Shape-Memory Effects of Radiation Crosslinked Poly(ε-caprolactone)

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ABSTRACT: Poly(ε-caprolactone) (PCL) with different molecular weight were crosslinked by γ-radiation. The radiation crosslinking features were analyzed by Soxhlet extraction with toluene and the Charlesby–Pinner equation. The crosslinking degree is relative to molecular weight and radiation dose; the relation between sol fraction and dose follows the Charlesby–Pinner equation. All the samples were crystalline at room temperature, and the radiation crosslinking had a little effect on the crystallinity and the melting behavior of PCL. The shape-memory results indicated that only those specimens that had a sufficiently high crosslinking degree (gel content is higher than about 10%) were able to show the typical shape-memory effect, a large recoverable strain, and a high final recovery rate. The response temperature of the recovery effect (about 55°C) was related to the melting point of the samples. The PCL shape-memory polymer was characterized by its low recovery temperature and large recovery deformation that resulted from the aliphatic polyester chain of PCL. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1589–1595, 2003

Key words: polycaprolactone; radiation; crosslinking; shape-memory effect

INTRODUCTION

As well known to those skilled in the art, both some alloys and some synthetic polymers show shape-memory effect. Known shape-memory alloys are , for example, the titanium–nickel alloy and copper–zinc–aluminum alloy. However, the shape-memory alloys are such metals that they are not easily processed and not suitable for mass production of resulting products. Another problem of the shape-memory alloys is in that they not only have high specific weight but also are so expensive that they are rarely generally used. Meanwhile, the shape-memory polymer is easily formed, is light in weight, is large in recoverable deformation, and shows good processing performance, so that it is known to be suitable for used in mass production of resulting products. The shape-memory polymer, as shape-memory alloy, may remember its original shape after being deformed. That is, when the shape-memory polymer, after being deformed, is heated to a temperature higher than a predetermined level, the stress imposed on the shape-memory polymer is relieved, thus making the shape-memory polymer recover its original shape. In this sense, it is called a thermally stimulated shape-memory polymer. The

first shape-memory polymer material of practical importance was made of polyethylene crosslinked by the reaction with ionizing radiation during processing.[1] It was used for cable joint, tube joint, and goods packing. Its response temperature related to the melting temperature of polyethylene is usually near or above 120°C. Various kinds shape-memory polymers are needed to match the requirements of different applications.

An interesting study is to lower the response temperature of the shape-memory effect. A shape-memory polymer of lower response temperature may be applied in daily life and may be important for applications of special biological or medical considerations where the use of high temperature should be avoided. An important approach to solve this is to use segmented copolymers. Hayashi and his coworkers[2–6] have studied the chemical structure and dynamic mechanical properties of two series of block polyurethanes (PUs) with shape-memory behavior. Kim, Lee et al.[7] have studied the effect of crystallization of polycaprolactone, as the reversible phase, on shape-memory behavior. Lee,[8] and Lin and Chen,[9,10] have studied the influence of hard segment content and soft segment molecular weight (MW) on the shape-memory behavior of polyether-based PUs and the influence of chemical crosslinking structures on the shape-memory behavior of polyester-based PUs. Their response temperatures were around −70∼+50°C, but these

lower temperature shrinking PUs are rarely available in market. Xu et al.[11] have studied the shape-memory behavior of chemical crosslinked ethylene–vinyl acetate copolymer. Its shape-recoverable temperature of 70°C was also too high to be tolerated by human body. There are other researchers[12,13] who have analyzed the mechanism of shape-memory effects and their applications.

Polycaprolactone (PCL) is a kind of biocompatible, biodegradable polymer material and is not toxic to living organisms.[14] PCL has a semicrystalline structure, and its crystalline melting point is 55–60°C. Once crosslinked, PCL, as crosslinked ethylene, may be made for shape-memory material with lower recoverable temperature. This kind material can be used for surgical fixation devices and drug delivery systems. However, no studies on the shape-memory behavior of PCL have been reported in the open literature. In this study, the PCLs with different molecular weight were crosslinked by γ-ray radiation, and their shape-memory behavior and their relationships with the radiation dose and the structure were investigated.

EXPERIMENTAL

Materials

PCL H4, H5, and H7 were products from Nippon Daicel Company; their weight average molecular weight (M_W) were 40,000, 50,000, and 70,000, respectively. These polymer samples were compressed into 2 mm plates in a steel mold by a 4.5 kN plate press machine. Toluene (AR grade) was bought from the Xi'an Chemical Reagent Plant.

The samples, enclosed in a PE bag with limited air; were irradiated using a cobalt-60 plate resource supplied by Xi'an Radiation Research Center, the dosage rate was 20 kGy/h. The radiation dose was 0, 50, 100, 200, 250, and 300 kGy, respectively. If some sample, for example H5, was radiated 100 kGy, it was marked as H5-100; the others were alike.
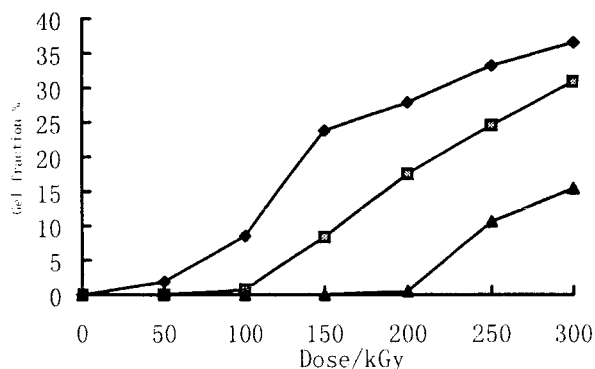

Figure 1 Gel fraction of irradiated PCL against dose: (◆) H7, (□), H5, and (▲) H4.
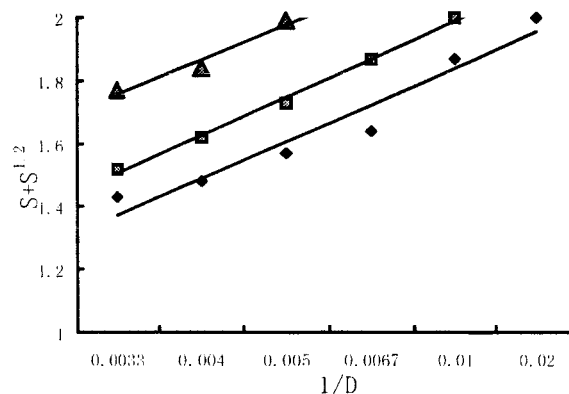

Figure 2 Relation between $S + S^{1/2}$ and $1/D$ of irradiated PCL. (◆) H7, (□) H5, and (△) H4.

Specimens for strain recovery measurements were prepared according to the following order. The compression-molded sheet was cut into 200×5×2 mm strip samples. The strip was first heated to 10°C above the melting point of the PCL crystals (actual temperature 65°C) and kept 3 min. When becoming transparent, the strip was stretched at this temperature to a double original length (deformation ϵ_0) and then cooled down immediately to a setting temperature under constrained conditions of constant length. In our work, room temperature was chosen as the setting temperature. At room temperature, withdrawing the external forces, the deformation of the samples could be maintained for a long time because the hardened crystal phase resisted the elastic recovery effectively. The deformed specimens were then used for studying the deformation recovery behavior in a process of constant heating rate.

Measurements and characterization

The gel content was determined by Soxhlet extractor with toluene (reflux 30–40 h). The ratio of insoluble material remaining mass (dried to constant weight in a vacuum oven) to original mass was defined as the gel content $G\%$ for the sample.

$$G\% = \frac{\text{mass of residue (g)}}{\text{original mass (g)}} \times 100\%$$

The thermal properties of the crosslinked PCLs were measured by using a modulated differential scanning calorimetry (MDSC, TA Instruments). The environment of the measured samples was purged with nitrogen gas, then quenched with liquid nitrogen. DSC was carried out over a temperature range from −40 to 100°C at a heating rate of 10°C/min.

Dynamic mechanical analysis (DMA) was carried out at 10 Hz and 2°C/min heating rate by using a

TABLE I
Gelation Dosage and Ratio of Degradation to
Cross linking of Different M_w PCL

Samples	M_w	Gelation dose (kGy)	p_0/q_0 (ratio of degradation to crosslinking)
H4	40,000	182	1.65
H5	50,000	91	1.38
H7	70,000	41	1.25

Figure 4 The temperature dependence of dynamic modulus for H5s with different doses. (♦) H5-0, (□) H5-100, (△) H5-200, and (×) H5-300.

Dynamic mechanical thermal analyzer (DDV-III-EA, Toyo Baldwin Co. Ltd.). The strip specimens of 20×3×2mm were used.

The shape-memory behavior was examined by a heat-shrinking test.[11] The heating rate used was around 2°C/min. The recovery process can be expressed by the temperature dependence of the strain $\epsilon(T)$ or the recovery rate $R(T)$, the percentage of the recovery strain at temperature T in the total fixed strain, $R(T) = [\epsilon_0 - \epsilon(T)]/\epsilon_0$. Through measuring the length of samples at different temperatures, the relation curves between strain recovering ratio and temperature can be drawn. Some important parameters are usually obtained from these measurements to characterize the shape-memory behavior of the samples. The final recovery rate R_f shows the recovery ability of the sample. On the recovery ratio–temperature curves, the temperature related to 50% R_f is defined as the shape-memory response temperature of the deformed samples.

RESULTS AND DISCUSSION

Radiation crosslinking of PCL

Figure 1 shows the formation of gel fraction as a function of dosage for different molecular weight PCLs. As the radiation dose increased, the gel content increased. At the same dose, the larger the molecular weight of PCL, the greater the gel fraction. The incipient gel dose of PCL with different molecular weights
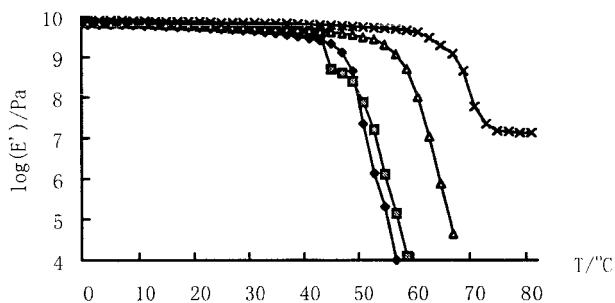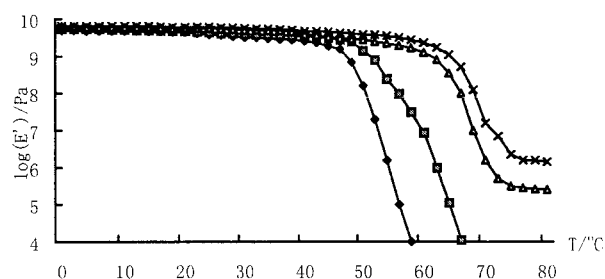
was found to be different: the higher the molecular weight, the lower the gelation dose.

Applying the Charlesby–Pinner equation,[15]

$$S + S^{1/2} = p_0/q_0 + 1/(q_0\mu_1 D)$$

(where S is sol fraction, D is radiation dose, p_0 and q_0 are constants, which indicate sensitivity of dissociation and crosslinking to radiation, respectively), the experiment data can be analyzed by plotting $S+S^{1/2}$ against $1/D$, and getting straight lines, as shown in Figure 2. This indicates that radiation crosslinking of PCL follows the law of random crosslinking. An upper extrapolation of these lines to $S+S^{1/2}=2$ gives gelation doses and the intercepts at $1/D = 0$ are p_0/q_0, these results are summarized in Table I.

From Table I, it can be clearly seen that the gelation dose of sample H7 is only 41 kGy; however, it needs 91 and 182 kGy for H5 and H4, respectively. In fact, the gel cannot be measured until the radiation dose is over 200 kGy for H4. The ratio of degradation to crosslinking (p_0/q_0) also gives the same result: the lower molecular weight PCLs have a larger p_0/q_0, the high molecular weight PCLs have a smaller p_0/q_0. These suggest that the high molecular weight PCL H7 is easier to crosslink than H5 and H4.
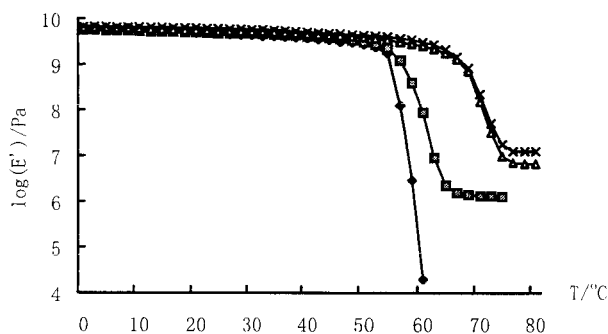

Figure 3 The DMA curves of H4s with different dosages. (♦) H4-0, (□) H4-100, (△) H4-200, and (×) H4-300.

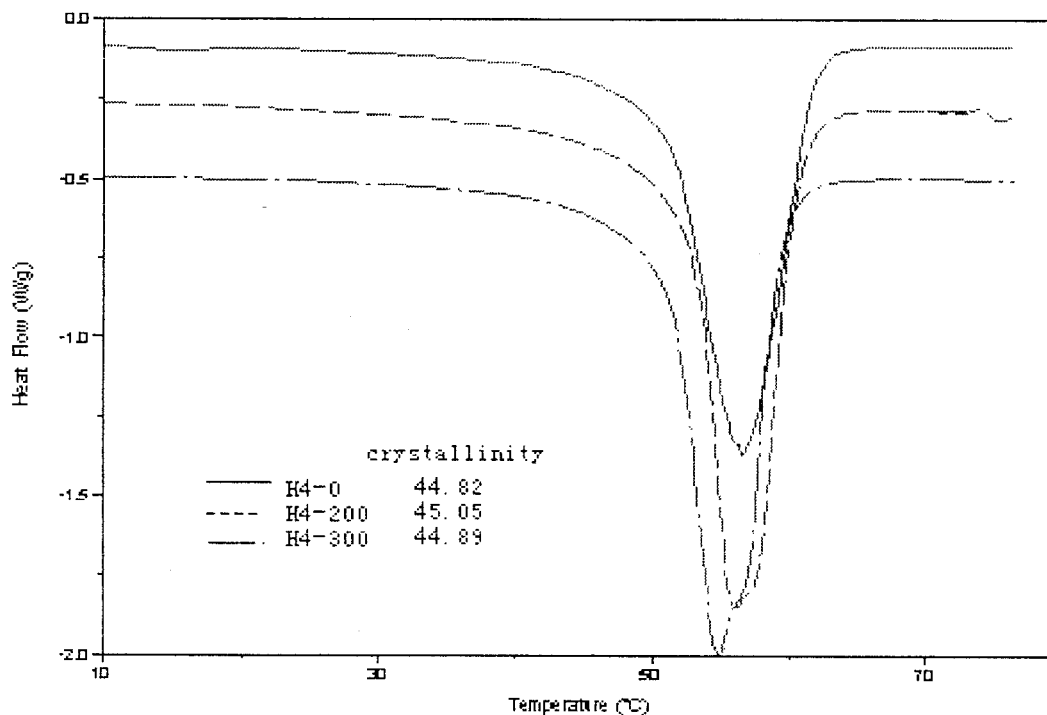**Figure 5** DMA curves of H7s with different dosages. (♦) H7-0, (□) H7-100, (△) H7-200, and (×) H7-300.

Figure 6 The DSC scanning curves of H4 samples with different radiation doses.

The heat mechanical behaviors of PCL after radiation

The temperature dependence of tensile modulus for PCLs with different molecular weights and radiation doses, displayed in Figures 3–5, show the following features.

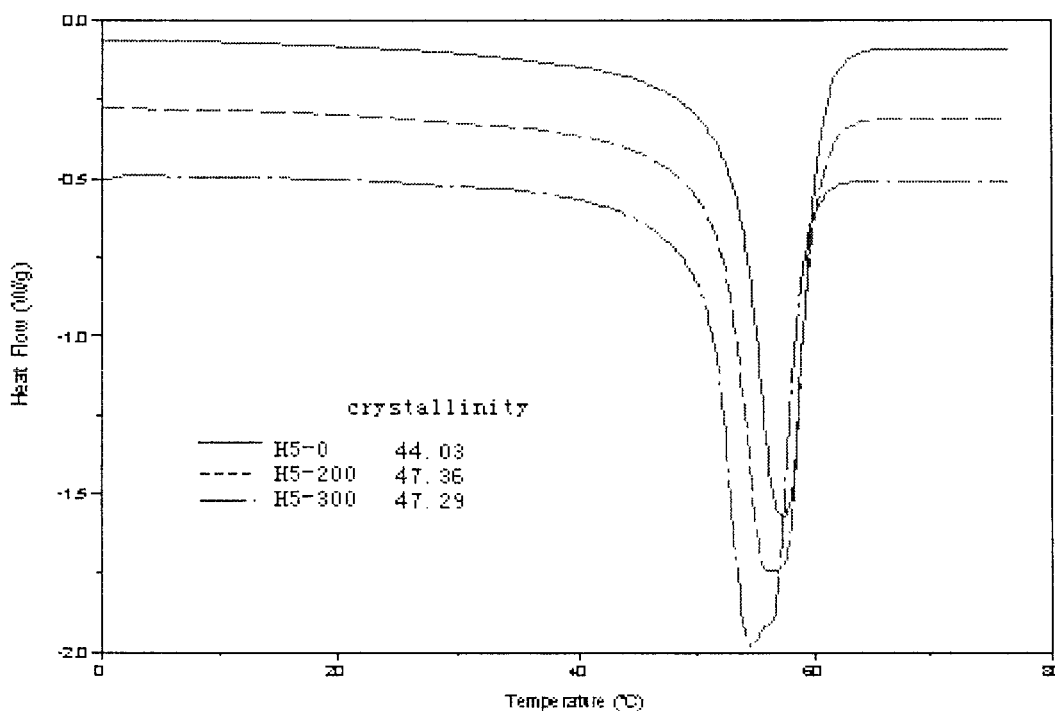The tensile modulus increases with the increase of radiation dose, this ascribes to the formation of

Figure 7 The DSC scanning curves of H5 samples with different radiation doses.
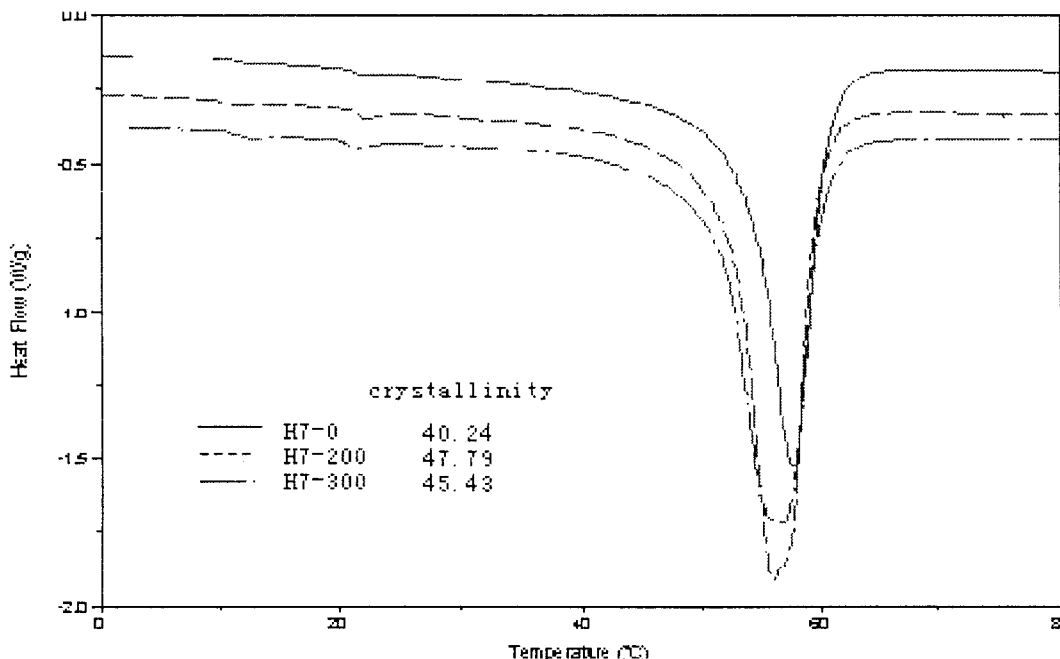
Figure 8 The DSC scanning curves of H7 samples with different radiation doses.

crosslinking network structure in the specimens. The temperature dependence of tensile modulus for crosslinked PCLs is related to the degree of crosslinking. The larger is the degree of crosslinking, the higher is the temperature of sharp transition of modulus. These sharp drops of the modulus over several decades in magnitude near 60°C are associated with the melting of crystalline. At higher a dose, the tensile modulus exhibits a plateau, the level of which is an increasing function of radiation dose (see Figs. 4 and 5). The exhibition of plateau is also attributed to the formation of net crosslinking structure at higher dose. According to an ideal rubber theory,[16]

$$G_N = \rho RT / Mc$$

(where G_N denotes the shear modulus, ρ is the polymer density, R is molar gas constant, T is absolute temperature, and Mc is the molecular weight between two junction points in the network), the modulus increases as Mc decreases. So, that the degree of crosslinking increases with the dose inevitably causes the Mc to decrease and G_N to rise. In the plateau region of the DMA curve, PCL does not melt, but presents a rubber-like state, so it can be deformed, after cooling below the crystalline melting point and releasing the external force; the deformation of PCL can be fixed because this hardened state resists the elastic recovering force of the fixed phase. The fixed phase is the crosslinked point. When heated above the melting point, the deformed PCL can recover its original shape

by the elastic recovering force of the crosslinked structure.

DSC analysis of crosslinked PCLs

The effects of radiation crosslinking on crystal melting temperature (T_m) and crystallinity of PCL were measured by using MDSC. To reduce the influence of the thermal history, all samples were heated to 100°C for 5 min, then these samples were cooled to −40°C quickly and reheated to 100°C at a heating rate of 10°C/min. The evaluation of DSC traces was based on the reported enthalpy of fusion of 139.5 J/g for 100% crystalline PCL.[14]
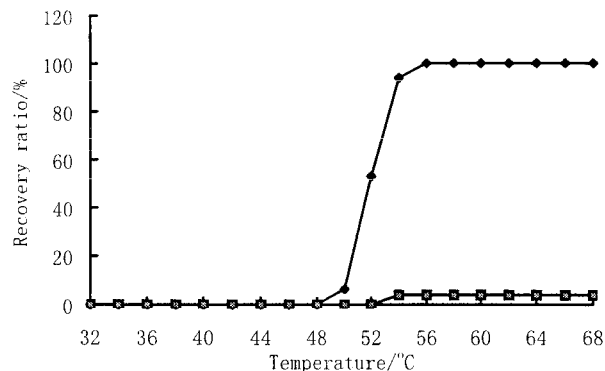

Figure 9 The strain recovery curves for PCL-H4 with different doses. (♦) H4-300 and (□) H4-200.
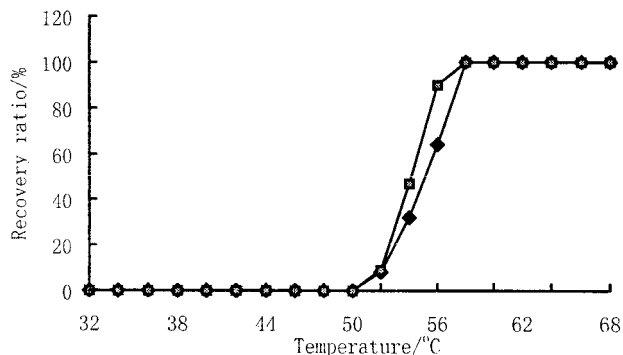
Figure 10 The strain recovery curves for PCL-H5 with different doses. (♦) H5-200 and (□) H5-300.

TABLE II
The Shape-Memory Properties: Recovered Temperature (T_r) and the Final Recovering Ratio (R_r) of the Studied Samples

Samples	The degree of cross linking (%)	T_r (°C)	Crystal melting point (DSC) (°C)	R_f (%)
H4–200	0.5	—	56.01	5
H4–300	15.4	52	54.84	100
H5–200	17.5	55	57.04	100
H5–300	30.9	54	54.69	100
H7–100	8.5	55	—	99
H7–200	27.9	54	55.97	100
H7–300	36.6	53	56.74	100

The scanning results of the different molecular weight PCLs with various radiation dose are displayed in Figures 6–8. In respect to the influences of radiation on crystal melting temperature (T_m), Figures 6–8 shows similar results—that is, the crystal melting point of PCL decreased with the increasing of radiation dose, which may be because the radiation causes crystal grain damage and confined crystallization,[17] so its melting temperature drops down. It also can be seen that the crystal melting point of crosslinked PCLs is lower—it is 56°C or so; this temperature is also the strain recovery temperature of deformed PCLs and it seems to have importance as a biomedical material because it is safe and feasible to use with human body. Molecular weight has slight influence on crystal melting point. The crystallinity decreases with the increasing of molecular weight; this is because the long chain polymer is easy to foil and fold, and difficult to arrange in crystal lattice.

As the radiation dose increases, the crystallinity increases slightly. This must be attributed to crystallization of tie segments made possible by the chain cleavage in the amorphous phase, facilitated by the radiation splitting action.[14]
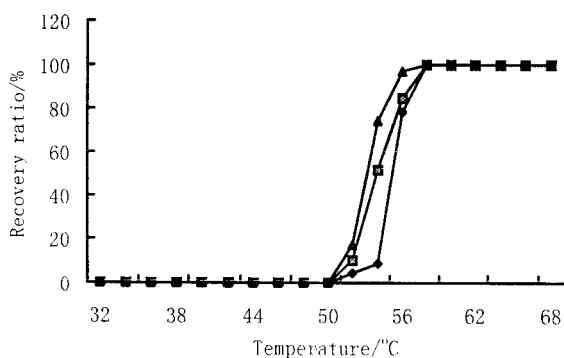
Shape-memory behavior

The shape-memory behavior of the crosslinked PCL with different molecular weights are showed in Figures 9–11. The shape recovery was measured at different temperatures. It was found that the recovery temperature of the specimens was around 56°C, which was closely related to their crystal melting temperature, and agreed with the DSC scanning results. The shape recovery approached a constant value after 62°C. This response temperature is tolerable to the human body. From Figure 9, it can be seen that the deformed strain of H4-300 sharply recovers its original shape in the vicinity of melting point of PCL, but because the recovery ratio of H4-200 is very low, it cannot recover its original shape. This means that in this case the fixed strain was mainly composed of the plastic or irreversible strain. Only when the gel content of the samples was high enough can the strain of polymer fully recover. This also suggested that the formation of a network structure for a polymer sample was very important to exhibit the typical shape-memory effect. It should be noted that the stain recovery temperature range of these PCL samples was quite narrow compared to that of EVA and segmented copolymer. The recovered temperature (T_r) decreased with the increase of radiation; this was because the crystal melting point of PCLs decreased with the increasing of radiation, and corresponded to DSC analysis. (See also Table II.)

CONCLUSION

PCL can be crosslinked by γ-radiation: the larger the molecular weight of PCL, the higher the degree of crosslinking. The relationship between gel content and radiation dose follows the Charlesby–Pinner equation. Radiation crosslinked PCL has a higher tensile modulus and heat resistance, and shows an elastic state, so it can be stretched and deformed; after cooling to room temperature, the deformation can be kept effec-

Figure 11 The strain recovery curves for PCL-H7 with different doses. (♦) H7-100, (□) H7-200, and (▲) H7-300.

tively, when heated again, the strain can recover to original shape, and render a better shape-memory behavior. The recoverable temperature of shape-memory PCL is lower than 60°C, so it is possible to prepare medical surgical fixation materials.

References

1. Ota, S. Radiation Physics Chemistry, 1981, 18(1–2), 81–87.
2. Takahashi, T.; Hayashi, N.; Hayashi, S. J Appl Polym Sci 1996, 60, 1061–1069.
3. Tobushi, H.; Hashimoto, T.; Hayashi, S.; Yamada, E. J Intelligent Material Systems and Structures 1997, 8(8), 711–718.
4. Hayashi, S.; Kondo, S. Plastics Eng 1995, (2): 29–32.
5. Hayashi, S. U.S. Pat., 5145935, 1992.
6. Hayachi, S. E.P. Pat., 0361419, 1990.
7. Kim, B. K.; Lee, S. Y.; Xu, M. Polymer 1996, 37, 5781.
8. Lee, B. S.; Chun, B. C.; Chung, Y.-C.; Sul, K. I.; Cho, J. W. Macromolecules 2001, 34 (18), 6431–6437.
9. Lin, J. R.; Chen, L. W. J Appl Polym Sci 1998, 69, 1563–1574.
10. Lin, J. R.; Chen, L. W. J Appl Polym Sci 1999, 73, 1305–1319.
11. Li, F. K.; Zhang, X.; Xu, M. J Appl Polym Sci 1999, 71, 1063–1070.
12. Bhattacharyya, A.; Tobushi, H. Polym Eng Sci 2000, 40(12), 2498–2510.
13. Hoffman, A. S.; Stayton, P. S.; Bulmus, V.; Chen, G.; Chen, J.; Cheung, C.; Chilkoti, A.; Ding, Z.; Dong, L. J Biomater Res 2000, 52(4), 577–586.
14. Pitt, C. G.; Chasalow, F. I.; Hibionada, Y. M.; et al. J Appl Polym Sci 1981, 26, 3779–3787.
15. Charlesby, A. Atomic Radiation and Polymers; London: Pergamon Press, 1960, 134–158.
16. Cowie, J. M. G. Polymers Chemistry and Physics of Modern Materials, 2nd ed.; New York: Chapman & Hall, 1991; p 314.
17. Jiang, S.; Ji, X.; An, L.; Jiang, B. Polymer 2001, 42, 3901–3907.