# Melting Bulk Reaction Between Poly(butylene terephthalate) and Poly(ethylene glycol)/ DL-Oligo(lactic acid)

**Yiwang Chen,[1,2] Xiangjun Zhu,[1] Licheng Tan,[2] Jiying Su[1]**

[1]*Institute of Polymer Materials, School of Materials Science and Engineering, Nanchang University, Nanchang 330031, People's Republic of China*
[2]*Department of Chemistry, School of Science, Nanchang University, Nanchang 330031, People's Republic of China*

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**ABSTRACT:** A reactive blend of poly(ethylene glycol) (PEG) and DL-oligo(lactic acid) (OLA) is obtained at high temperature to produce partial PEG/OLA multiblock copolymer without purification. The reactive blend of PEG and OLA easily reacts with poly(1,4-butylene terephthalate) (PBT) in the melt leading to the formation of high-molar mass poly(1,4-butylene terephthalate-*co*-ethylene oxide-*co*-DL-lactide) (PBTEOLA) copolymers. The analysis from $^1$H NMR and solubility test reveals that the transesterification between butylene terephthalate (BT), ethylene-oxide (EO), and lactide (LA) segments during synthesis is unavoidable. The copolyesters are segmented copolyesters with certain random properties, as confirmed by their thermal behavior. The copolyesters show only one melting temperature ($T_m$) on the second heating run and one crystallization temperature ($T_c$) on the cooling cycle from differential scanning calorimetry measurement. With increase of OLA feeding composition in PEG/OLA blend or increase of content of PEG/OLA blend, the $T_m$ and $T_c$ of copolyesters decrease, and solubility increases. The conventional size-exclusion chromatography polystyrene calibration estimates weight-averaged molecular weight of the copolyester to be as high as 66,600 g/mol. Mechanical tests indicate that the copolyesters exhibit high Young's modulus of 50–100 MPa and good elongation at break of 32–137%. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2171–2179, 2008

**Key words:** polyesters; biodegradable; poly(butylene terephthalate); blending

## INTRODUCTION

In the recent years, biodegradable synthetic polymers have been a subject of considerable interest for environmentalists and industrialists. Great efforts have also been made to obtain biodegradable polymers with properties appropriate for biomedical and environmental-friendly materials, such as bioabsorbable sutures, bone fixation, implants, agricultural mulch films, drink bottles, etc. Until now many kinds of biodegradable polymers have been synthesized for this purpose, including polylactide, polyglycolide, polycaprolactone, poly(α-amino acid)s, poly(orthoester)s, polyanhydrides, etc.[1–3] The environmentally degradable polymers that have been developed so far are either expensive or present physical and thermomechanical properties which are significantly lower than those of conventional thermoplastics, thus limiting their potential areas of application. The approach generally used to obtain degradable polymers with acceptable thermomechanical properties involves the incorporation of aromatic units into the main chain of degradable aliphatic polymers. Blending and copolymerization techniques have been tried to obtain biodegradable polymers with improved properties.[4–8]

Reactive blending of already existing homopolyesters has proven to be a successful and inexpensive tool to produce new aliphatic/aromatic copolyesters with intermediate properties. In fact, this technique has been recently used for the preparation of poly(1,4-butylene succinate)/poly(1,4-butylene terephthalate), poly(1,4-butylene adipate-*co*-succinate)/poly(1,4-butylene terephthalate), and poly(1,4-butylene glutarate-*co*-adipate-*co*-succinate)/poly(1,4-butylene terephthalate) copolyesters.[9–12] Poly(butylene terephthalate)/poly(ε-caprolactone) copolyesters were prepared by blend of poly(butylene terephthalate) (PBT) and poly(ε-caprolactone) (PCL), and followed transesterification at 257°C.[13] A copolyester, poly(butylene succinate-*co*-ethylene succinate-*co*-ethylene terephthalate) (PBEST), was synthesized via direct

*Correspondence to:* Y. Chen (ywchen@ncu.edu.cn).
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**TABLE I**
**Composition and Yields of the Resulted Copolyesters**

| Sample | Weight ratio PBT/PEG/OLA | Feed molar ratio PBT/PEG/OLA | Composition BT/EO/LA[a] | Yield (%) |
|---|---|---|---|---|
| PBTEO43LA9 | 70.0/17.4/12.6 | 35.2/48.1/16.7 | 48/43/9 | 80.0 |
| PBTEO47LA7 | 70.0/20.9/9.1 | 34.4/52.7/12.9 | 47/46/7 | 86.9 |
| PBTEO59LA5 | 70.0/24.7/5.3 | 33.1/60.6/6.3 | 36/59/5 | 93.0 |
| PBTEO66LA1 | 70.0/27.9/2.1 | 32.2/66.0/1.8 | 33/66/1 | 93.0 |
| PBTEO73LA0 | 70.0/30.0/0.0 | 31.8/68.2/0 | 27/73/0 | 95.3 |
| PBTEO15LA3 | 90.0/7.0/3.0 | 67.0/26.5/6.5 | 82/15/3 | 86.0 |
| PBTEO34LA5 | 80.0/14.0/6.0 | 47.4/42.3/10.3 | 61/34/5 | 90.0 |
| PBTEO62LA14 | 50.0/34.9/15.1 | 18.0/65.6/16.4 | 24/62/14 | 89.7 |
| PBTEO73LA20 | 30.0/48.9/21.1 | 8.8/73.3/17.9 | 7/73/20 | \ |

[a] The molar ratio of butylene terephthalate (BT), ethyleneoxide (EO), and lactide (LA) segments (or units) in resulting copolyesters.

polycondensation from three prepolymers of butylenes succinate, ethylene succinate, and ethylene terephthalate.[14] Poly(ε-caprolactone)/poly(ethylene terephthalate),[15–18], poly(succinic anhydride-*co*-ethylene oxide)/poly(ethylene terephthalate),[19] poly(ethylene adipate)/poly(ethylene terephthalate),[20,21] and poly (ethylene terephthalate)/poly(1,4-butylene succinate)[22] copolymers have been reported. More recently, poly (butylene terephthalate)/poly(1,4-butylene succinate),[23,24] poly(butylene terephthalate)/poly(1,4-butylene adipate),[25] poly(butylenes terephthalate/succinate/adipate),[26] poly(ethylene terephthalate)/cyclodi(ethylene succinate),[27] and poly(glycolic acid) and poly(lactic acid)/poly(ethylene terephthalate)[28,29] copolymers were prepared by means of melt-blending transesterification of already existing homopolymers.

In this study, we report on transesterification reactions of poly(butylenes terephthalate) (PBT) and poly (ethylene glycol)/DL-oligo(lactic acid) (PEG/OLA) blending product and the resulting properties of the copolymers. PEG/OLA blend was prepared by melting bulk reaction of PEG and OLA at 200°C without follow-up separation. PBT and PEG/OLA were subjected to reactive blending in the absence of any additional catalyst. The molecular structures of the resulting copolymers will be evaluated by combination of $^1$H NMR spectroscopy and solubility studies. The polymers were produced with the aim to obtain the materials showing enhanced mechanical performance and sufficient biodegradability.

## EXPERIMENTAL

### Materials and synthesis

Poly(butylene terephthalate) (PBT) (Aldrich, Milwaukee, WI) was powdered by cryogenic crushing and vacuum-dried overnight at 80°C before use ($T_m$ = 227°C, $T_g$ = 66°C, $M_\eta$ = 38,000 from inherent viscosity measurements in 40/60 tetrachloroethane/phenol at 30°C, using the molar mass–viscosity relationship $[\eta] = 1.166 \times 10^{-4} M^{0.871}$).[30] Ninety percent aqueous solution of racemic DL-lactic acid (Fluka) was heated stepwise to 200°C and kept at this temperature in vacuum for 4 h.[31] This procedure yielded α-hydroxy-ω-carboxyoligo(lactic acid) (OLA, $M_w$ = 4500, $M_n$ = 1700, $M_w/M_n$ = 2.60). Hydroxyl end-capped poly(ethylene glycol) 1000 (PEG, $M_n$ = 1000) was purchased from Lancaster and dried by vacuum at 40°C prior to use.

### Synthesis of copolyesters

Prior to synthesis of copolyesters, the reactive blend of PEG and OLA was prepared by melting bulk reaction of PEG and OLA to obtain PEG/OLA blend. An appropriate molar ratio of PEG and OLA were placed in a two-necked bottom equipped with nitrogen inlet and magnetic stirrer bar. A continuous nitrogen flow was maintained for the reaction system. The reaction mixture was kept at 200°C for 2 h under normal pressure, and subsequently stirred at 200°C for another 2 h under reduced pressure. Allowing mixture to cool to room temperature, the PEG/OLA blend was collected without further separation. The PEG/OLA blend was stored for next use even containing unreacted PEG and OLA in the blend.

PBT/PEG/OLA copolyesters were synthesized by reacting PBT and PEG/OLA blend in the bulk and at high temperature. 7.3 g (33 mmol) of PBT and certain amount of PEG/OLA blend according to an appropriate molar ratio (see Table I) were placed in a 50-mL glass reactor equipped with nitrogen inlet and outlet and a central mechanical stirrer. A slow nitrogen stream was passed through the system. The reactor was placed in a salt bath at 260°C and the reaction mixture was stirred for 1.5 h under nitrogen. The polymer was allowed to cool to room temperature, dissolved in 50 mL of chloroform/phenol (4/6 v/v), isolated by precipitation in 800 mL of

methanol, and collected on a filter. The white polymer was then dried at 40°C for 24 h in vacuum.

### Measurements

The proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded on a Brucker ARX 400 MHz NMR spectrometer using deuterated chloroform as solvent. The gel permeation chromatography (GPC), so-called size-exclusion chromatography (SEC) analysis, was carried out on a Breeze Waters system consisting of a Rheodyne injector, a 1515 Isocratic pump, and a Waters 2414 differential refractometer. SEC was performed in chloroform. Two hundred microliter of solution (about 3% w/v) was injected through a Styragel column set, Styragel HT3 and HT4 (19 mm × 300 mm, $10^3 + 10^4$ Å), at a flow rate of 1.0 mL/min, to separate $M_w$ ranging from $10^2$ to $10^6$. The temperature of columns (separation) was maintained at 40°C, while the temperature of refractometer detectors was set at 40°C. The instrument was calibrated with monodisperse polystyrene standards. Thermogravimetry (TG) was performed under nitrogen with a Perkin-Elmer TGA 7 (heating rate 20°C/min, sample size 8–10 mg). A temperature $T_d$ (−1.5 wt %) at which 1.5 wt % of original weight of a sample was lost due to its decomposition, was tentatively applied as an index to characterize its thermal stability. Differential scanning calorimetry (DSC) measurements of copolyesters were carried out on a Perkin–Elmer DSC 7 equipped with a liquid nitrogen cooling system under a nitrogen flow at a rate 40 mL/min. The samples of about 8–10 mg were encapsulated in the DSC aluminum pans and then thermally treated. Prior to the DSC characterization, heat histories of samples were removed and they were kept at ambient temperature for days to allow their crystallization to approach the equilibrium state. DSC thermal diagram was recorded at the heat speed of 10°C/min from −50 to 300°C, and glass transition temperature $T_g$, melting point $T_m$, and heat of fusing $\Delta H_m$ were determined from the endothermic curves by observing the second heating run. The crystallization temperature $T_c$ and crystallization enthalpy $\Delta H_c$ were recorded from cooling run (cooling rate 20°C/min). The surfaces of degraded samples after the hydrolytic degradation were observed with Philips 535 scanning electron microscopy (SEM) after gold vapor deposition onto the samples in an Edwards Auto 306. Mechanical properties were determined with a WDW universal test system, with electronic data evaluation on dumbbell-shaped specimen of 100-mm gauge length and 15-mm width that were cut from solution-cast and remolten films. The standard rate of elongation was 2 mm/min, and the films were tested at room temperature.

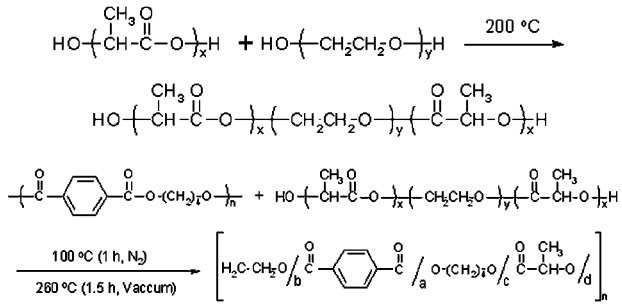
### Hydrolytic degradation

Films of polyesters were prepared by solution casting. Typically, a chloroform solution (30%) of the polymer was poured onto a glass plate and the solvent was slowly evaporated at room temperature. The formed film was separated from the glass plate. The residual solvent was evaporated under atmospheric pressure over 24 h at room temperature and then *in vacuo* for 48 h at 40°C. Hydrolytic degradation experiments of the polyesters were carried out at 37°C in a phosphate buffer solution (Fluka, pH 7.413 at 25°C). Square samples with dimensions of 1 mm × 4 mm were cut from the various films and placed in vials containing 20 mL of buffer solution. At predetermined degradation time intervals, the specimens were removed from the medium, rinsed with distilled water, dried under vacuum at room temperature for 1 week and weighed. Before continuing the experiment, the buffer solution was renewed. Weight loss percentages of the copolyesters were obtained according to the relationship (weight loss %) = $(W_0 - W_r) \times 100/W_0$, where $W_0$ is the initial weight and $W_r$ is the dry weight of the specimens after degradation.

## RESULTS AND DISCUSSION

### Synthesis of copolyesters

The scope of this article is the development of catalyst-free synthesis of high-molecular weight copolyesters with biodegradable and aromatic moieties based on existing polymers. The concept for achieving hydrolytical degradation is the combination of lactide (LA) and ethyleneoxide (EO) moieties into aromatic segments. Copolyesters have to contain a high content of aromatic units and a certain amount of LA and EO moieties to display improved physical properties and hydrolytic degradability, respectively. Prior to synthesis of copolyesters, blend of PEG and OLA were carried out at high temperature to obtain multiblock PEG/OLA copolymer. Without further purification, the PEG/OLA blend contained PEG/OLA multiblock copolymer and unreacted PEG and OLA. Because of enhanced thermal stability, the PEG/OLA reactive blend was used to replace simple mixture of PEG and OLA for next melting reaction at high temperature. Contrarily, if simple mixture of PEG and OLA without melting blend was used for next high-temperature reaction, the transesterification reaction would lead to color change of reaction mixture. The reactions between PBT and PEG/OLA were carried out at 260°C for 1.5 h in the bulk (Scheme 1). During the synthesis of copolyesters, the transesterification between the reactants was almost unavoidable. LA and EO units were built into the

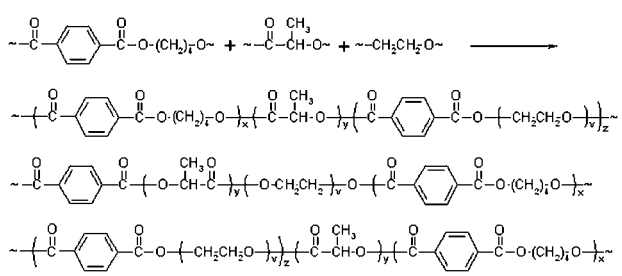



**Scheme 1** Synthesis of PEG/OLA reactive blend and copolyesters.

polymer chain during the reaction by transesterification, having the appropriate reactivity for incorporation and yielding a statistical product, poly (1,4-butylene terephthalate-*co*-ethyleneoxide-*co*-DL-lactide) (PBTEOLA). LA units have two different functional groups and ethylene glycol units have two hydroxyl end groups, so the polycondensation and the transesterification between butylene terephthalate (BT), EO, and LA units (or segments) may proceed as in Scheme 2. The reaction took place without any additional catalyst. Because of good solubility of PEG, OLA, and PEG/OLA copolymer in methanol, the copolyesters were reprecipitated from methanol. Any unreacted PEG, OLA, and PEG/OLA copolymer contained in copolyesters could be extracted completely.

### Structure characterization of copolyesters

The $^1$H NMR spectra of a PEG/OLA reactive blend and PBT are shown in Figure 1. We can see clearly that the $^1$H NMR spectrum of the PEG/OLA reactive blend is not simple additivity of that of PEG and OLA; the peaks centered at 1.51, 5.32, and 4.48 ppm should be assigned to the protons of C$H_3$ (b), C$H$ (c), and C$H$ (d) adjacent to end OH group of OLA, and the peak at 3.64 (a) ppm should belong to the contribution of C$H_2$ in PEG, respectively. Besides those peaks, peak at 3.50 ppm, attributable to C$H_2$ of PEG linked to COO of OLA, is a result of transesterification of PEG and OLA. The results indicated that not



**Scheme 2** Possible chemical structure in transesterification between PBT and PEG/OLA.

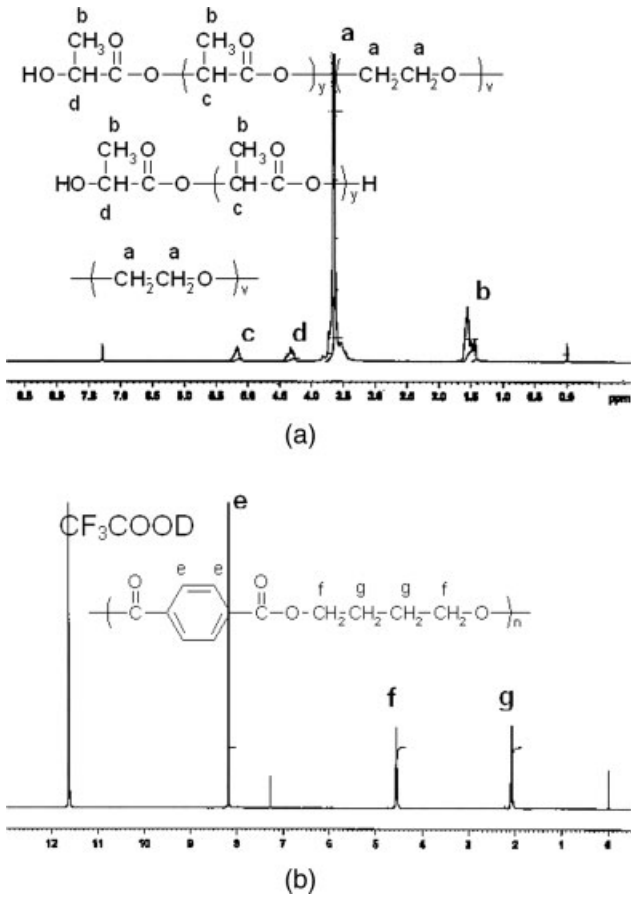



**Figure 1** 400 MHz $^1$H NMR spectra of the PEG/OLA reactive blend and PBT. (a): The results indicated that not only unreacted PEG and OLA but also PEG/OLA copolymer existed in PEG/OLA reactive blend. (b): In the 1H NMR spectrum of PBT, peaks centered at 8.14 (e), 4.55 (f), and 2.08 ppm (g) should be assigned to the protons of benzene ring, $OCH_2$, and adjacent $CH_2$ of PBT.

only unreacted PEG and OLA but also PEG/OLA copolymer existed in PEG/OLA reactive blend. In the $^1$H NMR spectrum of PBT, peaks centered at 8.14 (e), 4.55 (f), and 2.08 ppm (g) should be assigned to the protons of benzene ring, O$CH_2$, and adjacent C$H_2$ of PBT. However, in the $^1$H NMR spectrum of the copolyester without LA unit, which was prepared from melting reaction of PBT and PEG, except for the nuclear resonances mentioned earlier characteristic of PBT and PEG, there is a new peak appearing at 3.85 ppm (h) attributable to C$H_2$ of EO adjacent to terephthaloyloxymethylene (Fig. 2). In the $^1$H NMR spectrum of the copolyester prepared from melting bulk reaction of PBT and PEG/OLA blend, except for the nuclear resonances mentioned characteristic of PBT, PEG, and OLA, there are several new peaks appearing at 1.85, 3.85 (h), 4.35 ppm, attributed to C$H_3$ of LA adjacent to terephthalate, C$H_2$ of EO adjacent to terephthaloyloxymethylene, C$H_2$ of EO and butyleneoxide linked to LA, respectively, (Fig. 2). Because of the conjugative effect of

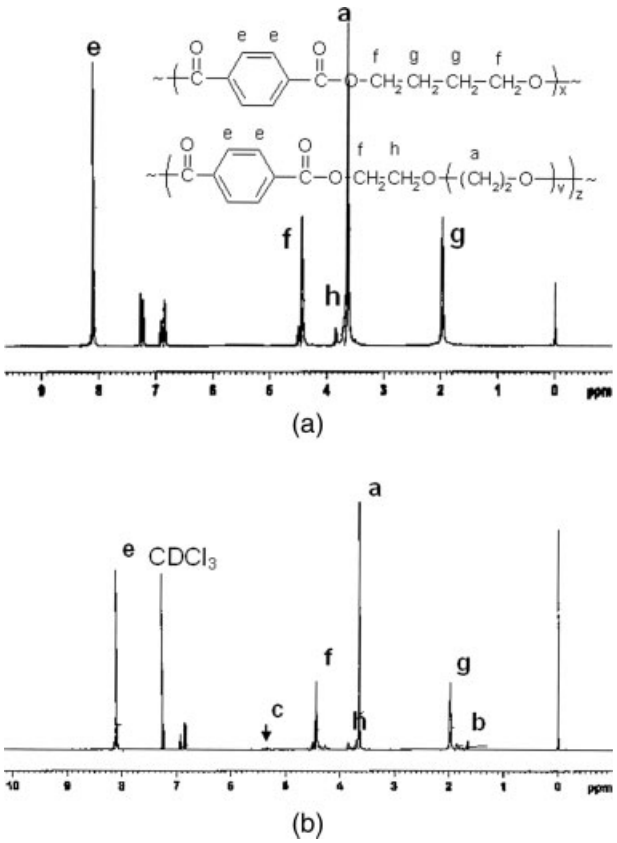



**Figure 2** 400 MHz $^1$H NMR spectra of the copolyester PBTEO73LA0 and PBTEO66LA1. (a): However, in the 1H NMR spectrum of the copolyester without LA unit, which was prepared from melting reaction of PBT and PEG, except for the nuclear resonances mentioned earlier characteristic of PBT and PEG, there is a new peak appearing at 3.85 ppm (h) attributable to $CH_2$ of EO adjacent to terephthaloyloxymethylene. (b): In the 1H NMR spectrum of the copolyester prepared from melting bulk reaction of PBT and PEG/OLA blend, except for the nuclear resonances mentioned characteristic of PBT, PEG, and OLA, there are several new peaks appearing at 1.85, 3.85 (h), 4.35 ppm, attributed to $CH_3$ of LA adjacent to terephthalate, $CH_2$ of EO adjacent to terephthaloyloxymethylene, $CH_2$ of EO and butyleneoxide linked to LA, respectively.

**TABLE II**
**The Solubility of the Resulted Copolyesters**

| Copolyester | MeOH | Toluene | THF | $CHCl_3$ | $CHCl_3$/Phenol (4/6 v/v) |
|---|---|---|---|---|---|
| PBTEO43LA9 | − | − | ± | + | + |
| PBTEO47LA7 | − | − | − | + | + |
| PBTEO59LA5 | − | − | − | + | + |
| PBTEO66LA1 | − | − | − | + | + |
| PBTEO73LA0 | − | − | − | + | + |
| PBTEO15LA3 | − | − | − | − | + |
| PBTEO34LA5 | − | − | − | − | + |
| PBTEO62LA14 | − | − | − | + | + |
| PBTEO73LA20 | − | − | ± | + | + |
| PEG | + | + | + | + | + |
| OLA | + | + | + | + | + |
| PBT | − | − | − | − | + |

+, soluble; −, insoluble; ±, swelling.

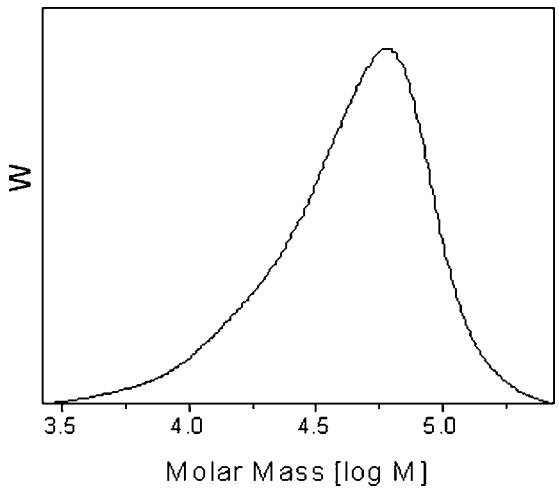



**Figure 3** GPC curves of the copolyester PBTEO59LA5 determined by chloroform-GPC with refractive index detection versus polystyrene standards.

the benzene ring, the terephthalate ester group has stronger electronegativity than LA ester group, so taking into account the relationship between chemical shifts in the $^1$H NMR spectrum and the chemical circumstances of different $OCH_2$ protons, peaks at 4.55 and 4.35 ppm are assigned to the $OCH_2$ protons of the butyleneoxide and EO group linking to a terephthaloyl and a LA, respectively. The integrals of the peaks at 2.08 ($CH_2$ of BT units), 3.64 ($CH_2$ of EO units), 5.32 ppm (CH of LA units) provided the actual content of BT, EO, and LA units (or segments) in the copolyesters. The calculated molar ratios of BT/LA are shown in Table I. For the synthesis of the copolyesters, the reaction temperature reached above 260°C, which was above the temperature of the ester bond cleavage in prepolymers, thus leaded to the possibility of ester exchange reaction. Meanwhile, a period of reaction time was also assumed to be in favor of the ester exchange reaction.

The copolyesters were synthesized by melting bulk reaction but with varying starting ratio of OLA/PEG and varying feeding amount of PEG/OLA blend. Yields were in the range of 80–95%. While the PEG/OLA blend starting amount increased to 91.2% (PBTEO73LA20, see Table I), the copolyester became too viscous colloid to filtration after precipitation with methanol due to incorporation of excess aliphatic segments. That became difficult for calculating yield of the viscous copolyester. With increasing starting ratio of OLA/PEG and amount of PEG/OLA blend, the copolyesters showed improved solubility in chloroform and tetrahydrofuran (THF), as shown in Table II. The copolyesters with composition of BT units below 60% are readily soluble in chloroform. However, the pristine PBT is soluble only in a chloroform/phenol (4/6 v/v) mixing solvent. Because of solubility of the copo-

**TABLE III**
**Molecular Weight of the Resulted Copolyesters**

| Copolyester | $M_w \times 10^{-4}$ | $M_n \times 10^{-4}$ | $M_w/M_n$ |
|---|---|---|---|
| PBTEO43LA9 | 1.22 | 0.72 | 1.69 |
| PBTEO47LA7 | 3.14 | 1.86 | 1.68 |
| PBTEO59LA5 | 6.51 | 4.24 | 1.54 |
| PBTEO66LA1 | 6.66 | 5.13 | 1.30 |
| PBTEO73LA0 | 8.07 | 5.07 | 1.59 |
| PBTEO62LA14 | 5.46 | 3.22 | 1.70 |
| PBTEO73LA20 | 0.70 | 0.41 | 1.69 |

lyesters in chloroform, a conventional GPC with chloroform as eluent can be used to measure molecular weight of the copolyester. All GPC traces of the copolyesters showed unimodal molecular weight distribution (Fig. 3). The weight-averaged molecular weights of the copolyesters are determined to be in range of 7000 and 66,600 with molecular weight distribution between 1.30 and 1.70 (Table III). With

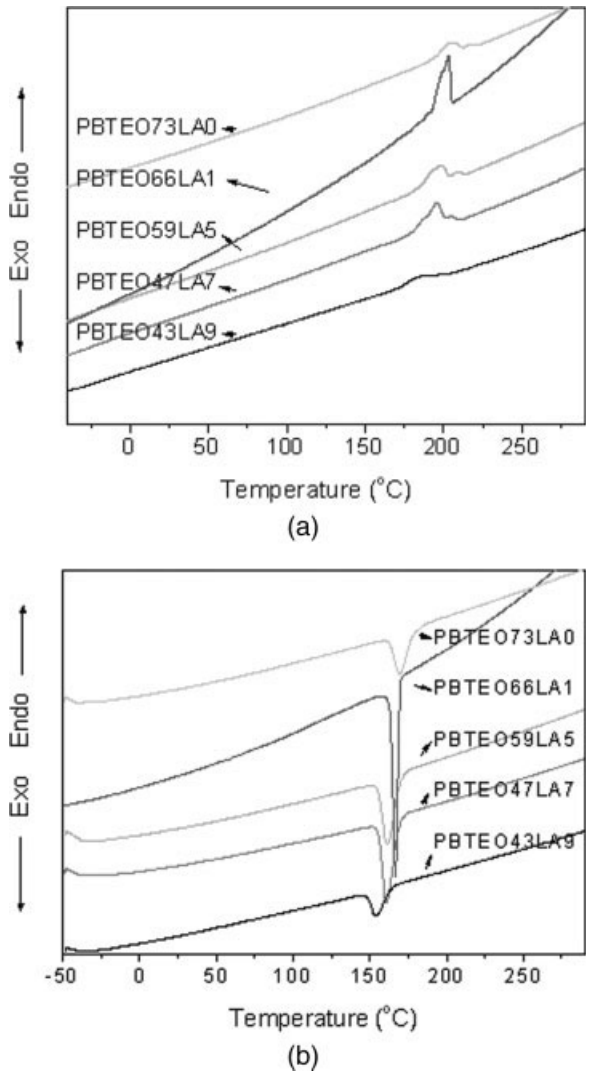



**Figure 4** DSC (a) second heating scan and (b) cooling run of copolyesters with different starting molar PEG/OLA ratio.

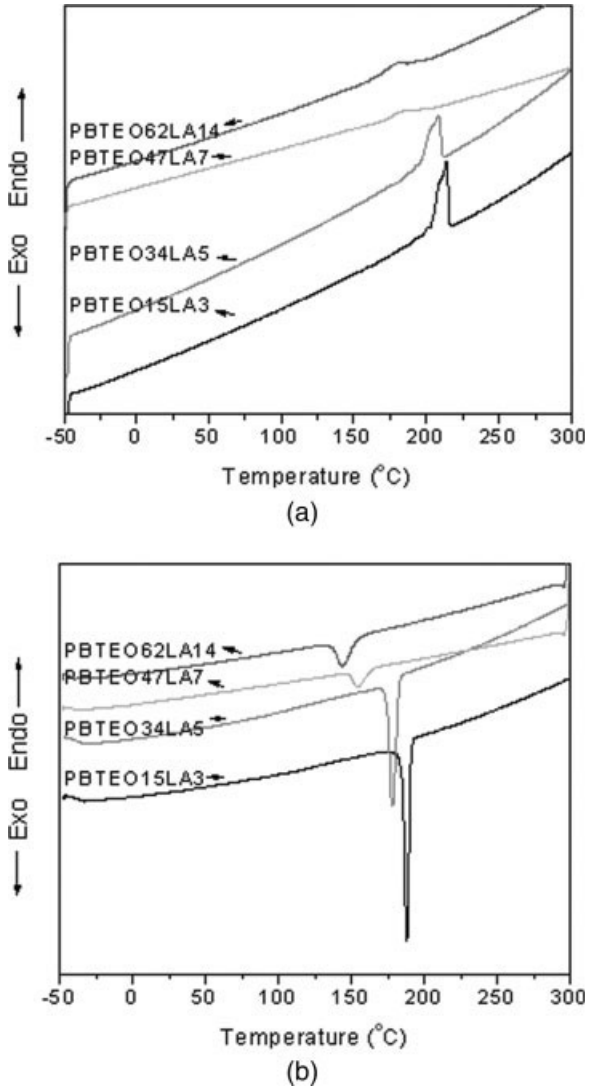



**Figure 5** DSC (a) second heating scan and (b) cooling run of copolyesters with different starting amount of PEG/OLA blend while fixing PEG/OLA starting molar ratio.

increase of starting ratio of OLA/PEG and amount of PEG/OLA blend, the molecular weight of the copolyesters decreased. During transesterification some butyleneoxide in PBT was replaced with EO moieties, and the molecular weights of the copolymers had greater change in comparison to pristine PBT due to rearrangement of BT units with EO and LA moieties.

### Thermal behavior of copolyesters

The thermal properties were characterized by means of DSC and TG for the copolyesters with different starting ratio of OLA/PEG and amount of PEG/OLA blend. Figures 4 and 5 show the DSC second heating and cooling thermograms of copolyesters, and the transition temperature values are listed in Table IV. As we can see in the DSC thermograms,

**TABLE IV**
**Thermal Properties of Copolyesters**

| Copolyester | $T_m$ (°C)[a] | $\Delta H_m$ (J/g) | $T_c$ (°C) | $T_d$ (°C)[b] |
|---|---|---|---|---|
| PBTEO43LA9 | 187.1 | 18.7 | 159.2 | 407.1 |
| PBTEO47LA7 | 195.6 | 25.9 | 162.3 | 407.8 |
| PBTEO59LA5 | 198.2 | 14.2 | 164.2 | 409.8 |
| PBTEO66LA1 | 202.2 | 38.4 | 167.6 | 408.5 |
| PBTEO73LA0 | 205.5 | 14.6 | 168.3 | 407.8 |
| PBTEO15LA3 | 213.8 | 30.4 | 187.8 | 402.6 |
| PBTEO34LA5 | 208.3 | 30.5 | 178.1 | 403.9 |
| PBTEO62LA14 | 175.1 | 11.7 | 141.2 | 409.8 |

[a] Melting temperature ($T_m$), crystallization temperature ($T_c$), and melting enthalpy ($\Delta H_m$) were registered by DSC at a cooling rate of 20°C/min or at a second heating rate of 10°C/min.
[b] $T_d$ (−1.5 wt %) was measured by TG at a heating rate of 20°C/min.

no glass transition was observed. All copolyesters exhibit only one melting temperature ($T_m$) from second heating run and one cooling-crystallization temperature ($T_c$) from cooling cycle. The $T_m$ and $T_c$ of the copolyesters shifted down to a low temperature as increase of starting ratio of OLA/PEG and amount of PEG/OLA blend. The few aromatic units in the copolyesters led to lower melting temperature and crystallization temperature while starting ratio of OLA/PEG and amount of PEG/OLA blend increased. Only one $T_m$ of the copolyesters and $T_m$'s change with variation of composition indicated that the melt bulk transesterification resulted in statistical copolyesters rather than physical blend. Figures 6 and 7 show TG curves of the copolyesters with starting ratio of OLA/PEG and amount of PEG/OLA blend. The copolyesters exhibit an almost similar decomposition temperature at around 400°C as the pristine PBT. In comparison to these results, OLA and PEG have as lower decomposition temperature as 220 and 300°C, respectively. However, the copolyester with PEG/OLA blend starting amount of 91.2% exhibited melting temperature close to room temperature and low decomposition temperature due to almost aliphatic units in the copolyesters.

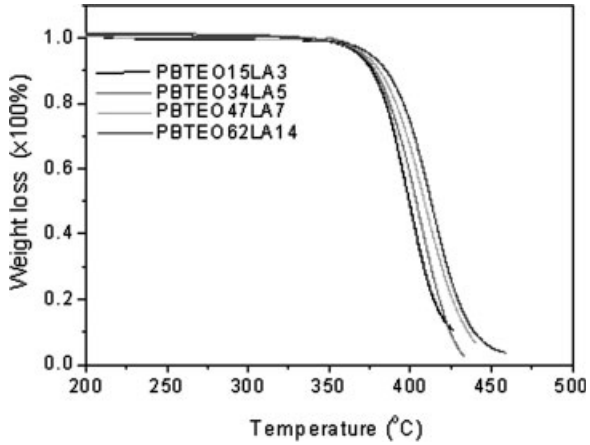



**Figure 7** TG traces of copolyesters with different starting amount of PEG/OLA blend while fixing PEG/OLA starting molar ratio (scanning rate of 20°C/min).

### Hydrolytic biodegradability of copolyesters

For preliminary test of hydrolytic degradability, films of the copolyesters with thickness of 300 μm and weight of about 1.5 g were placed in 20 mL of a phosphate buffer solution at 37°C. The samples were removed at various times, rinsed with distilled water, dried, and weighed. Before continuing the experiment, the buffer solution was renewed. All the copolyesters were distinctly degraded in phosphate buffer solution at 37°C even though they have many aromatic units in the main chain, and a weight loss of 10% was observed for the copolyester with 76% of EO and LA composition (PBTEO62LA14, see Table I), after immersion phosphate buffer solution at 37°C

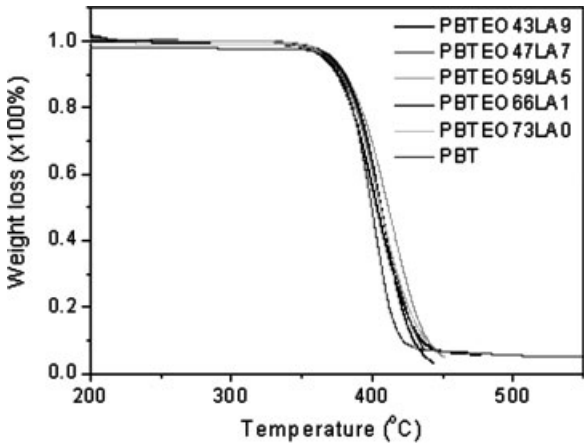



**Figure 6** TG traces of copolyesters with different starting molar PEG/OLA ratio (scanning rate of 20°C/min).

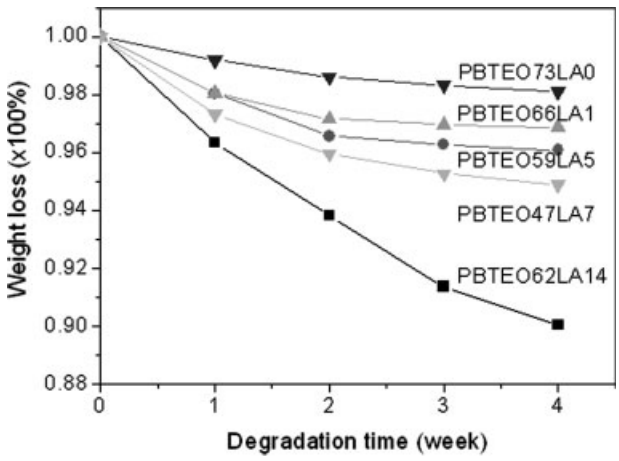



**Figure 8** Weight loss versus time during hydrolytic degradation of copolyesters.

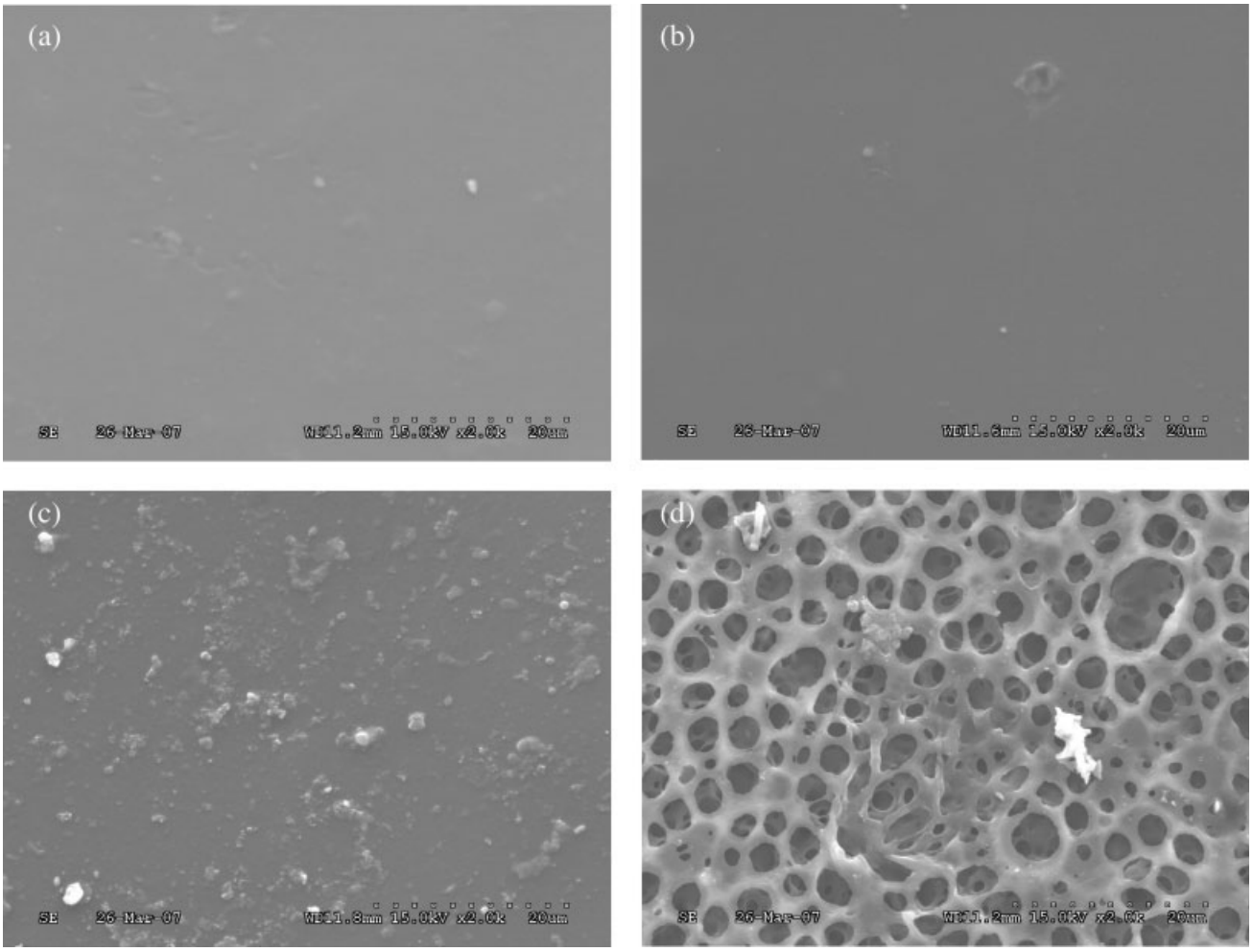



**Figure 9** Scanning electron micrographs of the surface of the copolyester PBTEO73LA0 (a) and PBTEO62LA14 (b) film before hydrolytic degradation and (c and d) corresponding images after hydrolytic degradation for 4 weeks.

for 4 weeks. The degradation rate revealed a composition dependency (Fig. 8). With increase of EO and LA composition, the copolyesters produced by melting bulk transesterification showed better biodegradability. This is due to the fact that the degradation of copolyesters occurs at aliphatic ester bond. The pristine PBT slightly displayed degradation under physiological conditions. Surface morphology changes were investigated by SEM. Photographs of the copolyester PBTEO73LA0 containing 73 mol % of EO composition and no LA composition and the copolyester PBTEO62LA14 containing 62 mol % of EO composition and 14 mol % of LA composition before and after immersion tests are shown in Figure 9. Dark areas and holes on the surfaces of the samples represented biodegraded parts. The surfaces of the films before degradation were smooth without holes. After degradation for 4 weeks, the smooth surface of the copolyester film with enough LA composition became cracked or porous. However, no obvious surface erosion was observed on the surface of the copolyester without LA composition. The results indicated that the LA units are in favor of hydrolytic degradation of the copolyesters. All copolyesters produced by transesterification showed good biodegradability. The degradation of copolyesters occurred on the film surfaces.

## Mechanical properties

Mechanical properties of the copolyesters have been measured, and the data are recorded in Table V. The Young's modulus ($E$), nominal tensile strength ($\sigma$), and elongation at break ($\varepsilon$) of the solution-cast and remolten film of the copolyester PBTEO73LA0 con-

**TABLE V**
**Mechanical Properties of the Resulted Copolyesters**

| Copolyester | Tensile strength (MPa) | Elongation (%) | Modulus (MPa) |
|---|---|---|---|
| PBTEO47LA7 | 21.3 | 31.8 | 100 |
| PBTEO66LA1 | 17.7 | 89.3 | 60 |
| PBTEO73LA0 | 14.5 | 136.8 | 50 |
| PBT | 53.3 | 14.5 | 1,200 |

taining 73 mol % EO and no LA composition are 50 MPa, 14.5 MPa, and 136.8%, respectively. Meanwhile, the Young's modulus, nominal tensile strength, and elongation at break of the solution-cast and remolten film of the copolyester PBTEO47LA7 containing 47 mol % EO and 7 mol % LA composition are 100 MPa, 21.3 MPa, and 31.8%, respectively. More EO composition, therefore less aromatic units in the copolyester, led to lower modulus and higher elongation due to flexibility of EO segments. Nevertheless, more aromatic units in the copolyester PBTEO47LA7, even though increasing LA composition, caused higher modulus and lower elongation. The industrial pristine PBT has tensile strength of 53 MPa and lower elongation at break of only 14%. Further research is being performed on improvement of mechanical properties by orientation and thermal treatment of the samples. The results will be reported in the following article.

## CONCLUSIONS

In this work, new biodegradable copolyesters were prepared through bulk melting reaction between reactive blend of PEG/OLA and PBT. The existence of new heterolinkages inside the backbones of the copolyesters, resulting from the transesterification reaction, was confirmed. The copolymers attained an almost statistical microstructure when melting bulk transesterification was performed at 260°C for 1.5 h. The $T_m$ and $T_c$ values of the copolyesters varied with the starting ratio of OLA/PEG and amount of PEG/OLA blend used for the transesterification reaction. The copolyesters exhibit increased solubility with increase of starting ratio of OLA/PEG and amount of PEG/OLA blend. The copolyesters with composition of BT units below 60% are readily soluble in chloroform, while pristine PBT is only soluble in chloroform/phenol mixing solvent. The copolyesters underwent significant hydrolytic degradation at 37°C, which increased with increase of the composition of LA and EO units. Hydrolysis occurs mainly on the aliphatic ester groups, especially on the LA ester bonds. After simple melting transesterification, the copolymers exhibit good biodegradability and better ductibility. The copolyesters have potential applications in environment-friendly packaging materials and tissue engineering.

## References


1. Gilding, D. K.; Reed, A. M. Polymer 1979, 20, 1459.
2. Brode, G. L.; Koleske, J. V. J. Macromol Sci Chem A 1972, 6, 1109.
3. Domb, A. J.; Langer, R. J Polym Sci Part A: Polym Chem 1987, 22, 3373.
4. Fukuzaki, H.; Aiba, Y.; Yoshida, M.; Asano, M.; Kumakura, M. Makromol Chem 1989, 190, 1553.
5. Imasaka, K.; Nagai, T.; Yoshida, M.; Fukuzaki, H.; Asano, M.; Kumakura, M. Makromol Chem 1990, 191, 2077.
6. Fukuzaki, H.; Yoshida, M.; Asano, M.; Kumakura, M.; Imasaka, K.; Nagai, T.; Mashimo, T.; Yuasa, H.; Imasi, K.; Yamanaka, H. Eur Polym J 1990, 26, 1273.
7. Pannu, R. K.; Tanodekaew, S.; Li, W.; Collett, J. H.; Attwood, D.; Booth, C. Biomaterials 1999, 20, 1381.
8. Bechtold, K.; Hillmyer, M. A.; Tolman, W. B. Macromolecules 2001, 34, 8641.
9. Park, S. S.; Chae, S. H.; Im, S. S. J Polym Sci Part A: Polym Chem 1998, 36, 147.
10. Kim, Y. J.; Park, O. O. J Appl Polym Sci 1999, 72, 945.
11. Kang, H. J.; Park, S. S. J Appl Polym Sci 1999, 72, 593.
12. Park, S. S.; Kang, H. J. Polym J 1999, 31, 238.
13. Ma, D.; Xu, X.; Luo, X.; Nishi, T. Polymer 1997, 38, 1131.
14. Deng, L. M.; Wang, Y. Z.; Yang, K. K.; Wang, X. L.; Zhou, Q.; Ding, S. D. Acta Mater 2004, 52, 5871.
15. Tokiwa, Y.; Ando, T.; Suzuki, T.; Takeda, T. Polym Mater Sci Eng 1990, 62, 988.
16. Jun, H. S.; Kim, B. O.; Kim, Y. C.; Chang, H. N.; Woo, S. I. J Environ Polym Degrad 1994, 2, 9.
17. Jun, H. S.; Kim, B. O.; Kim, Y. C.; Chang, H. N.; Woo, S. I. Stud Polym Sci 1994, 12, 498.
18. Chiellini, E.; Corti, A.; Giovannini, A.; Narducci, P.; Paparella, M.; Solaro, R. J Environ Polym Degrad 1996, 4, 37.
19. Maeda, Y.; Maeda, T.; Yamaguchi, K.; Kubota, S.; Nakayama, A.; Kawasaki, N.; Yamamoto, N.; Aiba, S. J Polym Sci Part A: Polym Chem 2000, 38, 4478.
20. Heidary, S.; Gordon, B., III. Polym Mater Sci Eng 1992, 67, 190.
21. Heidary, S.; Gordon, B., III. J Environ Polym Degrad 1994, 2, 19.
22. Niekraszewicz, A. Polimery (Warsaw) 1993, 38, 339.
23. Pisula, W.; Piglowski, J.; Kummerlöwe, C. Polimery (Warsaw) 2006, 51, 341.
24. Li, F.; Xu, X.; Hao, Q.; Li, Q.; Yu, J.; Cao, A. J Polym Sci Part B: Polym Phys 2006, 44, 1635.
25. Shi, X. Q.; Ito, H.; Kikutani, T. Polymer 2005, 46, 11442.
26. Shi, X. Q.; Aimi, K.; Ito, H.; Ando, S.; Kikutani, T. Polymer 2005, 46, 751.
27. Salhi, S.; Tessier, M.; Blais, J.-C.; Gharbi, R. E.; Fradet, A. Macromol Chem Phys 2004, 205, 2391.
28. Kint, D. P. R.; Alla, A.; Deloret, E.; Campos, J. L.; Muñoz-Guerra, S. Polymer 2003, 44, 1321.
29. Acar, I.; Kaşgöz, A.; Özgümüs, S.; Orbay, M. Polym Plast Technol Eng 2006, 45, 351.
30. Bormann, W. F. H. J Appl Polym Sci 1978, 22, 2119.
31. Asano, M.; Yoshida, M.; Kaetsu, I. Makromol Chem Rapid Commun 1985, 6, 509.