL and oxazoline without adding initiator and without extraction with xylene, and (3) spectra of (2) after extraction with xylene.

g–OXA after extraction with xylene. ^{1}H-NMR spectra of unmodified PCL and its chemical shift for all the protons were in accordance with the literature reports.[10] The assignments for protons in OXA, which might be of interest for the investigation of the possible mechanism for the grafting reaction between PCL and OXA in the presence of DCP, were made by using chemical shift parameters of suitable model compounds.[11] This was also accomplished by looking at ^{1}H-NMR spectra of corresponding products.[12] By observing the coupling relationship of protons in 2D NMR spectra (COSY) of OXA (Fig. 9), more information on the assignment of OXA protons can be obtained. The peaks of interest for this investigation that appeared in the ^{1}H-NMR spectra for OXA are designated in the structure of OXA (Fig. 1) by (a), (b), (c), etc. (from high to low field) and also are marked in the spectra of OXA [Fig. 8(II)]. The exact values of the chemical shifts ascribed to individual peaks in the ^{1}H-NMR spectra are listed in Table III. As seen from the spectra of the grafted PCL without extraction [Fig. 8(III)], the peaks of protons H_{a-e}, H_h, and H_i can apparently be found by comparing spectra II and III in Figure 8. However, there is a new peak which appears at δ 4.83 ppm, designated *e′* [Fig. 8(III)]. From the spectra of grafted PCL after extraction with xylene [Fig. 8(IV)], the peaks H_a, H_b, and H_e disappear, which suggests that the peaks a, b, and e should originate from unreacted monomers adhering to the grafted polymer but can be re-

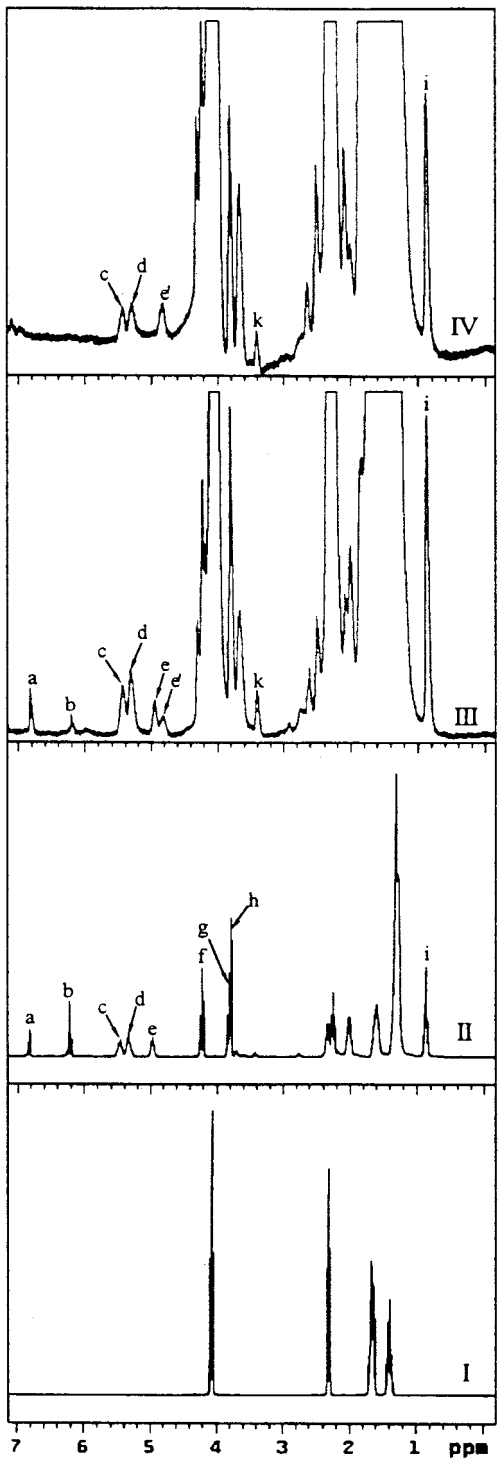


Figure 8 ^{1}H-NMR spectra of monomers and grafted polymer: (I) unmodified PCL, (II) OXA, (III) PCL–*g*–OXA without extraction, and (IV) PCL–*g*–OXA after extraction with xylene.

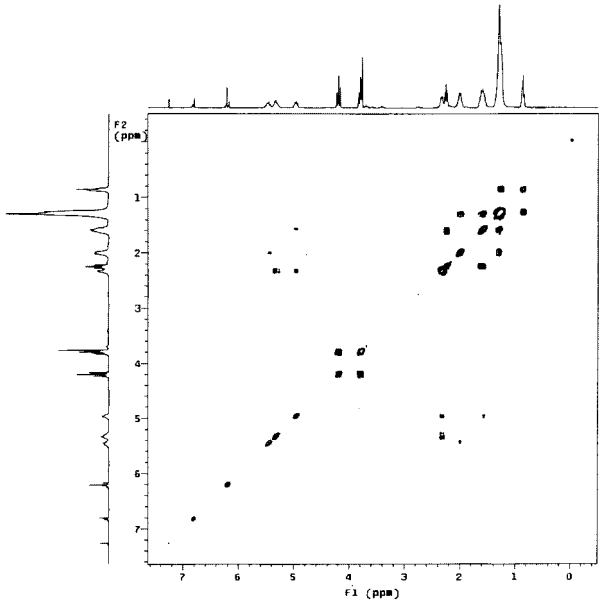


Figure 9 Correlation spectra of OXA at room temperature using $CDCl_3$ as reference.

moved by extraction procedure, as discussed earlier in the FTIR Spectra section. This result also indicates that the grafting reaction might take place in the olefinic link between H_a and H_b. This means the PCL free radical formed by the hydrogen abstraction of the α-carbon atom relative to the carbonyl group in PCL by the action of the homolytic scission of organic peroxide[8] will be added to the olefinic double bond. This reaction will lead to the opening of the conjugative system of $\alpha\beta$ unsaturated ester in the oxazoline moiety. The result would lead to a more up-field movement of H_e chemical shift to form the e' peak. By comparing the ^{1}H-NMR spectra of (II), (III), and (IV) in Figure 8, the peak in δ 3.41 ppm designated by k [Fig. 8(III)] could be assigned to the signal of the methine proton formed due to grafting reaction.[8,13] As seen from the grafting of maleic anhydride onto PCL, the insertion of a maleic anhydride unit into the polymer chain can result in succinic anhydride units with threo- or erythro-configuration. Apparently a similar reaction path is followed during the grafting reaction as the OXA unit is inserted into the PCL, but only the olefinic link between H_a and H_b takes part in this reaction. This is further illustrated by the existence of c and d signals after the grafting reaction. The slight lower shift of the methine proton in the present study, against the results reported by Komber,[13] shows that more electronegative groups are introduced, along with the influence of the ester carbonyl group in PCL. It is well known that free radicals from the thermal homolysis of dicumyl peroxides can be thought of as having nucleophilic properties,[14] which abstracts the hydrogen at the α-carbon atom relative to the carbonyl of PCL because of the stabilization of this radical due to its conjugation with the carbonyl group. From the above discussion, the steps involved in the grafting reaction can be summarized as follows (Fig. 10). The reaction starts with the homolytical scission of organic peroxide. The radical abstracts a hydrogen of the α-carbon atom relative the to carbonyl group, forming a PCL macroradical which can undergo quick β-scission with the simultaneous formation of a radical chain end and vinyldene chain end. The OXA grafting take place on the radical chain end at the olefinic bond between H_a and H_b and does not come about before β-scission. The addition reaction of macroradical before β-scission is sometimes suggested.[15] It

Table III Chemical Shifts δ ^{1}H (ppm) of OXA

Peak	Assignment (δ in ppm)
a	6.81
b	6.22
c	5.48
d	5.34
e	4.96
f	4.21
g	3.81
h	3.77
i	0.87

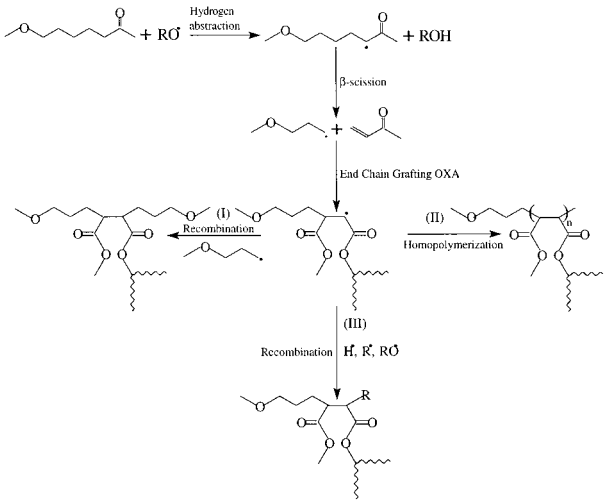


Figure 10 Proposed reaction pathway for the grafting reaction of OXA to PCL.

seems that grafting reaction in solution could favor this mechanism, but β-scission is predominant in the melt-grafting procedure in the presence of organic peroxide.[16] After the grafting of one OXA onto the macroradical, various termination reactions or oligomerization of OXA and transfer processes, along with other possible reactions, might take place. However, according to the spectroscopic, intrinsic viscosity, and GPC results, it can be concluded that steps I and III in Figure 10 best represent the grafting reaction of OXA moiety to the polymer chain. However, GPC results strongly support reaction path III as a possible mechanism for grafting reaction, because the number-average molecular weights before and after grafting are very close. This result is also in accordance with data obtained by Sun and associates[17] who grafted glycidyl methacrylate onto polypropylene. From the results, it can be concluded that not enough evidence is present to support the oligomerization reaction of oxazoline. The absence of oligomerization reaction is also supported by the results obtained by Vainio and coworkers.[6]

CONCLUSIONS

Oxazolines, oxazoline esters, and their vinyl derivatives can be grafted to polymer chains using an extruder or batch mixer. The grafting yield was found to vary with the experimental conditions. Temperature, monomer, and initiator concentrations affect the graft content, and the desired graft content can be obtained by controlling these factors. The grafted polymer will be an efficient compatibilizer for polymer blends. Enhanced mechanical and physical properties can be obtained for polymer blends using the grafted polymer as a compatibilizer with natural polymers. Completely biodegradable compositions can be obtained because the compatibilized polymer will serve as a significant energy source for microorganisms.

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