

Heat Resistance of Radiation Crosslinked Poly(ϵ -caprolactone)

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ABSTRACT: Polycaprolactone (PCL) was gamma-irradiated at different phases such as solid state at 30 to 55°C, molten state, and supercooled state, under vacuum or air atmosphere, to elucidate its crosslinking behavior. Irradiation in the molten state (80°C) gave higher gel content compared to room temperature. The resulting gel, however, contains many voids due to the gas evolved during irradiation. Conversely, irradiation of PCL in the supercooled state led to the highest gel content among the three irradiation conditions and it was free of voids. Based on these findings, to evaluate heat resistibility of crosslinked PCL prepared by irradiation in supercooled state, the crosslinked PCL was hot pressed at 200°C to form a film. Unirradiated PCL melted at 60°C. The film prepared from 160 kGy irradiated PCL (crosslinked sample) under an applied load of 0.667 MPa, at a temperature of 110°C did not break even after 3 h. At a temperature of 120°C, the film has a tensile strength of 3 MPa. Furthermore, the film extended by hot pressing is transparent and has high heat shrinkability. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 581–588, 1998

Key words: polycaprolactone; irradiation; crosslinking; molten state; heat stability

INTRODUCTION

In recent years, the rapidly expanding production and use of plastic materials has created massive problems in the area of waste disposal, especially due to the adverse environmental effect of non-biodegradable plastics. Biodegradable polymers, such as poly(3-hydroxybutyrate) (PHB), Poly(lactic acid) (PLA), and poly(ϵ -caprolactone) (PCL), are converted to carbon dioxide and water when in contact with soil that contains microorganisms; hence, they are known as environmental friendly polymers. These polymers, however, have some disadvantages; for instance, PHB and PLA

rapidly degrade during molding processes and PCL has a low melting point (60°C).

PCL, an aliphatic polyester, is derived from ring-opening polymerization of ϵ -caprolactone. The polymer is partially crystalline and melts at a relatively low temperature (60°C).^{1–3} It is well known that this polymer is biodegradable and has good compatibility with a wide range of other polymers.⁴ PCL has been used for plastics packaging, plant containers,⁵ and medical devices.⁶

Ionizing radiation is one of the methods used to improve certain properties of polymers by crosslinking or grafting. It has been reported that polypropylene irradiated by electron beam in the presence of polyfunctional monomers, results in a high melt strength material.⁷ Hot water resistance of PVA sheets was also improved by radiation crosslinking after an acetylation process.⁸

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PCL films produce an insoluble fraction when exposed to gamma irradiation even in air. At 600 kGy of irradiation dose under vacuum with a dose rate of 1.36 kGy/h, however, a relatively low gel content (30%) is formed.⁹ Lawton reported that when polyethylene is irradiated at a high temperature, near melting, a higher gel fraction is produced compared to that by irradiation at room temperature. He reported that crosslinking occurs mainly in the amorphous phase of polyethylene.¹⁰ Hence, increasing of the amorphous phase content by increasing the irradiation temperature to the molten state is preferable to get high gel content. Similar results were also found for polytetrafluoroethylene irradiated in the molten state (340°C).¹¹

In this article, the effect of phases such as solid state, supercooled state, and molten state on the radiation crosslinking behavior and heat resistance of crosslinked PCL have been investigated.

EXPERIMENTAL

Materials

Polycaprolactone used in this experiment was a commercial product, PCL-H7 (Daicel Co. Ltd., Japan). The number-average and weight-average molecular weights, measured by gel permeation chromatography (GPC), are 1.28×10^5 and 2.19×10^5 , respectively. It was dried under reduced pressure at 45°C for 72 h before use.

Irradiation

PCL pellets were sealed in a glass tube of 15 mm in diameter after evacuation of air to 10^{-3} torr or put on the glass without evacuation (in air). Irradiation of samples was carried out using gamma rays from a ⁶⁰Co source with a dose rate of 10 kGy/h in a temperature-controlled vessel. Irradiation was carried out by three methods. First was irradiation at a temperature range of 25 to 55°C (solid state); second was in molten state (above 60°C); and third was at a reduced temperature (30 to 55°C), after melting at 120°C. For the third method, the samples were kept at a given temperature for about 15 min prior to irradiation.

Film Preparation

Irradiated bulk PCL was hot pressed to make films at 200°C for 6 min with a pressure of 10

MPa and then cooled to room temperature by cold pressing using water as a coolant for 3 min. Unirradiated PCL was treated in the same way as irradiated PCL except the temperature used was 120°C.

Molecular Weight Measurement and Thermal Analysis

Molecular weight was measured by GPC (HLC-802A, Tosoh Co. Ltd., Japan). The instrument was equipped with a series of four Tosoh gel columns and a RI-8 differential refractometer at 38°C. The eluent was chloroform with a flow rate of 1 mL/min and the polymer concentration was 1 mg/mL. The average molecular weights were calibrated using polystyrene standards.

Melting and crystallization temperatures were measured using Differential Scanning Calorimetry (DSC-7, Perkin-Elmer) under nitrogen flow with a heating or cooling rate of 10°C/min. Isothermal crystallization of samples after melting at 80°C for 3 min were performed at various temperatures ranging from 25 to 55°C for 16 h. The cooling rate was 50°C/min.

Mechanical Property and Gel Content

Mechanical properties were analyzed with a tension meter (Strograph-R1 Toyoseiki, Co., Japan) at a crosshead speed of 100 mm/min according to ASTM D 882.¹² For measurement of mechanical properties at high temperature, an Instron-4302, series IX machine equipped with a temperature controller was used.

Gel content of irradiated PCLs were estimated by measuring the insoluble part in boiling chloroform for 48 h. The gel fractions were calculated as a ratio of dried gel to the initial weight of the polymer.

Heat Stability Test

Heat-resistance properties of irradiated PCL were measured using an oven at various temperatures. The film samples (0.3×2) cm² of area and 0.015 cm thickness prepared by hot press were hung in an oven with a given load and temperature. The deformation in elongation and the times required to break the samples were observed.

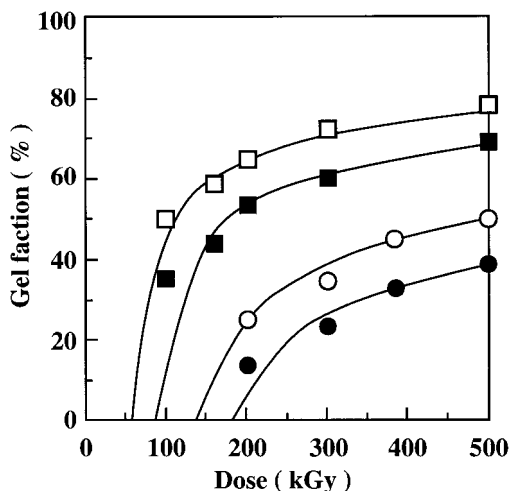


Figure 1 Gel fraction of PCL as a function of irradiation dose. Irradiation temperature ($^{\circ}\text{C}$): (○, ●) room temperature; (□, ■) molten state (80°C). Open and closed symbols are vacuum and air conditions, respectively.

RESULTS AND DISCUSSION

Crosslinking at High Temperature

Crosslinking and chain scission are among the chemical effects observed when polymers are subjected to ionizing radiation. The processes ultimately cause formation of an insoluble gel if crosslinking predominates over scission. PCL is a crosslinkable polymer, as evidenced by the formation of gel when exposed to gamma rays. The effect of irradiation dose in the temperature of 27 and 80°C on the gel content is shown in Figure 1. This irradiation corresponds to the effect of morphology of PCL in solid (below 60°C) and molten (above 60°C) phases during irradiation. Irradiation in the molten state (80°C) results in higher gel content compared to room temperature (27°C). Irradiation under vacuum also gives higher gel content than in air. At 100 kGy, gels of 50% are formed in the molten state, whereas no gel formation is observed for irradiation at room temperature. At room temperature, the polymer contains crystalline and amorphous parts. Crosslinking is rarely in the crystalline phase. At 80°C (above melting point), the polymer is converted from the crystalline to the completely amorphous state. Similar results are obtained when polyethylene is irradiated at several temperatures ranging from room temperature to above the melting point.¹⁰ Figure 2 shows the effect of irradiation temperature on the gel formation at a constant

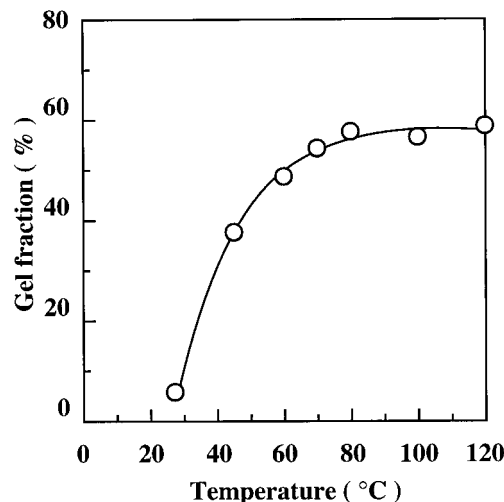


Figure 2 Effect of irradiation temperature on gel fraction of PCL irradiated with a dose of 160 kGy under vacuum.

irradiation dose of 160 kGy under vacuum. The gel fraction increases rapidly up to melting and then levels off. From these findings, it is suggested that crosslinking efficiency is largely affected by the temperature during irradiation. When temperature rises and approaches melting, the degree of crystallinity of the polymer decreases by the partial melting of the crystallites. The rates of chemical reactions increase with temperature due to the greater proportion of the molecules that have energies in excess of the activation energies, and this will cause irradiation-induced secondary reactions in polymer. Substantial changes in molecular mobility occur in the molten state, and the rates of chemical reactions are often greatly affected.¹³ Irradiation in the molten state, however, produces voids that result from gas evolved and trapped in the sample during irradiation, as can be seen in Figure 3(a). The presence of voids

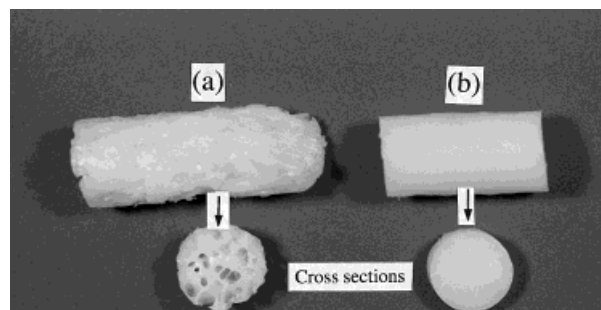


Figure 3 Photograph of 160 kGy irradiated PCL. (a) Irradiation in the molten state; (b) irradiation in the supercooled state.

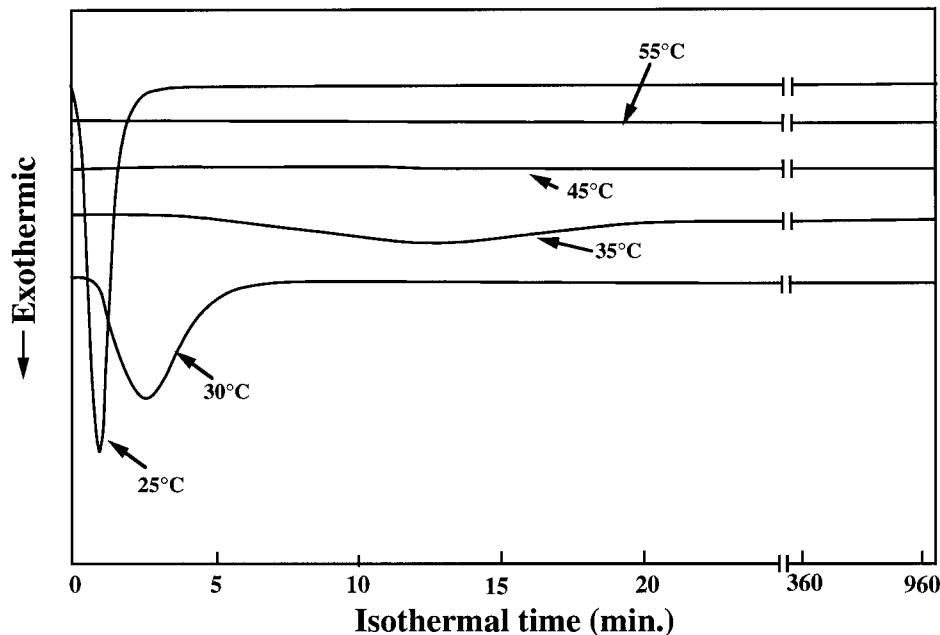


Figure 4 Isothermal crystallization curves at various temperatures for 16 h after melting at 80°C of unirradiated PCL.

may affect certain properties of the polymer. Weight-average molecular weight of PCL measured by GPC is 2.19×10^5 . In the pregelation state, the effect of irradiation on PCL result in increases of weight-average molecular weight. For instant, in irradiation in the molten state, weight-average molecular weights are 3.2×10^5 and 5.1×10^5 for an irradiation dose of 20 kGy and 50 kGy, respectively.

Crosslinking in the Supercooled State

In the previous section it was mentioned that irradiation of the molten state results in gel at low doses. However, during irradiation, voids are formed in the polymer due to the gases evolved, which cause a reduction in various physical properties of the polymer. To avoid the formation of voids, PCL was irradiated at 35 to 55°C after melting. Irradiation of PCL, at 45°C or lower results in free of voids gel [see Fig. 3(b)], while irradiation at 50 and 55°C produces gels that contain many voids. To elucidate phase structure of PCL at 25 to 55°C, isothermal crystallization of PCL after melting has been carried out, as can be seen in Figure 4. For isothermal curves at 25 to 35°C, exothermic peaks due to crystallization appear immediately in a few minutes, while for isothermal they are at 45 and 55°C and the crystalliza-

tion peaks do not appear even after a long time (16 h). From these findings it is clear that at 45°C or above, the samples remain in the amorphous phase during irradiation to give higher crosslinking. In this crosslinking, the whole sample remains amorphous after melting during irradiation. Hence, such irradiation condition is defined as a supercooled state. As shown in Figure 3(b), PCL obtained by irradiation in the supercooled state has a homogenous shape without voids. This may be due to smaller gas evolution compared to the molten state because of lower temperature; therefore, this irradiation yields higher gel content compared to that at room temperature and in the molten state, as shown in Figure 5. These findings imply that radiation crosslinking of PCL occurs effectively in irradiation in the supercooled state compared to that of the molten state because of lower molecular mobility. It was found that the gelation dose of PCL, irradiated under vacuum in the supercooled state, in the molten state, and at room temperature obtained from the Charlesby-Pinner plot of $S + S^{0.5}$ versus a reciprocal dose were 31, 55, and 139.5 kGy, respectively. The amount of gel fraction of PCL irradiated in the supercooled state is the same as polyethylene irradiated using electron beam under vacuum.¹⁴ For example, at 150 kGy, about 78% of the gels were formed in both cases.

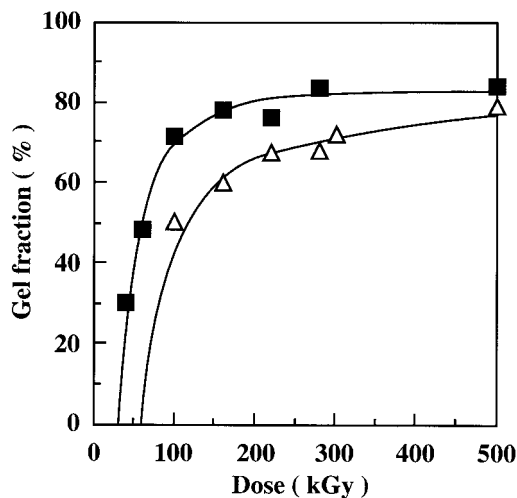


Figure 5 Effect of dose on the gel fraction of PCL irradiated in vacuum: (■) the supercooled state; (△) the molten state (80°C).

Heat Resistance of Crosslinked PCL

The irradiated PCL sample in the supercooled state is a cylindrical shape, as shown in Figure 3(b). Because this sample has network structure by crosslinking, it is difficult to mold by melt flow processing. Hence, a slice of cylindrical sample was expanded to make a film by compression under 100 kg/cm² at 200°C. Figure 6 shows the mechanical properties of the film obtained by the compression processing of irradiated PCL in the supercooled state. Tensile strength increases with irradiation dose up to 160 kGy and thereafter de-

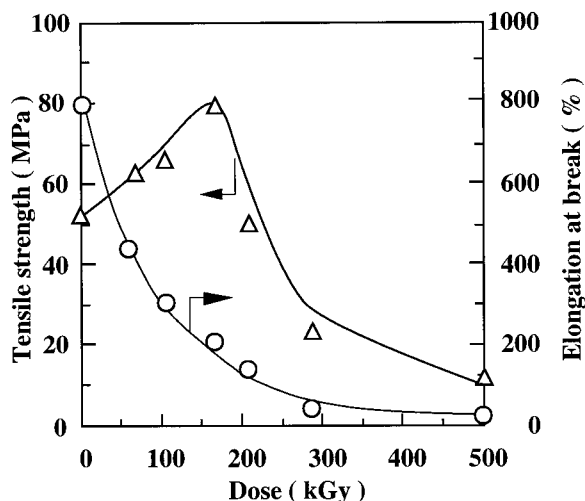


Figure 6 Tensile strength and elongation at break of PCL irradiated in the supercooled state as a function of dose.

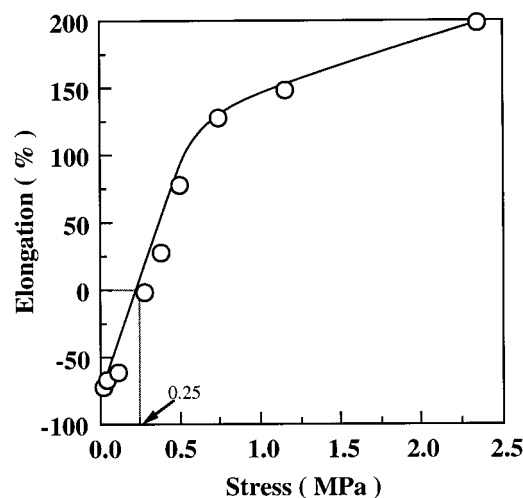


Figure 7 Stress-strain curve of irradiated PCL (160 kGy) in the supercooled state measured at 70°C for 3 min.

creases. Increasing of tensile strength is due to the possibility of rearrangement of polymer chains during the extension process. At a sufficiently high crosslink density, above 160 kGy, the rearrangement of polymer chains become much more difficult, and this results in a reduction of tensile strength. The elongation at break decreases as the irradiation dose increases, due to network structure of polymer chains formed by crosslinking.

Heat resistance of irradiated PCL was determined by measuring the deformation of PCL film at a given temperature using various loads, or at different temperatures with a constant load, and also by measuring the tensile properties at high temperature. The relationship between applied load (stress) and deformation (in elongation) of PCL irradiated in the supercooled state with a dose of 160 kGy is shown in Figure 7. The stress was calculated from the load divided by the cross-sectional area. The films (0.3 × 2) cm² of area and 0.015 cm thickness were hung in an oven at 70°C for 3 min using various loads, and the deformation in elongation was observed. Irradiated PCL has a heat-shrinkable property at low applied stresses. Without any applied stress, the film shrinks (negative elongation) up to 70% of initial length. Addition of applied stress decreases the shrinkability of films. At 0.25 MPa the film could maintain its initial length due to the equilibrium between internal and external stresses. Further increase in stress led to elongation of the film because the external stress is higher than the internal stress. At an applied stress of 2.35 MPa, the film has an

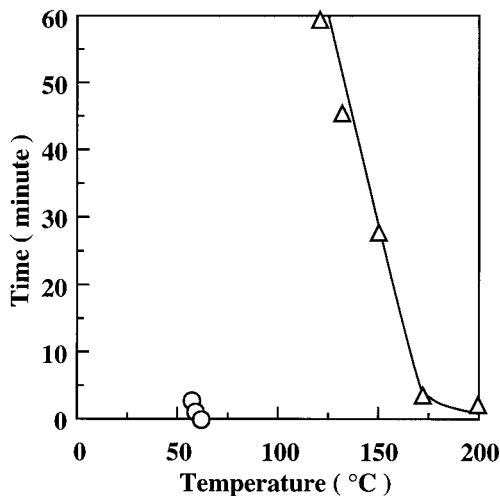


Figure 8 Relationship between temperature and breaking time of PCL with applied stress of 6.67 kg/cm²: (○) unirradiated; (△) irradiated with 160 kGy in the supercooled state.

elongation of 200%, after keeping at 70°C for 3 min, and the film did not break. To analyze the breaking time of PCL at different temperatures, a modified creep test was carried out. The films were kept at different temperatures with a constant stress (0.667 MPa) as shown in Figure 8. Unirradiated PCLs broke in 3.0, 1.5, and 0.3 min when held at 53, 57, and 60°C, respectively. Above melting, unirradiated PCL was converted into a viscous liquid, while PCL irradiated in the supercooled state has ultimately high heat stability. At 110°C it did not break even up to 180 min, while at 130, 150, 170, and 200°C the films broke in 45, 28, 3.5, and 2 min, respectively.

The plots of tensile strength and elongation at break as a function of temperature are shown in Figure 9. Tensile strength of unirradiated PCL drops to 0 MPa at 70°C and elongation at break increases as temperature increase up to 55°C. Tensile strength of PCL irradiated in the supercooled state with 160 kGy reduces sharply up to 70°C and thereafter slightly decreases. At 120°C, the film still maintains a tensile strength of 3 MPa. The elongation at break increases with temperature. The crosslinked PCL exhibits rubber-like elasticity when it is heated above 100°C. From these findings, it is concluded that irradiated PCL in the supercooled state has superior heat resistibility after crosslinking.

Transparency of Irradiated PCL

PCL films made from irradiated bulk PCL in the supercooled state have high transparency and

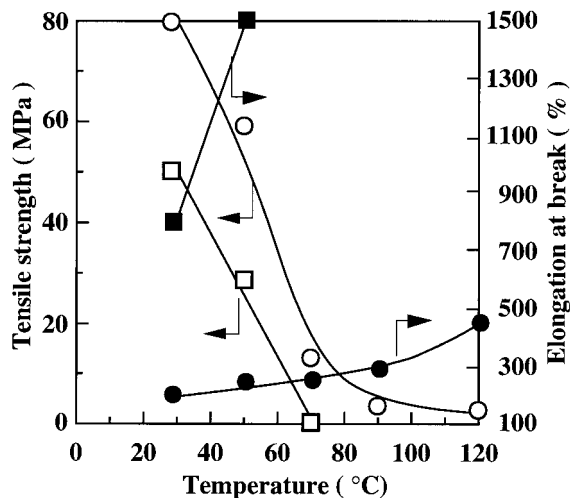


Figure 9 Tensile strength and elongation at break of PCL irradiated in the supercooled state as a function of temperature: (○,●) 160 kGy; (□,■) 0 kGy.

heat resistibility. Figure 10 shows a photograph of PCL films that were put on a written paper. The sentences located under the film prepared by hot pressing from irradiated bulk PCL with 160 kGy are readable due to transparency of the film [Fig. 10(a)], while sentences located under the unirradiated PCL film are unreadable [Fig. 10(b)]. Another way to determine the transparency is by haze measurement. Haze value decreases by increasing radiation dose, as shown in Figure 11. Low haze value reflects high transparency. When a crosslinked PCL sample is hot pressed to make a film, during the cooling process the formation of

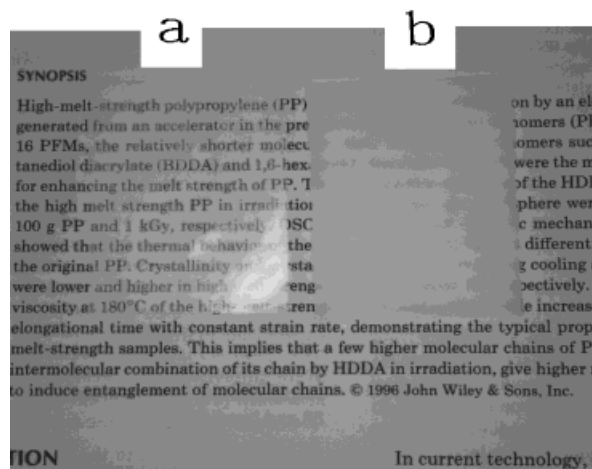


Figure 10 Photograph of PCL films prepared by a hot press from (a) irradiated bulk with 160 kGy in the supercooled state and (b) without irradiation.

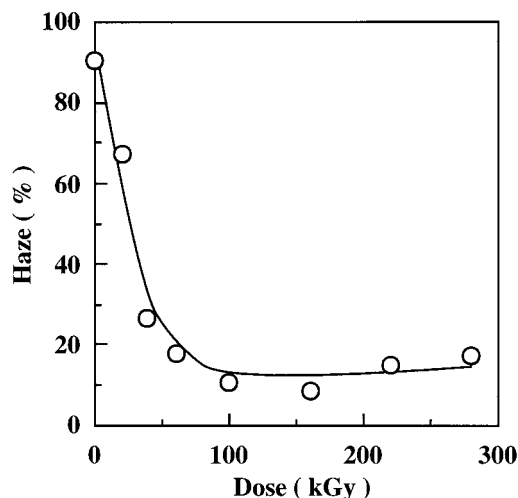


Figure 11 Haze value of PCL irradiated in the supercooled state.

crystals is disturbed by the crosslinked structure; as a result, small crystal size and imperfect crystals are formed. The limited formation of small crystals and imperfection of crystals led to the high transparency. However, even at low doses, below the gel point, the haze value also reduces. This may be due to the microgel formed at a pregelation dose that affects the crystal rearrangement.

Melting and Crystallization Behaviors of Crosslinked PCL

Crosslinked material such as polyethylene has a lower melting point (T_m) than uncrosslinked, and

network structures formed by crosslinking retard crystallization during cooling after melting. Figure 12 shows melting and crystallization behaviors of PCL and its crosslinked form. The DSC second run heating was performed directly after the cooling of the first run. The melting point of unirradiated PCL in the second run is lower than in the first run due to the very short time available, so that the crystallization is not completed, as shown in Figure 12(A) (No. 1). Increasing irradiation dose also depresses the melting point of PCL. Crystallization temperature becomes broader and shifts to lower temperature with increasing gel content as shown in Figure 12(B). It is understood that crosslinking imparts a remarkable influence on crystallization. Polypropylene copolymerized with ethylene of 2.5% have higher transparency due to smaller crystals size and lower crystallinity than homopolymer of propylene (PP)¹⁵ The melting point of PP is reduced by copolymerization with ethylene. The crosslinked PCL has crystalline structure even at higher gel fractions (80%), and the degree of crystallinity of crosslinked PCL, estimated from DSC measurement, is almost the same as the original one, that is c.a. 53%, but the melting point is remarkably reduced by crosslinking. It is assumed that the major factor for transparency and reduction of melting of crosslinked PCL is the production of smaller crystals during the crystallization (cooling) process for crosslinking.

CONCLUSIONS

Crosslinking of PCL by irradiation in the solid state at 27 to 55°C, in the supercooled state and

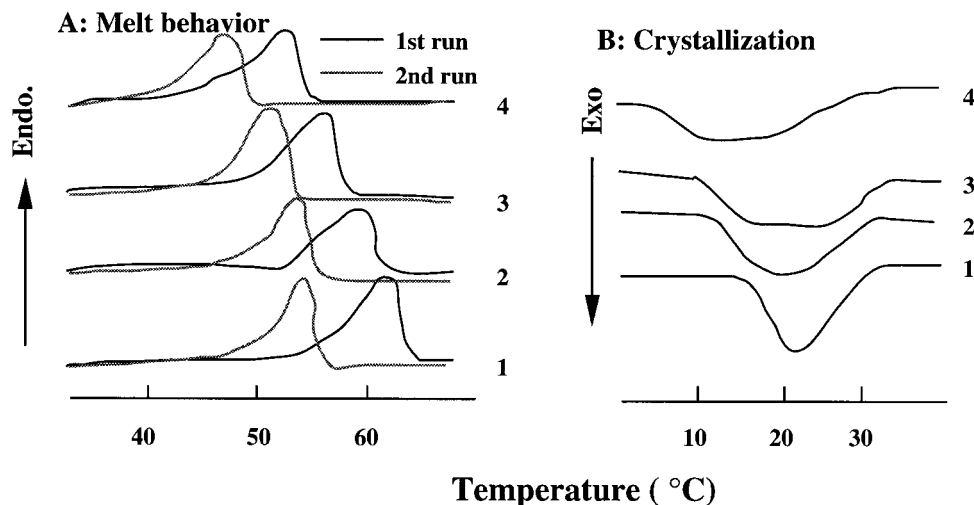


Figure 12 DSC curves of PCL irradiated in the supercooled state: 1, unirradiated; 2, 100 kGy; 3, 500 kGy; 4, 820 kGy.

in the molten state were investigated. In general, the crosslinking occurred predominantly in the amorphous region compared to the crystal region. It was found that isothermal heating of PCL, at 45 to 55°C after melting, retains an amorphous phase for a long time due to a slower crystallization rate. Hence, such a condition is favorable for radiation crosslinking. The films obtained by compression molding at 200°C of crosslinked PCL had high heat resistance and heat shrinkability. Furthermore, the films have high transparency due to the formation of the small crystal size because crystallization is disturbed by crosslinking during cooling from 200°C in the compression-molding process. From these findings, modification of PCL using radiation will be useful for a wide variety of industrial applications.

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