

SYNTHESIS OF POLY(ETHYLENE TEREPHTHALATE)- POLYCAPROLACTONE BLOCK COPOLYMER BY DIRECT COPOLYMERIZATION*

Shen-guo Wang** and Kai Tang

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Abstract Poly(ethylene terephthalate)-polycaprolactone block copolymer (PCL-*b*-PET) is a polyester with improved biodegradability. In the present paper, a new direct copolymerization method of ϵ -caprolactone (ϵ -CL) and bishydroxyethylene terephthalate (BHET) in the presence of $\text{Ti}(\text{OBu})_4$ was proposed for the synthesis of PCL-*b*-PET. The PCL-*b*-PET copolymer was characterized by IR, GPC and $^1\text{H-NMR}$ techniques, and the effects of synthesis conditions, such as temperature, reaction time and concentration of catalyst on the copolymerization were discussed.

Keywords Poly(ethylene terephthalate)-polycaprolactone block copolymer, Direct copolymerization, Biodegradable polymer

INTRODUCTION

Poly(ethylene terephthalate) (PET) possesses very good mechanical properties, so it is one of the most usable polymers not only as textile material, engineering plastic, packing material, film material, but also as a biomedical material. Now PET has become one of the most salable commercial plastics in the world. Since PET is an aromatic polyester and its biodegradation rate is very slow by nature, PET waste is increasing year after year. In fact it has become a major nuisance to the environment. Recently it has been reported that the biogradability of PET can be improved by copolymerization with polycaprolactone (PCL) to produce a biodegradable polymer-poly(ethylene terephthalate)-polycaprolactone block copolymer (PCL-*b*-PET)^[1,2]. In the PCL-*b*-PET molecules the PET segments serve as hard segments to form physical cross-linking, while the PCL segments serve as soft segments to contribute to the elasticity of the material. It is a new thermoplastic elastomer that shows similar morphological structure and properties as that of the aromatic polyester-polyether block copolymer or the polyurethane^[3-5]. There are some reports on the investigation of chemical structure, morphology and spectral features of the PCL-*b*-PET^[6,7], yet there is almost no discussion on the synthesis condition of this copolymer. Conventionally, PCL-*b*-PET copolymer was synthesized by a two-step procedure, whereby homo-PET or/and homo-PCL was first prepared, then either one or both of them (PET and PCL) were copolymerized with ϵ -caprolactone (ϵ -CL) or bishydroxyethylene terephthalate (BHET). These procedures are complex and the chemical structure of the obtained copolymers cannot be

* This work was supported by 863 Programme of China No. 715-002-0210 and the National Natural Science Foundation of China (No. 59773022).

** Corresponding author: Shen-guo Wang (王身国), E-mail: wangsg@hotmail.com

Received January 10, 1998

controlled. Therefore, the properties of the copolymer were also inconsistent. In the present paper, the PCL-*b*-PET copolymer was synthesized by direct copolymerization of ϵ -caprolactone (ϵ -CL) and BHET in the presence of $\text{Ti}(\text{OBu})_4$. The effects of synthesis conditions such as temperature, reaction time and catalyst content on the copolymerization were also discussed.

EXPERIMENTAL

Materials

ϵ -Caprolactone (ϵ -CL) (Acros Chemical Company, Inc.) was dried with calcium hydride for 24 h, then distilled at 64 °C /200 Pa. Bishydroxyethylene terephthalate (BHET) was synthesized by esterification of dimethyl terephthalate (DMT) and ethylene glycol (EG) according to a reported method^[8]. Tetra-*n*-butyl titanate (Beijing 89942 Chemical Factory, C.P.grade) was purified by distillation at 140 °C/27 Pa.

Synthesis and Purification of PCL-*b*-PET Copolymer

An example of copolymerization is given here. Under nitrogen, ϵ -CL, BHET and $\text{Ti}(\text{OBu})_4$ were introduced to a three-necked flask equipped with stirrer. The system was first dried under vacuum for 30 min. The flask was then purged with nitrogen and heated to 160 °C. The ϵ -CL was polymerized at 160–220 °C for 2–4 h, then the reaction system was heated to 250 °C and evacuated to 1.0×10^{-5} MPa to eliminate ethylene glycol for 1–4 h. Thus the copolymerization was completed. The raw PCL-*b*-PET product was purified by filtering a 5 wt% chloroform solution and then reprecipitating from ethanol. The reprecipitated polymer was extracted with ethanol and dried under vacuum at room temperature.

IR and ¹H-NMR Measurement

The samples were prepared by casting the PCL-*b*-PET copolymer solution in chloroform onto a glass plate and then desolvating in vacuum at room temperature. The IR spectra were performed with a Perkin-Elmer FT-IR2000 Infrared spectrometer. The ¹H-NMR measurements were performed with a Varian Unity 200 spectrometer with CDCl_3 as a solvent at room temperature.

Inherent Viscosity Measurement

The viscosity of the PCL-*b*-PET at a concentration of 0.5 g/dL in chloroform was determined by a Ubbelodhe viscometer at 30 °C, and the intrinsic viscosity was calculated from η_r by the “one point method”

$$[\eta] = \sqrt{2(\eta_{sp} - \ln \eta_r) / C}$$

and expressed in dL/g.

GPC Measurement

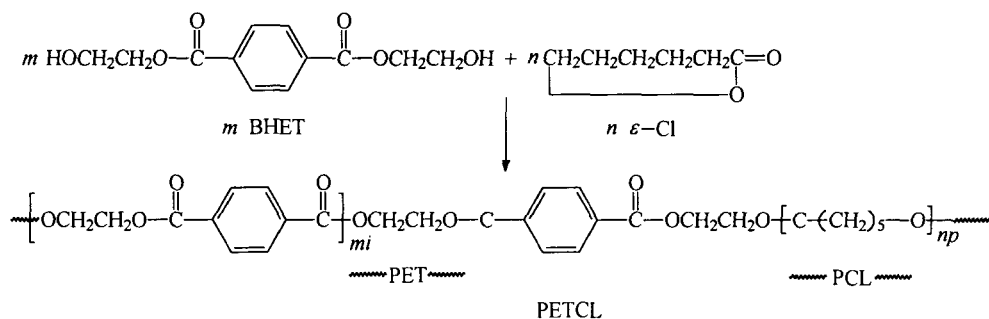
The molecular weight of PCL-*b*-PET was measured with Waters high-performance liquid chromatography, Model 510 at 35 °C at a chloroform flow rate of 1 mL/min through the Shodex GPC KF-800 series column. The number-average molecular weight (M_n), the weight-average molecular weight (M_w) and the molecular weight distribution (M_w/M_n) of PCL-*b*-PET copolymers were calibrated by using standard polystyrene samples.

RESULTS AND DISCUSSION

The tetra-*n*-butyl titanate ($\text{Ti}(\text{OBu})_4$) is a commonly used catalyst for esterification and polycondensation reactions^[9, 10]. In the present work an attempt was made to use the $\text{Ti}(\text{OBu})_4$ as copolymerization catalyst. The synthesis of PCL-*b*-PET copolymer is expressed in Scheme 1.

The purified PCL-*b*-PET copolymer was characterized by IR, ¹H-NMR and GPC techniques. It can be seen that the IR spectrum of the PCL-*b*-PET (Fig. 1(a)) is composed of all specific absorption at 1268 and 1122 cm^{-1} which belong to PET (Fig. 1(b)), and at 3021 and 756 cm^{-1} that

belong to PCL (Fig. 1 (C)). It is evident that the purified PCL-*b*-PET copolymer is composed of PET and PCL. Figure 2 shows that the GPC spectra of PCL-*b*-PET-50 and PCL-*b*-PET-55 have single and symmetrical peak, indicating the PCL-*b*-PET copolymer is a pure and unique copolymer, and there is no homo-PET or homo-PCL in the copolymer.



Scheme 1 Synthesis scheme of PCL-*b*-PET copolymer

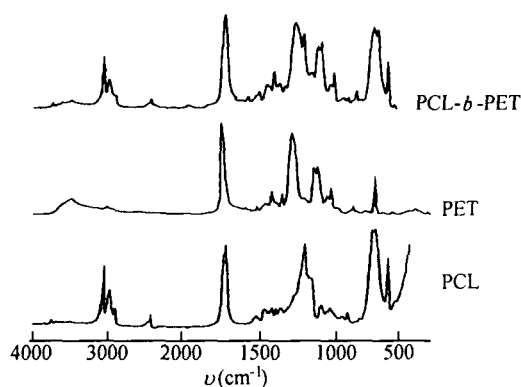


Fig. 1 IR spectra of PCL-*b*-PET, PET and PCL

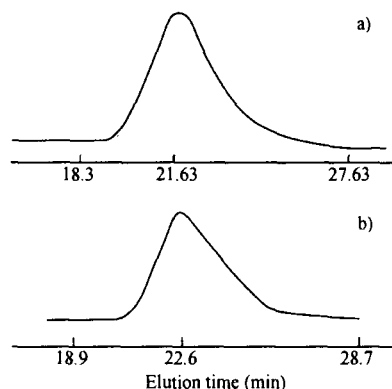


Fig. 2 GPC spectra of PCL-*b*-PET copolymer
a) PCL-*b*-PET-50, b) PCL-*b*-PET-55

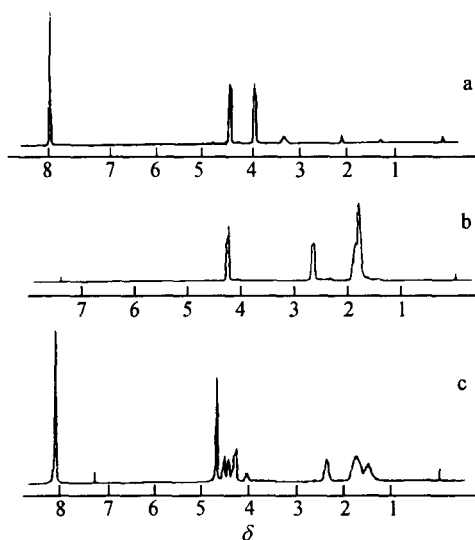


Fig. 3 ^1H -NMR spectra of PCL-*b*-PET copolymer and monomers
a) BHET, b) ϵ -CL and c) PCL-*b*-PET-55

The composition of the PCL-*b*-PET copolymer was determined by $^1\text{H-NMR}$ technique as shown in Fig. 3. According to the ratio of hydrogen number in an ethylene terephthalate unit (ET, at $\delta = 8.08$ for benzene ring (4H)) to that in a caprolactone unit (CL, at $\delta = 1.45\sim 1.75$ for the trimethylene (6H)), the component ratio of ET to CL can be calculated. The composition of PCL-*b*-PET copolymers is indicated by their molar ratio of the ET unit. For example, PCL-*b*-PET-55 signifies that the copolymer is composed of 55% molar ratio of ET units and 45% molar ratio of CL units.

Effects of reaction conditions such as temperature, reaction time and catalyst amount on the copolymerization were investigated by determining the inherent viscosity of PCL-*b*-PET products. It can be seen that at ϵ -CL polymerization stage, the higher the reaction temperature, the higher the yield of PCL-*b*-PET copolymer will be, which is shown in Fig. 4. At a higher reaction temperature the copolymer with higher inherent viscosity can be obtained, but the color of the product becomes dark and the CL content in the copolymer is lowered because ϵ -CL monomer is partly distilled off.

The effect of reaction time on the copolymerization can also be seen from Fig. 5. The mole ratio of CL to ET of the produced PCL-*b*-PET decreases with increasing reaction time. It is due to the fact that the amount of ϵ -CL monomer distilled off increases with increasing reaction time under the high vacuum and high temperature reaction condition.

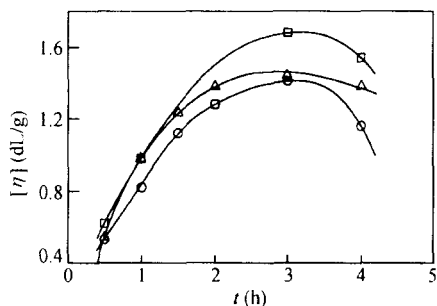


Fig. 4 Effect of temperature on synthesis of the PCL-*b*-PET copolymer

Feeding dose: BHET/ ϵ -CL = 50/50 mol%
 -○- 160°C, -△- 200°C, -□- 240°C

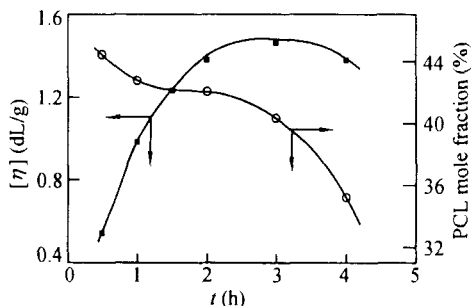


Fig. 5 Effect of reaction time on composition of PCL-*b*-PET copolymer

Feeding ratio of BHET/ ϵ -CL = 50/50 (mol%) at 250°C

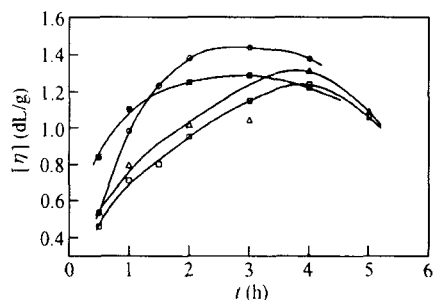


Fig. 6 Dependence of inherent viscosity of PCL-*b*-PET product on concentration of catalyst

Weight ratio of $\text{Ti}(\text{OBu})_4$ to BHET ($\times 10^4$)
 -□- $\times 1$, -△- $\times 5$, -○- $\times 10$, -■- $\times 20$

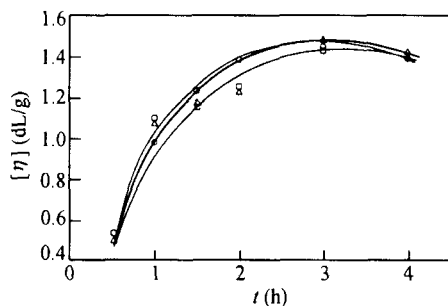


Fig. 7 Repeatability of the direct copolymerization method

Feeding dose: BHET/ ϵ -CL = 50/50 (mol%),
 BHET/ $\text{Ti}(\text{OBu})_4 = 10^3$ (wt) at 250°C
 -□- No.1 reaction, -○- No.2 reaction,
 -△- No.3 reaction

In the presented synthesis method the concentration of catalyst is another important factor for obtaining a copolymer with high inherent viscosity because $\text{Ti}(\text{OBu})_4$ is a good catalyst not only for the copolymerization, but also for the depolymerization. Within a certain concentration range of $\text{Ti}(\text{OBu})_4$ the inherent viscosity of obtained PCL-*b*-PET copolymer increases with increasing amounts of catalyst, then decreases when the amount of catalyst exceeds the range as shown in Fig. 6.

In the optimum reaction condition the reproducibility of the presented synthesis method is quite good (Fig. 7). According to the described procedures and reaction conditions, a series of PCL-*b*-PET copolymers with various unit ratio of ET to CL, as shown in Table 1, were obtained.

Table 1. PCL-*b*-PET copolymer formed by direct copolymerization

No.	Design unit ratio (mol%)		Actual unit ratio* (mol%)		[η] (dL/g)
	ET	CL	ET	CL	
PCL	0	100	0	100	1.38
PCL- <i>b</i> -PET-11	11.1	88.9	18.6	81.4	2.12
PCL- <i>b</i> -PET-30	20.0	80.0	30.8	69.2	0.88
PCL- <i>b</i> -PET-45	33.3	66.7	45.2	54.8	1.38
PCL- <i>b</i> -PET-50	40.0	60.0	50.0	50.0	1.34
PCL- <i>b</i> -PET-55	50.0	50.0	55.8	44.2	0.97
PCL- <i>b</i> -PET-73	66.7	33.3	73.1	26.9	0.96
PCL- <i>b</i> -PET-83	80.0	20.0	83.6	16.4	
PET	100	0	100	0	

* Measured by $^1\text{H-NMR}$ technique

CONCLUSIONS

A comparison between the direct copolymerization method with the conventional methods the following conclusions can be drawn: (1) The PCL-*b*-PET copolymer can be synthesized simply by direct copolymerization of ϵ -CL and BHET with $\text{Ti}(\text{OBu})_4$ as catalyst; (2) the composition of PCL-*b*-PET copolymer can be easily adjusted by controlling the feeding dosage and (3) the direct copolymerization method has several advantages; i.e. simple operation, short reaction time, good reproducibility and uniform composition.

REFERENCES

- 1 Nakanishi, M. and Sato, T., 1988, Japan Pat., S63-65869
- 2 Takiyama, E. and Hatano, Y., 1993, Japan Pat. Kokai, H5-279446
- 3 Hoeschele, G.K., Polym. Eng. Sci., 1988, 14, (12): 848
- 4 Lilaonitkul, A. and West, J.C., J. Macromol. Sci. Phys., 1976, B12 (4): 563
- 5 Vanbogart, J.C. and Gibson, P.E., J. Polym. Sci., Polym. Phys. Edi., 1980, 21: 65
- 6 Luo, X.L. and Ma, D.Z., ACTA Polymerica Sinica, 1986, 6: 676
- 7 Zhang, R.Y. and Luo, X.L., Polym. Mater. Sci. and Eng., 1995, 11(6): 66
- 8 Dinov, K. and Terlemezyan, E., J. Polym. Sci., Part A-1, 1972, 10 (11): 3133
- 9 Wang, S.G., Polym. J., 1989, 21(2): 179
- 10 Wang, S.G. and Qiu, B., Polymers for Advanced Technologies, 1993: 4, 363