Synthesis and Characterization of Fullerene Grafted Poly(ε-caprolactone)

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ABSTRACT: The fullerene grafted poly(ε-caprolactone) (PCL) was successfully synthesized with a graft efficiency of 80%. The fullerene moieties grafted onto the PCL chain aggregate into 1–2 μm particles so that a physical *pseudo*-network is formed. Because of the existence of the network structure, the fullerene grafted PCL film can retain its shape at much higher temperatures than that of pure PCL film, as observed in dynamic mechanical tests. It shows a hydrophobic gelling behavior in chloroform solution. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 4029–4035, 2008

Key words: poly(ε-caprolactone); fullerene grafted poly(ε-caprolactone); network; hydrophobic gel; biodegradable

INTRODUCTION

Fullerene and its derivatives have attracted much attention because of their promising applications in many fields such as solar energy conversion and storage, fuel cells, macromolecular materials, and biomedical and life sciences.[1–6] However, its poor solubility and processability pose difficulties in utilizing fullerene for practical applications.[7,8] Incorporation of fullerene into polymers is a useful method to improve the solubility of the fullerene moiety.[9–11] Fullerene-containing polymers have been prepared by grafting the polymer with reactive end-groups onto the fullerene.[3] The attachment of the fullerene onto the polymer chains results in attractive properties.[6,12,13] For instance, Kojima et al. found that an incorporation of fullerene grafts onto polystyrene greatly improved the optical limiting property of polystyrene.[14] Fullerene-functionalized π-conjugated polyester has been used as the photovoltaic cells and the electroluminescent devices.[15,16] Fullerene containing poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) membrane has a much higher gas permeability than that of original PPO.[17]

Recently, fullerene containing polymers have aroused much research interest.[18–22] Wang and coworkers found that the single end-capped poly(*tert*-butyl acrylate) shows good photoconductive properties.[23] Because of the aggregation behavior of the fullerene moiety at the chain end of the double-fullerene end-capped polymers, a network-like structure will be formed, which will greatly increase the physical properties of the polymers.[24] Goh and coworkers have successfully attached the fullerene onto the end of poly(ethylene oxide) (PEO) chain. The resulted double-fullerene end-capped PEO (FPEOF) showed excellent mechanical properties.[25–29] The aggregation of the fullerene moieties in the double capped polymer leads to the formation of network-like structures so that a combination of a double-fullerene capped polymer and a linear polymer is expected to give rise to a *pseudo*-semi-interpenetrating polymer network (*p*-SIPN). Poly(methyl methacrylate) (PMMA) blended with FPEOF shows a good reinforced toughness. This FPEOF effect is comparable to the effect of nanotubes on PMMA.[30] The introduction of fullerene into these commonly used engineering plastics has achieved much success, but there has been less report on the incorporation of fullerene in to biodegradable polyesters.

Aliphatic polyesters have attracted much research interest because of their biodegradability and biocompatibility.[31–33] Poly(ε-caprolactone) (PCL) is one of typical such aliphatic polyesters.[34] It is fully biodegradable, biocompatible, and nontoxic to living organisms.[34] Also, PCL has good resistant ability to water, oil, solvent, and chlorine. The unique properties of PCL give it high potential for use in biomedical fields and it has been used in the development of controlled drug delivery system as well as in surgical sutures and other resorbable fixation devices.[34,35] Recently, the introduction of carbon nanomaterials into PCL to afford hybrids is a good way to improve the properties of PCL. Zeng et al. have successfully incorporated the carbon nanotube into PCL.[36]

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According to Goh's and our previous work,[30,37–39] fullerene capped polymers are good additives for improving the mechanical properties of other polymers. Recently, Stoilova et al. investigated the fabrication of microstructured fiber of fullerene containing PCL by electron spinning and the fullerene molecules were found to aggregate into particles in the fiber.[40] Since the fullerene end-capped polymers have limitation on the fullerene content, as the molecular weight of the polymer increases, the fullerene content of the fullerene end-capped polymer decreases, so that, the advantages of fullerene incorporated into the fullerene/polymer hybrid decrease with increasing the polymer molecular weights.

To solve this problem and to create the fullerene/polymer hybrid with adjustable fullerene content, the synthesis of fullerene grafted polymer should be the best one of possible methods. Here, we developed the method to synthesize fullerene-grafted PCL. The introduction of the fullerene moieties onto the PCL chain is expected to give it fascinating properties for advanced biomedical and engineering uses such as biosensor, gas separation membrane, bio-optical limiter, etc. Furthermore, the fullerene-grafted PCL is expected to be a good additive to reinforce other polymers. In this study, the synthetic method of fullerene grafted PCL is developed by using the poly(α-chloro-ε-caprolactone-co-ε-caprolactone) (PCL-Cl).[41] The synthesis, thermal properties, dynamic mechanical properties, and fullerene aggregation behavior of fullerene grafted PCL (PCL-g-Fullerene) are presented.

EXPERIMENTAL

Materials

The fullerene (Lot: 4A0248-A) was purchased from the Frontier Carbon Corporation (Tokyo, Japan). ε-Caprolactone was purchased from Kanto Chemical Co. (Tokyo, Japan) and distilled over CaH_2 before use. Tin 2-ethylhexanoate [$Sn(Oct)_2$], sodium azide, α-chlorocyclohexanone, and m-chloroperoxybenzoic acid (mCPBA) were purchased from Kanto Chemical Co. (Tokyo, Japan) and used as received. Reference PCL sample (PCL$_R$; $M_n = 1.15 \times 10^5$ g mol^{-1}, $M_w/M_n = 1.47$) was supplied by Daicel Chemical (Japan) and used after precipitation.

Synthesis of α-chloro-ε-caprolactone

The synthesis of α-chloro-ε-caprolactone was performed as described by Lenoir et al.[41] The α-chlorocyclohexanone was reacted with mCPBA in dichloromethane for 96 h. Then, the reaction mixture was cooled to −20°C to precipitate the m-chlorobenzoic acid. After filtration, the solution was washed three times with a saturated aqueous solution of $NaHSO_3$,

three times with an aqueous solution of $NaHCO_3$, and finally with water. After dying over $MgSO_4$, the organic phase was filtered and the solvent was removed under reduced pressure so that the α-chloro-ε-caprolactone was obtained.

Preparation of poly(α-chloro-ε-caprolactone-co-ε-caprolactone) copolymer (PCL-Cl)

Copolymer of α-chloro-ε-caprolactone with ε-caprolactone was performed by using ring opening polymerization (ROP) in presence of 1-laury alcohol as ring opening initiator.[41] The mixture of α-chloro-ε-caprolactone (0.3 g), ε-caprolactone (10 g), and 1-laury alcohol (0.03 g) was put into a three-necked flask (previously dried in vacuum oven at 150°C) and tin 2-ethylhexanoate catalyst was added under nitrogen gas flow. The flask was capped and heated at 120°C for 48 h, and then cooled to room temperature to afford white solid. The white solid was dissolved in chloroform and precipitated in ethanol for three times to afford the copolymer, PCL-Cl ($M_n = 3.6 \times 10^4$, Pd = 1.2).

Introduction of azide group into poly(ε-caprolactne) (PCL-N$_3$)

The azide group was introduced into PCL by a similar method as described in Goh and coworkers.[25] The PCL-Cl copolymer (5 g) was mixed with sodium azide (1 g) and tetra-n-butylammonium iodide (0.2 g) in DMF solution and then heated at 65°C for 72 h. The reaction mixture was centrifuged, filtrated, and precipitated into ethanol to afford faint yellow solid.

Synthesis of fullerene grafted poly(ε-caprolactone)

The azide group introduced PCL (3 g) was reacted with 0.5 g fullerene in 100 mL chlorobenzene at 135° under nitrogen purging for 24 h. The solution was ultra centrifugated, and then filtered and distilled to remove most of the chlorobenzene. After distillation, the tetrahydrofuran (THF) was poured into the flask, then the solution was again centrifugated, and filtered. The clear filtrate was cast on the dishes and dried under air to afford wine red product.

Characterizations

^{1}H NMR spectra were measured at room temperature in CDCl$_3$ solution on Bruker Avance 600 MHz spectrometer with 30° pulse, 3.7 s-pulse repetition time, 32K data points, and 256 FID accumulations.

Molecular weight was determined by a Toso HLC-8020 gel permeation chromatography (GPC) system (Toso, Tokyo, Japan) with a SC-8010 controller and a refractive detector with TSK gel G2000HXL columns

at 40°C. Chloroform was used as the eluent at a flow rate of 1 mL/min, and the sample concentration was 1 mg/mL. Polystyrene standards of low polydispersity were used to construct a calibration curve. GPC data were processed on a SC-8010 data processor in order to calculate the number average (M_n) and weight average molecular weight (M_w).

The measurement of thermogravimetry (TG) was carried out with a Seiko (Tokyo, Japan) TG/DTA 220U with the Exstar 6000 Station. The samples (10 mg) were heated from 25 to 600°C at a heating rate 5°C/min.
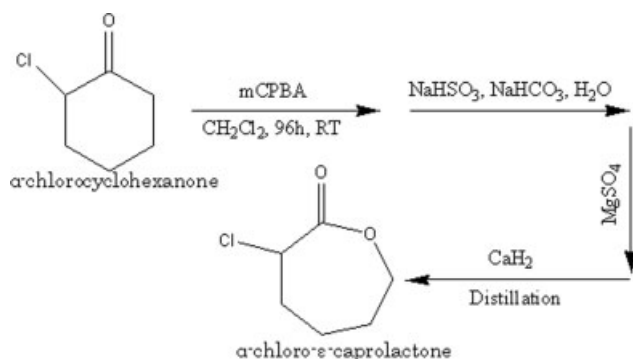
The melt crystallization temperature (T_{mc}) was measured through crystallization from the melt on the PYRIS DIAMOND DSC (Perkin-Elmer). The sample was directly heated to 100°C in the DSC cell and held for 3 min, followed by cooling at a rate of 10°C/min until the completion of melt crystallization, after this it was heated from 0 to 100°C at the heating rate 10°C/min. The peak temperature of the DSC melt crystallization curve was recorded as the T_{mc}. The crystallization enthalpy (ΔH) was determined from peak of the crystallization.

Dynamic mechanical analysis was performed on a SEIKO-DMS210 instrument (Seiko Instrument, Tokyo, Japan) under the tensile mode at 5 Hz and a thermal scanning rate of 2°C/min. The samples were cut into the dimension of 30 × 10 × 0.2 mm^3 for the test.
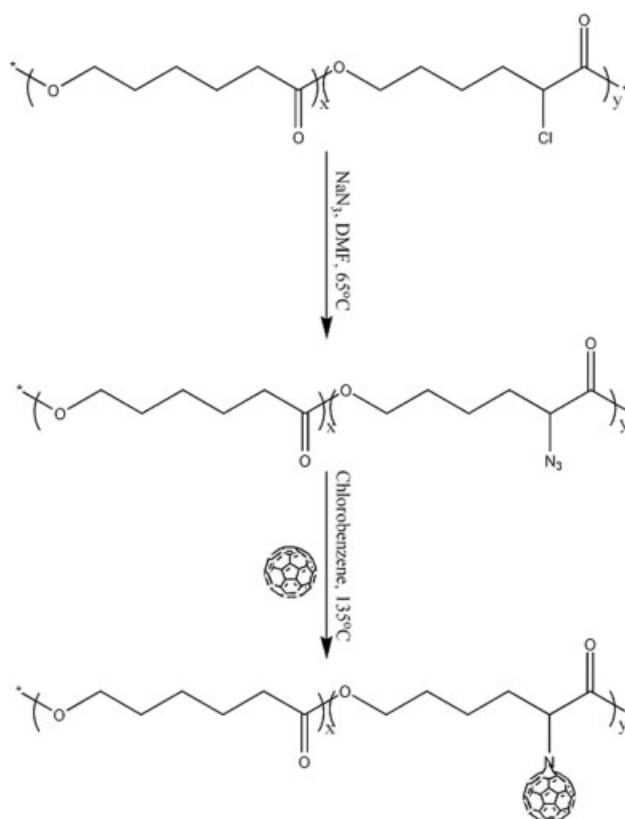
Scanning electron microscope (SEM) observation of the morphology of gel samples were performed on a scanning electron microscope (SEM: JEOL JSM-5200, Japan).

RESULTS AND DISCUSSION

α-chloro-ε-caprolactone was synthesized by the method of Lenoir et al.,[41] as shown in Scheme 1. The ^{1}H NMR spectrum of α-chloro-ε-caprolactone synthesized here fits well with that reported by Lenoir et al., and it was not shown here.[41] The fresh-made α-chloro-ε-caprolactone was copolymerized with ε-caprolactone at 120°C with laury alcohol as the

Scheme 2 Route for the synthesis of fullerene grafted poly(ε-caprolactone) (PCL-*g*-Fullerene).

initiator and tin 2-ethylhexanoate as the catalyst, to afford the PCL-Cl. The ^{1}H NMR spectrum of PCL-Cl was consistent with that shown by Lenoir et al. The peak corresponding to the methine group bonded to the chlorine atom appeared at 4.25 ppm. From the relative intensity of this peak, it is easy to calculate the content of α-chloro-ε-caprolactone monomeric unit in the copolymer, that is, about 2.6%. Because of the large size of fullerene molecules, the content of chlorine content is controlled to be low, in order to avoid the steric effect caused by the addition of fullerene onto the PCL chain.

The synthesis of PCL-*g*-Fullerene follows the steps indicated in the Scheme 2. The PCL-Cl was reacted with sodium azide in DMF to afford PCL-N$_3$. The ^{1}H NMR spectrum of PCL-N$_3$ was shown in Figure 1. The peak of methine group bonded to the chlorine atom disappeared while a new peak appeared at 3.83 ppm, corresponding to the methine group bonded to the azide group. From the ^{1}H NMR spectrum, the yield of substitution of the chlorine atom with the azide group is very high, approaching 100%. After azidation, PCL-N$_3$ was reacted with fullerene to afford the fullerene grafted PCL. After casting, PCL-*g*-Fullerene was hard to redissolve in chloroform, THF, etc. So, the measurement of solution ^{1}H NMR is impossible to perform. To estimate the
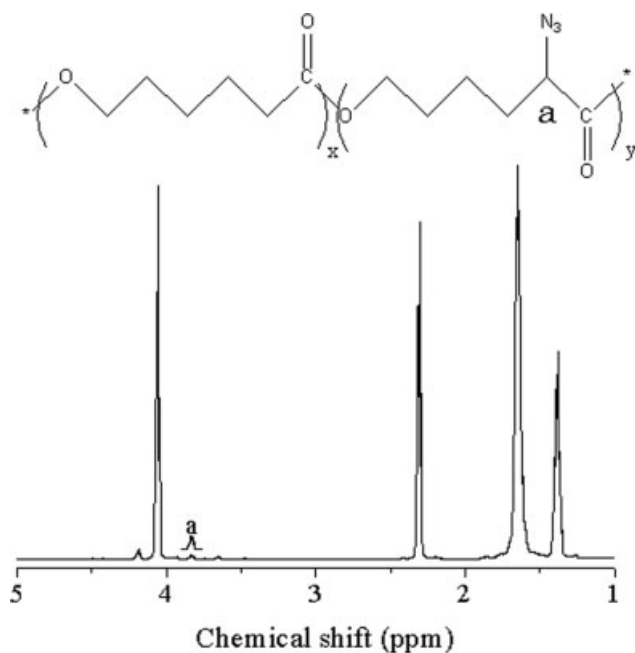
Scheme 1 Synthetic route for α-chloro-ε-caprolactone.

Figure 1 600 MHz ^{1}H NMR spectrum of PCL-N$_3$ in CDCl$_3$ at 19°C.

larger than that of PCL$_R$ when the temperature is less than 70°C. And it is hard to detect for PCL$_R$ sample at the temperature higher than 70°C, due to the melting of the PCL$_R$, while the modulus of the PCL-*g*-Fullerene was possible to detect until a much higher temperature, 140°C. Similar results were observed in tan δ curves for PCL$_R$ and PCL-*g*-Fullerene. The temperature for the break of the sample is 70 and 140°C for PCL$_R$ and PCL-*g*-Fullerene, respectively. The value of tan δ became larger at the temperature higher than 70°C for PCL-*g*-Fullerene sample. The higher temperature for the mechanical break of PCL-*g*-Fullerene is due to the introduction of the fullerene into the PCL chain and the fullerene molecules probably aggregate into the fullerene particles so that a network structure was formed. This network structure supported PCL-*g*-Fullerene, resisting break at the melting temperature of PCL. The peak temperature of tan δ of PCL-*g*-Fullerene is higher than that of PCL$_R$. The peak temperature of tan δ is always looked as the glass transition temperature. So the shift of the peak temperature of tan δ

graft efficiency, the TG was performed to estimate the weight percent of fullerene in PCL-*g*-Fullerene. The TG curves of PCL-Cl and PCL-*g*-Fullerene are shown in Figure 2. Because the PCL was almost degraded after the temperature is higher than 400°C, whereas the fullerene is thermally stable up to 600°C. So, it is very easy to estimate the fullerene content in PCL-*g*-Fullerene. Here, the fullerene content is estimated to be about 11 wt %, so the graft efficiency is roughly estimated to be higher than 80% of the available azide group.

Figure 3 shows the dynamic mechanical curves of PCL$_R$ and PCL-*g*-Fullerene. In Figure 3(a), the storage modulus of PCL-*g*-Fullerene was not noticeably
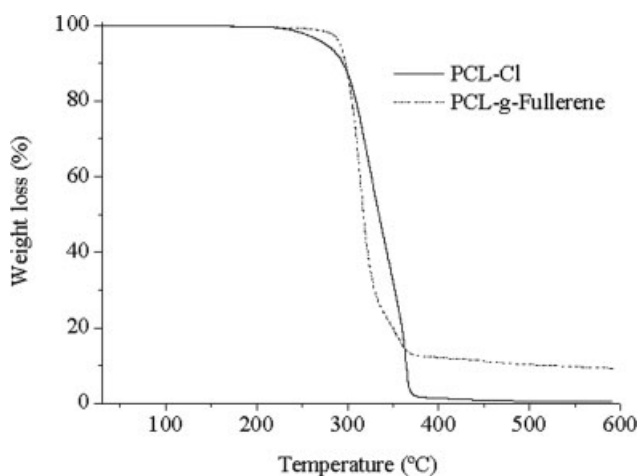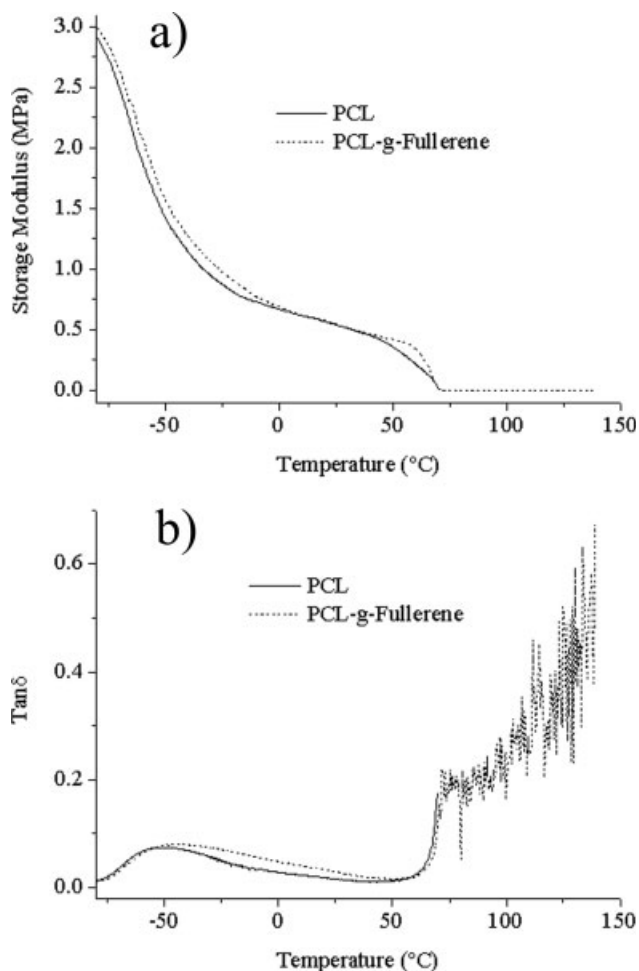

Figure 3 Dynamic mechanical curves of PCL$_R$ and PCL-*g*-Fullerene.

Figure 2 TG curves of PCL-Cl and PCL-*g*-Fullerene.

indicates the shift of glass transition temperature of PCL-g-Fullerene. The fullerene particles formed by the aggregation of fullerene moieties confine the mobility of the PCL segments, so that the glass transition temperature of PCL-g-Fullerene increases. That is the confinement effect of fullerene.

The DSC curves of the PCL-Cl and PCL-g-Fullerene were shown in Figure 4. The nonisothermal crystallization curves were shown in Figure 4(a). The T_{mc} of PCL-g-Fullerene was higher than that of PCL-Cl. Generally, a higher T_{mc} means a higher crystallization rate. So, the crystallization rate of PCL-g-Fullerene is higher than that of PCL-Cl. But the crystallization enthalpy of PCL-g-Fullerene is lower than that of PCL-Cl, 65.5 J/g for PCL-Cl and 55.4 J/g for PCL-g-Fullerene (normalized based on the PCL content in PCL-g-Fullerene), indicating the confinement effect of fullerene, as shown in Figure 3.
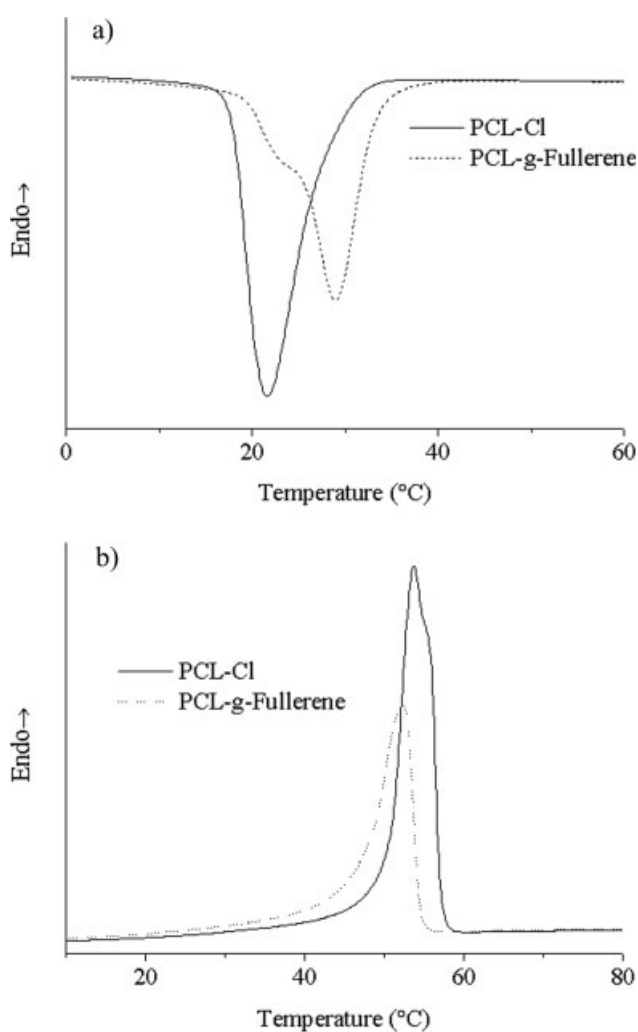

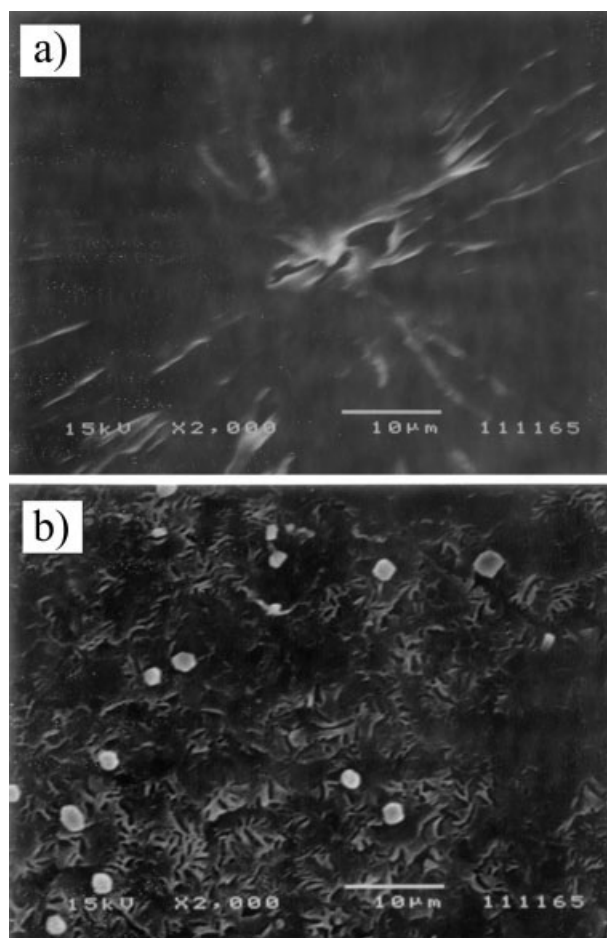**Figure 5** SEM pictures of the surface of the (a) PCL-Cl and (b) PCL-g-Fullerene film after hydrolysis in 1N NaOH for 3 days.

Figure 4 DSC curves of PCL-Cl and PCL-g-Fullerene, (a) nonisothermal crystallization with the cooling rate 10°C/min after melted at 100°C for 3 min, and (b) heating curves with the heating rate 10°C/min after nonisothermal crystallization.

The melting temperature of the PCL-Cl is higher than that of PCL-g-Fullerene as shown in Figure 4(b). As the crystallization temperature of PCL-g-Fullerene is higher than that of PCL-Cl, it is reasonable to assume that the crystalline order of PCL-Cl is higher than that of PCL-g-Fullerene. But, the melting temperature of PCL-g-Fullerene is lower than that of PCL-Cl. This contradictory is probably due to the introduction of fullerene in the PCL side chain. PCL is a semicrystalline polymer, meaning that within the material there are crystalline and amorphous regions. As the polymer melt starts to cool, the spherulit, crystals starts to grow in the crystalline regions. Here, the grafted fullerene acts like a nucleation agent, and it serves as an initiation point for these crystal growth. The crystals grow faster, are smaller, and are more numerous. Enhanced heterogeneous nucleation raises the crystallization onset temperature of polymer. Therefore, the T_{mc} of PCL-g-Fullerene is increased more than PCL-Cl. However, an increment of nucleation density due to the constraints imposed on the polymer chains by fullerene

surface leads to an increase in crystal defects so that a decrease in melting temperature.

To study the state of fullerene in the PCL matrix, the SEM photo graphs of PCL-Cl and PCL-g-Fullerene surfaces after degradation were observed as shown in Figure 5. The PCL-Cl and PCL-g-Fullerene sample were prepared by dipping the PCL-g-Fullerene and PCL-Cl films into 1N NaOH solution for 3 days, then washed with large quantity of water, and finally dried in the vacuum oven. In Figure 5(a), the SEM picture of the surface of PCL-Cl shows just a spherulite while in Figure 5(b), the SEM picture shows much more spherulites, than that of PCL-Cl sample. This finding is consistent with previous DSC study that the fullerene introduced into PCL has a nucleating effect on the crystallization of PCL. Also, in Figure 5(b), a lot of the fullerene aggregates were observed on the surface of PCL-g-Fullerene sample, with the sizes ranged from 1 to 2 μm. It is similar to the fullerene aggregates observed for the fullerene capped PEO.[29] The fullerene aggregates were formed by the aggregation of fullerenes grafted to the PCL chain. This result verified our previous prediction that the fullerene introduced onto the PCL grafts can aggregate into the fullerene particles. Also, for PCL-g-Fullerene samples, the surface after hydrolysis, it shows that the number of spherulites is higher than that of PCL-Cl samples. It verified our previous DSC study, that the introduction of fullerene onto the PCL chain has a nucleating effect on the crystallization of PCL.

Figure 6 shows the swelling of the PCL-g-Fullerene film in chloroform. The original size of the PCL-g-Fullerene film is about 1.0 × 1.0 × 0.1 cm³ as shown in Figure 6(a). After dipping into chloroform, it swelled and increased in its size to about 2.0 × 2.0 × 0.2 cm³ quickly within 5 min as shown in Figure 6(b). After about 1 h, it maintained its size 2.0 × 2.0 × 0.2 cm³ as shown in Figure 6(c). Upon drying, it recovered its original size, to about 1.0 × 1.0 × 0.1 cm³, as shown in Figure 6(d). PCL and PCL-Cl, they are soluble in chloroform, but upon introduction of fullerene moieties onto the PCL chain, the PCL-g-Fullerene became insoluble in chloroform. This phenomena is similar to that the fullerene double end-capped PEO forms gel in the water.[26]

Considering the formation of fullerene aggregates in the PCL matrix due to the aggregation of fullerene moieties grafted onto the PCL chain, the peculiar properties of PCL-g-Fullerene, such as crystallization behavior, dynamic mechanical properties, and swelling behavior of PCL-g-Fullerene, will be readily interpreted. In the crystallization process, the fullerene aggregates have two possible effects on the crystallization of PCL, i.e., confinement effect and nucleating effect. The increased crystallization temperature T_{mc} indicates a higher crystallization rate of PCL-g-Fullerene than that of PCL-Cl. This is due to the nucleating effect of the fullerene aggregates. The crystallization enthalpy of fullerene-grafted PCL decreases compared with the original PCL-Cl. Because the segments
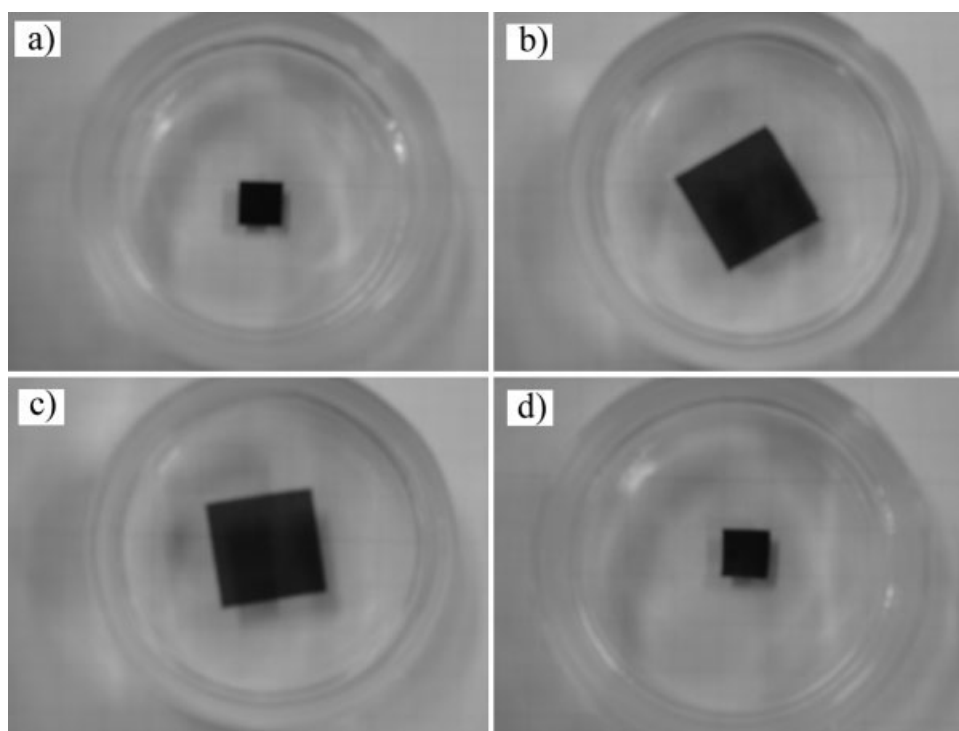

Figure 6 Gelation of PCL-g-Fullerene film: (a) original film, (b) film in chloroform for 5 min, (c) film in chloroform for 1 h, and (d) film after drying the film of (c).

of PCL chain connected with fullerene particles, is very hard to crystallize, resulting in the reduction of crystallization enthalpy. This is caused by the confinement effect of the fullerene aggregates.

In dynamic mechanical study, the temperature, at which the mechanical break of the PCL_R sample occurs due to melting, is much lower than that of the PCL-g-Fullerene sample. The aggregation of fullerene onto the PCL chain, resulted in the formation of *pseudo*-network structure (*p*N), so that even after the melting temperature of PCL crystal, this *p*N still supported the PCL-g-Fullerene film up to 140°C. The storage modulus of PCL-g-Fullerene sample is not noticeably larger than that of PCL_R due to the decrease in the crystallinity as indicated by DSC study. Also, just due to the formation of this *p*N structure, the film of PCL-g-Fullerene swelled in chloroform, forming a hydrophobic gel.

CONCLUSION

The synthesis of fullerene grafted PCL with the grafted efficiency about 80% was successfully achieved. The SEM picture indicate that the fullerene moieties, grafted on the PCL chains, aggregate, and form the fullerene particles with the size about 1–2 µm. Because of the nucleating and confinement effects of the fullerene aggregates on the PCL chain, the crystallization temperature and the crystallinity of the fullerene-grafted PCL were found to be higher and lower than those of original copolymer, respectively. The film of the fullerene-grafted PCL shows a *p*N structure and forms hydrophobic gel in chloroform, while it recovers its original shape upon drying. Considering the biocompatible and biodegradable nature of PCL, the fullerene grafted PCL has the potential to be used as biosensor, bio-optical limiter materials, etc.

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