

Block Copolyetheresters. Part 3: Preparation of Block Copolyetheresters by a Terephthalic Acid Process in the Presence of Salts

SHINN-JEN CHANG, FENG-CHIH CHANG *and*
HONG-BING TSAI*

*Institute of Applied Chemistry
National Chiao Tung University
Hsinchu, Taiwan, Republic of China*

** Union Chemical Laboratories
Industrial Technology Research Institute
Hsinchu, Taiwan, Republic of China*

The block copolyetheresters with hard segments of poly(butylene terephthalate) and soft segments of poly(tetramethylene ether) were prepared by a terephthalic acid (TPA) process in the presence of some salts. The preparations of a block copolyetherester under various conditions were first studied in a 1 L stainless steel reactor to find the best method. Then, the preparations of four block copolyetheresters were run in a pilot plant comprising a 200 L polyesterification reactor and a 200 L polymerization reactor under the suitable condition. The presence of some salts reduced the formation of tetrahydrofuran (THF), and also reduced the total reaction time in the pilot plant. The thermal properties and various mechanical properties of the block copolyetheresters prepared by the pilot plant were investigated to evaluate the feasibility of this method.

INTRODUCTION

The concept of block copolymer can be used to design thermoplastic elastomers. Typical examples are styrene-diene-styrene triblock copolymers (1-4), block copolyurethanes (1, 2, 5), block copolyetheramides (1, 2, 6), and block copolyetheresters (1, 2, 7-10). In our laboratories, the designs of various block copolymers as thermoplastic elastomers have become our major aims, and some block copolymers, such as block copolyetheramides (11), block copolyesters (12), and thermotropic block copolyetheresters (13) have been developed. It is an alternative approach intended to improve the preparation of the well-known commercial block copolymers.

The block copolyetheresters with hard segments of poly(butylene terephthalate) and soft segments of poly(tetramethylene ether) have been commercialized as thermoplastic elastomers for a period of time (1, 2, 10). They are produced by melt polycondensation of dimethyl terephthalate (DMT), 1,4-butanediol, and a poly(tetramethylene ether)glycol (PTMEG), namely a DMT process. However, the preparation of these block copolyetheresters by melt polycondensation of terephthalic acid (TPA), 1,4-butanediol, and a PTMEG, namely a TPA process, has been given little attention by the industry. The situation may be simi-

lar to the case of preparation of poly(butylene terephthalate) (PBT) by a TPA process in which the formation of tetrahydrofuran (THF) by cyclization is a severe problem. We have used some salts to reduce the formation of THF in the preparation of PBT by a TPA process, and some good results were found (14). In this study, we use some salts to improve the preparation of the block copolyetheresters by a TPA process, and a better condition was set up in a 200 L pilot plant to evaluate this modified TPA process. The thermal and mechanical properties of these block copolyetheresters were also investigated.

EXPERIMENTAL

Poly(tetramethylene ether) glycol (PTMEG1000) with a molecular weight of 1000 (Terathane 1000) and 1,4-butanediol were obtained from DuPont, terephthalic acid was supplied by China America Petrochemical Co. Ltd. (Taiwan), and isophthalic acid was supplied by Sisas (Italy). Irganox 1010 (an antioxidant), Tinuvin 770 (a UV stabilizer), and Tinuvin 370 (a UV stabilizer) were obtained from Ciba-Geigy. Tetrabutyl orthotitanate (TBT) and other chemicals were all Merck reagent grade. All the chemicals were used as received.

The block copolyetherester was prepared by melt polycondensation of terephthalic acid, 1,4-butanediol,

and PTMEG1000, similar to a process for PBT described previously (14). The reactions of 166 g (1.0 mol) of terephthalic acid, 162 g (1.8 mol) of 1,4-butanediol, 123 g (0.123 mol) of PTMEG1000 in the presence of catalysts and various salts in a 1 L stainless steel reactor were carried out to evaluate the effect of the salts. The content of THF of the distillate (containing water and THF) at the esterification stage and the conversion of esterification were determined as described previously (14). After the evaluation in the 1 L reactor, a better condition was chosen to scale up the process in a stainless steel pilot plant, which is composed of a 200 L esterification reactor and a 200 L polymerization reactor.

The products of the block copolyetheresters produced by the pilot plant were evaluated. The intrinsic viscosity of the products in phenol/syn-tetrachloroethane (60/40 wt/wt) was determined by an Ubbelohde viscometer at 30°C. The thermal properties from 50 to 250°C were measured by a DuPont DSC 910 at a heating rate of 10°C/min under nitrogen. Their ¹H NMR spectra were determined by a Bruker AM-400 NMR.

The products were injection molded into test specimens by an injection molding machine (Fu Chen Shine KT-150, Taiwan) under suitable conditions depending on the composition. The test specimens were used for the determination of tensile properties, flexural modulus, and hardness. The tensile properties were determined according to ASTM D-638, the Shore D hardness was measured according ASTM D-2240, and the flexural modulus was determined according to ASTM D-790.

RESULTS AND DISCUSSION

In the 1 L reactor, the reactions in the presence of various amounts of salts were carried out to evaluate the effect of the salts. Considering the reduction of the content of THF in the distillate, and the time required to reach a conversion of esterification at about 90%, we found that in the presence of some salts the reactions gave a lower content of THF and a shorter time of esterification. In the presence of 0.332 g (0.2 wt% based on terephthalic acid) of TBT as the catalyst system, 0.019 g (0.0115 wt% based on terephthalic acid) of sodium phosphate, and 0.0083 g (0.005 wt% based on terephthalic acid) of potassium

terephthalate as the salt system, the reaction gave a better result. Thus, this condition was chosen to scale up the TPA process.

Four block copolyetheresters were prepared in the pilot plant under a condition based on the above evaluation. The charged compositions are shown in Table 1. Three additional stabilizers were also used to improve the aging resistance.

To check the significance of the effect of the salts, a blank reaction with the same charged composition as that of TPEE3 but without salt was also carried out in the pilot plant. Figure 1 shows the process of the blank reaction and that of TPEE3. In the 200 L esterification reactor, the temperature was held at 220°C and the reactants were charged. The reaction temperature first decreased as a result of the charge of the

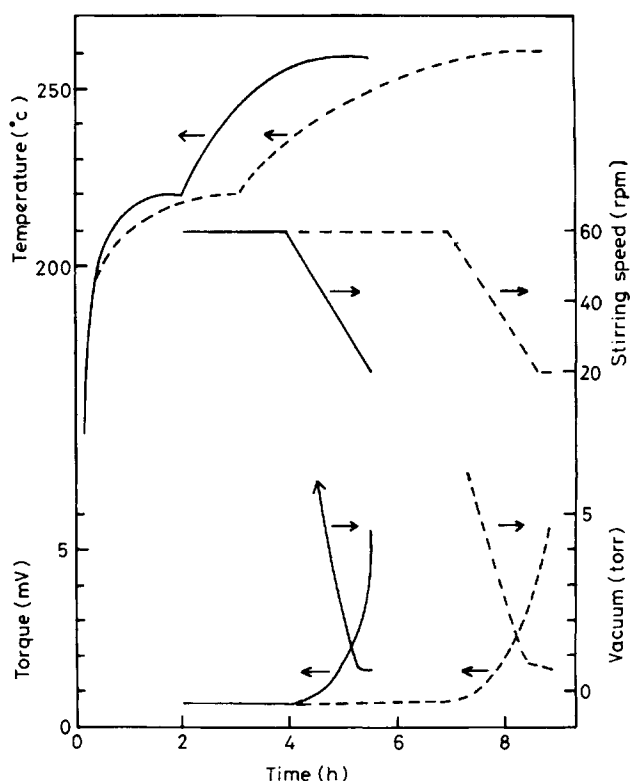


Fig. 1. Process curves of the preparation of TPEE3 in the presence of the salt system (solid lines) and the blank reaction (dash lines).

Table 1. The Charged Composition and Intrinsic Viscosity of the Block Copolyetheresters.

	TPEE1	TPEE2	TPEE3	TPEE4
Terephthalic acid (g)	23,100	22,150	18,670	15,000
Isophthalic acid (g)	0	0	0	60 00
1,4-Butanediol	22,540	21,620	18,220	20,494
PTMEG1000 (g)	4744	7964	13,890	16,193
TBT (g)	46.2	44.3	37.3	42.0
Irganox 1010 (g)	127.7	129.3	127.0	144.2
Tinuvin 770 (g)	127.7	129.3	127.0	144.2
Tinuvin 370 (g)	127.7	129.3	127.0	144.2
Sodium phosphate (g)	2.66	2.55	2.15	2.42
Potassium terephthalate (g)	1.16	1.11	0.93	1.05
Intrinsic viscosity (dL/g)	1.14	1.31	1.12	1.34

four block copolyetheresters are shown in Fig. 3. An endotherm corresponding to the melting of the hard polyester segments was observed for the block copolyetheresters. Their melting point (T_m) and heat of fusion are listed in Table 5. Their thermal properties were significantly affected by the composition. There was no isophthalate unit in TPEE1, TPEE2, or TPEE3. For these three block copolyetheresters, as the content of the polyether segment increased, TPEE1 < TPEE2 < TPEE3, the sequence length of the poly(butylene terephthalate) hard segment decreased (10), and thus the melting point (T_m) decreased (Table 5). The heat of fusion also decreased as the content of the polyether segment increased as a result of the decreasing order of both the content and the sequence length of the poly(butylene terephthalate) segment. TPEE4 showed a considerably lower T_m . The charged molar ratio of diacids (TPA and IPA) to PT-

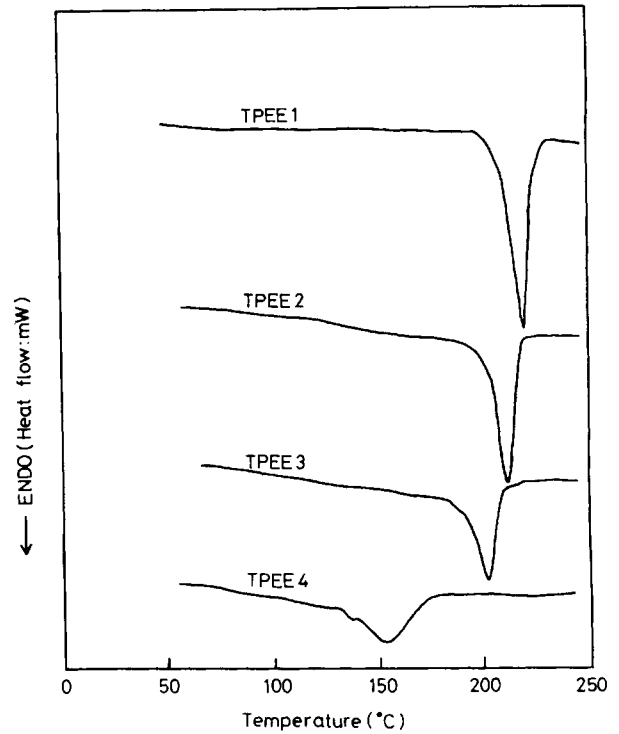


Fig. 3. DSC heating curves of the block copolyetheresters.

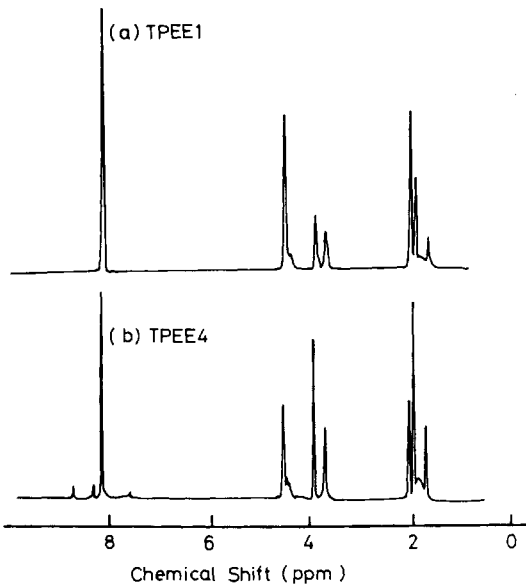


Fig. 2. ¹H NMR spectra of TPEE1 and TPEE4.

MEG was 1.0:0.128 for TPEE4, and that of TPA to PTMEG was 1.0:0.123 for TPEE3. Thus the content of the polyether segment of TPEE4 was close to that of TPEE3. However, TPEE4 showed a considerably lower T_m (153°C) than that of TPEE3 (202°C). It was due to the copolymerization effect in the polyester hard segment. For TPEE4, the presence of the isophthalate unit rendered a random structure in the polyester segment and affected the crystallization. Thus, TPEE4 showed a considerably lower T_m and also a lower heat of fusion when compared to TPEE3.

The tensile stress-strain curves and the corresponding tensile properties of the injection molded specimens are shown in Fig. 4 and Table 5 respectively. The measured flexural modulus and Shore D hardness are also listed in Table 5. As the content of polyether segment increased, the tensile yield strength, tensile modulus, flexural modulus, and Shore D hardness decreased as expected. This trend could correlate with the decreasing crystallinity as indicated by the heat of fusion (Table 5).

Table 4. The Ratios of H1 : H2 : H3 : H4 Calculated, Based on Charged Compositions and Determined by ¹H NMR.

	Calculated Ratio	Determined Ratio
TPEE1	1.0:1.0:0.44:1.44	1.0:1.04:0.48:1.54
TPEE2	1.0:1.0:0.78:1.78	1.0:1.05:0.71:1.79
TPEE3	1.0:1.0:1.60:2.60	1.0:1.03:1.55:2.69
TPEE4	1.0:1.0:1.66:2.66	1.0:1.05:1.76:2.80

Table 5. The Thermal Properties and Mechanical Properties of the Block Copolyetheresters.

Properties	TPEE1	TPEE2	TPEE3	TPEE4
T_m (°C)	219	211	202	153
Heat of fusion (J/g)	41.4	30.1	21.3	12.5
Yield strength (MPa)	44	27	17	13
Tensile modulus (MPa)	1250	440	200	84
Elongation (%)	> 500	> 500	> 500	> 500
Flexural modulus (MPa)	1040	420	200	62
Hardness (Shore D)	80	73	63	50

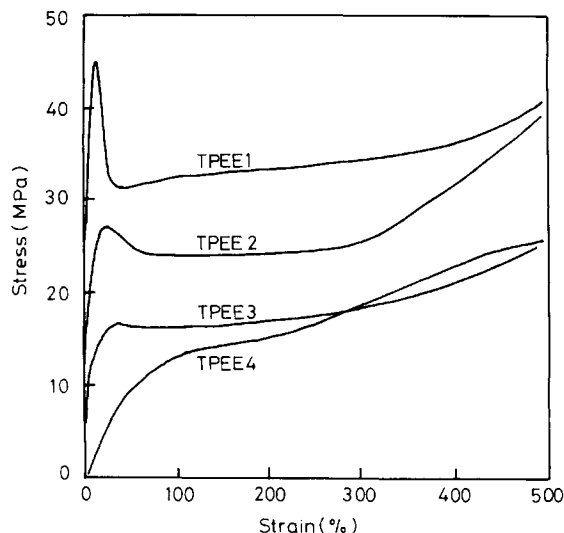


Fig. 4. Tensile stress-strain curves of the block copolyetheresters.

CONCLUSION

The block copolyetheresters were prepared successfully in a pilot plant by a TPA process in the presence of a salt system. The presence of this salt system reduced the formation of THF, and also reduced the reaction time of the whole process. The compositions of the block copolyetheresters deter-

mined by ^1H NMR agreed well with the charged compositions. The thermal properties and mechanical properties were measured and found to be dependent on the composition.

REFERENCES

1. N. R. Legge, G. Holder, and H. E. Schroeder, Eds., *Thermoplastic Elastomers: A Comprehensive Review*, Hanser Publishers, New York (1987).
2. A. K. Bhowmick and H. L. Stephens, Eds., *Handbook of Elastomers: New Developments and Technology*, Marcel Dekker, New York (1988).
3. L. M. Porter, U.S. Pat. 3,149,182 (1964).
4. R. F. Zelinski, U.S. Pat. 3,281,383 (1966).
5. G. Oertel, *Polyurethane Handbook*, Hanser Publishers, New York (1985).
6. P. Foy, C. Jungblut, and G. Deleens, U.S. Pat. 4,332,920 (1982).
7. J. C. Shivers and W. Chester, U.S. Pat. 3,023,192 (1962).
8. W. K. Witsiepe, U.S. Pat. 3,651,014 (1972).
9. G. K. Hoeschele, U.S. Pat. 3,801,547 (1974).
10. H. Schroeder and R. J. Cella, in *Encyclopedia of Polymer Science and Engineering*, 2nd Ed., Vol. 12, pp. 75-117, H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. I. Kroschwitz, Eds., Wiley, New York (1988).
11. L. Z. Chung, D. L. Kuo, A. T. Hu, and H. B. Tsai, *J. Polym. Sci. Part A: Polym. Chem.*, **30**, 951 (1992).
12. H. B. Tsai, H. C. Li, S. J. Chang, and F. S. Yu, *Polym. Bull.*, **27**, 141 (1991).
13. H. B. Tsai, C. Lee, and N. S. Chang, *Polym. J.*, **24**, 157 (1992).
14. S. J. Chang and H. B. Tsai, *J. Appl. Polym. Sci.*, **45**, 371 (1992).

Received Nov. 15, 1992