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Grafting of glycidyl methacrylate onto polycaprolactone: preparation and characterization

C.-H. Kim, K.Y. Cho, J.-K. Park*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1, Kusung-dong, Yusung-gu, Daejon 305-701, South Korea

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Abstract

Polycaprolactone-*graft*-glycidyl methacrylate (PCL-*g*-GMA) copolymer was prepared by grafting GMA onto PCL in a batch mixer using benzoyl peroxide as an initiator. The graft content was determined with the ^{1}H-NMR spectroscopy by calculating the relative area of the characteristic peaks of PCL and GMA. The graft content increased with the increase of GMA concentration. The methine proton peak appearing at 3.65 ppm in ^{1}H-NMR spectra could be assigned as a grafting site of GMA by the correlation spectra (H,H-COSY). Molecular weight determination was also carried out for the pure and grafted polymers using gel permeation chromatography to determine chain scission reaction. The detailed grafting reaction mechanism was discussed based on the results of GPC and NMR measurements. © 2001 Published by Elsevier Science Ltd.

Keywords: Polycaprolactone; Chemical grafting; Glycidyl methacrylate

1. Introduction

Development of biodegradable plastics has been considered to be an ultimate solution to the environmental problem caused by the disposal of plastic wastes. Many of the candidates for biodegradable polymers, however, have some limitations in their properties or costs. Among the many kinds of candidates including aliphatic polyesters, natural polymers, and their derivatives, starch is one of the most promising materials for biodegradable plastics because of its natural abundance and low cost. However, starch-based plastics have some drawbacks including poor mechanical properties and processability for practical applications. To solve some of these problems, blending of starch-based plastics with synthetic polymers has been considered [1–12].

To prepare completely biodegradable blends, starch has often been blended with aliphatic polyesters such as polycaprolactone (PCL) [5–12]. However, due to the hydrophilic nature of starch, blends with PCL have poor mechanical properties due to poor interfacial adhesion [5–8]. To enhance the compatibility between PCL and starch, compatibilizers had been synthesized and applied to the blend [9,10,12]. Their compatibilizing effect on the mechanical properties of the blend had been also investigated [9,10,12].

The chemical modification of aliphatic polyester by grafting has been also considered as another way of improving the compatibility between starch and aliphatic polyester in the blend [13,14].

In this paper, we report on the preparation of the modified PCL by grafting glycidyl methacrylate (GMA) which is expected to have a good interaction with starch and on the characterization of the modified PCL. The grafting reaction mechanism is also discussed.

2. Experimental

2.1. Preparation of the grafted PCL

Commercial grade PCL (TONE 787) was purchased from Union Carbide and GMA, benzoyl peroxide (BPO), and dicumyl peroxide (DCP) were obtained from Aldrich Chemical.

The graftings were proceeded by melt reaction of PCL and GMA with a Brabender mixing head. The torque of the reaction medium was recorded continuously during the reaction. The 40 g of PCL was premixed with GMA/BPO solution where the BPO content was fixed at 10 wt% of the GMA amount. The GMA content was varied in the range of 5–20 wt% of the PCL weight. The mixture of PCL, GMA, and BPO was then introduced into the chamber of Brabender Mixer. Mixing speed was kept constant at

* Corresponding author. Tel.: +82-42-869-3302; fax: +82-42-869-3910.
E-mail address: pjk@sorak.kaist.ac.kr (J.-K. Park).

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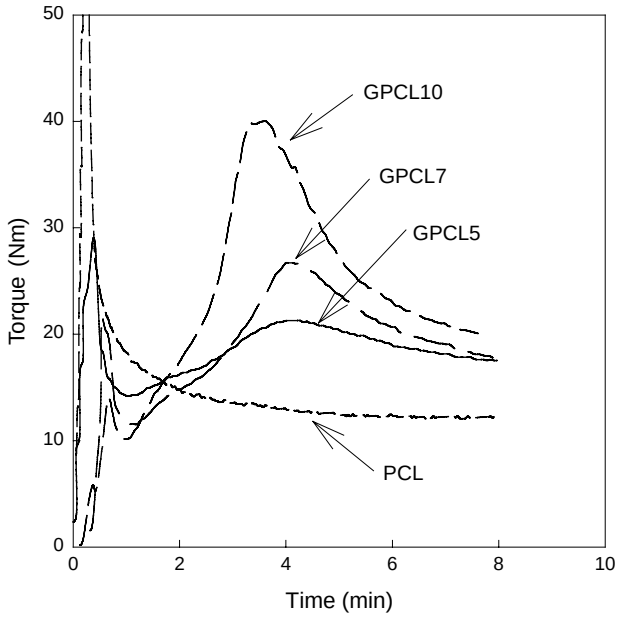

Fig. 1. Torque curves obtained during grafting reaction with different GMA concentration.

80 rpm. The grafting reaction was carried out at 130°C for about 8 min. After completion of the grafting reaction, the reaction product was dissolved in tetrahydrofuran (THF). The solution was poured into a large excess of methanol and the white precipitate, PCL-*g*-GMA (GPCL), was obtained and vacuum dried. All the unreacted GMA and traces of initiator present in the reaction product were removed by washing with methanol. The obtained GPCLs are denoted in this paper as GPCLX where X represents the wt% of GMA in the GPCL.

2.2. NMR spectroscopy

The structural characterization of PCL-*g*-GMA was conducted by using one- and two-dimensional NMR spectroscopy. The one-dimensional ^{1}H-NMR spectra were obtained on a Bruker AMX 500 operating at 500 MHz for proton. The PCL-*g*-GMA samples were dissolved in $CDCl_3$ for NMR measurements. All the chemical shifts for resonance peaks are reported in parts per million (ppm) using TMS as a reference.

The two-dimensional homonuclear correlation spectroscopy (H,H-COSY) was also used to obtain the detailed information on the coupled pairs of protons.

2.3. GPC measurements

A waters 600 was used with a refractive index detector to measure the molecular size of the PCL and the grafted products. The eluent, THF, was used with a flow rate of 1.0 ml/min through four Waters Styragel columns of HR1, HR2, HR4, and HR5. The average molecular weight of the sample was calculated using the calibration curve established from standard samples of polystyrene.

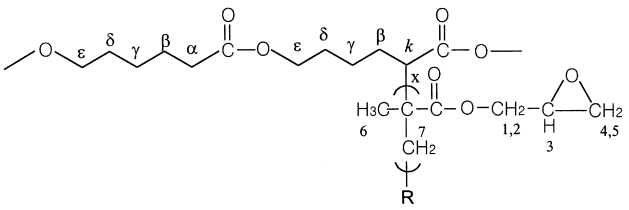

Fig. 2. Structure of PCL-*g*-GMA.

2.4. Mechanical properties

The PCL-*g*-GMA samples were compression molded at 150°C to make sheets with 1 mm thickness and then the specimens for tensile measurements were cut from the sheets and shaped into dog-bone type bars using a cutter. The actual dimensions of tensile specimens were the same as those described in ASTM-D1708 method.

The tensile properties of all samples were measured with Instron (Model-4204) tensile tester at a crosshead speed of 10 mm/min. A minimum of five specimens was tested and the results were averaged.

2.5. DSC measurements

DSC thermal analysis was carried out to measure the heat of fusion of the PCL and the graft product using a Du Pont 2000 thermal analyzer at a heating rate of 10°C/min under nitrogen from −100 to 150°C.

3. Results and discussion

3.1. Characterization of PCL-g-GMA

Fig. 1 shows the change of torque for the PCL solution containing various amounts of GMA/BPO with reaction time during grafting reaction. For the pure PCL, the torque decreased continuously until it reaches a constant value, while in the PCL solution containing GMA/BPO the torque increased significantly after the initial melting of PCL, and reached a maximum and then decreased with reaction time. Such an increase in the torque at earlier stage of the reaction is expected to be due to grafting of GMA onto PCL backbone and crosslinking of PCL, since branched or crosslinked macromolecules having a higher melt viscosity compared to linear macromolecules would be produced during the reaction. The reaction mechanism that describes the GMA grafting and the PCL crosslinking will be discussed in detail in the latter section of the manuscript. It is also found that the torque increase is more pronounced in the grafting reaction with higher GMA/BPO content. It is because the grafting reaction becomes more prominent with increase of the GMA content in the feed.

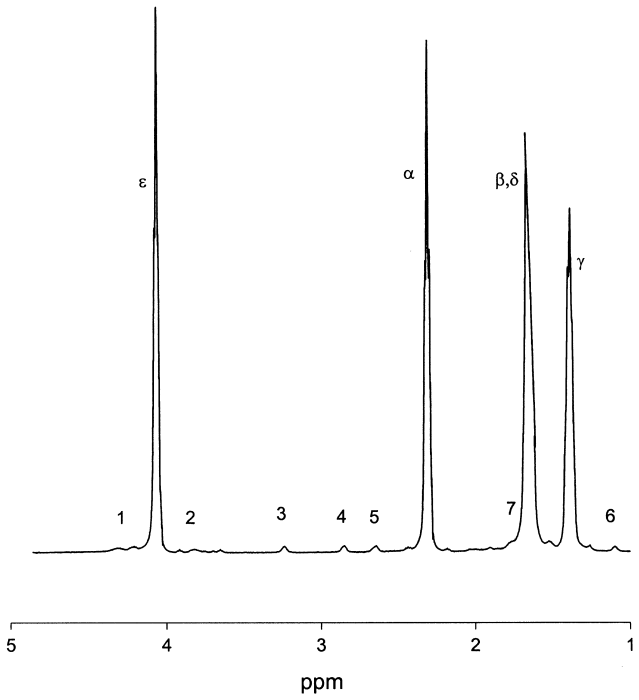

Fig. 3. ^{1}H-NMR spectrum of PCL-*g*-GMA.

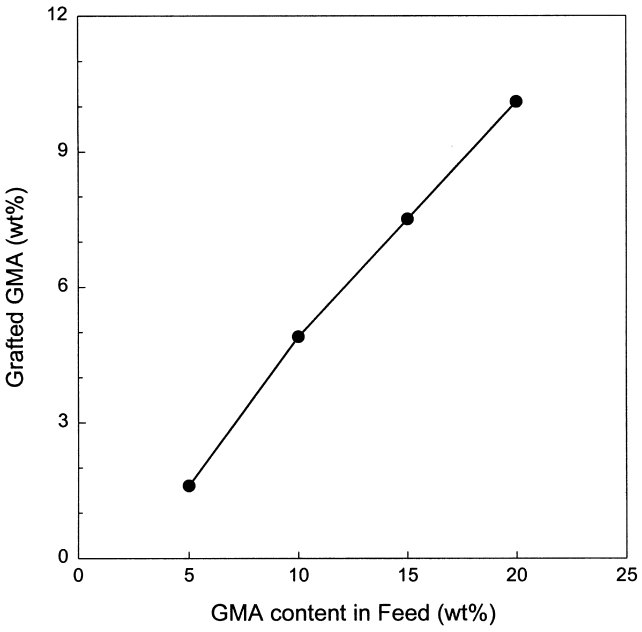

Fig. 4. The influence of GMA concentration on percentage GMA grafted at 130°C.

The structure of PCL-*g*-GMA and its NMR spectrum are shown in Figs. 2 and 3, respectively. The methylene proton peaks of PCL, denoted by α to ε, appeared at the chemical shifts completely separated from those of the proton peaks of the grafted GMA unit which were denoted by 1–7. From the relative peak area of the methylene proton of α-carbon atom to the carbonyl of PCL and the methine proton of GMA, denoted by 3, we could calculate the content of GMA grafted onto PCL.

The content of GMA grafted onto PCL is shown in Fig. 4 as a function of GMA content in the feed. It is found that the graft content increases from 1.6 to 10.1 wt% as the GMA concentration in the feed varies from 5 to 20 wt% at a melt temperature of 130°C and screw speed of 80 rpm. This ^{1}H-NMR result well supports the torque increase with increase of the GMA content.

The thermal characteristics of the grafted polymers with different GMA content were investigated by using DSC. As shown in Fig. 5, the increase of graft content resulted in the decrease of the crystallinity of PCL. This is due to the hindrance of PCL crystallization by the increase of chain structural irregularity caused by grafting reaction.

In addition to structural and thermal characterization, mechanical properties of the modified PCL were also considered. The bulk polymers obtained from the grafting reaction were compression-molded to make 1 mm sheet. The specimens for tensile measurements were cut from the sheets and shaped into dog-bone type bars using a cutter. The tensile properties of the pure and grafted polymers are summarized in Table 1. The tensile strength and elongation at break of PCL-*g*-GMA were comparable to those of the unmodified PCL except for GPCL10. It indicates that there is probably no reduction in the molecular weight and thus no change in the tensile properties. It was also found that the tensile strength at yield decreased with increase of the GMA content at least up to 7.5 wt% of GMA content. This decrease of tensile strength at yield is attributed to the decrease of crystallinity with the GMA content as is shown in Fig. 5. For GPCL10, the crosslink by the

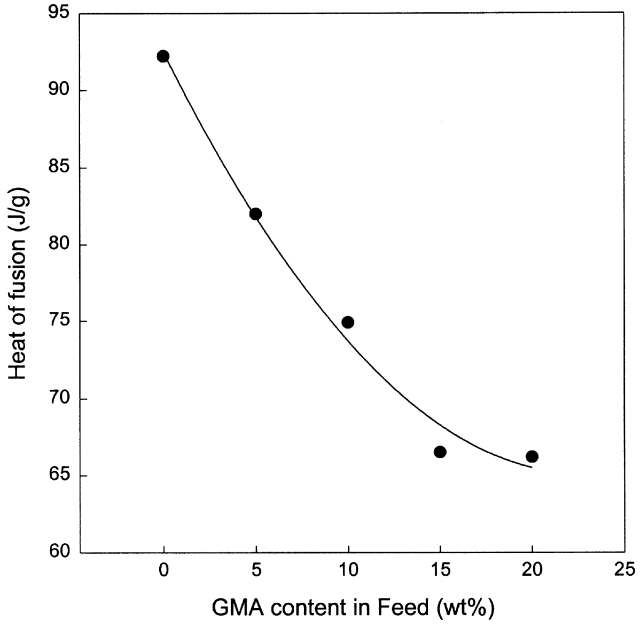

Fig. 5. Heat of fusion change of PCL-*g*-GMA as a function of GMA content.

Table 1
Tensile properties of PCL-*g*-GMA as a function of GMA content

	Tensile strength at yield (MPa)	Tensile strength at break (MPa)	Elongation at break (%)
PCL	15.8	33.0	1330
GPCL2	14.4	33.6	1350
GPCL5	13.9	34.3	1300
GPCL7	11.7	32.5	1290
GPCL10	13.6	27.2	820

recombination of macroradicals during the grafting reaction may occur and thus the tensile strength and the elongation at break were much lower than those for the other GPCLs studied. It is due to the limitation of chain orientation and strain-hardening of GPCL10. The molecular weight change and the crosslink formation during the grafting reaction will be discussed in more detail in the following section with the results of NMR and GPC measurements.

3.2. Grafting mechanism of PCL-g-GMA

The ^{1}H-NMR spectra of GMA, unmodified PCL, and PCL-*g*-GMA are shown in Fig. 6. The ^{1}H-NMR spectrum of the unmodified PCL and the chemical shift for all the protons were in accordance with the literature data [15]. The peaks 7 and 7′ shown in Fig. 6(a) corresponding to the methylene protons in the double bond of GMA appeared at the different positions in the NMR spectra as shown in Fig. 6(c) and the peak 6 of GMA is shifted up-field. It is due to the addition of double bond on a macroradical of PCL generated from the hydrogen abstraction caused by the action of the homolytic scission of organic peroxide. The peak position of methylene proton in the main chain of grafted p-(GMA) would be overlapped with the methylene proton peak of β- or δ-carbon atom of PCL and it could not be pointed out. From the comparison of the ^{1}H-NMR spectra (a), (b), and (c) in Fig. 6, the peak at δ 3.65 ppm designated by *k* (Fig. 6(c)) is found to newly appear and can be

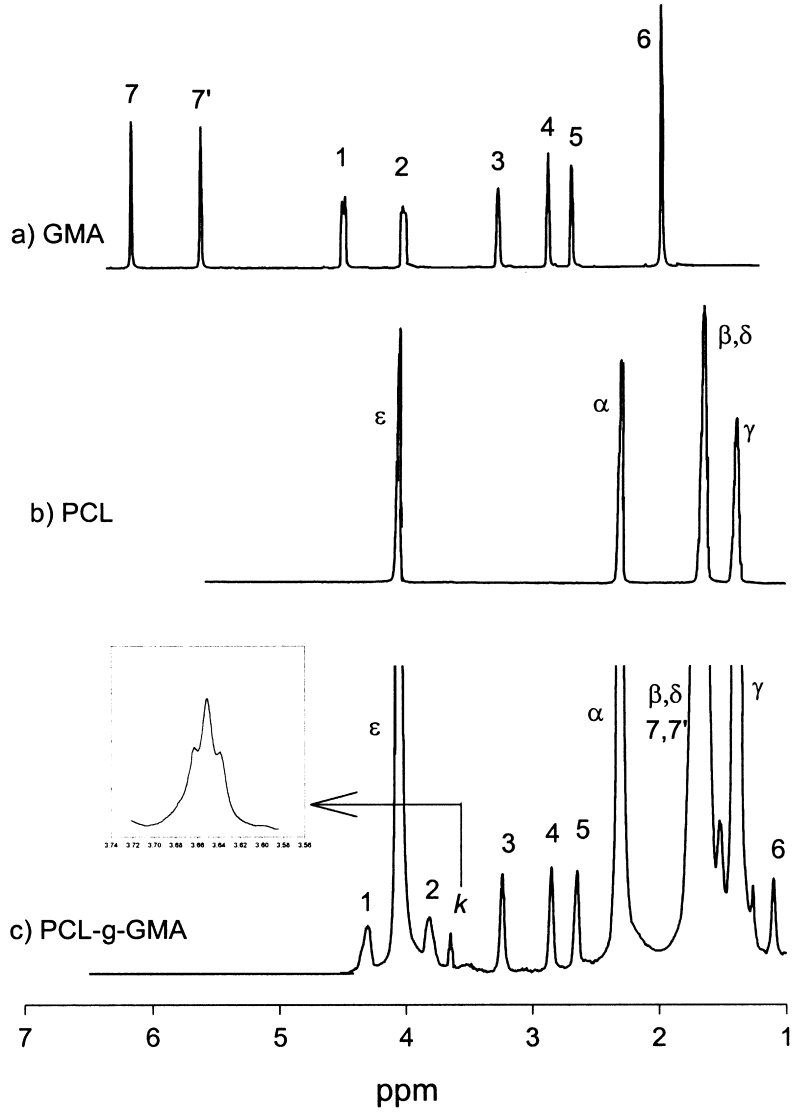

Fig. 6. ^{1}H-NMR spectra of: (a) GMA, (b) unmodified PCL, and (c) PCL-*g*-GMA.

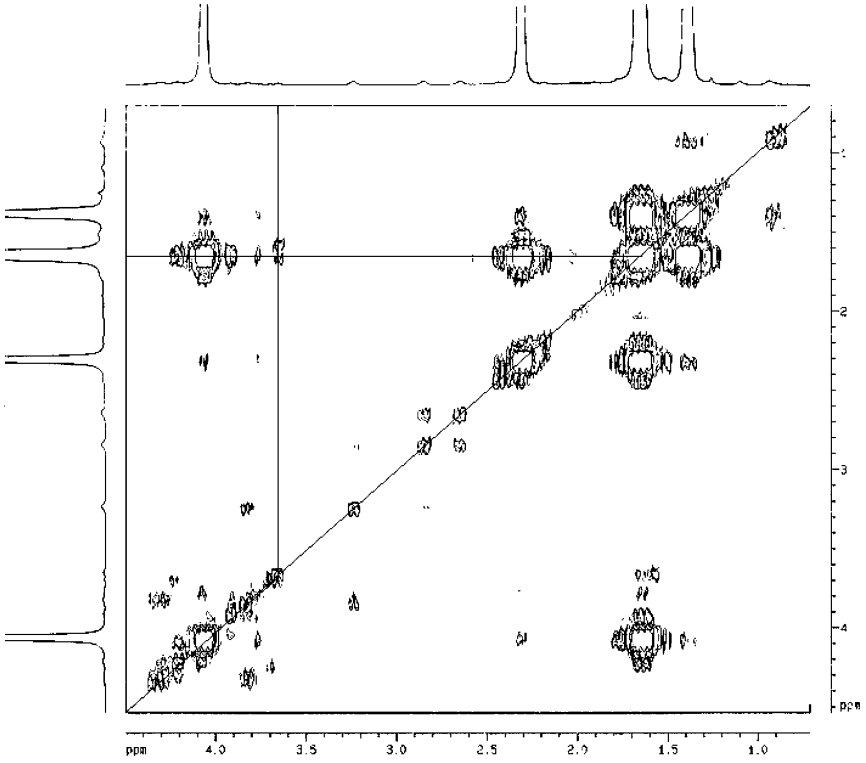

Fig. 7. Correlation spectra (H,H-COSY) of PCL-*g*-GMA.

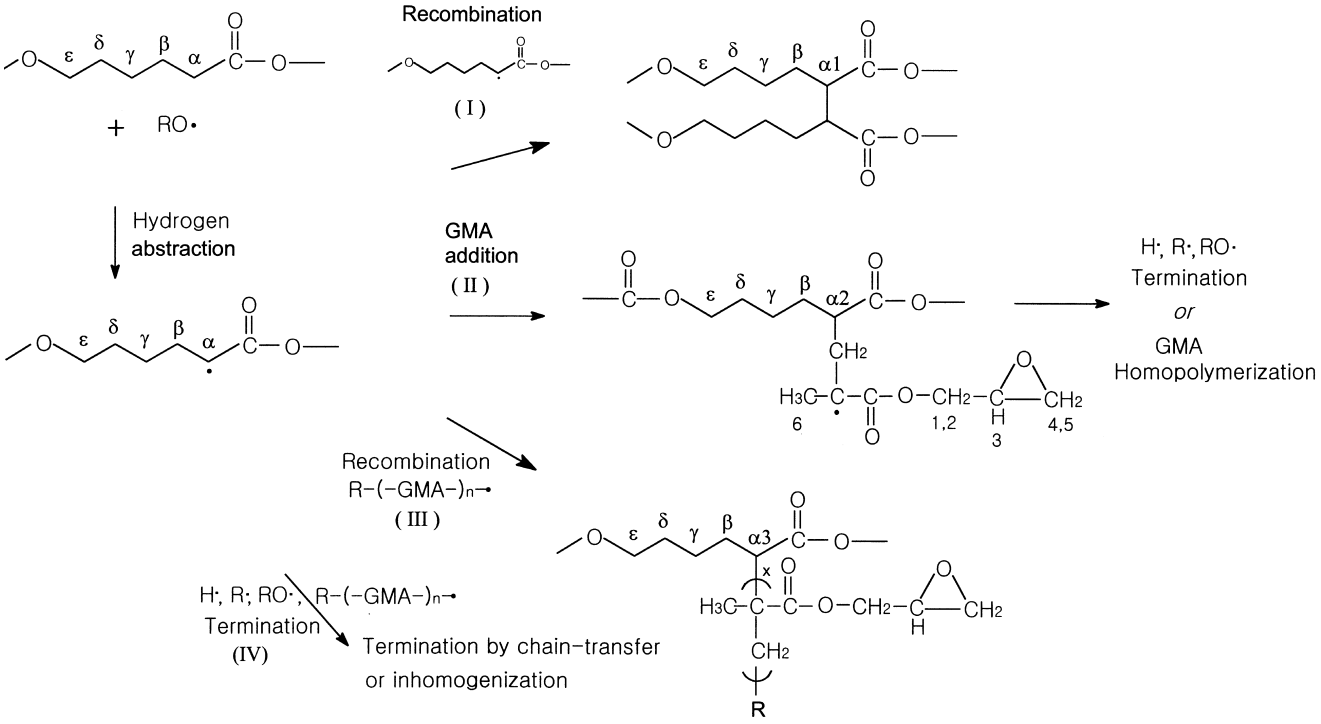

Fig. 8. Proposed reaction pathway for the grafting reaction of GMA to PCL.

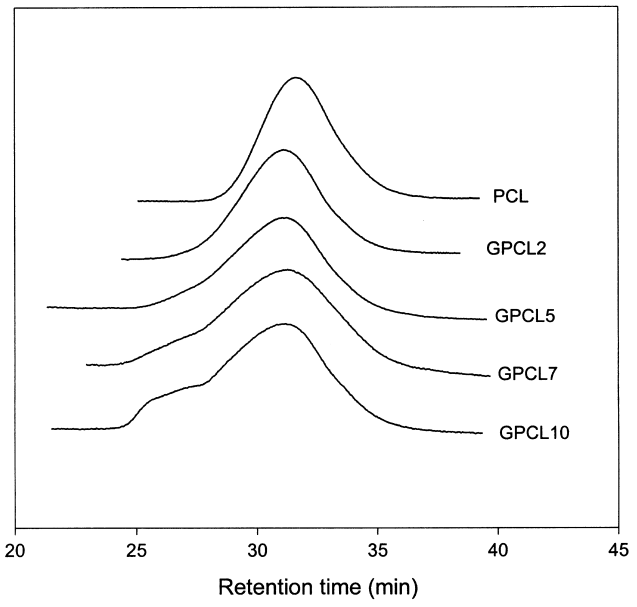

Fig. 9. Gel permeation chromatogram of pure PCL and PCL-*g*-GMAs at room temperature using THF as the mobile phase.

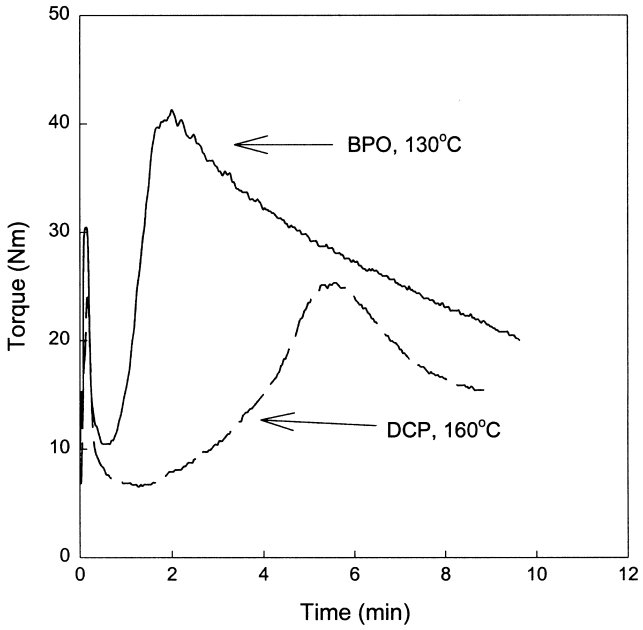

Fig. 10. Torque curves obtained during the mixing in the batch mixer only in the presence of organic peroxide.

assigned to the methine protons formed during the grafting reaction. The previous studies on the grafting mechanism of maleic anhydride or oxazoline maleinate showed a similar result that the new peak corresponding to the methine proton formed from the grafting reaction appears at a similar chemical shift to the one for the methine protons of PCL-*g*-GMA [13,14]. This peak assignment was also confirmed by observing the coupling relationship of protons in two-dimensional NMR spectra (H,H-COSY) of PCL-*g*-GMA (Fig. 7). As shown in Fig. 7, the new peak at δ 3.65 ppm was correlated with the methylene proton of β-carbon atom relative to the carbonyl group in PCL. It indicates that 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 will attack the double bond in the methacrylate unit. It is well known that free radicals from the thermal homolysis of BPOs can be thought of as having nucleophilic properties [16], and they can abstract the hydrogen at the α-carbon atom relative to the carbonyl of PCL, leading to the stabilization of the resulting radical by forming conjugation with the carbonyl group.

From the above discussion, the possible steps involved in the grafting reaction can be depicted as shown in Fig. 8. The reaction starts with the homolytic scission of organic peroxide. The peroxy radical can abstract hydrogen at the α-carbon atom relative to the carbonyl group and form a PCL macroradical. After the generation of PCL macroradical, various termination reactions through GMA grafting or chain-transfer processes, along with other possible reactions, might take place as shown in Fig. 8.

The previous studies suggested that the PCL macroradical could undergo quick β-scission with the simultaneous formation of a radical chain end and vinylidene chain end [13,14,17]. If the chain scission reaction takes place, small linear molecules will be formed and detected as multiple peaks in chromatograph measurements. To investigate the change of molecular weight by the grafting reaction, GPC measurement of pure PCL and PCL-*g*-GMA was proceeded. Fig. 9 represents gel permeation chromatograms of pure PCL and PCL-*g*-GMAs and the results are summarized in Table 2. The molecular weight and polydispersity of PCL-*g*-GMA increased with increase of the GMA content in PCL-*g*-GMA. As is seen from Fig. 9, the fractions that have lower molecular weights than the unmodified PCL were not obtained from PCL-*g*-GMAs. This indicates that the chain scission reaction did not occur during the grafting reaction. Instead, it is found that the fractions that have higher molecular weight than the unmodified PCL were produced from the grafting reaction. It implies that the chain extension (i.e. the crosslinking reaction) through the step (I) in Fig. 8 may occur during the grafting reaction. The chain extension would increase with the increase of GMA content since we added the BPO content proportionally to the GMA content during the grafting reaction.

Table 2
Summary of grafting reactions at different GMA content

	Number average (M_n)	Weight average (M_w)	PDI (M_w/M_n)
PCL	70,900	120,900	1.71
GPCL2	103,500	202,500	1.96
GPCL5	105,700	256,100	2.42
GPCL7	98,900	321,700	3.25
GPCL10	115,300	403,300	3.50

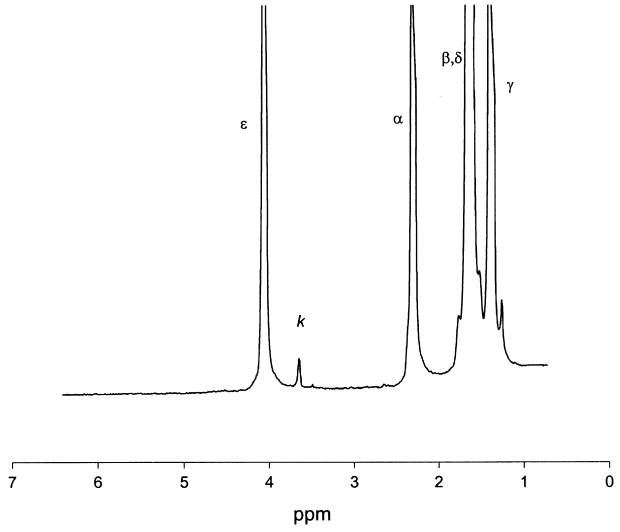

Fig. 11. ^{1}H-NMR spectrum of PCL obtained after mixing with BPO.

To investigate the chain extension mechanism through the step (I) in Fig. 8, we measured torques of the reacting mixture of the unmodified PCL and the organic peroxide (BPO or DCP) with reaction time. Fig. 10 shows the torques of the reacting mixture as a function of reaction time. It is found from this figure that the torque decreases at initial stage of the reaction due to the melting of PCL and then increases sharply with reaction time. This is expected to originate from the increase of the molecular weight through a chain extension (crosslinking reaction). At the end of the mixing, the torque decreases and is stabilized since the temperature of the reaction medium increases and is stabilized by heat generation during mixing process. The chain extension through the step (I) was also confirmed by the NMR spectrum of the PCL mixed with BPO. Figs. 11 and 12 show one- and two-dimensional (H,H-COSY) ^{1}H-NMR spectra of the PCL which was prepared from the mixing at 130°C with 1 wt% BPO of the PCL amount. It is found from Fig. 12 that the peak denoted by *k* at δ 3.65 ppm appears and

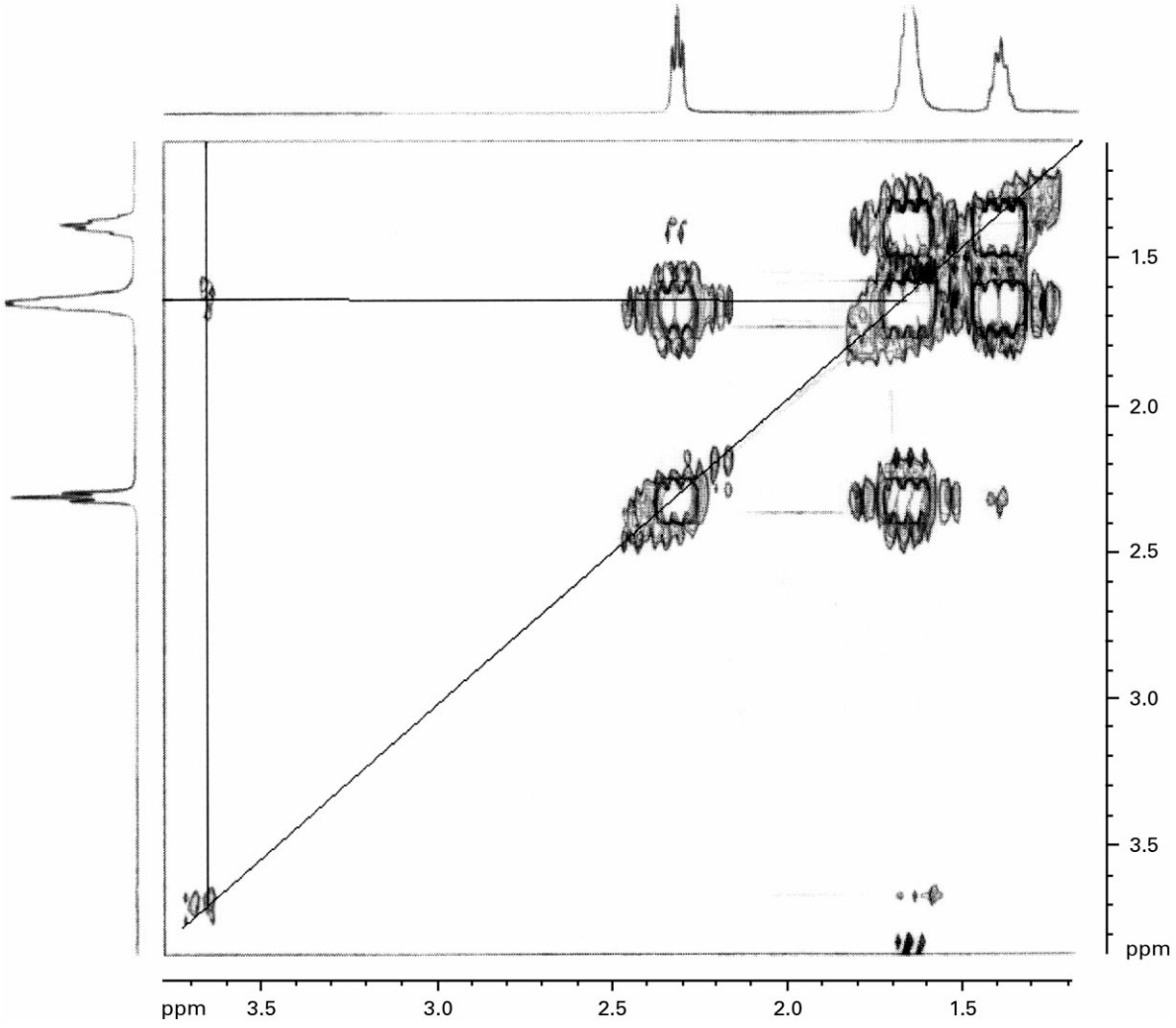

Fig. 12. Correlation spectra (H,H-COSY) of PCL obtained after mixing with BPO.

is correlated with the methylene peak of β-carbon relative to the carbonyl group of PCL. This indicates that the radical from the homolytic scission of BPO abstracts a hydrogen of the α-carbon atom relative to the carbonyl group to form the macroradical and this macroradical combines with the other macroradical through recombination reaction. The molecular weight of PCL can thus increase and the torque of the medium becomes increased. This recombination reaction will be more prominent with the increase of GMA content in PCL-*g*-GMA.

The GMA grafting can also take place on the PCL macroradical through step (II) or step (III) in the proposed mechanism (Fig. 8). The step (II) is the addition reaction of GMA monomer on the macroradical of PCL to transfer the macroradical to the position of tertiary carbon and thus the chain propagation will continue until the termination of the macroradical occurs. The step (III) is the recombination reaction between the PCL macroradical and the polyGMA radical which is produced by homopolymerization of GMA. The GMA is well known to be an active monomer which can be homopolymerized by a free radical polymerization [18]. The step (III) could thus be one of the possible mechanisms for GMA to graft onto the PCL backbone. The difference in the structure of the graft polymers which are produced by step (II) or step (III) is in the direction of GMA addition. For the graft polymers obtained through step (II), the methylene carbon of GMA is attached to methine carbon of the PCL backbone, while the quaternary carbon is attached to methine carbon of the PCL backbone of the graft polymer produced by step (III). If the GMA grafting proceeds through the step (II), NMR peak for the methine proton formed by the grafting reaction would split into quintet. However, as shown in Fig. 6(c), the peak for the methine proton formed by the grafting reaction, which is denoted by *k* in NMR spectra (δ 3.65 ppm) splits only into triplet. From this result, it seems that the GMA grafting can also occur through the step (III). From the above NMR and GPC results, it is concluded that the steps (I) and (III) well describe the grafting reaction of GMA moiety to the PCL chain.

Acknowledgements

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References

[1] Vaidya UR, Bhattacharya MB. J Appl Polym Sci 1994;52:617.
[2] Ramkumar D, Vaidya UR, Bhattacharya M, Hakkarainen M, Albertsson AC, Karlsson S. Eur Polym J 1996;32:999.
[3] Bhattacharya M, Vaidya UR, Zhang D, Narayan R. J Appl Polym Sci 1995;57:539.
[4] Bikiaris D, Panayiotou C. J Appl Polym Sci 1998;70:1503.
[5] Koenig MF, Huang SJ. Polym Mater Sci Engng 1992;67:290.
[6] Tokiwa Y, Iwamoto A, Koyama M. Polym Mater Sci Engng 1990;63:742.
[7] Bastioli C, Cerutti A, Guanella I, Romano GC, Tosin M. J Environ Polym Deg 1995;3(2):81.
[8] Koenig MF, Huang SJ. Polymer 1995;36(9):1877.
[9] Choi EJ, Kim CH, Park JK. Macromolecules 1999;32(22):7402.
[10] Choi EJ, Kim CH, Park JK. J Polym Sci, Polym Phys Ed 1999;37:2430.
[11] Kim CH, Choi EJ, Park JK. J Appl Polym Sci 2000;77(9):2049.
[12] Kim CH, Cho KY, Park JK. Polym Eng & Sci 2001 (in press).
[13] John J, Tang J, Yang Z, Bhattacharya M. J Polym Sci, Polym Phys Ed 1997;35:1139.
[14] John J, Tang J, Bhattacharya M. J Appl Polym Sci 1998;67:1947.
[15] Tho Pham Q, Petiand R, Waton H. Proton and carbon NMR spectra of polymers. London: Penton Press, 1991.
[16] Pryor WA. Introduction to free radical chemistry. Englewood Cliffs, NJ: Prentice-Hall, 1966 (chap. 6).
[17] Pabedinskas A, Cluett WR, Balke ST. Polym Engng Sci 1998;28:170.
[18] Pan Y, Ruan J, Zhou D. J Appl Polym Sci 1997;65:1905.