Copolymerization of P-Hydroxybenzoic Acid and Poly (Butylene Succinate): Effect of Catalysts

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Abstract. P-Hydroxybenzoic acid (HBA) and poly (butylene succinate) (PBS) were chosen to synthesize aromatic/aliphatic copolyester HBA/PBS. The effect of catalyst on the structure and properties of copolymers was studied. It is shown that HBA can have transesterification reaction with PBS and some HBA was easy to self-polymerize to form insoluble and infusible homopolyester. Tetrabutyl titanate is more effective than zinc acetate as catalyst. The reaction time has a certain impact on the polymerization reaction. The longer reaction time was, the more HBA/PBS copolyesters were obtained.

1. Introduction
Compared with common polyesters, thermotropic liquid crystalline polyesters (TLCPs) have better mechanical properties and chemical stabilities because of the aromatic structures in molecular chain [1, 2]. TLCPs can be easy to be processed because of their liquid crystallinity while melting. However, a large number of rigid structure of TLCPs make them difficult to be degraded, which limits their further application. Aliphatic polyesters have good biodegradability because of their aliphatic chain segment and ester linkage which can be degraded by microorganisms in natural conditions [3]. But the existence of long flexible chain makes the polyesters to show poor mechanical properties, which limits their application in many aspects. Therefore, considering the advantages and disadvantages, the liquid crystal polyester and biodegradable polyester could be copolymerized to get a new kind of polymer which both has biodegradability and liquid crystallinity [4, 5]. This new type material may have potential application in many areas because of its good properties. HBA with simple structure is much cheaper than other mesogenic units [6, 7]. PBS is one of the best biodegradable material in the world [8]. In this paper HBA and PBS were chosen as liquid crystalline monomer and aliphatic polyesters unit, respectively. The effect of catalyst on the polyester HBA/PBS was studied.

2. Experiment

2.1. Materials
HBA (polymer grade) was purchased from Shengxiao Chemical Co., Ltd. HBA was acetylated before reaction. PBS was obtained by polycondensation with succinic acid (CP) and butanediol (CP). Other
reagents like alcohol, acetic anhydride, zinc acetate and tetrabutyl titanate (TBT) were all commercially available.

2.2. Polycondensations

HBA, PBS and acetic anhydride (molar ratio 2: 1: 2) were added into a flask placed into an oil bath. Zinc acetate and TBT were used as catalysts respectively. The reaction mixture was heated slowly under nitrogen atmosphere with stirring. The temperature was raised to 200°C, afterwards to 240°C, 260°C, 270°C with time intervals of 1h. Vacuum was finally applied for 0.5h at 270°C. The cold polyester was crushed, washed with alcohol and dried at 80°C. And 5 polyesters with different reaction time were obtained (P-2h, P-4h, P-6h, P-8h, P-10h). The temperature was raised to 200°C for 1h and heated slowly to 270°C. Then kept 2h, 4h, 6h, 8h and 10h at 270°C respectively before vacuuming. TBT was used as catalyst.

2.3. Measurement

The DSC measurements were obtained on a Netzsch DSC214 and the heating rate was 20°C/min. The 600MHz 1H NMR spectra were obtained on a Bruker Avance 400 spectrometer. Trifluoroacetic acid-D (TFA) was chosen as solvent. The thermogravimetric analysis were obtained on a Q5000IR at a heating rate 20°C/min in nitrogen atmosphere. The XRD measurements were obtained on a powder diffractometer D2 PHASER. The liquid crystalline property were investigated by a BX51 thermal platform microscope.

3. Results and Discussion

In order to confirm the effect of different catalysts, zinc acetate and TBT were chosen as catalysts. DSC heating curves are shown in Figure 1. There is an exothermic peak before the melting peak which belongs to the crystallization of PBS. The melting peak of ‘HBA/PBS-Zinc acetate’ curve belongs to PBS. The melt temperature of polyesters using TBT was significantly lower than using zinc acetate, which means that the efficiency of TBT was better than zinc acetate (Figure 1 b).

Figure 1 c shows DSC heating curves of polyesters with different reaction time with TBT as catalyst. There are still PBS cold crystallization peaks between 60 and 70°C which the intensity decreased with the increase of reaction time. It means that more PBS reacted with HBA and the content of rich PBS segment decreased with the increase of reaction time. The endothermic peaks between 90 and 100°C belong to HBA/PBS copolyesters. Two decomposition stages in TG curves indicated the incomplete transesterification of PBS and HBA (Figure 2 a). Besides, the DTG curves of P-4h and P-6h have more than one peak at 325°C and 575°C compared with other three curves (Figure 2 b). The explanation might be that samples with short reaction time might be ester exchanged incompletely. The transesterification was better after 4h and much more polyesters with rich PBS segment and HBA segment were obtained. The longer reaction time was, the more HBA/PBS copolyesters were synthesized.
Figure 1. DSC heating curves of polyesters: (a) PBS; (b) Polyesters with different catalysts; (c) Polyesters with different reaction time using TBT as catalyst

Figure 2. TG and DTG curves of copolyesters
The structure of the polyesters were analyzed by $^1$H NMR spectra (Figure 3). The absorption peaks belonging to PBS appeared splitting peaks. HBA homopolymer cannot be dissolved in TFA, so the existence of signals at 8.4-8.1ppm and 7.6-7.0ppm indicates that HBA reacted with PBS.

![Figure 3. $^1$H NMR spectra of polyester P-10h](image)

The XRD curves of 5 samples (Figure 4) were very similar in diffraction peak position, intensity, interplanar spacing, crystallinity and other characteristics, which means that the reaction time had no significant effect on samples crystal structures.

![Figure 4. X-ray Diffraction of polyesters with different reaction time](image)
4. Conclusion
HBA/PBS polyesters were synthesized by melt polymerization. In this reaction system, tetrabutyl titanate is more effective than zinc acetate as catalyst. HBA can have transesterification reaction with PBS to format rich PBS segment and HBA segment polyesters. The reaction time has a certain impact on polymerization, but not impact on crystal structures. When the reaction time is about 8-10 hours, the system can react more completely.

Acknowledgments
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