

Crystallization Behavior and Mechanical Properties of Crosslinked Plasticized Poly(L-lactic acid)

Zhiyuan Jia, Kunyu Zhang, Juanjuan Tan, Changyu Han, Lisong Dong, Yuming Yang

Polymer Engineering Laboratory, Changchun Institute of Applied Chemistry, Graduate School of the Chinese Academy of Sciences, Changchun 130022, China

Received 3 January 2008; accepted 16 July 2008

DOI 10.1002/app.29171

Published online 30 October 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Enhancing the stability of plasticized poly(L-lactic acid) (PLLA) with poly(ethylene glycol) (PEG) is necessary for its practical application. In this study, plasticized PLLA (PLLA/PEG 80/20 wt/wt) was crosslinked under γ -ray (Co^{60}) in the presence of triallyl isocyanurate (TAIC) as crosslinking agent. FTIR analysis revealed that PLLA, PEG, and TAIC formed a cocrosslinking structure. Crystallization behavior and mechanical properties of the crosslinked plasticized PLLA were investigated by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), scanning electron microscopy (SEM), and tensile tests. Experimental results indicated that the crystallization behaviors of both PEG and PLLA in the blends were restrained after irradiation. The melting peak of PEG in the crystallized samples

disappeared at a low irradiation doses about 10 kGy. Although PLLA still owned the behavior of crystallize, its cold crystallization temperature and glass transition temperature shifted to higher temperature. Mechanical properties of the plasticized PLLA were strengthened through crosslinking. Both yield strength and elastic modulus of the samples increased after crosslinking. Elongation at break of the crosslinked plasticized PLLA decreased with the increase of crosslinking density but remained a high value over 200%. SEM images of fracture surfaces confirmed that the ductile fracture behavior of plasticized PLLA was kept after suitable crosslinking. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1530–1539, 2009

Key words: crosslinking; crystallization; plasticized PLLA

INTRODUCTION

Poly(lactic acid) (PLA), a biodegradable polyester, which is biocompatible in the human body and renewable from nature materials, has received a lot of attention.^{1,2} PLA exists in L- and D-form, which are optical isomers. PLLA with large amount of L-form isomer is highly crystalline. Its inherent brittleness is a major disadvantage for potential industrial applications. Nevertheless, the flexibility of PLLA can be improved by modifying its physical properties through several approaches including copolymerization and blending. Blending with other biodegradable polymers might offer a cost-effective way of modifying the properties of hard and brittle PLLA. Previously, several blend systems containing PLLA have been investigated, such as PLLA/PEG,^{3–7} PLLA/poly(D-lactide) (PDLA),^{8,9} PLLA/poly(propylene oxide) (PPG),¹⁰ PLLA/poly(3-hydroxybutyrate) (PHB),¹¹ and PLLA/poly(ϵ -caprolactone) (PCL).^{6,12,13} PEG as an effective plasticizer for PLLA has better modifying effect than other polymers. However, there is evidence that this blend is not stable and the attractive mechanical properties are lost over time.

One possible reason is the process of slow crystallization of PEG from the homogeneous blends. Because the crystallization temperature of PEG is approximated to room temperature, PEG has the tendency to form a stable crystalline structure.^{3,14} In the case of melt-quenched PLLA/PEG blends, PEG is miscible with PLLA and allows a high mobility of the PLLA molecule chains before PEG crystallizing. Blends of PLLA with 20% of PEG having molecular weight of 8 kDa are unstable because of slow crystallization of PEG that depletes the plasticizer of the amorphous phase.³ The apparent change of thermal behaviors of the same blend was observed only after aging 48 h at ambient condition.³ But direct crystallization of PEG from melt-quenched blends with PLLA is very slow at room temperature. Rapid crystallization and the maximum of crystallinity of PEG can be obtained only after slowly cooling the blends from melting state following with the crystallization of PLLA.⁴ Another possible reason for the instability of plasticized PLLA is the cold crystallization of PLLA that occurs at a relative high plasticizer content.¹⁵ Cold crystallization of PLLA influences the distribution of plasticizers and reduces the plastic deformation ability of PLLA.

Crosslinking the PLLA/PEG blends may be a method to eliminate their drawbacks. Physical properties, such as crystallinity, melting point, and glass transition temperature, are affected by introducing

Correspondence to: Y. Yang (ymyang@ciac.jl.cn).

crosslinking into macromolecular chains. It is well known that crosslinking of polymer chains results in a reduction in the crystallinity of polymer,^{16–19} and the main reason for this is that the diffusion of molten polymer chains participating in the crystallization is greatly restricted because of the presence of crosslinks. When the crosslinking density is high enough, that is, the molecular weight between two neighbor crosslinks is low enough, there will be no crystallization.²⁰ The crystallinity of PEG decreases dramatically in the crosslinked networks. It was reported that PEG could not be crystallized at all when the molecular weight between two neighbor crosslink dots decreased to 1000.²¹ Similar results were also observed in PLLA, which were irradiated to crosslink in the presence of crosslinking agent triallyl isocyanurate (TAIC).^{22,23} Crosslinked PLLA show very low crystallinity because of wide formation of molecular chain network that inhibited molecular motion for crystallization.

Certainly, the biodegradability of PLLA might be influenced by the crosslinking structure. It has been reported that crosslinked PLLA with 83% gel degraded about 30% after 140 h of immersion in the enzyme bath, whereas the uncrosslinked PLLA degraded about 60% after the same processing.²⁴ It indicated that crosslinked PLLA would undergo biodegradation by naturally existing microorganisms, but needed more time. Generally, the existence of PEG can make PLLA biodegrade more rapidly for it absorbing moisture. Because of the fact that the main part of the blends is PLLA, it can be inferred that the plasticized PLLA have suitable biodegradability after crosslinking.

This work is dedicated to introducing crosslinking structure into melt-quenched PLLA/PEG blends in the presence of TAIC. So that the crystallization of PEG and PLLA could be suppressed, and then, a more stable plasticized PLLA may be obtained. Differential scanning calorimeter (DSC) and wide-angle-X-ray diffraction (WAXD) were applied to study the crystallization behavior of the crosslinked blends. A promising result was obtained that the crystallization of PEG in the blends did not appear at all, and the cold crystallization temperature of PLLA shifted to higher temperature with a moderate irradiation dose, and the crosslinked plasticized PLLA still kept the attractive mechanical properties.

EXPERIMENTAL

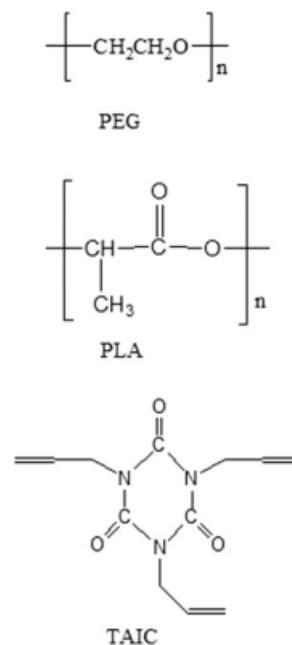
Materials

The PLLA utilized in this study was purchased from Mitsui Fine Chemicals (Tokyo, Japan) which had high optical purity about 99% L-lactide content. The PLLA exhibited a number-average molecular weight

(\bar{M}_n) of 80 kDa and polydispersity index of 1.34 (SEC analysis). The glass transition temperature (T_g) and melting temperature (T_m) of PLLA were 59.8 and 163.1°C (DSC analysis), respectively. PEG with a molecular weight of ~ 10 kDa was obtained from Fluka. Triallyl isocyanurate (TAIC) with 99% purity was friendly supplied by Shanghai Fangruida Chemicals Co. (Shanghai China) and used as received. The chemical structures of PEG, PLLA, and TAIC were shown at Scheme 1.

Sample preparation

The polymers were dried at 40°C in a vacuum oven for 24 h before use. Blending of PLLA, PEG, and TAIC was performed using a Haake mixer (Haake Rheomix 600, Germany). The melting mixing was carried out at 180°C for all the blends, the rotor speed was 60 rpm, and mixing time was 5 min. TAIC was added to the PLLA/PEG 80/20 (wt/wt) binary blend at different weight percentages (1.0, 3.0, 5.0 wt %), so, the actual PLLA/PEG/TAIC weight ratios were 79.2/19.8/1.0, 77.6/19.4/3.0, and 76.0/19.0/5.0, respectively. Addition of more than 5% of TAIC is not reasonable considering industrial application aspects. The reason for the selection of blending ratio of PLLA/PEG (80/20) is that lower content of PEG will not have enough plasticization effect on the blends, whereas higher content of PEG will make the quenched plasticized PLLA aging rapidly because of high molecular mobility of PLLA.



Scheme 1 Chemical structures of PEG, PLA and TAIC.

All the blends were pressed into 0.5-mm thick plate by pressing at 180°C for 3 min and then quenched between two thick metal blocks. The film samples were heat-sealed in the nylon/polyethylene bags with removal of the air. Then, irradiation was performed at room temperature with ^{60}Co γ -rays at a dose rate of 2.5 kGy/h and four different doses of ^{60}Co γ -rays (5 kGy, 10 kGy, 20 kGy, and 40 kGy) were directed at the films.

Characterization

The gel content of the crosslinked samples was estimated by measuring the amount of insoluble material in chloroform after 48 h with a Soxhlet extraction cycle. The gel fraction was calculated as follows:

$$\text{Gel fraction(\%)} = W_d/W_i \times 100 \quad (1)$$

where W_i is the initial weight of the dried sample after irradiation, and W_d is the weight of the dried insoluble part of sample after extraction.

Swelling behavior of crosslinked samples was revealed with the ratio of the weight of the swollen sample (W_s) and the weight of the dry samples (W_d). Here, we defined this value as “ q ” which can reflect the crosslink density indirectly. Because of the difficulty to obtain the accurate values of density of these blends, the degree of swelling generally defined was not calculated. But it would not influence the analysis of the crosslink density change of these parallel samples.

FTIR spectra (4000–500 cm^{-1} , resolution 4 cm^{-1}) was recorded in reflective absorbance mode with a Bruker Vertex 70 RTIR spectrometer for verifying the structure of crosslinked samples. Both extracted and original samples were investigated.

DSC measurements were performed on a Perkin-Elmer Diamond differential scanning calorimeter using indium and tin as the standard calibration, and nitrogen atmosphere was used throughout. To obtain the thermal behavior of samples, specimens were held at 190°C for 3 min, quenched to -50°C at 100°C/min, and then heated to 190°C at 10°C/min. The crystallization behavior of PLLA/PEG blends was studied using the following processes. The specimens were annealed at 190°C for 3 min, cooled to -50°C at 10°C/min or 2°C/min, and then, reheated to 190°C with a rate of 10°C/min. Percent crystallinity was calculated from the melting or crystallization enthalpy using heats of fusion of 197.0 Jg^{-1} for PEG²⁵ and 93.7 Jg^{-1} for PLA.²⁶

WAXD patterns were recorded in the reflection mode at room temperature on Phillips PW1700 automatic power diffractometer with Ni-filtered $\text{Cu}_{k\alpha}$ radiation. The scans were obtained with a step scan-

ning rate of 5°/min. Measurements were performed in the range $5^\circ < 2\theta < 40^\circ$. The samples were obtained by cooling in a Linkam hot stage (THMS 600) from 190°C to -50°C at 2°C/min.

Tensile tests were carried out on an Instron 1185 tensile testing machine at a rate of 10 mm/min at room temperature. Oar-shaped specimens with 20.0 mm gauge length, and width of 4.0 mm, were cut from 0.5 mm thick films for this test. At least three samples of each type were drawn to fracture.

The fracture surfaces of tensile specimens were observed using a field emission-scanning electron microscopy (FESEM, XL 30, Philips). All the fracture surfaces were sputter coated with gold to provide enhanced conductivity.

RESULTS AND DISCUSSION

Thermal properties and crystallization behavior of plasticized PLLA

Exemplary heating thermograms of the films of melt-quenched PLLA and plasticized PLLA are shown in Figure 1. As it has been known, PEG was an efficient plasticizer for PLLA, which decreased T_g from about 59.1°C for neat PLLA to 42.4°C and 28.1°C for the blends with 10 and 20 wt % of PEG, respectively. And it can be seen that TAIC had also a plasticizing effect on PLLA. The glass transition of the blends shifted to lower temperature with the content of TAIC increasing. The T_g decreased from 28.1°C for quenched PLLA/PEG 80/20 blend to 20.5°C for PLLA/PEG/TAIC 76/19/5 blend. All of the blends exhibited single glass transition, and no

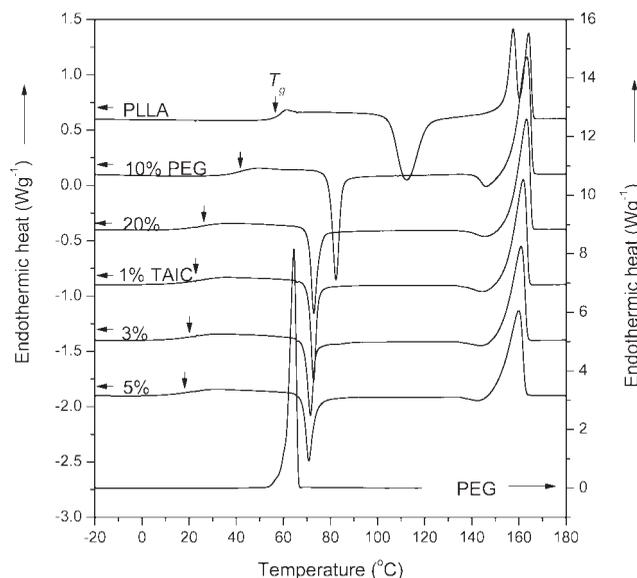


Figure 1 Thermograms of quenched PLLA and plasticized PLLA obtained with a heating rate of 10°C/min.

separate melting of PEG or TAIC crystals were found in these blends. The cold crystallization temperature of PLLA also shifted to the low temperature paralleling with the decrease of T_g dependent with the content of plasticizers.

It was noticed that quenched PLLA cold-crystallized at 114.7°C with crystallization enthalpy of 27.7 Jg⁻¹, and subsequent melting at 163.1°C with melting crystallization of 32.5 Jg⁻¹ when heating at 10°C/min. It appeared that this PLLA had a good crystallizable ability, which corresponded to its high optical purity. The double melting peak of PLLA has been attributed to melt-reorganization,^{27–29} which resulted in the excess of melting enthalpy over the crystallization enthalpy of PLLA. Quenched neat PEG was still highly crystalline; it achieved 90% crystallinity with melting temperature of 66.0°C. However, PEG did not crystallize in the blends during quenching or during subsequent heating.

Thermograms of PLLA/PEG/TAIC 76/19/5 with different cooling rates are shown in Figure 2(a). The results were similar with Hu et al.'s work,⁴ except that the utilized PLLA had a better crystallizable ability. Generally, with PEG content lower than 30 wt %, melt-quenched PLLA/PEG blends are amorphous without any crystallization. When this blend is cooled from melt with a slow cooling rate, PLLA firstly crystallizes from the blends, and then, PEG crystallizes. PLLA can crystallize in a slow cooling process or cold-crystallize in the heating process, then melt at higher temperature. So, its melting temperature is almost not influenced by the cooling rates. Although the crystallization of PEG is influenced by the crystallization of PLLA, it can not crystallize without the crystallization of PLLA. The cooling rate influenced the crystallization of PLLA in the cooling process, and then the crystallization of PEG is also affected. But PEG can not cold-crystallize in the heating process, so the melting temperature of PEG is also influenced. As it can be seen from this figure that PLLA crystallized during cooling process when the cooling rate was 20°C/min or less, and followed by the crystallization of PEG at a lower temperature. Crystallization temperature of PLLA increased as the cooling rate decreased. The effect of cooling rate on the subsequent heating thermogram is shown in Figure 2(b). As the cooling rate decreasing, an endothermic peak corresponding to melting of PEG appeared at about 50°C in the heating thermogram. The melting enthalpy of PEG in the heating thermogram corresponded to its crystallization enthalpy in the cooling thermogram. As observed, the melting peak of PEG almost did not change when the cooling rate was lower than 10°C/min, and the cold crystallization peak of PLLA disappeared entirely when the cooling rate was 10°C/min or less. The subsequent melting temperature

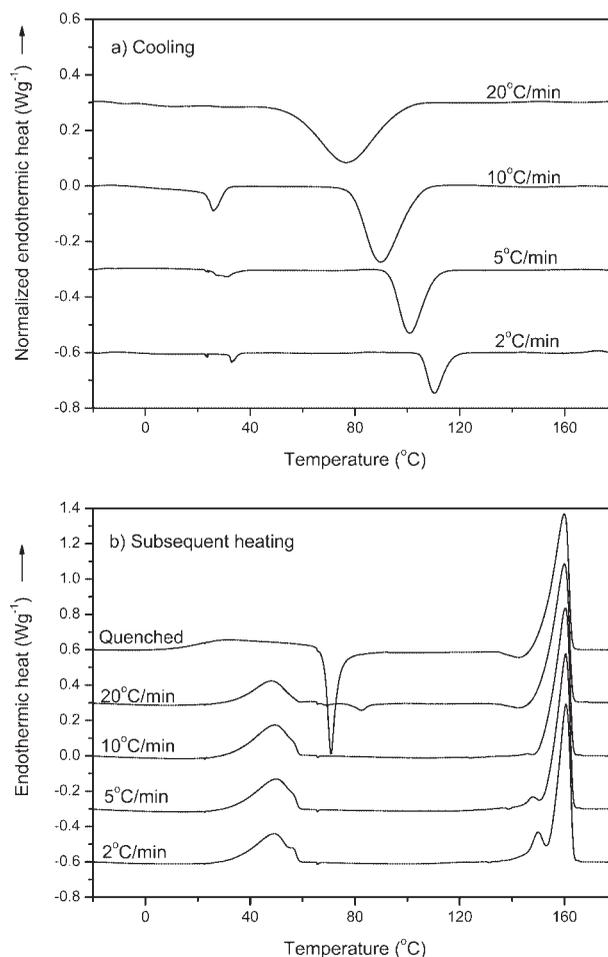


Figure 2 Effect of cooling rate on crystallization and melting thermograms of PLLA/PEG/TAIC 76/19/5: (a) Cooling thermograms obtained with the cooling rate indicated; and (b) Subsequent heating thermograms obtained with a heating rate of 10°C/min.

and melting enthalpy of PLLA almost kept constant. Only the double melting peak of PLLA became more pronounced at lower cooling rate.

Qualitatively, it appeared that if the cooling rate was slow enough, PLLA was able to crystallize during cooling. Slower cooling increased the amount of PLLA crystallization, and the melting enthalpy did not continue increasing when the cooling rate was lower than 10°C/min. So, it can be assumed that essentially complete crystallization of PLLA was achieved at a cooling rate of 10°C/min or less. If the cooling rate was such that PLLA incompletely crystallized during cooling, crystallization was completed during subsequent heating, as indicated by a cold-crystallization exotherm. Crystallization of the PLLA during cooling facilitated crystallization of PEG. Increasing PLLA crystallinity paralleled increasing PEG crystallinity as the cooling rate became slower. However, if PEG incompletely

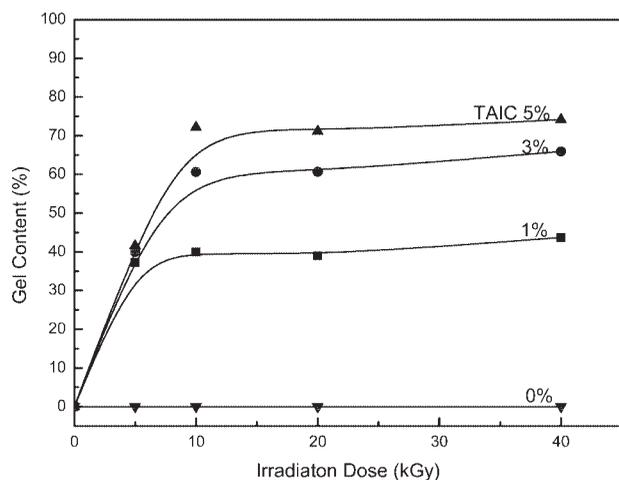


Figure 3 Gel contents of crosslinked PLLA/PEG 80/20 blends in the presence TAIC as a function of irradiation dose. The contents of TAIC are indicated in the figure.

crystallized during cooling, it did not crystallize further during subsequent heating.

Crosslinking behavior and structure

TAIC has been proved to be a good crosslinking agent for PLLA in combination with γ -irradiation.²² In case of PLLA/PEG blends, it also showed good crosslinking effect. Figure 3 shows the gel content of irradiated PLLA/PEG 80/20 blend containing different amounts of TAIC. It can be seen that gels were not formed for irradiated "pure" PLLA/PEG 80/20 blend until the irradiation doses was 40 kGy. However, with the presence of TAIC, the gel contents increased significantly. Crosslinking of this blend started at a low content (1.0 wt %) of TAIC and low irradiation dose (lower than 5 kGy). The gel fraction of PLLA/PEG 80/20 blends are 40.0, 60.6, and 72.2% at 10 kGy by adding 1, 3, and 5% of TAIC, respectively. The gel content increased with the increase of irradiation dose up to 10 kGy at the same content of TAIC. But the gel content did not continue increasing and almost kept constant when the irradiation dose was more than 10 kGy. The blends containing 5.0% TAIC had higher gel content than blends containing 1.0 and 3.0% TAIC at the same irradiation dose. The maximum value of gel fraction was achieved in the presence of 5% TAIC at dose of 40 kGy for the blends.

The swelling behavior of the crosslinked samples is shown in Table I. The q was defined as the ratio of the weight of the swollen sample (W_s) and the weight of the dry samples (W_d), which can indicate the crosslinking density indirectly. If the crosslink density of parallel samples is higher, the value of q is lower. It is interesting that the q value of cross-

TABLE I
Swelling Behavior of Crosslinked PLLA/PEG/TAIC Blends

| Irradiation dose (kGy) | TAIC 1% | TAIC 3% | TAIC 5% |
|------------------------|---------|---------|---------|
| 5 | – | 20.4 | 21.5 |
| 10 | 16.0 | 12.4 | 6.8 |
| 20 | 29.2 | 10.6 | 6.2 |
| 40 | 31.9 | 15.0 | 9.8 |

The values of q are indicated in the table.

linked samples with the same content of TAIC decreased with the increase of irradiation doses firstly, then significantly augmented when the irradiation dose was more than 20 kGy. However, the gel content almost remained constant at the same time. This is ascribed to the change of crosslinking density in the gel. The effect of radiation on polymer is generally divided into main-chain scission (degradation) and crosslinking (polymerization). PLA mainly undergoes chain-scissions at doses below 250 kGy,^{30,31} but PLA is able to crosslink at a low irradiation dose with the presence of TAIC.²² Crosslinking and main-chain scission took place simultaneously in the PLLA/PEG/TAIC blends under irradiation. Because of the presence of TAIC, crosslinking was dominant in the blends firstly. However, TAIC was continuously consumed with the increase of irradiation dose, then, the effect of irradiation gradually changed from crosslinking to decomposition. As a result, the change of crosslinking density varied from increase to decrease when the irradiation dose was high enough.

For determining the structure of the crosslinked blends, reflective FTIR spectra of original samples and extracted samples were investigated and shown in Figure 4. The peaks at 1756, 1690, and 1083 cm^{-1}

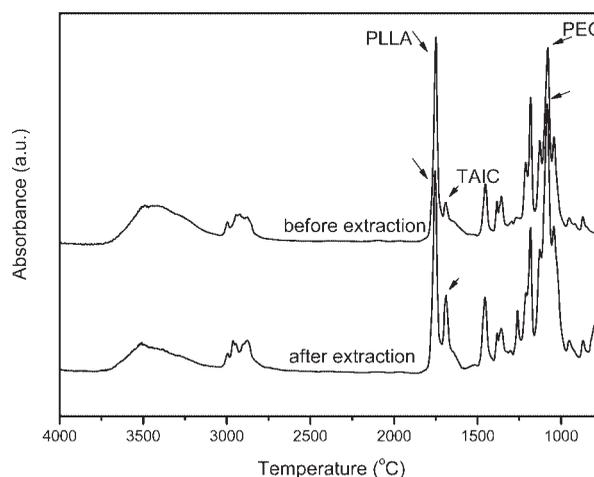
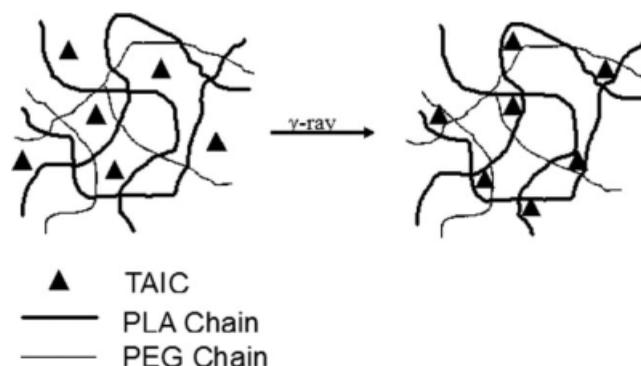


Figure 4 FTIR spectra of extracted and original PLLA/PEG/TAIC 76/19/5 with 20 kGy irradiation dose.



Scheme 2 Basic forms of PLLA and PEG cocrosslinking networks in the presence of TAIC.

corresponded to the C=O stretching mode of PLLA, the C=O stretching mode of TAIC, and the C—O—C stretching mode of PLLA and PEG in the blends, respectively. All these three peaks existed after extraction. Hereby, the presence of TAIC, PEG, and PLA in the gel can be confirmed. The enhanced peak at 1690 cm^{-1} after extraction indicated that the content of TAIC was higher than that of the original sample. Furthermore, the ratio of peak intensity of 1756 cm^{-1} and 1083 cm^{-1} decreased after extraction suggested higher content of PEG in the gel compared with the original sample. So, the crosslinking structure of the blend is imagined as shown in Scheme 2, which is a cocrosslinking networks composed by PLLA, PEG, and TAIC.

Thermal properties and crystallization behavior of crosslinked plasticized PLLA

Thermograms of crosslinked quenched PLLA/PEG/TAIC blends with different irradiation doses are shown in Figure 5. With the content of TAIC increasing, the change of thermal property of the blends irradiated at the same dose became more notable. The glass transition and cold-crystallization temperature of all the blends shifted to higher temperature through crosslinking. Especially for PLLA/PEG/TAIC 76/19/5, the cold crystallization temperature increased over 100°C with 20 kGy irradiation dose, which is only little lower than that of neat PLLA. The glass transition temperatures of all the blends were lower than 35°C , which was considered as the transition temperature for plasticized PLLA from brittle to ductile behavior.⁷ However, T_g and T_{cc} of these blends did not increase linearly with the increase of irradiation doses. The changes of T_g , T_{cc} , and T_m of plasticized PLLA after irradiation are plotted in Figure 6. The values of T_g and T_{cc} of all the blends decreased when the irradiation dose was more than 20 kGy. This result should be attributed to the change of crosslinking density. Both the glass

transition temperature and cold crystallization temperature increased with the increase of crosslinking density. Melting temperature of crosslinked PLLA/PEG/TAIC blends decreased with increasing the irradiation dose, but increased slightly when the dose was 40 kGy.

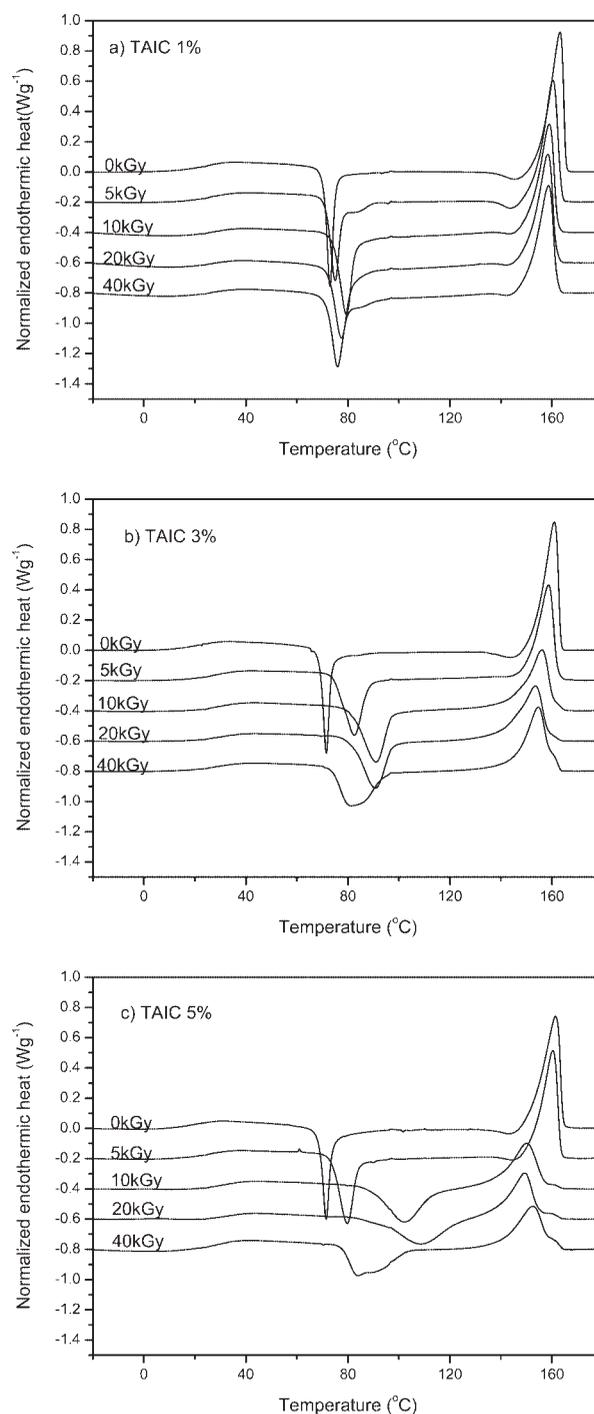


Figure 5 DSC thermograms of quenched PLLA/PEG 80/20 blends with different content of TAIC after irradiation obtained with a heating rate of $10^\circ\text{C}/\text{min}$: (a) TAIC 1%; (b) TAIC 3%; and (c) TAIC 5%.

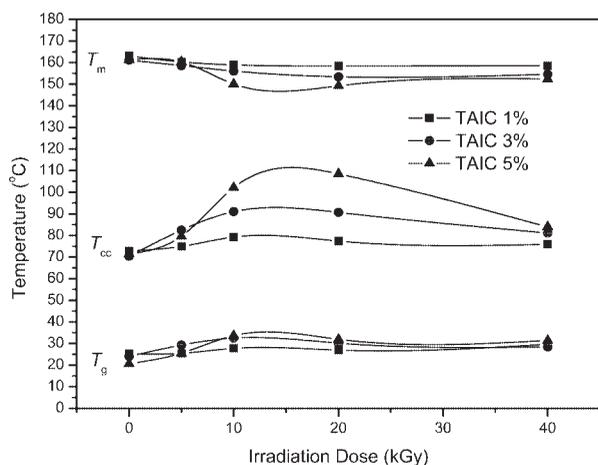


Figure 6 The change of T_g , T_{cc} , and T_m of plasticized PLLA after irradiation.

Because thermal properties of PLLA/PEG/TAIC 76/19/5 had tremendous changes after irradiation, their crystallization behaviors were investigated in detail subsequently. Thermograms of crystallized PLLA/PEG/TAIC 76/19/5 with different irradiation doses are shown in Figure 7(a,b) with cooling rate of $10^\circ\text{C}/\text{min}$ and $2^\circ\text{C}/\text{min}$, respectively. It is apparent that the crystallization of PEG in the blends was suppressed. Melting peak of PEG in the crystallized samples disappeared when the irradiation doses were more than 5 kGy. When the cooling rate was $2^\circ\text{C}/\text{min}$, PLLA already completely crystallized during the cooling process, but still not followed by crystallization of PEG at a lower temperature. PEG molecules were mostly fixed by crosslinks in amorphous state, so that no crystallization or melting was permitted. PLLA still had the ability to crystallize in the crosslinking networks, but was also suppressed. The cooling rate of $10^\circ\text{C}/\text{min}$ was not slow enough for PLLA to crystallize at the cooling process. The cold crystallization appeared and shifted to higher temperature with increasing crosslinking density. Table II shows the thermal properties of PLLA/PEG/TAIC 76/19/5 after a cooling process ($10^\circ\text{C}/\text{min}$) with different irradiation doses. The values are normalized to the amount of the constituent in the blend. It was noticed that the T_g of crosslinked plasticized PLLA can increase over 30°C and the enthalpy of melt of PLLA decreased significantly, which was helpful for improving their stability.

For further identifying the crystallization behavior of crosslinked plasticized PLLA, WAXD was used. All the samples were heated to 190°C for 3 min then cooled to -50°C at $2^\circ\text{C}/\text{min}$ using Linkam hot stage THMS 600. The cooling process was slow enough to ensure that PLLA and PEG could sufficiently crystallize from the blends. One interesting result we can see clearly from the WAXD patterns in Figure 8 is

that PEG in the PLLA/PEG/TAIC 76/19/5 blend only showed one diffraction peak at about 23.1° , and this peak disappeared with irradiation dose 20 kGy. The reason for this result is that another main peak of PEG was covered up by the peak of PLLA at 18.8° , and the crystallization of PEG was suppressed by the presence of crosslink networks. This investigation further confirmed the results from DSC.

Mechanical properties

The mechanical properties of PLLA/PEG/TAIC 76/19/5 blend with different irradiation doses were studied. Test samples were obtained by compression molding at 190°C and subsequently quenched between two thick metal blocks. After irradiation crosslinking, tensile test was performed on these samples. The average values of yielding strength and elongation at break are presented in Figure 9.

Generally, PLLA shows high elastic modulus and tensile strength and is quite brittle with elongation at break only about 3–5%. PEG as an effective

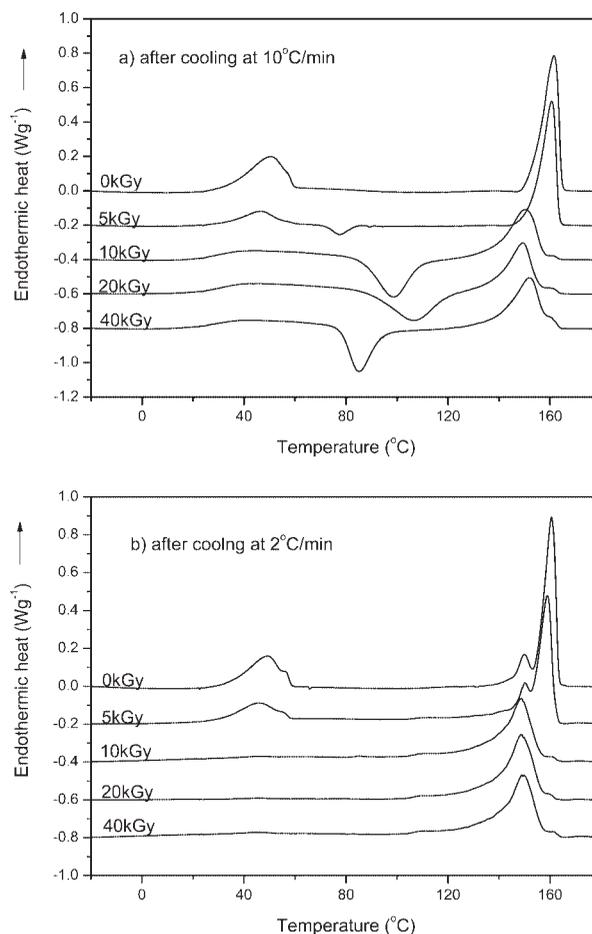


Figure 7 DSC thermograms of irradiated PLLA/PEG/TAIC 76/19/5 after different cooling process obtained with a heating rate of $10^\circ\text{C}/\text{min}$: (a) the cooling rate is $10^\circ\text{C}/\text{min}$; and (b) $2^\circ\text{C}/\text{min}$.

TABLE II
Thermal Properties of PLLA/PEG/TAIC 76/19/5 after a Cooling Process (10°C/min) with Different Irradiation Doses

| Irradiation Dose (kGy) | Blends T_g (°C) | PEG melting | | | PLA cold crystallization | | | PLA melting | | |
|------------------------|-------------------|-------------|--------------------------------|-----------|--------------------------|--------------------------------|-----------|-------------|--------------------------------|-----------|
| | | T_m (°C) | ΔH (Jg ⁻¹) | X_C (%) | T_C (°C) | ΔH (Jg ⁻¹) | X_C (%) | T_m (°C) | ΔH (Jg ⁻¹) | X_C (%) |
| 0 | – | 50.5 | 16.6 | 44.3 | – | – | – | 161.6 | 35.4 | 49.7 |
| 5 | – | 46.4 | 6.3 | 16.8 | 77.2 | –1.4 | 2.0 | 160.7 | 30.1 | 42.3 |
| 10 | 32.5 | – | – | – | 98.6 | –22.4 | 31.4 | 150.4 | 24.4 | 34.3 |
| 20 | 32.2 | – | – | – | 106.3 | –22.0 | 30.9 | 149.2 | 22.3 | 31.3 |
| 40 | 33.1 | – | – | – | 85.0 | –17.4 | 24.4 | 152.1 | 24.5 | 34.4 |

plasticizer of PLLA improves the mobility of PLLA segment and enhances its plastic elongation. As shown in Figure 9, the elongation at break of plasticized PLLA without irradiation was about 320%, which was about 100 times of the value of neat PLLA. It is well known that crosslinking has tremendous influence on the mechanical properties of polymer. After crosslinking, the plasticized PLLA was apparently strengthened. The yielding strength increased from about 10 MPa for the uncrosslinked samples to 30 MPa for the samples with irradiation dose 10 kGy. The elongation at break of plasticized PLLA decreased after crosslinking, but it still kept a high value over 200%, which indicated that crosslinked plasticized PLLA still kept a good ductile behavior.

It is noticed that the elongation at break of crosslinked plasticized PLLA firstly decreased in dependence on the irradiation dose, then increased when the irradiation dose was over 20 kGy. This phenomenon should be attributed to the change of crosslinking density as mentioned. Because of the bondage to the polymer chains of crosslinking, the elongation at break of the blends decreased with the increase of crosslinking density. But it is interesting that yield-

ing strength did not always increase with the increase of crosslinking density, it also decreased when the irradiation dose was more than 10 kGy, which suggested that too high crosslinking density might not have a positive effect on the yielding strength.

As it is well-known, fracture surfaces can reflect the mechanical properties of polymer blends. To further study the mechanical properties, the fracture surfaces of the tensile specimens was investigated by SEM and shown in Figure 10. Fracture surfaces of neat PLLA revealed features typical of brittle fracture of a glassy polymer with little plastic deformation. On the contrary, a large amount of plastically deformation was apparently visible on the fracture surfaces of the specimens of PLLA/PEG/TAIC 76/19/5. The ductile behavior of plasticized PLLA was expected to remain after irradiation crosslinking. We can see that PLLA/PEG/TAIC 76/19/5 with 20 kGy irradiation dose, which had the biggest crosslinking density also showed typical features of ductile materials from the SEM figure. But the fracture surfaces of irradiated sample were not as notable as that of the unirradiated samples, which may be attributed to the crosslinking strengthening.

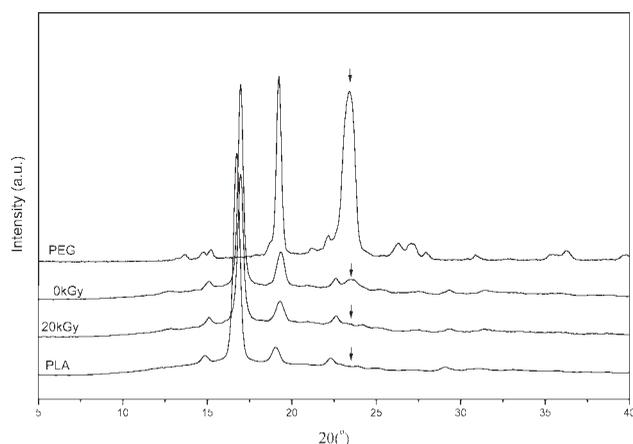


Figure 8 WAXD patterns for crystallized PEG, PLLA, and irradiated PLLA/PEG/TAIC 76/19/5. The irradiation doses are indicated in the figure.

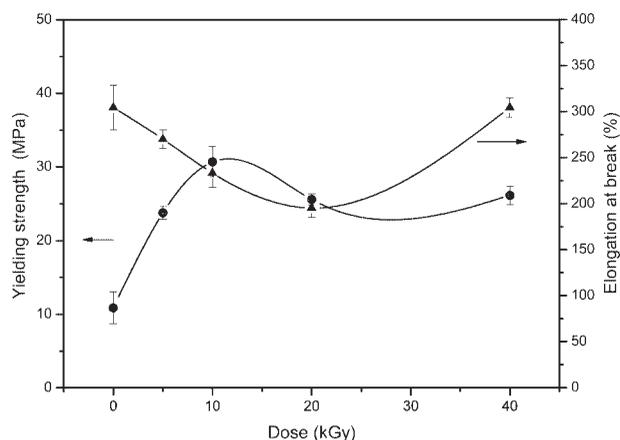


Figure 9 Tensile properties of PLLA/PEG/TAIC 76/19/5 blend with different irradiation doses.

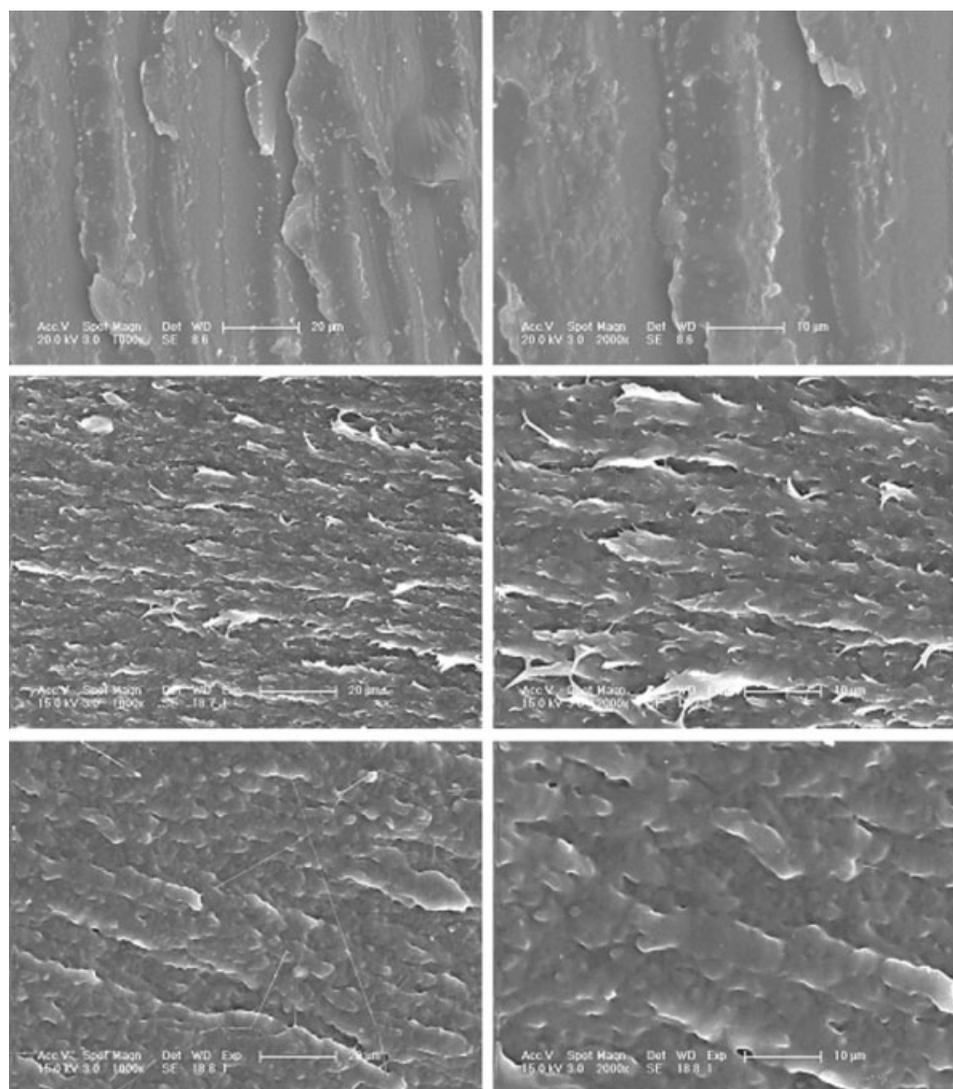


Figure 10 SEM micrographs of fracture surfaces of tensile specimens: neat PLLA (A,B), PLLA/PEG/TAIC 76/19/5 (C,D), and PLLA/PEG/TAIC 76/19/5 with 20 kGy irradiation dose (E,F).

CONCLUSIONS

PLLA/PEG 80/20 blend can be induced to crosslink by γ -irradiation in the presence of TAIC. Through crosslinking, the thermal behavior and crystallization of the blends varied significantly. It was found that the melting peak of PEG in the plasticized PLLA with TAIC content of 5% disappeared at the second heating thermogram even after a 2°C/min cooling process when the irradiation doses were more than 5 kGy. It indicated that the crystallization behavior of PEG in the blends was restrained. The same conclusion can be reached from the WAXD results. The crystallization behavior of PLLA in the blends was also influenced. The glass transition and cold crystallization temperature of plasticized PLLA shifted to higher temperature through crosslinking. FTIR data indicated that PLLA, PEG, and TAIC had formed a cocrosslinking structure. The ductile behaviors of

plasticized PLLA were kept after crosslinking, which was identified by tensile tests and the analysis of SEM microphotos. This method may be useful for obtaining more stable plasticized PLLA.

References

1. Sodergard, A.; Stolt, M. *Prog Polym Sci* 2002, 27, 1123.
2. Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv Mater* 2000, 12, 1841.
3. Hu, Y.; Hu, Y. S.; Topolkaev, V.; Hiltner, A.; Baer, E. *Polymer* 2003, 44, 5711.
4. Hu, Y.; Hu, Y. S.; Topolkaev, V.; Hiltner, A.; Baer, E. *Polymer* 2003, 44, 5681.
5. Sheth, M.; Kumar, R. A.; Dave, V.; Gross, R. A.; McCarthy, S. P. *J Appl Polym Sci* 1997, 66, 1495.
6. Yang, J. M.; Chen, H. L.; You, J. W.; Hwang, J. C. *Polym J* 1997, 29, 657.
7. Baiardo, M.; Frisoni, G.; Scandola, M.; Rimelen, M.; Lips, D.; Ruffieux, K.; Wintermantel, E. *J Appl Polym Sci* 2003, 90, 1731.
8. Tsuji, H. *Biomaterials* 2003, 24, 537.

9. Tsuji, H.; Hyon, S. H.; Ikada, Y. *Macromolecules* 1991, 24, 5651.
10. Kulinski, Z.; Piorkowska, E.; Gadzinowska, K.; Stasiak, M. *Bio-macromolecules* 2006, 7, 2128.
11. Blumm, E.; Owen, A. *J Polymer* 1995, 36, 4077.
12. Rusa, C. C.; Tonelli, A. E. *Macromolecules* 2000, 33, 5321.
13. Tsuji, H.; Mizuno, A.; Ikada, Y. *J Appl Polym Sci* 1998, 70, 2259.
14. Hu, Y.; Rogunova, M.; Topolkaev, V.; Hiltner, A.; Baer, E. *Polymer* 2003, 44, 5701.
15. Kulinski, Z.; Piorkowska, E. *Polymer* 2005, 46, 10290.
16. Takahashi, H.; Shibayama, M.; Fujisawa, H.; Nomura, S. *Macromolecules* 1995, 28, 8824.
17. Shibayama, M.; Takahashi, H.; Yamaguchi, H.; Sakurai, S.; Nomura, S. *Polymer* 1994, 35, 2944.
18. Weimann, P. A.; Hajduk, D. A.; Chu, C.; Chaffin, K. A.; Brodil, J. C.; Bates, F. S. *J Polym Sci Part B: Polym Phys* 1999, 37, 2053.
19. Hamley, I. W.; Fairclough, J. P. A.; Ryan, A. J.; Bates, F. S.; Towns Andrews, E. *Polymer* 1996, 37, 4425.
20. Treloar, L. R. G. *The Physics of Rubber Elasticity*, 2nd ed.; Clarendon Press: Oxford, 1958, p 287.
21. Qiao, C. D.; Jiang, S. C.; Dong, D. W.; Ji, X. L.; An, L. J.; Jiang, B. Z. *Macromol Rapid Commun* 2004, 25, 659.
22. Jin, F. Z.; Hyon, S. H.; Iwata, H.; Tsutsumi, S. *Macromol Rapid Commun* 2002, 23, 909.
23. Mitomo, H.; Kaneda, A.; Quynh, T. M.; Nagasawa, N.; Yoshii, F. *Polymer* 2005, 46, 4695.
24. Nagasawa, N.; Kaneda, A.; Kanazawa, S.; Yagi, T.; Mitomo, H.; Yoshii, F.; Tamada, M. *Nucl Instrum Methods Phys Res B* 2005, 236, 611.
25. Campbell, C.; Viras, K.; Richardson, M. J.; Masters, A. J.; Booth, C. *Makromol Chem* 1993, 194, 799.
26. Tsuji, H.; Ikada, Y. *Macromol Chem Phys* 1996, 197, 3483.
27. Di Lorenzo, M. L. *J Appl Polym Sci* 2006, 100, 3145.
28. Yasuniwa, M.; Tsubakihara, S.; Iura, K.; Ono, Y.; Dan, Y.; Takahashi, K. *Polymer* 2006, 47, 7554.
29. Martin, O.; Averous, L. *Polymer* 2001, 42, 6209.
30. Collet, J. H.; Lim, L. Y.; Gould, P. L. *Polym Prepr* 1989, 30, 468.
31. Gupta, M. C.; Deshmukh, V. G. *Polymer* 1983, 24, 827.