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Copolyesters

VI. Block copolyesters of poly(butylene terephthalate) and poly(butylene adipate)

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SUMMARY

In an attempt to prepare the block copolyesters of poly (butylene terephthalate)(PBT) and poly(butylene adipate) (PBA), melt transesterification between PBT and PBA was chosen first. However, PBT and PBA were found to be immiscible within the reaction temperature range. This hindered their transesterifi-cation reaction. Various parameters such as catalyst, reaction temperature, reaction time, degree of vacuum and stirring speed all failed in preparing the block copolyesters of PBT and PBA. However, when some amount of 1,4-butanediol was added at the melt mixing stage, followed by a vacuum stage at high temperature, block copolyesters could be prepared. The chemical structure and thermal properties of the block copolyesters were characterized by NMR and DSC respectively. As the degree of randomness of the block copolyesters increased, the melt transition temperature of PBT segment decreased, and that of PBA segment decreased considerably. When, the degree of randomness reached as high as 0.35, the melt transition of PBA segment disappeared.

INTRODUCTION

The controlled melt transesterification between two poly-esters is one of the methods of preparation of block copolyesters. The transesterification reactions at the melt state between an aromatic polyester(as hard segment) and an aliphatic polyester(as soft segment) are typical examples [1,2]. In our laboratory, an attempt was made to prepare the block copolyesters of poly(butylene terephthalate)(PBT) and poly (butylene adipate)(PBA) by a similar method. However, when high molecular weight PBT and PBA were mixed at the melt state and stirred for a period of time in the presence of a transesterification catalyst, no significant transesterification reaction was observed. But, when some amount of 1,4-butanediol was added at the melt mixing stage, and then vacuum was applied, we observed that significant transesterification reaction occurred and block copolyesters could be obtained. In this paper, we present this modified method of preparation of block copolyesters of PBT and PBA. The chemical structure and the thermal properties of the block copolyesters are also described.

EXPERIMENTAL

All the reagents used were Merck reagent grade otherwise will be specified. PBT and PBA were prepared by melt polycondensation of 1,4-butanediol with terephthalic acid(supplied by China American Petrochemical Co., Ltd., Taiwan) and adipic acid respectively in the presence of 0.1 wt% of tetrabutyl orthotitanate(TBT) as the catalyst similar to a method described in a previous paper[3]. The intrinsic viscosity values of PBT and PBA were found to be 0.81 and 0.86 dL/g respectively.

A melt mixing method via two stages was used to prepare the block copolyesters. A typical reaction procedure is as follows. 92.7 g(0.4215 mole) of PBT, 84.3 g(0.4215 mole) of PBA, 1.855 g(0.0206 mole) of 1,4-butanediol and 0.4637 g (0.00136 mole) of TBT were charged into a 1 liter stainless steel reactor. The temperature was raised to 275°C under nitrogen and the stirring speed was held at 200 rpm for 0.5 hour. Then, vacuum(0.5mmHg) was applied and held for 1.5 hours. The conditions of other experiments were the same except the amounts of 1,4-butanediol and TBT were varied. When no 1,4-butanediol was added, all batches resulted opaque products. In the presence of 1,4-butanediol, some of the products were semitransparent.

The intrinsic viscosity of the products in phenol/syn-tetrachloroethane(60/40 wt/wt) at 30°C was determined by a Ubbelohde viscometer. The proton NMR spectrum of the products in CF_3COOD was determined by a Bruker 400 Mhz NMR as described in a previous paper[4]. The thermal properties of all the products were measured by a Du Pont DSC 910 at a heating rate of 10°C/min under nitrogen.

RESULTS AND DISCUSSION

Various parameters such as reaction temperature (from 230 to 280°C), stirring speed(from 100 to 500 rpm), reaction time(from 0.5 to 8 hours), and amount of catalyst (TBT)(0.1 to 2 wt % based on PBT) were first tried to prepare the block copolyesters of PBT and PBA by the melt mixing method. However, all the products were found to be opaque and very brittle when no 1,4-butanediol was added. Possibly no significant transesterification occurred. This can be verified by the NMR data and thermal properties.

Typical proton NMR data of PBA, PBT and random copolyesters of PBT and PBA have been presented in a previous paper[4]. The peaks at 2.59, 2.45, and 2.32 ppm correspond to the resonance signals of the TBT, hetero(TBA and ABT), and ABA sequences respectively. Thus, the content of hetero sequence, (f_{hetero}), and the degree of randomness (B) can be determined:

$$f_{hetero} = I_{hetero}/(I_{TBT}+I_{hetero}+I_{ABA}) \qquad \text{------ } 1$$

$$P_{AT} = (I_{hetero}/2)/[(I_{hetero}/2)+I_{ABA}]$$

$$P_{TA} = (I_{hetero}/2)/[(I_{hetero}/2)+I_{TBT}]$$

$$B = P_{AT} + P_{TA} \qquad \text{------ } 2$$

Where I_{TBT}, I_{hetero} and I_{ABA} are the integrated intensities of the resonance peaks at 2.59, 2.45, and 2.32 ppm respectively. The content of hetero sequence will indicate the extent of transesterification. The degree of randomness will describe the block nature of the products. For a random copolymer, B=1; for a blend, B=0; and for a block copolymer, B is close to zero.

The conditions, transparent appearance and apparent property of some batches are listed in Table 1. B1 was prepared in the absence of 1,4-butanediol. The proton NMR spectrum of B1 within 2 to 3 ppm is shown in Figure 1. No resonance peak of hetero sequence was detected. Thus, no significant transesterification occurred in B1. The DSC heating curve of B1 is shown in Figure 2. The DSC heating curve of B1 is just an overlapped profile of those of PBT and PBA. Thus, B1 would be only a physically immiscible blend of PBT and PBA. This would be due to the immiscibility between PBT and PBA at the reaction temperature.

B2 was prepared in the presence of large amounts of 1,4-butanediol, and no TBT catalyst was added(see Table 1). Its proton NMR spectrum is shown in Figure 1. B1 showed a strong resonance peak of hetero sequence. The content of hetero sequence of B2 was as high as 50.1 mole%. This means that considerably significant transesterification reaction occurred in the presence of large amount of 1,4-butanediol. The degree of randomness of B2 was found to be 1.01 as shown in Table 2. Thus, it would be a random copolyester. The DSC heating curve of B2 is shown in Figure 2. The melt transition of PBA segment disappeared, and the melt transition temperature of PBT segment was lowered to 134°C. As a comparison, the melt transition temperature of pure PBT was found to be 225°C. Obviously, the presence of 1,4-butanediol enhanced the transesterification reaction.

Table 1. The conditions, transparent appearance and apparent property of various batches.

Batch	BDO[a] (g)	TBT[b] (g)	Appearance	Property
B1	0	0.464	opaque	brittle
B2	15.33	0	semitransparent	tough
B3	0.0927	0.464	opaque	medium[c]
B4	0.464	0.464	semitransparent	tough
B5	0.927	0.464	semitransparent	tough
B6	1.855	0.464	semitransparent	tough
B7	4.637	0.464	semitransparent	tough

a. 1,4-butanediol
b. tetrabutyl orthotitanate
c. brittle to tough

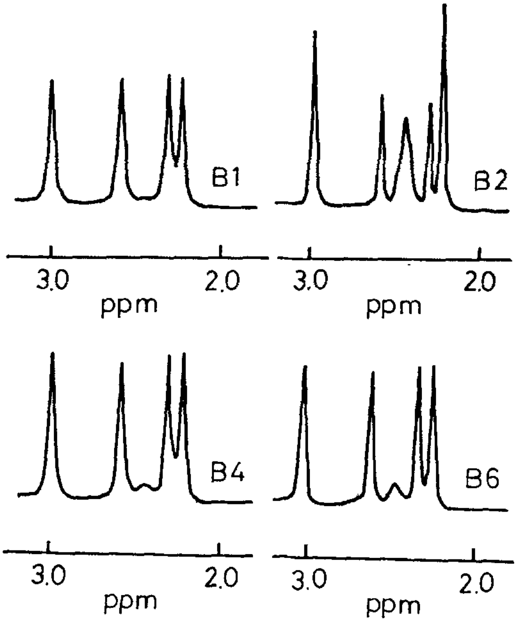

Figure 1. Proton NMR spectra of B1, B2, B4, and B6.

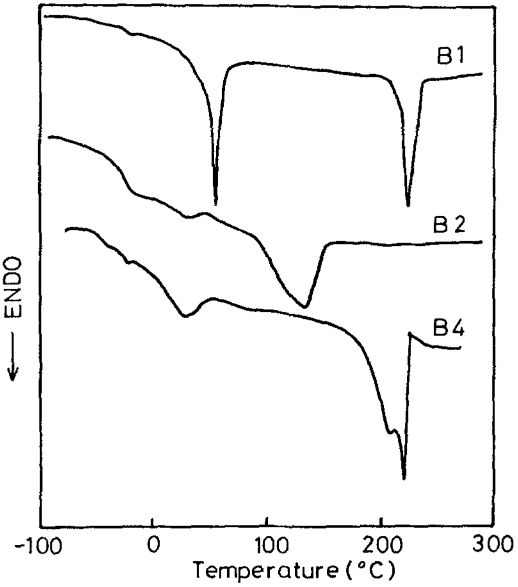

Figure 2. DSC heating curves of B1, B2, and B4.

B3-B7 were prepared in the presence of 0.454 g of TBT catalyst and various amounts of 1,4-butanediol(see Table I). Typical proton NMR spectra and DSC heating curves are shown in Figure 1 and Figure 2 respectively. The apparent properties, intrinsic viscosity, melt transition temperatures, content of hetero sequence and degree of randomness are shown in Table 1 and Table 2. In the presence of some amount of 1,4-butanediol, significant amount of hetero sequence was detected, thus, significant transesterification occurred. The content of hetero sequence increased monotonically as the amount of 1,4-butane-diol increased as shown in Table 2. Thus, the extent of transesterification could be controlled by the amount of 1,4-butanediol. The presence of 1,4-butanediol gave very complex behavior. First, it might change the phase equilibrium, and second, it might react with the two polyesters to form oligomers, and this may further change the phase equilibrium. However, it did render transesterification reaction.

Although the presence of 1,4-butanediol rendered some degree of transesterification reaction to be occurred, it also decreased the molecular weight of the polyesters. Thus, after melt mixing in the presence of 1,4-butanediol for 0.5 hour, vacuum(0.5 mm Hg) was applied for another 1.5 hours to increase the molecular weight. The intrinsic viscosity values of various batches were found to be higher than 0.6 dL/g as shown in Table 2.

The melt transition temperatures of the block copolyesters are shown in Table 2. The melt transition temperatures were highly dependent on their chemical structure. This can be described as the effect of sequence length. When the degree of randomness increased, the sequence length of both PBT and PBA segment decreased, thus the melt transition temperatures decreased accordingly. However, the effect of the degree of randomness on the melt transition temperature of these two segments behave differently. As the degree of randomness increased, the melt transition temperature of PBT segment of the block copolyesters decreased to a much less

Table 2. The intrinsic viscosity(IV), melt transition temperatures of PBA segment(T_1) and PBT segment(T_2), content of hetero sequence(f_{hetero}) and degree of randomness(B) of the products.

Batch	IV(dL/g)	T_1(^oC)	T_2(^oC)	f_{hetero}(mole%)	B
B1	0.70	59	225	0	0
B2	0.87	——	134	50.1	1.01
B3	0.67	51	226	4.8	0.10
B4	0.62	29	222	7.5	0.15
B5	0.67	15	216	13.4	0.27
B6	0.61	——	210	17.5	0.35
B7	0.98	——	140	42.9	0.83

extent than that of PBA segment. As the degree of randomness increased, the melting transition temperature of the PBA segment decreased considerably. The melt transition of PBA segment disappeared as the degree of randomness reached about 0.35.

In conclusion, the block copolyesters of PBT and PBA could be prepared by melt mixing of PBT and PBA in the presence of some amount of 1,4-butanediol, followed by the application of vacuum. The sequence distribution of these block copolyesters could be controlled by the amount of 1,4-butanediol.

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