Surface-Initiated Ring-Opening Polymerization of ε-Caprolactone from the Surface of PP Film

Yuan Sui,[1,2] Jingbo Zhao,[1,2] Shenghua Gan,[1,2] Hongchi Zhao,[1,2] Wantai Yang[1,2]

[1]State Key Laboratory of Chemical Resource Engineering, Ministry of Education, Beijing 100029, People's Republic of China
[2]Department of Polymer Science, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

ABSTRACT: This article presents the ring-opening polymerization of ε-caprolactone (ε-CL) from PP film modified with an initiator layer composed of —OSn(Oct) groups. This method consists of two steps: (1) Sn(Oct)$_2$ exchanged with the hydroxyl groups on the surface of PP film, forming the —OSn(Oct) groups bonded on the surface; (2) surface-initiated ring-opening polymerization of ε-CL with the —OSn(Oct) groups. The initiator layer is characterized by attenuated total reflectance-Fourier transform infrared (ATR-FTIR), contact angles, and X-ray photoelectron spectroscopy (XPS). The growth of PCL chains from the initiator layer through ring-opening polymerization is successfully achieved. ATR-FTIR, XPS, and scanning electron microscope (SEM) are also used to characterize the grafted film. XPS results reveal that the PCL chains cover the surface of PP film after 4 h. The SEM images reveal that the PCL chain clusters grow into regular spheroidal particles, which can be changed into other different morphology by treated with different solvents. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 877–884, 2007

Key words: surface-initiated; ring-opening polymerization; poly(propylene); modification

INTRODUCTION

Surface modification of polymers is of great importance in many fields such as printing, coating, fibers, membranes, and biomedical technologies.[1] Many methods including physical deposition, coating, chemical modification, graft polymerization were used for surface modification. Of these methods, the surface graft polymerization has been extensively studied. Generally, there are two common methods for graft polymerization. One is "grafting to" technology, i.e., end-functionalized polymer molecules react with an appropriate substrate to form grafted copolymer; this method is limited by the steric hindrance from the surface because macromolecules do not easily reach to the reactive sites. The other method is "grafting from," which is a very promising approach for the preparation of the surface grafted copolymers. Immobilized initiators on the surface of polymer substrate can in situ generate grafted polymer. By this method, higher surface grafting densities can be obtained, because

monomers can more easily diffuse toward the reactive centers. Various polymerization methods have been applied to surface-initiated polymerization (SIP), including radical,[2] cationic,[3–5] anionic,[6–8] ring-opening metathesis,[9] and ring-opening polymerization (ROP).[10–14] Recently, biocompatible and/or biodegradable polymers grown from solid substrate surface by ring-opening polymerization have been investigated.[10,12–15] Langer and Choi demonstrated that Sn(Oct)$_2$-catalyzed, surface-initiated polymerization of L-lactide (LA) from gold and silicon oxide surfaces to coat the surfaces with a biocompatible and biodegradable poly(lactic acid) (PLA).[12] Hedrick and coworkers reported Sn(OTf)$_2$-catalyzed SIP of LA, where PLA was grown from a gold surface in a living fashion.[11] Poly(p-dioxanone) (PPDX) was also grown from gold and silicon oxide surface by AlEt$_3$-catalyzed, ring-opening polymerization.[14]

Polycaprolactone (PCL) is a synthetic aliphatic polyester, which is a biodegradable and biocompatible polymer, and widely used in biomedical field. Coating of solid substrates with PCL has also been investigated recently. Dubois and coworkers reported a living ring-opening polymerization of ε-caprolactone (ε-CL) from the surface of starch granules with various metallic compound catalysts including AlEt$_3$, Al(OiPr)$_3$, and Sn(Oct)$_2$.[16] Inorganic nanoparticles such as silica and/or cadmium sulfide[17–19] were also been chosen as substrate on which ε-CL was initiated with metallic compound catalysts by ring-opening

polymerization. Choi et al. demonstrated enzyme-catalyzed, surface-initiated polymerization of ε-CL from gold surfaces to coat the surfaces with PCL.[15] Over the past few years, controlled surface-initiated ring-opening polymerization of ε-CL was used to fabricate patterned polymer brush on patterned SAMs surface.[13] Up to now, the substrates of SIP are restricted to gold, silver, or silicon oxide,[11–14] other substrates such as polymers[10] have still little been used.

Stannous(II) octoate (Sn(O(O)CCH(C_2H_5)C_4H_9)$_2$, denoted as Sn(Oct)$_2$, is the most often used initiator in the ring-opening polymerization of ε-CL because of its approval from FDA as a food stabilizer. Two mechanism on Sn(Oct)$_2$-catalyzed ring-opening polymerization of lactones have been proposed: an activated monomer mechanism and a coordination-insertion mechanism. In the activated monomer mechanism, Sn(Oct)$_2$ activated monomer by forming a donor–acceptor complex, which participated directly in the propagation. Sn(Oct)$_2$ is liberated in every step of the propagation.[20–23] In the coordination-insertion mechanism, a compound containing a hydroxyl group reacts with Sn(Oct)$_2$ to formed the actual initiator, i.e., tin(II) alkoxide or hydroxide.[24–30] Recent mechanistic studies support the coordination-insertion mechanism. For example, Penczek and coworkers reported that the solution polymerization of ε-CL is initiated by a —Sn(OR) species that derives from a carboxylate (Sn(Oct)$_2$)-alcohol(ROH) exchange reaction.[28,30]

In this study, we chose hydroxylated PP film as substrate and carried out subsequent surface initiated ring-opening polymerization of ε-CL catalyzed by Sn(Oct)$_2$, resulting in PCL grafted on PP film. This method consists of two simple steps: (1) Sn(Oct)$_2$ exchanged with the hydroxyl groups on the surface of PP film, forming the —OSn(Oct) groups bonded on the surface; and (2) surface-initiated ring-opening polymerization of ε-CL with the —OSn(Oct) groups (Fig. 1). It is well-known that the surface of PP film has a low surface energy and is very inert. Grafting with polar monomers is an effective method to tailor surface properties such as wettability, printability, and adhesion. However, surface modification of PP film with PCL with SIP technique, to our knowledge, has yet not been reported.

EXPERIMENTAL

Materials

Polypropylene films of 20-μm thickness were cut into circular shape of about 40 mm in diameter and Soxhlet extracted with acetone for 48 h to remove the additives and impurities. The films were then vacuum-dried. ε-CL was purchased from Fluka Chemika AG CH-9471 Buchs and used without further purification. Stannous octoate (Sn(Oct)$_2$) was purchased from Sigma-Aldrich and used as received. Toluene and petroleum ether were dried by refluxing over Na and distilled under a nitrogen atmosphere. PEG2000 was purchased from Shanghai Chemical Reagent Company. The actual number average molecular weight (M_n) of this PEG was 1300 determined by gel-permeation chromatograph (GPC).

Graft polymerization of ε-CL on hydroxylated PP film with Sn(Oct)$_2$

The PP films were modified by UV-irradiation according to the literature[31,32] to obtain hydroxylated film. The hydroxylated PP films (denoted as PP-OH film in short) were put into Sn(Oct)$_2$ toluene solution, purged with N$_2$ for 15 min to remove O$_2$, and reacted for 1 h at 60°C under N$_2$ atmosphere. After the reaction, the films were rinsed with toluene two times, and then
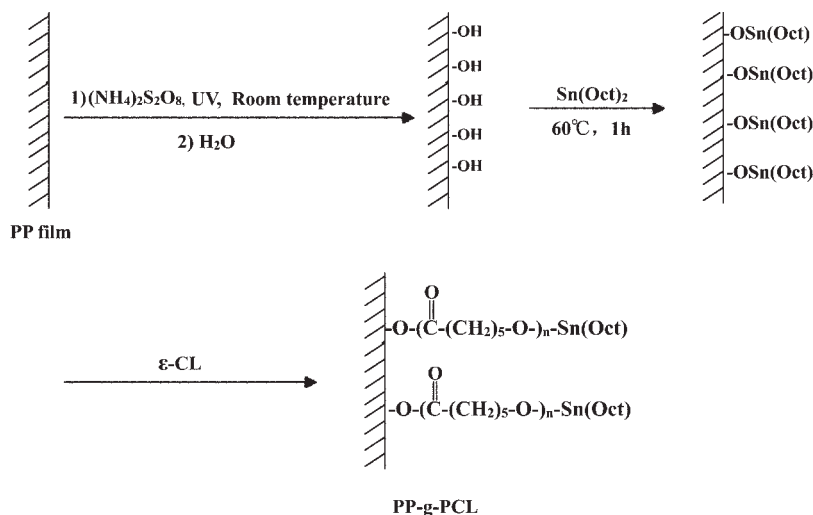

Figure 1 Schematic representation for surface-initiated ring-opening polymerization of ε-CL on PP film.

putted into a flask containing 5 mL ε-CL and 10 mL toluene solution. Reaction was kept at a temperature ranging from 60°C to 100°C for predetermined time.

The grafted films were taken out and Soxhlet-extracted with acetone for 24 h to remove the unreacted monomer and homopolymer adhered on the films, and dried to constant weight in a vacuum oven at 40°C.

Model polymerization:

PEG (2.5 mmol)and Sn(Oct)$_2$ toluene solution (5 mmol) were mixed under dry nitrogen in a three-necked flask equipped with magnetic stirring. The flask was emerged in oil bath at 60°C for 1 h. When the reaction time was over, the mixture was precipitated with petroleum ether, filtrated, washed several times with petroleum ether, and then OctSnO-PEG-OSnOct **1** was obtained.

The compound **1**, ε-CL, and toluene were introduced into a three-necked flask under N$_2$ atmosphere. The molar ratio of compound **1** to CL was 1 : 5, and the polymerization was conducted at 100°C for 10 h. The reaction product was precipitated with petroleum ether, filtrated, washed several times with petroleum ether, and dried for GPC measurement.

Characterization

ATR-FTIR spectra of PP and PP-*g*-PCL film were obtained with a Nicolet Nexus 670 spectrometer equipped with variable angle horizontal ATR accessory, on which a 50° rectangle ZnSe crystal was used. For each spectrum obtained, a total of 64 scans were accumulated at a resolution of four wavenumbers. The surface composition was analyzed using X-ray photoelectron spectroscopy (XPS). The samples were measured on ESCALAB 250 spectrometer with an Al Kα X-ray source. Water contact angles of the modified PP films were measured by Dataphysics OCA20 contact angle system (Germany) at the room temperature.

The volume of the drop of tridistilled water used was 2 μL. Fifteen measurements were carried out and the resulting values were averaged. The surface morphology of films were observed by SEM using a S250HK3 (Cambridge, UK) instrument. The GPC measurement was conducted at 25°C with a Waters 150C Model gel-permeation chromatography using tetrahydrofuran as eluent: flow rate, 1.0 mL/min. Molecular weight and molecular weight distribution were calibrated with polystyrene standards.

RESULTS AND DISCUSSION

Linked initiator layer

One of the basic requirements for the synthesis of controlled polymer film by graft polymerization from surface-linked initiators is the control of the chemical composition and grafting site density of the surface. As reactions in surface-linked monolayers are not easily quantified, it is desirable to achieve the immobilization of the initiator in a one-step procedure. Additionally, the surface reaction has to be self-limited otherwise uncontrolled multilayer formation will occur. To obtain a high graft density, it is desirable that the reactivity of the initiator molecule is high under the given reaction conditions.

The synthesis of PP-*g*-PCL film was performed by the synthetic route shown in Figure 1. First, the PP film was pretreated with ammonium persulfate under UV light. After hydrolyzed, PP-OH films were obtained.[31,32] As it is known from the literature, the Sn(Oct)$_2$ will reacted with alcohol to produce 2-ethylhexanoic acid and/or butyl 2-ethylhexanoate (OctBu) and —SnOR species at 80°C in THF.[28] Immersed the PP-OH film into the solution of Sn(Oct)$_2$ for 1 h and rinsed with toluene for several times to remove physical attached Sn(Oct)$_2$ from the film, —OSn(Oct) groups will covalently linked to the PP film. It is a fast reaction. So a layer of initiator on
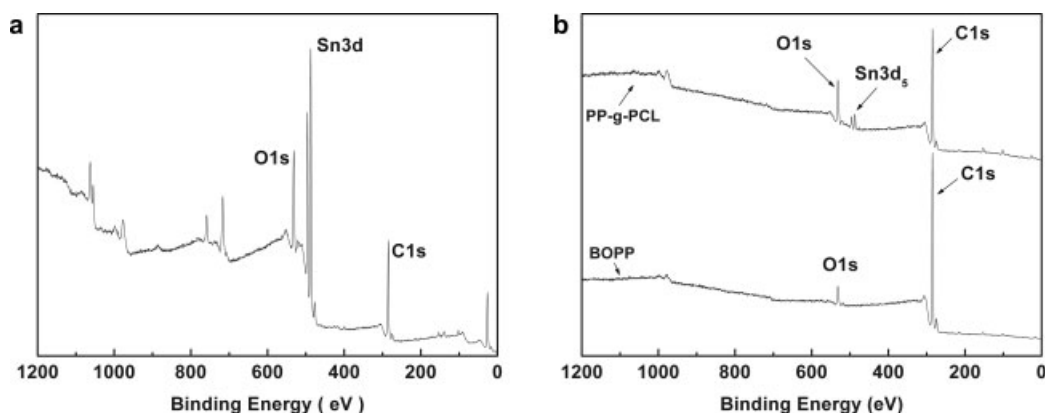

Figure 2 XPS spectrum for (a) the initiator layer on the surface of PP film, and for the (b) pristine PP film surface, as well as PP-*g*-PCL film surface.
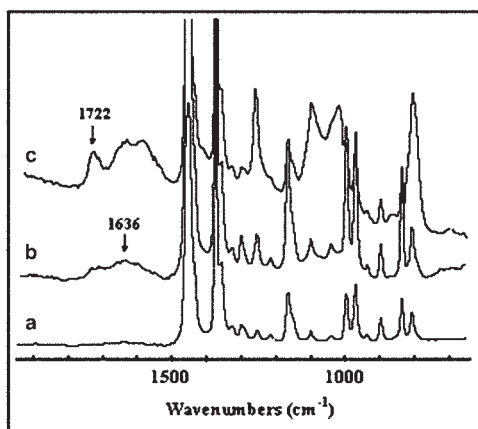
Figure 3 ATR-FTIR spectra of (a) PP, (b) PP-OSn(Oct), and (c) PP-g-PCL film.

the PP film is facile to be obtained. ATR-FTIR, contact angles, and XPS were used to characterize the layer of initiator. ATR-FTIR analysis [Fig. 3(a)] revealed that a wide adsorption peak appeared at 1636 cm^{-1}, which is attributed to the carboxylate groups of —OSn(Oct). The PP film is hydrophobic of which the water static contact angle is 105–110°, while the PP-OH film is hydrophilic (70–85°). But after bonded with —OSn(Oct) groups, the contact angle increased again because of the presence of the longer alkyl chain. The change of the water static contact angle also suggests that the exchange reaction between PP-OH film and Sn(Oct)$_2$ exists.

Trace (a) of Figure 2 displays the XPS spectrum of the initiator layer. The spectrum shows the stannous signal at 485 eV associated with the initiator. If the initiator evenly bonded on the PP film, the surface of PP film will be covered by —OSn(Oct), and the area ratio of O1s/C1s will be 0.375. From the spectrum of the initiator layer, the ratio area of O1s/C1s is 0.367 in agreement with the theoretical value. So, the —OSn(Oct) group was thought linked to the PP film evenly.

Surface-initiated ring-opening polymerization

In polymerization process, ε-CL will insert into the tin (II)-oxygen (i.e., Sn—O) bonds directly linked on the PP film and the graft chains grow gradually. The PP-g-PCL film was obtained. After the polymerization, the sample was removed from the polymerization mixture and cleaned with toluene and extracted with acetone for 24 h to remove homopolymer PCL.

To prove that the PCL was grafted on the PP film, ATR-FTIR spectra were used to characterize the PP-g-PCL film. Figure 3 shows the ATR-FTIR spectra of PP, PP-OSn(Oct), and PP-g-PCL film. In the spectra, the nonmodified PP film shows no signal at the range of 1500–2000 cm^{-1}. The PP-OSn(Oct) film shows a wide adsorption peak appeared at 1636 cm^{-1}, which is attributed to the carboxylate group of —OSn(Oct) above-mentioned. After grafted PCL, there is a little spiculate absorption peak at 1722 cm^{-1}, which corresponds to the C=O stretching vibration of PCL. This result indicates that the PCL has been grafted on the surface of the PP film.

XPS spectra of PP and PP-g-PCL were showed in trace (b) of Figure 2. The C1s (285 eV) peak and O1s (533 eV) peak were detected on the nonmodified PP film, but O1s peak was very weak. The weak O1s peak was attributed to the slightly oxidation of PP film surface. After grafting PCL, the increase of the intensity of oxygen peaks relative to the carbon signal indicates the presence of the PCL at the PP surface. Besides that, on the spectrum of PP-g-PCL film, a set of additional peaks appeared at 485–500 eV due to Sn 3d. It was ascribed to the terminal groups of the grafting chains and unreacted initiators linked on the film.

Figure 4 shows the respective C1s core-level spectra of pristine PP and PP-g-PCL film surface. In the case of pristine PP film, the C1s core level spectrum contains one major peak components of which the binding energy at 285 eV is attributed to the C—H species. The C1s peak of PP-g-PCL was broken down into the following: a component at 285 eV due to the
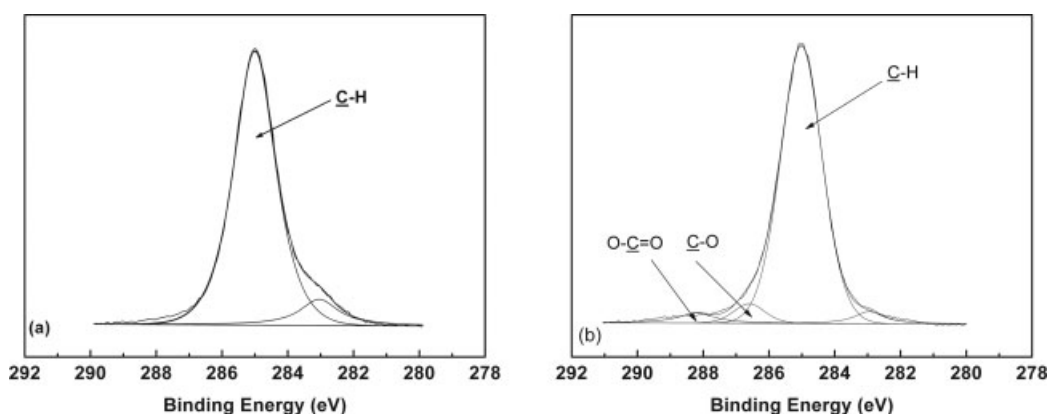

Figure 4 XPS C1s core-level spectra of (a) PP film surface and (b) PP-g-PCL film surface.

C—H species, a component at 286.5 eV for the C—O species, a component at 288.2 eV for the O—C=O species. The peaks of the C—O and O—C=O were attributed to the ester groups of the PCL chains. These results also clearly indicated the PCL chains were successfully grafted on the PP film.

Figure 5 shows that the atomic composition of PP-g-PCL surface varied with reaction time. We can notice an increase in oxygen concentration and decrease in carbon content with reaction time. After 4 h, the content of oxygen and carbon tend to constant: the content of C1s is nearly 76% and that of O1s almost kept at 21.5%. These values are approximate to that of PCL (the theoretical contents of C1s and O1s of PCL are 75 and 25%, respectively). These results indicate that the PCL chains have covered the surface of PP film after 4 h. In the whole reaction time, the content of Sn(II) is almost unchanged. Treated the grafted film (reaction time was 8 h) with dilute HCl, the content of Sn(II) decreased from 0.87% to 0.21%. From the SEM image, the shape of PCL particles still kept spheroid after

treated with dilute HCl [Fig. 8(c and c′)]. It meant that in the polymerization processing, the —Sn(Oct) group was always bonded at the end of growing chain and could be hydrolyzed down by dilute HCl. These results suggested that the —OSn(Oct) group was truly the active center. Monomer inserted into the Sn(II)—O bond and the grafting chains grew.

The mechanism of the graft polymerization on the PP-OH films was further studied by the model polymerization. Hydroxy-terminated PEG (HO-PEG-OH, $M_n = 1300$, $M_w/M_n = 1.7$) was used as model compound. HO-PEG-OH was reacted with Sn(Oct)$_2$ in toluene solution at 60°C for 1 h and was precipitated with petroleum ether. OctSnO-PEG-OSnOct **1** was obtained. Polymerization of ε-CL initiated by OctSnO-PEG-OSnOct **1** was performed in toluene solution at 100°C for 10 h (the CL and 1 at a molar ratio of 5 : 1). After precipitation with petroleum ether, copolymer PCL-b-PEG-b-PCL **2** with M_n of 18,500 and M_w/M_n of 1.81 was obtained. The model polymerization was described as follows:

$$\text{HO}\!-\!(\text{CH}_2\text{CH}_2\text{O})_{\overline{n}}\!-\!\text{H} \ + \ 2\,\text{Sn(Oct)}_2 \ \underset{60°C}{\rightleftharpoons} \ \text{OctSnO}\!-\!(\text{CH}_2\text{CH}_2\text{O})_{\overline{n}}\!-\!\text{SnOct} \tag{1}$$
$$\mathbf{1}$$

$$\text{OctSnO}\!-\!(\text{CH}_2\text{CH}_2\text{O})_{\overline{n}}\!-\!\text{SnOct} \ + \ 2m \ \overset{\text{O}}{\underset{(\text{CH}_2)_5}{\overset{\|}{\text{C}\!-\!\text{O}}}} \ \xrightarrow{100°C} \tag{2}$$

$$\underset{\text{PCL}}{\sim\!\sim\!\sim}(\text{CH}_2\text{CH}_2\text{O})_{\overline{n}}\!-\![\text{C(O)CH}_2(\text{CH}_2)_3\text{CH}_2\text{O}]_{\overline{m}}\!-\!\text{SnOct}$$
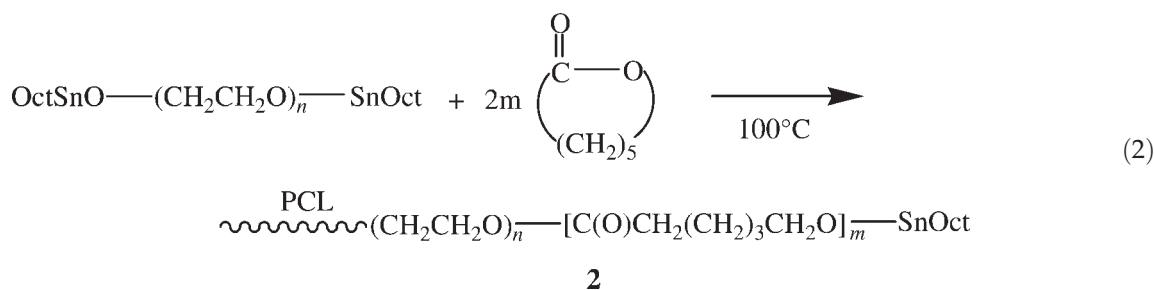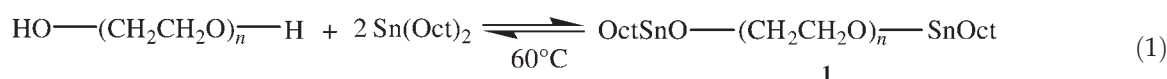$$\mathbf{2}$$

Figure 6 shows the GPC curve of PCL-b-PEG-b-PCL and original PEG. The peak shape of the block copolymer was different from that of PEG, and the M_n of PCL-b-PEG-b-PCL was much higher than that of original PEG. It was concluded that OctSnO-PEG-OSnOct could initiate the ring-opening polymerization of ε-CL. This model polymerization could support the grafting mechanism described in Figure 1. These results conformed that the mechanism of Sn(Oct)$_2$-catalyzed, ring-opening polymerization of ε-CL was coordination-insertion mechanism.

Topography of the graft surfaces

Temperature is an important factor that influences ε-CL ring-opening polymerization. Figure 7 presents a set of SEM images of the nonmodified PP and the PP-g-PCL produced at different temperature.
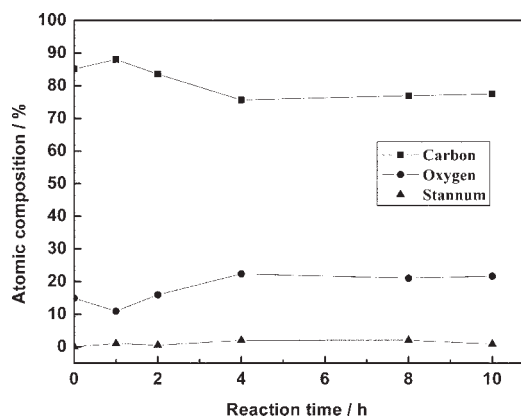
Figure 5 XPS elemental composition for PP-OH and PP-g-PCL film surface as a function of grafting reaction time. Report values for each condition are averages of at least three measurements for a take off angle of 45°. The grafting reaction temperature is 100°C.
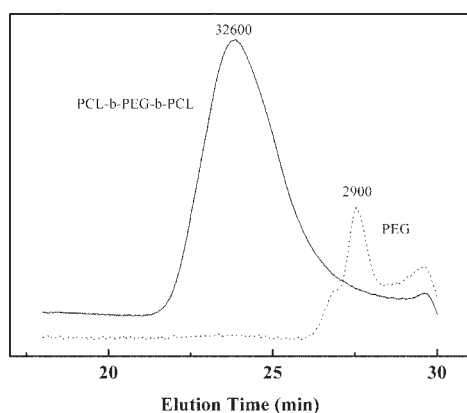
Figure 6 GPC curves of PEG and PCL-*b*-PEG-*b*-PCL copolymer.

Figure 7(a) was SEM images of nonmodified PP film. It was a flat surface and no particles on it. After grafted with PCL, there were a lot of less regular particles on the surface of the grafted PP film [Fig. 7(b)–(d)]. When the polymerization temperature increased from 60 to 100°C by a step of 20°C, the particles grew regularly into spheroidal particles. Figure 8 presents the reaction time effect on the images of the surface at 100°C. The longer the reaction time, the bigger the particle size was. It was revealed that when the polymerization temperature increased, the polymerization rate increased. The polymer chains became longer and entangled each other into spheroidal particles. At 100°C, when the reaction time increased, the particles on the surface of PP grew bigger, but the size of the spheroidal particles was not uniform. These results suggested that the initial attempt to control polymer growth from the surface bound initiators at this reaction conditions was unsuccessful, perhaps because the extremely large molar ratio of ε-CL to the initiating sites leaded to little control over the degree of polymerization of the grafting chains. Furthermore, the
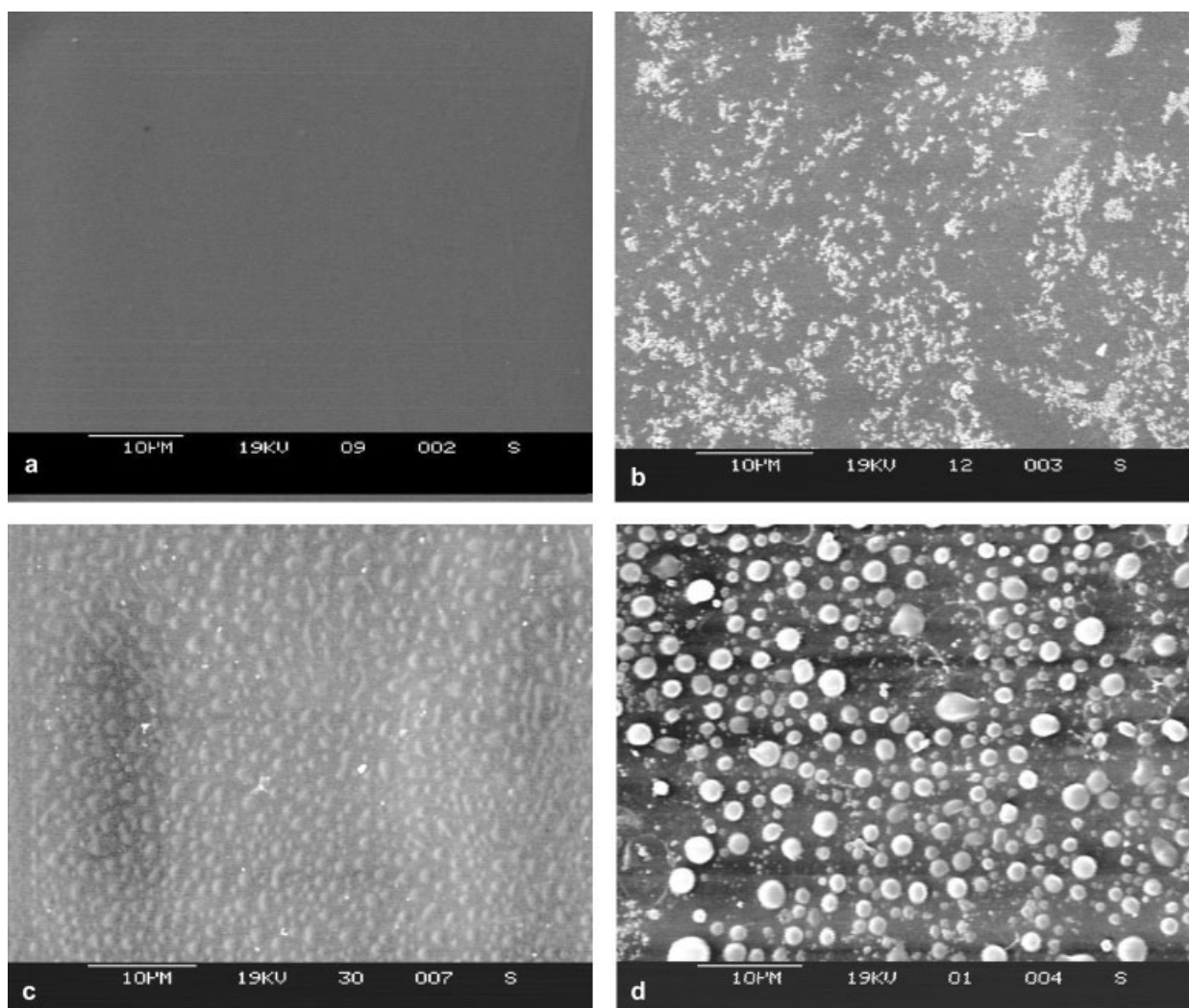

Figure 7 SEM images of nonmodification PP (a) and PP-*g*-PCL film prepared with different reaction temperature (b, 60°C; c, 80°C; d, 100°C; reaction time: 6 h).
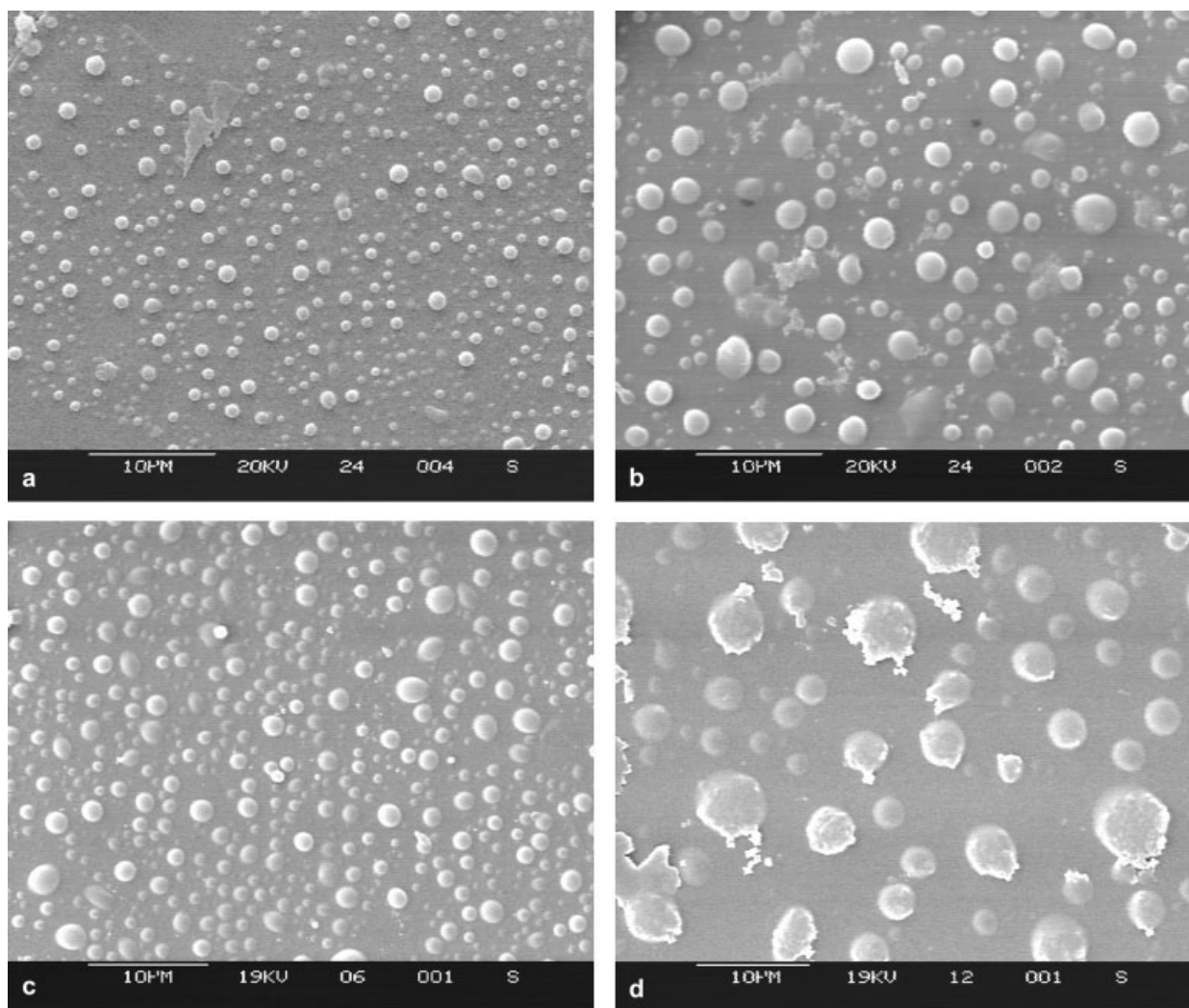
Figure 8 SEM images of PP-*g*-PCL film prepared with different reaction time at 100°C (a, 2 h; b, 4 h, c, 8 h, c′, sample c treated with HCl).
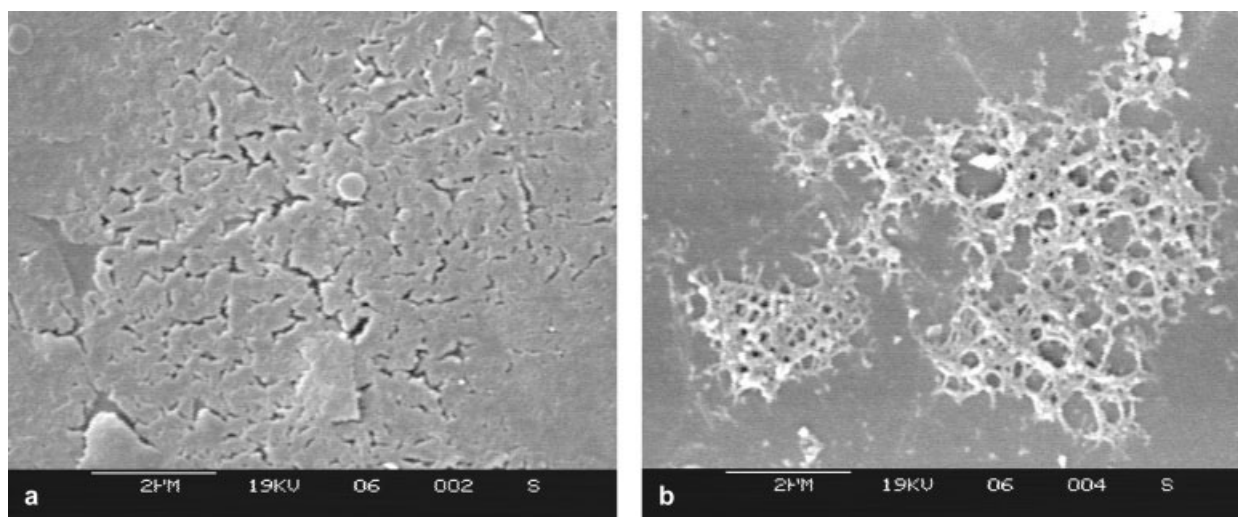

Figure 9 SEM images of PP-*g*-PCL film prepared at 100°C for 8 h after treatment with THF at 40°C for 1 h (a) and emerged into hexane at room temperature (b). The films after solvent treatment was dried with a clean air stream.

extremely low concentration of initiating sites on the substrate would lead to susceptibility to trace impurities, which also induced the termination of growing chains.[13]

The PP-*g*-PCL sample became transparent after THF treatment at 40°C for 1 h and drying under air. In Figure 9(a), the SEM result showed that the spheroidal particles on the surface have been changed into a thin flat film after this treatment. THF is a good solvent for PCL. THF solvated the PCL spheroid and made the polymer chains disentanglement and stretched in the solvent. Removed THF from the sample, the polymer chains condensed and kept the stretched state. If the PP-*g*-PCL sample solvated with THF was immerged in hexane at room temperature, a poor solvent for PCL, the SEM image changed into sparse mesh structure [Fig. 9(b)]. This result could be explained that in a poor solvent, the stretched polymer chains would crimp and wrap each other. After removed the hexane, the sparse structure formed. These results denoted that the spheroidal particles were not crosslinked. The morphology of PCL grafted on the surface of PP film could be changed by the treatment with different solvents.

CONCLUSIONS

In this study, we demonstrated a novel and efficient approach to graft PCL on the PP film by surface initiated ring-opening polymerization. ATR-FTIR and XPS analysis demonstrated that we successfully obtained PP-*g*-PCL film with little side products by this method. This results and the model polymerization indicated that the true initiators were —OSn(Oct) groups linked to the PP film, thereby confirmed that the mechanism of Sn(Oct)$_2$-catalyzed, ring-opening polymerization of ε-CL was coordination-insertion mechanism. But the polymerization was not well-controlled because the extremely low concentration of initiating sites with respect to the monomer concentration. SEM images revealed that the polymerization temperature and grafting reaction time have effect on the graft polymerization. The grafted PCL chains would entangled into spheroidal particles on the PP film. By treatment with different solvents, these spheroidal particles would change into different morphologies.

References

1. Sugawara, T.; Matsuda, T. Macromolecules 1994, 27, 7809.
2. Prucker, O.; Rühe, J. Macromolecules 1998, 31, 592.
3. Jordan, R.; West, N.; Ulman, A.; Chou, Y. M.; Nuyken, O. Macromolecules 2001, 34, 1606.
4. Zhao, B.; Brittain, W. J. J Am Chem Soc 1999, 121, 3557.
5. Jordan, R; Ulman, A. J Am Chem Soc 1998, 120, 243.
6. Yee, C.; Scotti, M.; Ulman, A.; White H.; Rafailovich, M.; Sokolov, J. Langmuir 1999, 15, 4314.
7. Zhou, Q.; Fan, X.; Xia, C.; Mays, J; Advincula, R. Chem Mater 2001, 13, 2465.
8. Jordan, R; Ulman, A; Kang, J. F.; Rafailovich, M. H.; Sokolov, J. J Am Chem Soc 1999, 121, 1016.
9. Weck, M.; Jackiw, J. J.; Rossi, R. R.; Weiss, P. S.; Grubbs, R. H. J Am Chem Soc 1999, 121, 4088.
10. Lahann, J.; Langer, R. Macromol Rapid Commun 2001, 22, 968.
11. Möller, M.; Nederberg, F.; Lim, L. S.; Kånge, R.; Hawker, C. J.; Hedrick, J. L.; Gu, Y. D.; Shah, R.; Abbott, N. L. J Polym Sci, Part A: Polym Chem 2001, 39, 3529.
12. Choi, I. S.; Langer, R. Macromolecules 2001, 34, 5361.
13. Husemann, M.; Mecerreyes, D.; Hawker, C. J.; Hedrick, L. J.; Shah, R.; Abbott, N. L. Angew Chem Int Ed 1999, 38, 647.
14. Yoon, K. R.; Chi, Y. S.; Lee, K.-B.; Lee, J. K.; Kim, D. J.; Koh, Y.-J.; Joo, S.-W.; Yun, W. S.; Choi, I. S. J Mater Chem 2003, 13, 2910.
15. Yoon, K. R.; Lee, K.-B.; Chi, Y. S.; Yun, W. S.; Joo, S.-W.; Choi, I. S. Adv Mater 2003, 15, 2063.
16. Dubois, P.; Krishnan, M.; Naraya, R. Polymer 1999, 40, 3091.
17. Carrot, G.; Rutot-Houzé, D.; Pottier, A.; Degée, P.; Hilborn, J.; Dubois, P. Macromolecules 2002, 35, 8400.
18. Joubert, M.; Delaite, C.; Bourgrat-lami, E.; Dumas, P. J Polym Sci, Part A: Polym Chem 2004, 42, 1976.
19. Martin, E.; Dubois, P.; Jerome, R. Macromolecules 2003, 36, 7094.
20. Du, Y. J.; Lemstra, P. J.; Nijenhuis, A. J.; Van Aert, H. A. M.; Bastiaansen, C. Macromolecules 1995, 28, 2124.
21. Kricheldorf, H. R.; Kreiser-Saunders, I.; Boettcher, C. Polymer 1995, 36, 1253.
22. In't Veld, P. J. A.; Velner, E. M.; Van De Witte, P.; Hamhuis, J.; Dijkstra, P. J.; Feijen, J. J Polym Sci, Part A: Polym Chem 1997, 35, 219.
23. Schwach, G.; Coudane, J.; Engel, R.; Vert, M. J Polym Chem, Part A: Polym Chem 1997, 35, 3431.
24. Leenslag, J. W.; Pennings, A. J. Makromol Chem 1987, 188, 1809.
25. Zhang, X.; Wyss, U. P.; Pichora, D.; Goosen, M. F. A. Polym Bull 1992, 27, 623.
26. Storey, R. F.; Taylor, A. E. J Macromol Sci Pure Appl Chem 1998, 35, 723.
27. Kowalski, A.; Libiszowski, J.; Duda, A.; Penczek, S. Polym Prepr 1998, 39, 74.
28. Kowalski, A.; Duda, A.; Penczek, S. Macromol Rapid Commun 1998, 19, 567.
29. Penczek, S.; Duda, A.; Kowalski, A.; Libiszowski, J. Polym Mater Sci Eng 1999, 80, 95.
30. Kowalski, A.; Duda, A.; Penczek, S. Macromolecules 2000, 33, 689.
31. Yang, P.; Deng, J. Y.; Yang, W. T. Polymer 2003, 44, 7157.
32. Zhao, H. C.; Yang, P.; Deng, J. P.; Liu, L. Y.; Zhu, J. W.; Sui, Y.; Lu, J. M.; Yang, W. T. Langmuir 2007, 23, 1810.