

Copolyesters: 5. Poly(butylene terephthalate-co-isophthalate-co-adipate)s with different molecular weights

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The copolyesters of 1,4-butanediol, terephthalic acid, isophthalic acid, and adipic acid with different molecular weights were prepared by melt polycondensation in the presence of a monocarboxylic acid which was benzoic acid, *p*-phenylbenzoic acid or stearic acid. Both *p*-phenylbenzoic acid and stearic acid were successful in controlling the molecular weight predictably. T_g decreased as the molecular weight of the copolyesters decreased. The decrease in T_g due to decrease in molecular weight was more significant for the copolyesters with stearate end group (SA series) than *p*-phenylbenzoate end group (PBA series). The Brookfield melt viscosity was found to decrease significantly as the molecular weight decreased. The copolyesters were used as hot melt adhesives. It was found that the lap shear strength increased as the molecular weight increased and levelled off as intrinsic viscosity reached above 0.6 dl/g.

(Keywords: copolyesters; molecular weight control; glass transition temperature; melt viscosity; lap shear strength)

INTRODUCTION

The copolyesters of 1,4-butanediol, terephthalic acid, isophthalic acid, and adipic acid have been used as hot melt adhesives¹⁻⁵. The molecular weight is an important factor in determining their performance. As the molecular weight is very high, the melt viscosity is very high and it is difficult to process. But if the molecular weight is very low, no sufficient properties such as adhesion strength can be provided.

In this paper, copolyesters of 1,4-butanediol, terephthalic acid, isophthalic acid, and adipic acid were prepared by melt polycondensation. The molecular weight of the copolyesters was controlled by various monocarboxylic acids with very high boiling point. The influence of molecular weight on T_g , melt viscosity and adhesion strength was studied.

EXPERIMENTAL

p-Phenylbenzoic acid was obtained from Jansen Chemica (Belgium) and terephthalic acid was supplied by China American Petrochemical Co., Ltd. (Taiwan). Stearic acid, benzoic acid, 1,4-butanediol, isophthalic acid, adipic acid, and tetrabutyl orthotitanate (TBT) were all Merck reagent grade.

The copolyesters were prepared by melt polycondensation of 1,4-butanediol, terephthalic acid, isophthalic acid, adipic acid, and monocarboxylic acid (benzoic acid, *p*-phenylbenzoic acid or stearic acid) with TBT as the catalyst. A typical example is as follows.

Into a 2 l stainless reactor were introduced 162.0 g (1.8 mol) of 1,4-butanediol, 74.7 g (0.45 mol) of terephthalic acid, 49.8 g (0.3 mol) of isophthalic acid, 36.5 g

(0.25 mol) of adipic acid, and 0.6 g of tetrabutyl orthotitanate. The reactants were heated to 220°C, water was then distilled. After 3 h, most water was distilled out. The vacuum was slowly applied and the reaction temperature was raised to 260°C. Excess 1,4-butanediol was distilled at this period. Afterward, high vacuum (0.5 mmHg) was applied for 1.5 h. The resultant molar composition was 1,4-butanediol: terephthalic acid: isophthalic acid: adipic acid = 1:0.45:0.30:0.25. In other batches, various amounts of monocarboxylic acid were added additionally.

The intrinsic viscosity was determined at 30°C in phenol/TCE (1,1,2,2-tetrachloroethane) by a Ubbelohde viscometer. \bar{M}_n and \bar{M}_w were determined by g.p.c. with *m*-cresol/chloroform (1/3 vol/vol) as the eluent at flow rate of 1 ml/min followed by a method described previously⁶ except the molecular weight was further calibrated with standard poly(ethylene terephthalate). The thermal properties were determined by a Du Pont 910 differential scanning calorimeter at a heating rate of 10°C/min. The melt viscosity at various temperatures was determined using a Brookfield Viscometer (Brookfield Laboratories, Inc.) with a RV Series SC4-28 spindle. The adhesion bonding was applied by pressing two pieces of aluminium substrate within which copolyester film was located. The lap shear strength at room temperature was measured by a standard method according to ASTM D 1002-72.

RESULTS AND DISCUSSION

Previously in our laboratory, the molecular weight of copolyesters prepared by the melt polycondensation method was controlled by the reaction time at the high vacuum stage. Three batches were carried out to check this method, the reaction temperature at high vacuum

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stage was held at 260°C and high vacuum (0.5 mmHg) was applied for 10 min. The resultant intrinsic viscosity (*IV*) values were 0.23, 0.51 and 0.42 dl/g respectively for these three batches. Thus, the reproducibility was rather poor by this method.

The use of monofunctional monomers such as benzoic acid, *p*-phenylbenzoic acid, and stearic acid was considered for control of the molecular weight. Based on 1 mol of diacids, the added amounts of benzoic acid (BA series), or *p*-phenylbenzoic acid (PBA series), or stearic acid (SA series) of various batches are listed in Table 1. The plots

Table 1 The added amounts of monocarboxylic acids, the corresponding molar ratio of monocarboxylic acid to diacids and *IV* value

Notation ^a	Monocarboxylic acid (g)	Molar ratio, <i>S</i>	<i>IV</i> (dl/g)
BA1	8.13	0.0667	0.38
BA2	8.13	0.0667	0.26
BA3	4.06	0.0333	0.50
BA4	1.63	0.0133	0.86
BA5	0.82	0.0067	0.82
PBA1	19.80	0.10	0.21
PBA2	14.85	0.075	0.24
PBA3	9.90	0.050	0.31
PBA4	6.93	0.035	0.41
PBA5	3.96	0.020	0.54
PBA6	1.98	0.010	0.67
SA1	28.45	0.10	0.20
SA2	18.97	0.0667	0.25
SA3	9.47	0.0333	0.40
SA4	3.78	0.0133	0.65
SA5	1.91	0.0067	0.77
Blank	0	0	1.02

^a BA series for benzoic acid, PBA series for *p*-phenylbenzoic acid, and SA series for stearic acid

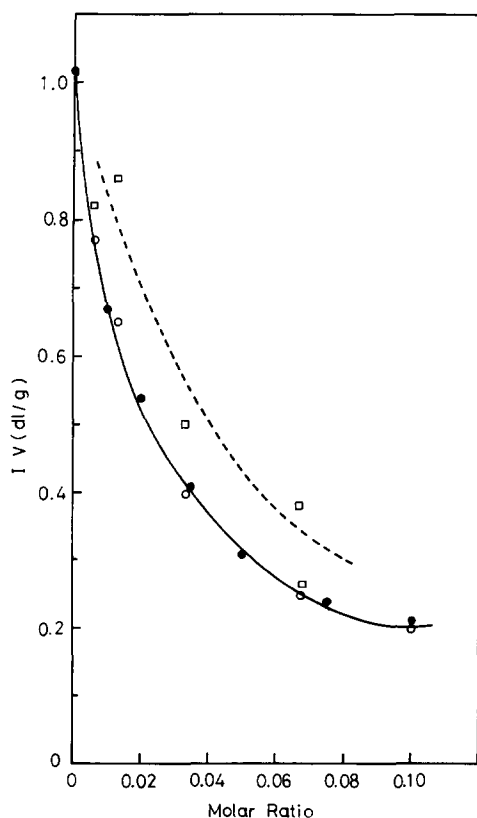


Figure 1 The effect of molar ratio of monocarboxylic acid to diacids on *IV* values. □, BA; ●, PBA; ○, SA

Table 2 $2/S$, \bar{M}_n , \bar{M}_w and T_g of the copolyesters

Notation	$2/S$	\bar{M}_n	\bar{M}_w	T_g (°C)
PBA1	20.0	4500	9500	-4
PBA2	26.7	5800	12400	-3
PBA3	40.0	8000	14500	-3
PBA4	57.1	9800	19500	-1
PBA5	100	12900	27300	-1
PBA6	200	17400	36900	0
SA1	20.0	4500	9300	-18
SA2	30.0	6400	13000	-14
SA3	60.0	10000	20700	-10
SA4	150	14700	32100	-6
SA5	300	19700	40400	-2
Blank	-	26000	59400	0

of *IV* versus molar ratio of monocarboxylic acid to diacids for the three series are shown in Figure 1. Two types of relationship between *IV* and molar ratio of monocarboxylic acid to diacids were found. In the presence of benzoic acid, *IV* could not be predicted well from the molar ratio of benzoic acid to diacids. This is probably due to the lower boiling point of benzoic acid. The boiling point of benzoic acid is 249°C, and under the preparation conditions, the high temperature (260°C) and vacuum caused some of the benzoic acid to be distilled out, thus it failed in controlling the molecular weight predictably.

Although the preparation conditions were similar for batches B1 and B2, the resultant values of *IV* were rather different (0.38 and 0.26 dl/g, respectively). Thus, the reproducibility of use for benzoic acid in controlling the molecular weight was poor.

The second type of relationship was much different. In the presence of both *p*-phenylbenzoic acid and stearic acid, the relationship between *IV* and molar ratio of monocarboxylic acid to diacids was found to fall into a smooth curve. Because the boiling points of both *p*-phenylbenzoic acid (> 300°C) and stearic acid (383°C) are very high, there would be little tendency for them to be distilled out under such preparation conditions. Thus, the two monocarboxylic acids were successful in controlling the molecular weight of the copolyesters predictably. In addition, the reproducibility was also found to be very good. In the presence of additional 9.47 g of stearic acid (molar ratio of stearic acid to diacids equal to 0.0333), three batches similar to the typical example were carried out. The resultant *IV* values were 0.40, 0.39 and 0.42 dl/g, respectively. The variation in *IV* values between various batches was small. Thus, the use of such high boiling point monocarboxylic acids would provide a good method for controlling the molecular weight of copolyesters prepared by melt polycondensation.

The number average molecular weight (\bar{M}_n) and weight average molecular weight (\bar{M}_w) of each copolyester determined by g.p.c. are shown in Table 2.

The concept of molecular weight control is very simple. After polymerization reaction, the monocarboxylic acid capped the polymer chain end. For the system of interest, *S* mol of monocarboxylic acid was added in the presence of 1 mol diacids (the molar ratio of monocarboxylic acid to diacids was equal to *S*). If all the copolyester molecules were capped by the monocarboxylic acid, each copolyester molecule possessed two end groups capped by the monocarboxylic acid. Statistically, 1 mol of repeat units corresponded to *S*/2 mol of polymer molecules. If the influence of end groups on the molecular weight can be

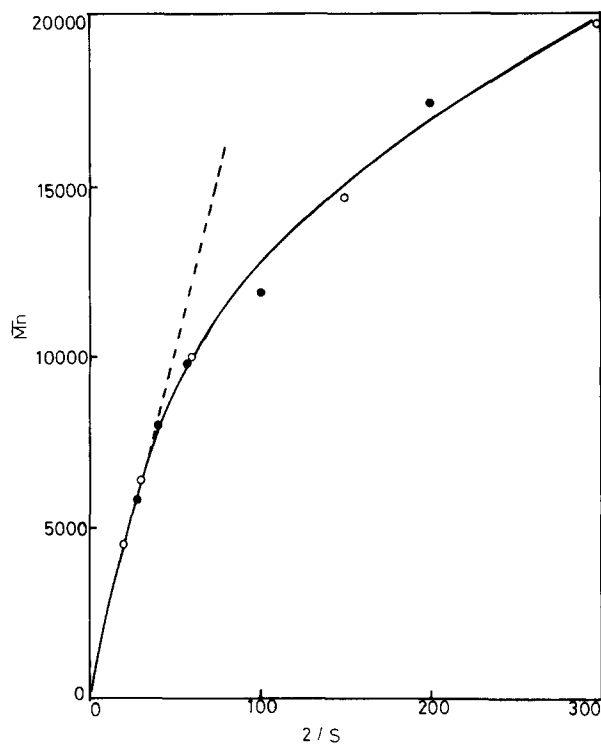


Figure 2 The plot of \bar{M}_n versus $2/S$ for PBA (●) and SA (○) series

neglected, the average degree of polymerization \bar{DP} will be

$$\bar{DP} = 1/(S/2) = 2/S \quad (1)$$

The plot of \bar{M}_n versus $2/S$ for PBA and SA series is shown in Figure 2. As $2/S$ was below 40, the relationship between \bar{M}_n and $2/S$ fitted a straight line. Thus, the concept of equation (1) was able to predict the molecular weight of copolyesters controlled by both *p*-phenylbenzoic acid and stearic acid when $2/S$ was below 40. The slope of the straight line in Figure 2 was found to be about 200, which is close to the molecular weight of repeat unit (215). In other words, as the molar ratio of monocarboxylic acid to diacids was greater than 0.05, the degree of polymerization was governed by equation (1).

When $2/S$ was above 40, the relationship between \bar{M}_n and $2/S$ deviated from the original straight line. \bar{M}_n levelled off for larger $2/S$. The end groups were all assumed to be capped by monocarboxylic acid in deriving equation (1). In fact, some end groups were not capped by monocarboxylic acid. When $2/S$ was small, the contribution of these end groups other than capped by monocarboxylic acid could be neglected, thus equation (1) held. But the amounts of these end groups which were not capped by monocarboxylic acid were significant when $2/S$ was large, thus deviation from equation (1) was found.

Typical d.s.c. thermograms of the copolyesters are shown in Figure 3. T_m (melting temperature) and heat of fusion (compared to that of indium taken as 6.8 cal/g) of all the copolyesters were found to be about 110°C and 5 cal/g, respectively. There was no explicit trend of effect of molecular weight on T_m and crystallinity. The copolyesters prepared by this melt polycondensation method would be random copolymers due to transesterification^{7,8}, and the sequence length of different segments would not be interrupted by the end groups significantly. Thus, the

effect of molecular weight on the T_m and crystallinity was possibly forbidden because the effect of copolymerization was a dominant term.

T_g (glass transition temperature) was taken as the midpoint of the inflection and is listed in Table 2. The effect of molecular weight of PBA and SA series on T_g is also shown in Table 2. For the same type of end group, the influence of molecular weight on T_g can be described as the effect of number of chain end group. In general, as the molecular weight decreases, the number of end groups increases and the free volume increases; thus T_g decreases accordingly. T_g of the PBA series decreased slightly as the molecular weight decreased, but T_g of the SA series decreased more significantly as the molecular weight decreased.

It was found that the copolyesters with similar molecular weights (i.e. PBA4, BA1 and SA3) but different end groups had rather different values of T_g (-1, -7 and -10°C, respectively). The different effect of molecular weight on T_g for the two series would be attributed to the structure of end group. The rigidity of *p*-phenylbenzoate end group (-O-CO-C₆H₄-C₆H₅) is greater than that of benzoate (-O-CO-C₆H₅) which is, in turn, greater than that of stearate end group (-O-CO-(CH₂)₁₄-CH₃). In the case of SA series of copolyesters, the stearate end group was more flexible than the end groups of original polymer. In addition to the effect of number of end groups, the more flexible stearate group would act like diluent or plasticizer and thus decrease T_g to a greater extent. Because the weight fraction of stearate group increased as the molecular weight decreased for the SA series of copolyesters, the net result was that T_g was more sensitive to the molecular weight. The presence of a very rigid end group would result in a very different behaviour. Thus the T_g of the PBA series of copolyesters was more insensitive to molecular weight than SA series.

The Arrhenius plots of melt viscosity versus temperature for the PBA and SA series are shown in Figures 4 and 5, respectively. The flow activation energy was found to be about 6-7 kcal/mol. As might be expected, the melt

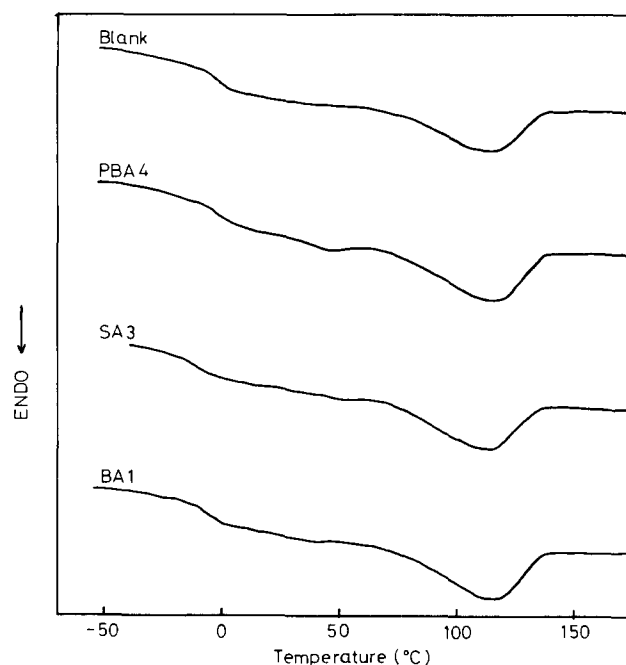


Figure 3 D.s.c. thermograms of some samples

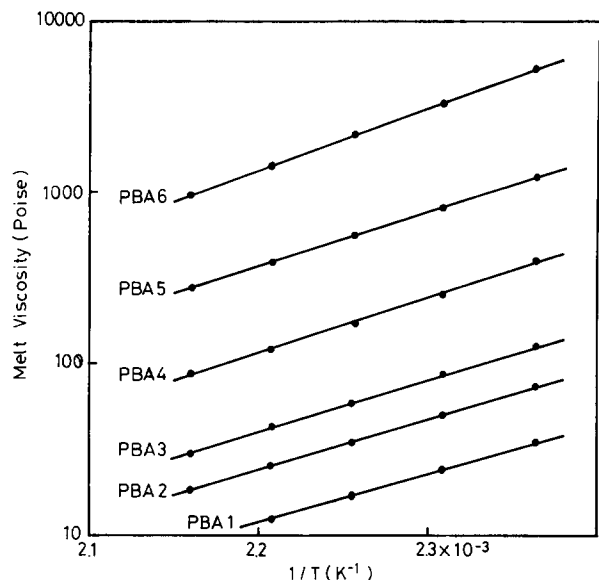


Figure 4 The effect of temperature on the melt viscosity of PBA series (Arrhenius plot)

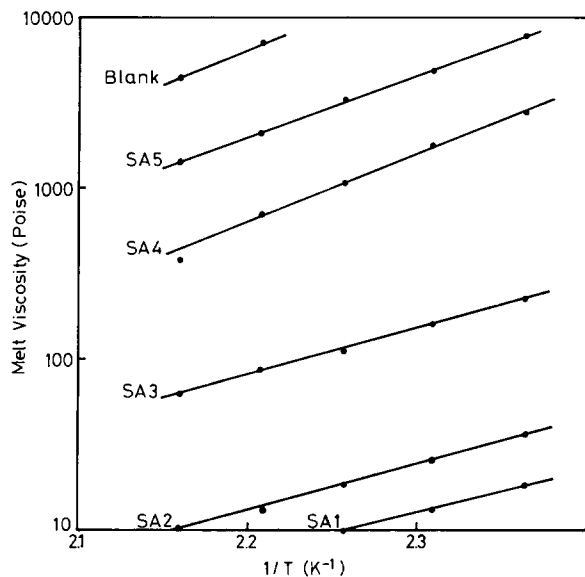


Figure 5 The effect of temperature on the melt viscosity of SA series (Arrhenius plot)

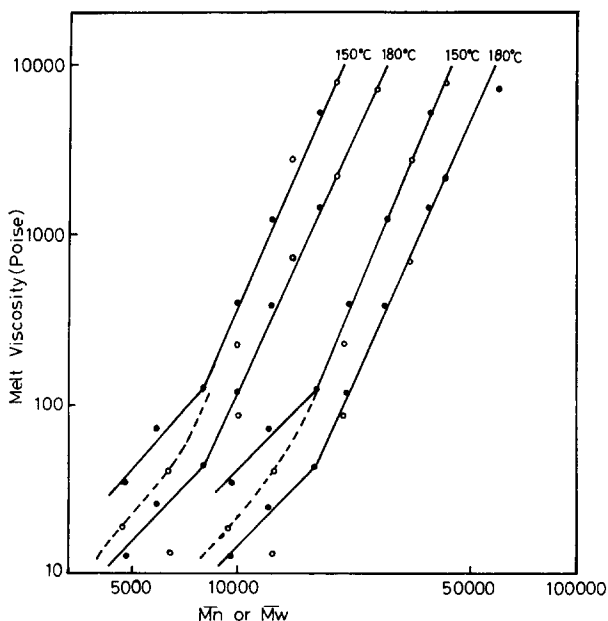


Figure 6 The effect of temperature on the melt viscosity of PBA (●) and SA (○) series at 180 and 150°C

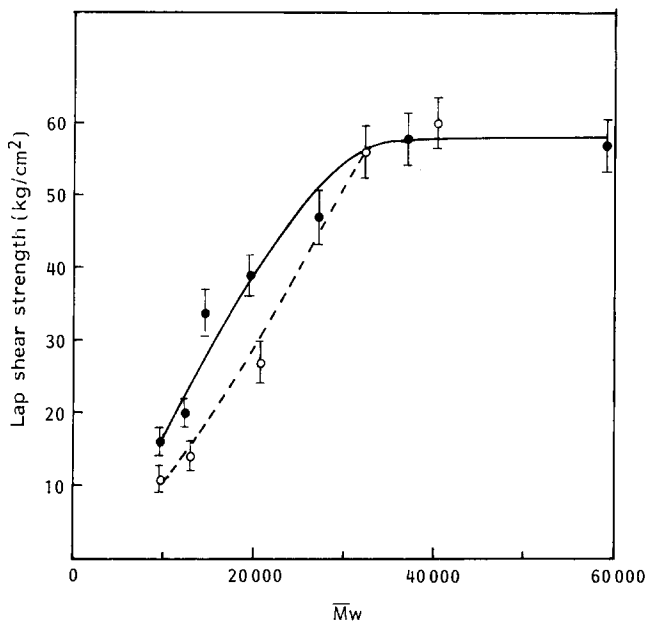


Figure 7 The effect of molecular weight on the lap shear strength. ●, —, PBA; ○, ----, SA

viscosity decreased considerably as the molecular weight decreased.

The logarithmic plots of melt viscosity at 150°C and 180°C versus \bar{M}_n and \bar{M}_w for PBA and SA series are shown in Figure 6. The slope of the plot for the high molecular weight range was greater than that for the low molecular weight range. This is probably due to the chain entanglement in the high molecular weight range. When \bar{M}_w was above 15000, the logarithmic relationship between melt viscosity and molecular weight (\bar{M}_n and \bar{M}_w) of both the PBA and SA series fitted a straight line at a given temperature. Because the weight fraction of end groups capped by monocarboxylic acid decreased as the molecular weight increased, the effect of different end groups on the melt viscosity could be neglected for high molecular weight range, and a single line was found for both PBA and SA series. But the effect of different end groups was significant for low molecular range. When \bar{M}_w was below 15000, the plot of the PBA series (solid line) lay above that of SA series (dashed line), in Figure 6. Within the low molecular weight range, the difference in melt viscosity between the PBA and SA series would be due to the different rigidity of the end groups. The weight fraction of the end groups capped by monocarboxylic acid increased as the molecular weight decreased. Because the rigidity of *p*-phenylbenzoate end groups is much higher than the stearate end groups, the melt viscosity of the PBA series was found to be higher than the SA series at low molecular weights.

The influence of \bar{M}_w on the lap shear strength for PBA and SA series is shown in Figure 7. At lower molecular weights, the lap shear strength increased considerably as the molecular weight increased for both series. When \bar{M}_w was greater than 30000 ($IV > 0.6$ dl/g), there was no significant difference in lap shear strength. At low molecular weights, the lap shear strength versus \bar{M}_w curve of the PBA series lay above that of SA series, as shown in Figure 7. This could be attributed to the more rigid nature of the *p*-phenylbenzoate end groups.

CONCLUSION

The copolyesters of 1,4-butanediol, terephthalic acid, isophthalic acid, and adipic acid of different molecular weights which were prepared by melt polycondensation were successfully controlled by a monocarboxylic acid, either *p*-phenylbenzoic acid (PBA series) or stearic acid (SA series). T_g was found to decrease more significantly as the molecular weight decreased in the SA series than in the PBA series due to the more rigid nature of end groups in the PBA series. The melt viscosity of the PBA and SA series decreased considerably as the molecular weight increased. The lap shear strength increased significantly as the molecular weight increased, and then levelled off when *IV* was greater than 0.6 dl/g. At low molecular weights, the melt viscosity and lap shear

strength of the PBA series were found to be higher than those of the SA series. This is attributed to the different rigidity of the end groups of the two series.

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