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Synthesis, characterization and hydrolytic degradation of degradable poly(butylene terephthalate)/poly(ethylene glycol) (PBT/PEG) copolymers*

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Abstract Hydrolytic degradable PBT/PEG copolymer was synthesized by macromolecular transesterification method from PBT and PEG macromonomers. The resultant copolymers were characterized by ^{1}H-NMR and GPC. The non-isothermal crystallization behavior of these copolymers was studied by differential scanning calorimetry (DSC). The water absorption and hydrolytic degradation behavior of PBT/PEG copolymers were also studied in detail.

1 Introduction

In recent years, great efforts have been taken to develop biodegradable polymers for the industrial or academic purpose due to more and more serious environmental problems. There are many kinds of biodegradable polymers, including aliphatic polyesters [1, 2], poly(α-amino acid)s [3], poly(ortho ester)s [4], polyanhydrides [5], and etc. But unfortunately, due to their high cost, their wider industrial application was restricted. Recently, poly(ethylene glycol) (PEG) was incorporated into aromatic polyester backbone to increase the hydrophilicity and biodegradability of these raw materials. Poly(ethylene terephthalate)/poly(ethylene glycol) (PET/PEG) copolymers and poly(butylene terephthalate)/poly(ethylene glycol) (PBT/PEG) copolymers were studied more extensively [6–11]. Due to its low cost and good biodegradability, these materials might have a potential application in biomedical and ecological fields. PBT/PEG and PET/PEG copolymers were mainly synthesized from ethylene diol (or: butylene diol), dimethyl terephthalate, and poly(ethylene glycol) [6–8]. But during the process, the byproduct–methanol would be released. In this work, we prepared PBT/PEG multiblock copolymer by macromolecular transesterification method, starting from PBT and PEG macromers. These resultant copolymers were characterized by ^{1}H-NMR and DSC. Water absorption and *in vitro* degradation behaviour were also studied in detail. This article is an extension of our previous work [9–11].

Fan LY is the co-first author for this work.

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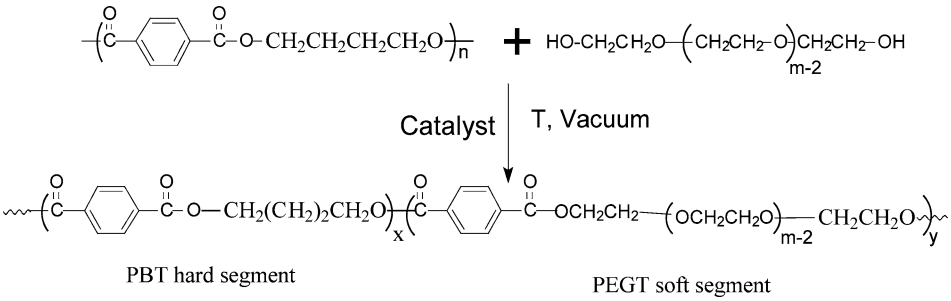
Scheme 1 Synthesis scheme of PBT/PEG multiblock copolymers from PBT and PEG macromonomers.



2 Experimental

2.1 Materials

PBT ($[\eta] = 0.81$ measured in *m*-cresol, Yizheng Chem. Co., P.R. China), PEG ($M_n = 600$–4000), tetrabutyl titanate and *m*-cresol were analytical pure agents. PBT was dried in vacuum for 12 h before use, and the others were used as received.

2.2 Synthesis of PBT/PEG copolymers

PBT/PEG copolymer was synthesized by macromolecular transesterification method shown in Scheme 1 [10, 11]. The mixture of PBT, PEG ($M_n = 600$–4000), and tetrabutyl titanate was added into a four-necked flask under nitrogen atmosphere, and then was gradually heated to 230°C to get a homogeneous melt. At this temperature, the reaction mixture underwent a transesterification reaction for 30 min with constant stirring. The temperature was then elevated to 270°C under high vacuum for 1–2 h. At the end, the resultant melt was poured into cold water and then vacuum dried for 12 h. The resulting copolymers were kept in desiccators before use. All the samples prepared in this work are listed in Table 1.

2.3 Intrinsic viscosity measurement

Intrinsic viscosity $[\eta]$ was measured by using an Ubbelohde viscometer at 30 ± 0.1°C. All the copolymers were dissolved in *m*-cresol to prepare solutions of ca.0.5 g/dL. $[\eta]$ was calculated according to Equation (1):

$$[\eta] = \frac{\sqrt{2(\frac{t}{t_0} - 1 - \ln\frac{t}{t_0})}}{C} \tag{1}$$

Where C is concentration of solution, t is flow time of solution, and t_0 is flow time of pure solvent.

2.4 ^{1}H-nuclear magnetic resonance (^{1}H-NMR)

^{1}H-NMR spectra (in $CDCl_3$) were recorded on Bruker 300 spectrometer (Bruker, Rheinstetten, Germany) at 300 MHz using trimethylsilane (TMS) as internal standard.

2.5 GPC analysis

GPC analysis was used to characterize the molecular weight of PBT/PEG copolymers. The experiments were carried out with a Shimadzu SCL-10A and LC-10AT system equipped with two Phenogel 5 μm 100 Å and 10000 Å columns (size: 300 × 4.6 mm) in series and a RID-10A refractive index detector. Chloroform was used as eluent at a flow rate of 0.30 ml/min at 40°C. Monodispersed poly(ethylene glycol) standards were used to obtain a calibration curve.

2.6 Differential scanning calorimetry (DSC)

The nonisothermal crystallization behavior of PBT/PEG copolymers was characterized on a DSC instrument

Table 1 The PBT/PEG copolymers prepared in this work

Sample	Weight fraction of PBT in feed (%Wt)	Molecular Weight of PEG (g/mol)	Intrinsic Viscosity ([η], dl/g)	Mn (*) (g/mol)	Mw/Mn (*)
PBT50/600	50	600	0.58	13,387	2.511
PBT50/PEG1000	50	1000	0.70	10,245	2.612
PBT50/PEG1540	50	1540	0.84	14,443	2.543
PBT50/PEG4000	50	4000	0.70	10,620	2.361
PBT40/PEG1000	40	1000	0.74	13,271	2.074
PBT60/PEG1540	60	1540	0.71	12,319	2.268

*Which were obtained from GPC results.

(NETZSCH DSC 204). The specimens were first heated to 220°C from room temperature, then were cooled to −55°C, and then were reheated to 220°C. The heating rate and cooling rate are both 10°C/min. The crystallinity (X_c) of the sample was calculated according to the heat of fusion of the second heat run:

$$X_{c,PBT}\,(\%) = \frac{\Delta H_{m\text{-}PBT}}{\Delta H^{\circ}_{m\text{-}PBT}} \times 100 \tag{2}$$

Where $\Delta H^{o}_{m\text{-}PBT} = 144.5$ J/g is for the 100% crystalline PBT according to Zhang Y *et al.* [12].

$$X_{c,PEG}\,(\%) = \frac{\Delta H_{m\text{-}PEG}}{\Delta H^{o}_{m\text{-}PEG}} \times 100 \tag{3}$$

Where $\Delta H^{o}_{m\text{-}PEG} = 197$ J/g is for the 100% crystalline PEG according to Hu Y *et al.* [13].

2.7 Water absorption behaviour

The copolymer samples were immersed in distilled water at 37°C for predetermined period, and then were taken out and the surplus surface water were removed by a filter paper. The water absorption was calculated according to equation (4):

$$\text{Water absorption}\,(\%) = \frac{W_{ht} - W_d}{W_d} \times 100 \tag{4}$$

Where W_d is the initial weight of dry sample, and W_{ht} is the weight of humid sample at time t.

2.8 Hydrolytic degradation

The copolymer samples were placed in a small bottle containing 10 ml of degradation medium (PBS solution, pH = 4.0, 6.88, 9.23 respectively) at 37°C. PBS solution was refreshed every two weeks. The samples were removed from the bottles at predetermined time, rinsed thoroughly with distilled water and then dried *in vacuo* for 12 h at 60°C. The degree of degradation was denoted as weight loss:

$$\text{Weight loss}\,(\%) = \frac{W_0 - W_t}{W_0} \times 100 \tag{5}$$

Where W_0 is the dry weight before degradation, W_t is the dry weight at time t.

2.9 Alkaline degradation

Alkaline degradation experiment of the samples was conducted in 0.01 mol/L aqueous sodium hydroxide (NaOH) solution at 37°C. Degradation behavior was studied by weight loss according to Equation 5 too.

3 Results and discussion

3.1 Synthesis of PBT/PEG copolymers

The as-polymerized PBT/PEG copolymer was characterized by ^{1}H-NMR. A typical ^{1}H-NMR spectrum of the PBT50/PEG1540 copolymer was shown in Fig. 1. Seven

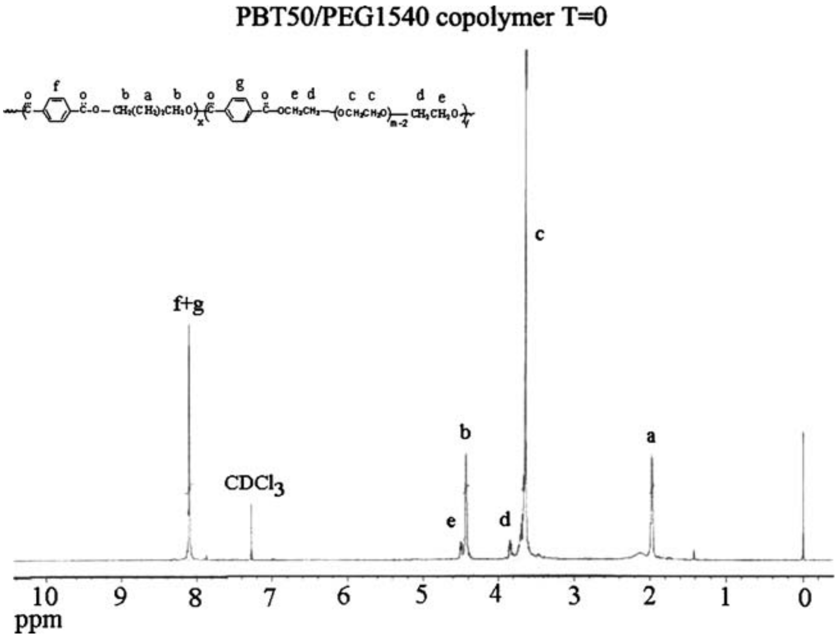


Fig. 1 ^{1}H-NMR spectrum of PBT50/PEG1540 copolymer.

signals were observed. Three of them were for the protons of the PEG blocks: at 3.68 ppm (peak “c”), 3.83 ppm (peak “d′”), and 4.69 ppm (peak “e”). The peaks at 1.96 ppm (peak “a”) and 4.46 ppm (peak “b”) were for the methylene protons of the PBT block respectively, the peak at 8.1 ppm (peak “$f + g'$”) was for the aromatic protons of PBT and PEGT blocks, and the chemical shift at 7.26 was assigned for the d-$CHCl_3$. The ^{1}H-NMR spectrum confirmed the production of PBT/PEG copolymers.

The inherent viscosity and molecular weight of the prepared PBT/PEG copolymers were listed in Table 1. According to Table 1, the inherent viscosity of the samples was in the range of 0.58–0.84, and the molecular weight was in the range of 10,000–15,000.

3.2 Non-isothermal crystallization behavior of PBT/PEG copolymers

For this semicrystalline PBT/PEG copolymer, its thermal property of PBT/PEG copolymers was mainly influenced by the content of PBT segment, and molecular weight of PEG segment.

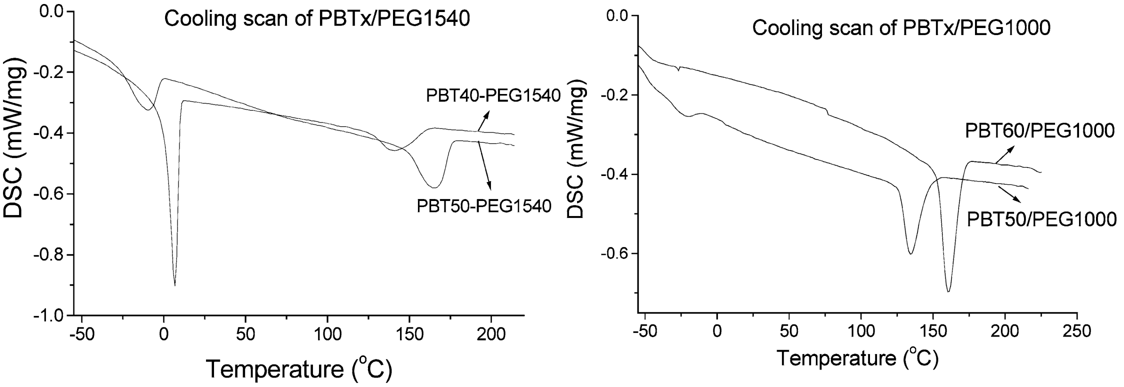
3.2.1 Effect of content of PBT segment

According to previous work, the crystallization behavior of PBT/PEG copolymer was mainly determined by crystalline PBT segment [10, 14]. With the increase in PBT content, the crystalline domain increased then. As was shown in Fig. 2 and Table 2, with the increase in PBT content, the crystallinity, the melting temperature, and crystallization temperature of PBT segment increased, but which of PEG segment decreased accordingly, and there is no obvious change in the glass transition temperature of PEG segment.

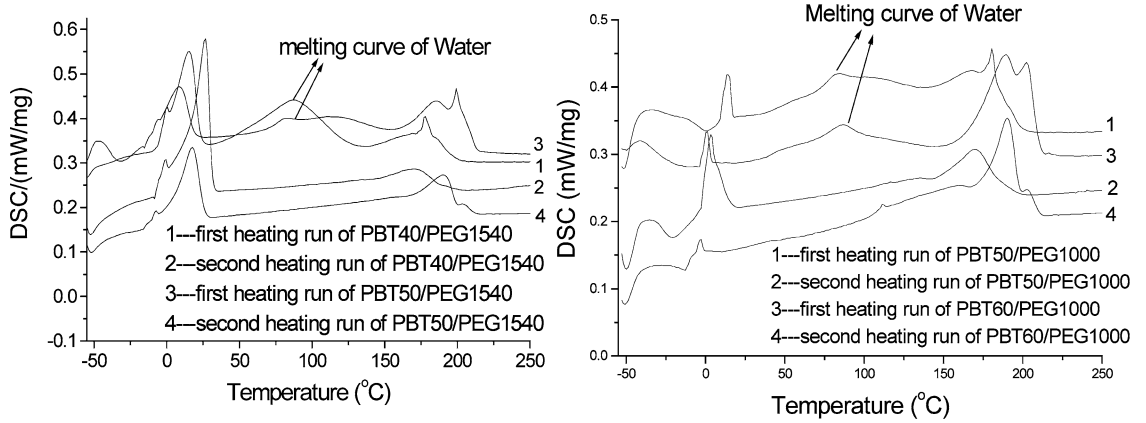
From Fig. 2b we could find that there was an endothermal peak at ca.100°C in the 1st heating run of PBT/PEG copolymers, but it disappeared in the 2nd heating run. So, we think that this peak might be due to the melting of water entrapped in PBT/PEG copolymers. In this article, 2nd heating run was used to study the thermal property of PBT/PEG copolymers.

3.2.2 Effect of molecular weight of PEG segment

According to Fig. 3 and Table 3, when the weight content PBT segment was kept constant, the crystallization temperature,



a) Cooling run



b) Heating run

Fig. 2 DSC curves of PBTx/PEG copolymers: (a) Cooling run; (b) Heating run.

Table 2 Thermal properties of PBT/PEG block copolymers[a]

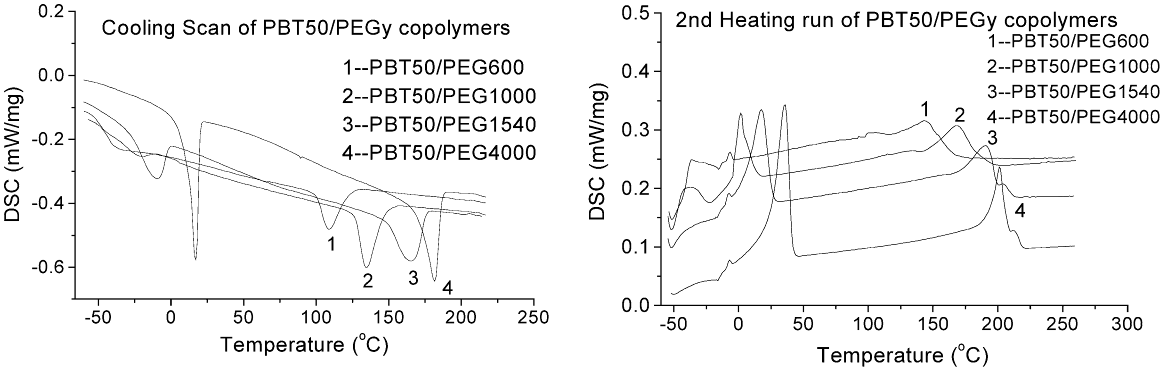
	PBT50/PEG1000	PBT60/PEG1000	PBT40/PEG1540	PBT50/PEG1540
$T_{g,PEG}$ (°C)	−46.9	−46.1	–	−47.9
$T_{c,PEG}$ (°C)	−22.7	–	7.0	−9.7
$T_{c,PBT}$ (°C)	134.8	160.6	141.6	166.1
$T_{m,PEG}$ (°C)	1.8	−3.6	27.0	17.6
$\Delta H_{m,PEG}$ (J/g)	6.2	0.9	33.5	17.7
$X_{c,PEG}$ (%)	3.1	0.4	17.0	9.0
$T_{m,PBT}$ (°C)	168.3	190.3	172.3	190.5
$\Delta H_{m,PBT}$ (J/g)	7.8	11.2	4.4	9.4
$X_{c,PBT}$ (%)	5.4	7.7	3.0	6.5

[a] The data of heating run was obtained according to the 2nd heating scan of PBT/PEG copolymers.

Table 3 Thermal properties of PBT/PEG copolymers[a]

	PBT50/PEG600	PBT50/PEG1000	PBT50/PEG1540	PBT50/PEG4000
$T_{g,PEG}$ (°C)	−40.3	−46.9	−47.9	–
$T_{c,PEG}$ (°C)	–	−22.7	−9.7	16.9
$T_{c,PBT}$ (°C)	109.0	134.8	166.1	181.9
$T_{m,PEG}$ (°C)	−7.0	1.8	17.6	35.5
$\Delta H_{m,PEG}$ (J/g)	0.4	6.2	17.7	26.8
$X_{c,PEG}$ (%)	0.2	3.1	9.0	13.6
$T_{m,PBT}$ (°C)	127.1	168.3	190.5	201.4
$\Delta H_{m,PBT}$ (J/g)	5.3	7.8	9.4	16.2
$X_{c,PBT}$ (%)	3.7	5.4	6.5	11.2

[a] The data of heating run was obtained according to the 2nd heating scan of PBT/PEG copolymers.



a) Cooling run

b) Heating run

Fig. 3 DSC curves of PBT50/PEGy copolymers: (a) Cooling run; (b) Heating run.

the melting temperature, and crystallinity of PBT and PEG increased accordingly with the increase in PEG molecular weight. This DSC data confirmed that the microphase separation between PBT and PEG segment enhanced with the increase in PEG molecular weight. This result was consistent with the results obtained by Deschamps *et al.* [8], and is very similar to multiblock PET/PEG copolymers [10].

3.3 Water absorption of PBT/PEG copolymers

PBT is a kind of hydrophobic polyesters, but its hydrophilicity increased dramatically with the incorporation of hydrophilic PEG segment into the PBT main chain. For these amphiphilic hydrolytic degradable PBT/PEG copolymers, the hydrophilicity was greatly affected by the PBT and PEG segment. So, the water absorption of this copolymer was mainly determined by two parameters: the weight fraction of PBT segment and PEG molecular weight.

3.3.1 Effect of weight fraction of PBT

According to Fig. 4, with the decrease in weight content of PBT segment, there is an increase in PEG. As a result, amorphous phase region increased, and then the hydrophilicity increased accordingly. So, the water absorption increased accordingly with the decrease in PBT content.

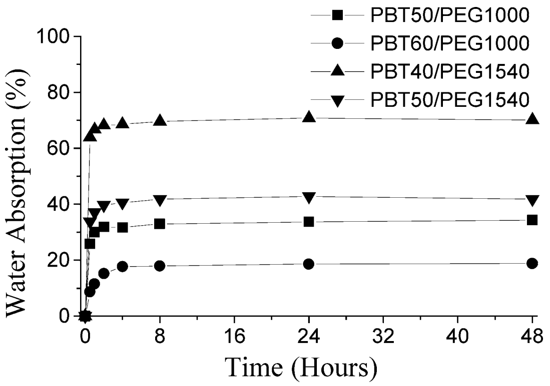


Fig. 4 Effect of weight fraction of PEG on the water absorption of PBT/PEG copolymers at 37°C in distilled water.

3.3.2 *Effect of molecular weight of PEG*

For this PBT/PEG copolymer, when the molecular weight and weight fraction of PBT in these copolymers was kept constant, the molecular weight of PEG segment had diverse effects on the water absorption behavior. At one side, with the increase in molecular weight of PEG segment, the molar content of PEG decreased then, which decreased the water absorption. But, with the increase in molecular weight of PEG, the microphase separation enhanced between PBT and PEG segments, which in turn increased the water absorption of PBT/PEG copolymers. According to Fig. 5, we could find that the water absorption increased with the increase in molecular weight of PEG segment. That's to say, the microphase separation had a dominant effect on the water absorption behavior of the sample. This phenomenon was consistent with the water absorption behavior of PET/PEG copolymers [10] and poly(1,4-butanediol succinate)/poly(ethylene glycol) [14] copolymers.

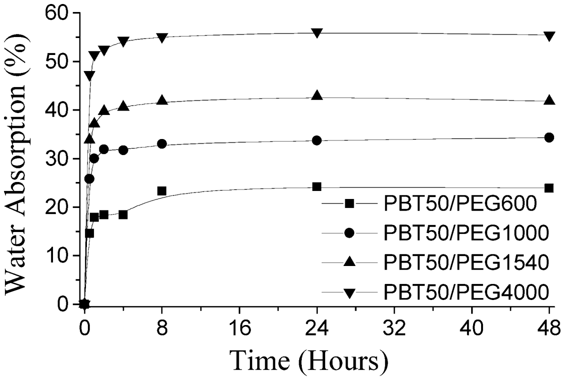


Fig. 5 Effect of molecular weight of PEG on water absorption behavior of PBT50/PEGy copolymers at 37°C in distilled water.

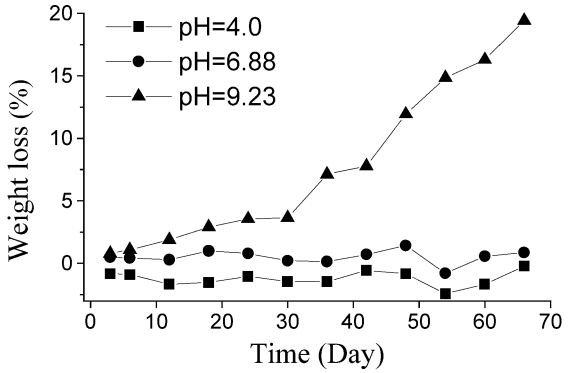


Fig. 6 Effect of pH value of PBS degradation medium on the degradation profile of PBT50/PEG1540 copolymers at 37°C.

3.4 Hydrolytic degradation behavior of PBT/PEG copolymers

For these amphiphilic copolymers, its hydrolytic degradation behavior was mainly determined by some factors, such as degradation medium, the chemical structure (e.g.: the weight fraction of PBT and PEG content), the molecular weight of PEG, and etc. The details were shown as following.

3.4.1 *Effect of pH value*

pH value of the degradation medium has a great effect on the degradation behavior of PBT/PEG copolymers. According to Fig. 6, with the increase in pH value of the degradation medium, the degradation rate of PBT50/PEG1540 copolymer increased quickly.

3.4.2 *Effect of weight fraction of PBT*

According to Fig. 2 and Table 2, the crystallization behavior of this PBT/PEG copolymer was greatly determined by the weight fraction of PBT segment. With the increase in PBT content, the melting temperature and the crystallinity of PBT segment increased accordingly. The increase in crystallization phase region would restrict the degradation of this PBT/PEG copolymer. So, as a result, the degradation rate would decrease with the increase in PBT content, which could be confirmed by Fig. 7.

3.4.3 *Effect of molecular weight of PEG*

For these PBT/PEG copolymers, when the weight fraction of PEG and PBT was kept constant, with the increase in molecular weight of PEG segment, the molar content of PBT segment increased, which would decrease the degradation rate; but at the same time, the microphase separation between PBT and PEG segments was enhanced, and then the degradation rate would increase.

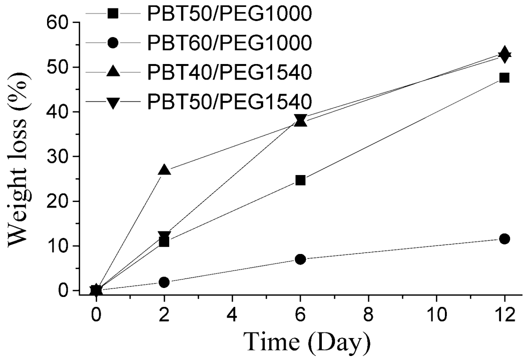


Fig. 7 Degradation of PBT/PEG copolymers in 0.01 mol/L NaOH solution at 37°C.

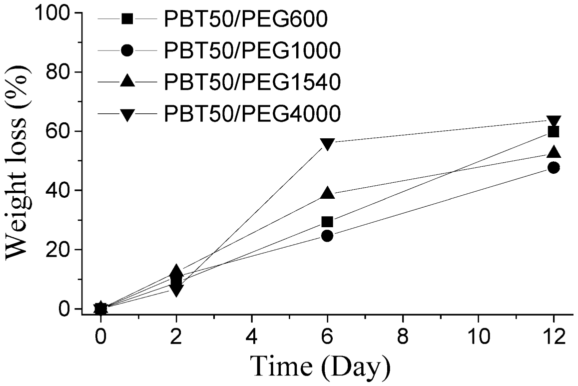


Fig. 8 Degradation of PEG PBT50/PEGy copolymer in 0.01 mol/L NaOH solution at 37°C.

According to Fig. 8, for PBT50/PEG600 and PBT50/PEG1000, with the increase in molecular weight of PEG segment, the degradation rate decreased then. But for the PBT50/PEG1000, PBT50/PEG1540, and PBT50/PEG4000, the degradation rate increased dramatically with the increase in PEG's molecular weight.

4 Conclusion

In this article, semicrystalline PBT/PEG copolymers were synthesized by macromolecular transesterification method. The resultant copolymers were confirmed by ^{1}H-NMR. The non-isothermal crystallization behavior was studied by DSC. With the increase in PBT content, the melting temperature, crystallinity increased then. Hydrolytic degradation was controlled by the content of PBT segment and the molecular weight of PEG segment. Water absorption decreased with increase in concentration of PBT segment, and it increased with molecular weight of PEG segment via microphase separation. The degradation rate increased with decrease in PBT concentration. PEG molecular weight had diverse effects on degradation rate.

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