Effect of the Sb_2O_3 Catalyst on the Solid-State Postpolycondensation of Poly(ethylene terephthalate)

DEMETRIS E. KOKKALAS, DEMETRIS N. BIKIARIS, and GEORGE P. KARAYANNIDIS*

Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-540 06, Thessaloniki, Greece

SYNOPSIS

The effect of Sb_2O_3, which is used as the main catalyst in the production of poly(ethylene terephthalate) (PET) by melt polymerization, was studied on solid-state postpolycondensation. It was observed that the catalyst works efficiently even in the solid state. The number-average molecular weight of a PET prepolymer with an Sb_2O_3 content of 2000 ppm was increased from 18,350 to 40,800 after heating at 210°C for 8 h under vacuum (2–3 Pa), whereas when the catalyst was absent, the molecular weight of the same prepolymer under the same conditions was just increased to 22,500. The activation energies and the frequency factors of the esterification and ester interchange reactions, which take place simultaneously during solid-state postpolycondensation, were determined. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene terephthalate) (PET) possesses physical and mechanical properties that are of considerable interest for various applications. For each application, a certain number-average molecular weight ($\bar{M}_n$) is needed: $\bar{M}_n = 13,000$ or $[\eta] = 0.55$ for films (Mylar, Melinex, etc.) destined for audio or video tapes, photographic films, food packaging films, and insulating material for capacitors; $\bar{M}_n = 17,000$ or $[\eta] = 0.65$ for synthetic fibers (Dacron, Terylene, Trevira, etc.); $\bar{M}_n = 20,000$ or $[\eta] = 0.73$ for carbonated soft-drink bottles and, recently, for carbonated alcoholic drink bottles, e.g., beer; and $\bar{M}_n > 25,000$ or $[\eta] > 0.85$ for industrial tire cords where the highest mechanical strength is needed.

This relatively high average molecular weight PET is usually produced by "solid-state polycondensation" (SSP) of a prepolymer and not by continuation of the melt polymerization, because the longer time in the melt state causes an excessive degradation of the final product.

The main chemical reactions that can take place during solid-state polycondensation are esterification and transesterification (ester interchange) in which water or/and ethylene glycol are released as byproducts. To increase the rate of these reactions, the removal of these byproducts by diffusion out of the solid semicrystalline polymer is necessary. So, the polycondensation rate in the solid state depends on both chemical and physical processes and is determined by the slower process. This depends on various reaction parameters such as reaction temperature and time, but also on sample size, crystallinity, end-group content, initial molecular weight, and the catalyst system used for its preparation.[1-14]

It was noted in the past[2] that any type of catalyst that affects the polymerization of PET in the melt state should also be effective in the solid state as long as the reaction temperature is high enough to activate the terminal hydroxyl and carboxyl groups or those ester linkages nearest the ends of the chains. In spite of the so many articles relative to the SSP of PET, there is no published information on the role that Sb_2O_3 or other catalysts play during this kind of reaction. Therefore, it was of interest to investigate the influence of the catalyst content on the solid-state polycondensation process, keeping constant all the other aforementioned factors, e.g., sample size and crystallinity. For this reason, four PET prepolymer samples were prepared, and after addition of different quantities of Sb_2O_3 into these samples, they were subjected to solid-state polycon-

---

* To whom correspondence should be addressed.

densation. From this investigation, it was concluded that the action of the catalyst is significant even in the solid-state polycondensation.

EXPERIMENTAL

Preparation of PET Prepolymer Samples

PET prepolymer was prepared in two stages from dimethyl terephthalate (DMT) (0.50 mol) and ethylene glycol (EG) (1.10 mol), i.e., (DMT/EG = 1/2.2). Both stages, transesterification and polycondensation, were catalyzed by manganese acetate tetrahydrate, $Mn(CH_3COO)_2 \cdot 4H_2O$ (Ref. 15) (1 × 10^{-4} mol based on DMT 127 ppm), and were carried out in the same reaction tube of a polymerization apparatus similar to that used by Günther and Zachmann.[16] For the transesterification stage, the reactions were heated at 200°C for 1 h, 220°C for 1 h, 240°C for 30 min, 260°C for 30 min, and, finally, 270°C for 30 min. The methanol that was also formed in this stage was continually removed by distillation and collected in a volumetric cylinder. The volume of methanol distilling out of the reactor served as an estimate for the conversion rate of DMT. When the theoretical amount of methanol had distilled (40.4 mL), polycondensation was carried out by gradually reducing the pressure of the system to 4.0 Pa over a period of 30 min. The polymerization tube was maintained under vacuum and stirring for 90 min at 270°C.

The prepolymer received was analyzed by the methods described below and showed the following characteristics: [η] = 0.76; carboxyl content = 38 mmol/kg; and hydroxyl content = 72 mmol/kg. This quantity of the PET prepolymer was divided into four, about equal, parts, and then 500, 1000, or 2000 ppm of the Sb_2O_3 catalyst was added to the second, third, and fourth sample after melting at 280°C and with stirring (60 rpm) for 10 min under an argon atmosphere. The first sample was subjected exactly to the same treatment but without addition of Sb_2O_3 (blank). After cooling, the samples were delivered from the glass particles. It must be pointed out that in every experiment the glass reaction tube is broken itself on cooling, because of the very strong adherence between PET and glass and the contraction of PET during crystallization. Then, the samples were ground and sieved and the particle size fraction of −0.40 + 0.16 mm was chosen. After a thorough drying (12 h at 110°C), all four samples underwent solid-state postpolycondensation.

Solid-state Polycondensation (SSP)

The reaction apparatus was described previously.[14] Two grams of the PET sample was introduced in each flask and the vacuum stabilized between 3 and 4 Pa. The reaction temperature was kept constant at 180, 190, 200, or 210°C. The reaction flasks were withdrawn successively from the bath after 2, 4, 6, and 8 h and were allowed to be cooled to room temperature. The resulting samples were measured for the intrinsic viscosity and hydroxyl and carboxyl content.

Measurements

All viscosity measurements were conducted at 25.0 ± 0.1°C in an Ubbelohde-type viscometer on solutions in 60%/40% w/w phenol/tetrachloroethane, at a polymer concentration of 0.25%. The intrinsic viscosity of each sample was calculated by using the Solomon–Ciuta[17] equation of a single-point measurement:

$$[\eta] = [2(\eta_{sp} - \ln \eta_{rel})]^{0.5}/c \qquad (1)$$

The number-average molecular weight ($\bar{M}_n$) of the samples was calculated from [η] values, using the Berkowitz[18] equation:

$$\bar{M}_n = 3.29 \times 10^4 [\eta]^{1.54} \qquad (2)$$

The $\bar{M}_n$ was also calculated from the end-group content of the samples as

$$\bar{M}_n = 2/[OH] + [COOH] \qquad (3)$$

where the concentration of hydroxyl and carboxyl groups is expressed in mmol/kg.

The carboxyl end-group content was determined according to Pohl's method.[19] The hydroxyl end-group content was determined according to the method proposed by Zimmermann and Kolbig,[20] reported also by Weisskopf.[21] The latter method is based on the reaction of the hydroxyl end-groups of PET with o-sulfobenzoic acid cyclic anhydride.

RESULTS AND DISCUSSION

The PET prepolymer used was prepared according to the method described in the experimental part and showed an intrinsic viscosity [η] = 0.76, corresponding to a molecular weight $\bar{M}_n$ = 21,600. This prepolymer was divided into four, about equal, parts

Table I   Analytical Data of PET Prepolymer Samples

PET Sample	Sb$_2$O$_3$ (ppm)	[COOH] (mmol/kg)	[OH] (mmol/kg)	[COOH] + [OH] (mmol/kg)	$\bar{M}_n$[a]	[η] (dL/g)	$\bar{M}_n$[b]
Prepolymer	—	24	73	97	20,600	0.76	21,600
A	—	38	72	110	18,200	0.70	19,000
B	500	39	71	110	18,200	0.70	19,000
C	1000	38	72	110	18,200	0.70	19,000
D	2000	37	72	109	18,350	0.70	19,000

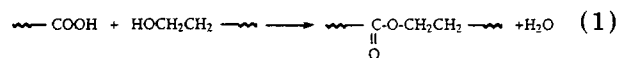[a] $\bar{M}_n$ was calculated from the end-group content.
[b] $\bar{M}_n$ was calculated from the [η] value.

(A, B, C, and D) and then 500, 1000, or 2000 ppm of Sb$_2$O$_3$ were added to the second (B), third (C), and fourth (D) sample correspondingly. The characteristics of four PET samples are presented in Table I.

It is obvious that after the aforementioned melting the number-average molecular weight of the PET samples was decreased from 21,600 to 19,000 or from 20,600 to 18,200, determined by end-group content, but it changed to about the same degree in all samples. The latter is very important, because in this work, we tried to have similar PET samples with the only difference between them the different Sb$_2$O$_3$ content. These PET samples, after SSP at four different temperatures (180, 190, 200, and 210°C) and for different times (2, 4, 6, and 8 h), were measured for intrinsic viscosity and carboxyl and hydroxyl content (Table II).

As one can see, the decrease of carboxyl content at 210°C after heating for 8 h is the same ($\approx$ 10 mmol/kg) for all samples. This means that esterification [Reaction (1)] is independent of the presence of Sb$_2$O$_3$:

$$\text{—COOH} + \text{HOCH}_2\text{CH}_2\text{—} \longrightarrow \text{—}\underset{\underset{\text{O}}{\overset{\|}{}}{}}{\text{C}}\text{-O-CH}_2\text{CH}_2\text{—} + \text{H}_2\text{O} \quad (1)$$

Table II   Carboxyl and Hydroxyl Group Contents and $\bar{M}_n$ of SSP Samples

Temp. (°C)	Time (h)	[COOH] (mmol/kg) A	B	C	D	[OH] (mmol/kg) A	B	C	D	$\bar{M}_n \times 10^{-3}$ A	B	C	D
Initial values		**38**	**39**	**38**	**37**	**72**	**71**	**72**	**72**	**18.2**	**18.2**	**18.2**	**18.35**
180	2	37	38	37	36	71	69	68	65	18.5	18.7	19.0	19.8
	4	36	37	36	35	70	67	65	56	18.9	19.2	19.8	22.0
	6	35	36	36	34	69	66	60	52	19.2	19.6	20.8	23.3
	8	35	36	35	34	68	65	57	45	19.4	19.8	21.7	25.3
190	2	35	37	36	36	70	67	59	50	19.0	19.2	21.0	23.3
	4	34	36	35	35	68	64	53	44	19.6	20.0	22.7	25.3
	6	33	35	35	35	66	62	49	37	20.2	20.6	23.8	27.8
	8	32	34	34	33	65	61	45	34	20.6	21.0	25.3	29.9
200	2	33	36	35	35	67	64	52	41	20.0	20.0	23.0	26.3
	4	32	35	34	33	66	61	44	38	20.4	20.8	25.6	28.2
	6	30	34	34	32	64	58	35	31	21.3	21.7	29.0	31.7
	8	29	33	33	32	63	53	30	26	21.7	23.3	31.7	34.5
210	2	33	34	34	34	67	54	42	33	20.0	22.7	26.0	29.9
	4	30	33	32	31	65	44	38	29	21.0	26.0	28.6	33.3
	6	29	31	29	29	63	41	30	25	21.7	27.8	33.9	37.0
	8	28	29	28	27	61	38	26	22	22.5	29.9	37.0	40.8

By examining the differences,

$$\Delta[COOH] = [COOH]_0 - [COOH]_t$$

and

$$\Delta[OH] = [OH]_0 - [OH]_t$$

which express the mmol of carboxyl and hydroxyl groups per kg of polymer, reacted in time t, it is shown that only for sample A they are about equal, i.e., the only reaction that takes place in sample A is esterification, obviously, because the specific catalyst for ester interchange (Sb_2O_3) is absent.

When Sb_2O_3 is present and its content is increasing progressively from sample B to D, a second parallel reaction, the ester interchange [Reaction (2)], begins to take place:

$$(2)$$
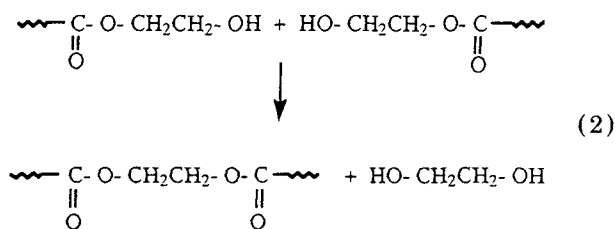
These two parallel Reactions (1) and (2) were studied using the carboxyl and hydroxyl contents of the solid-state postpolycondensated samples and the very important work of Chen and Chen.[10] In this article, the authors succeeded to determine the rates of esterification and ester interchange separately. The kinetic results of our work are presented in Table III.

The activation energy (E_{10}) and frequency factor (f_{10}) obtained for ester interchange could not be estimated for sample A because there is no such reaction in the absence of Sb_2O_3, as mentioned previously. For the other samples, the activation energy

Table III   Values of the Activation Energies and Frequency Factors of the SSP of PET with Different Sb_2O_3 Content

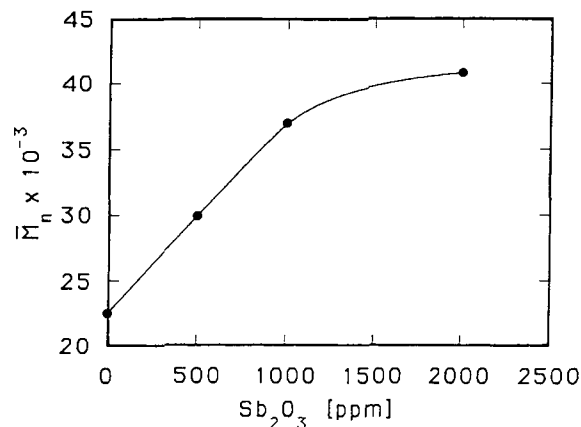|	Ester Interchange		Esterification	
Sample	E_{10}	f_{10}	E_{20}	f_{20}
A	—	—	26.9	6.39×10^7
B	39.5	1.12×10^{15}	25.1	6.96×10^6
C	30.1	1.30×10^{11}	25.3	9.28×10^6
D	24.3	6.58×10^8	27.4	8.32×10^7

Figure 1   Ultimate number-average molecular weight vs. Sb_2O_3 content for SSP of PET samples A, B, C, and D.

decreases as the Sb_2O_3 content increases. At a content of 2000 ppm, this activation energy is 24.3 kcal/mol, i.e., about the same as that found by Chen and Chen and very close to that of the reaction at the melt state: about 22.5 kcal/mol.[22]

The activation energy (E_{20}) of esterification is about the same for all samples ($\approx$ 26 kcal/mol). This value is significantly higher than that of the reaction of terephthalic acid and EG, 17.1 kcal/mol,[23] and that found by Chen and Chen, 19.1 kcal/mol.

In Figure 1, the ultimate number-average molecular weight, which was achieved after heating for 8 h at 210°C, is plotted against the Sb_2O_3 content. It is shown in this figure that Sb_2O_3 can catalyze the polycondensation of PET even in the solid state. Moreover, the 2000 ppm content of Sb_2O_3 must be a limiting one because the slope of the curve in this region was sensibly decreased. The slight increase of the $\bar{M}_n$ of the blank sample (from 18,200 to 22,500) must be attributed to the presence of manganese acetate that was used in its preparation and/or the solid-state postpolycondensation reaction conditions (high temperature and vacuum).

REFERENCES

1. D. A. S. Ravens and I. M. Ward, *Trans. Faraday Soc.*, **57**, 150 (1961).
2. L. C. Hsu, *J. Macromol. Sci.-Phys.*, **B1**(4), 801 (1967).
3. F. C. Chen, R. G. Griskey, and G. H. Beyer, *AIChE J.*, **15**, 680 (1969).
4. C. H. Bamford and R. P. Wayne, *Polymer*, **10**, 661 (1969).

5. T. M. Chang, *Polym. Eng. Sci.*, **10**, 364 (1970).

6. M. Dröscher and G. Wegner, *Polymer*, **19**, 43 (1978).

7. M. Dröscher, *Makromol. Chem.*, **181**, 789 (1980).

8. S. Chang, M. F. Sheu, and S. M. Chen, *J. Appl. Polym. Sci.*, **28**, 3289 (1983).

9. S. A. Jabarin, and E. A. Lofgren, *J. Appl. Polym. Sci.*, **32**, 5315 (1986).

10. S. A. Chen and F. L. Chen, *J. Polym. Sci.*, **25**, 533 (1987).

11. G. Cohn, *J. Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.*, **30**(2), 160 (1989).

12. K. Ravindranath and R. A. Mashelkar, *J. Appl. Polym. Sci.*, **39**, 1325 (1990).

13. G. Karayannidis, I. Sideridou, D. Zamboulis, G. Stalidis, D. Bikiaris, N. Lazaridis, and A. Wilmes, *Angew. Makromol. Chem.*, **192**, 155 (1991).

14. G. Karayannidis, D. Kokkalas, and D. Bikiaris, *J. Appl. Polym. Sci.*, **50**, 2135 (1993).

15. K. Yoda, *Kobunshi Kagaku*, **24**, 472 (1967).

16. B. Günther and H. G. Zachmann, *Polymer*, **24**, 1008 (1983).

17. O. F. Solomon and I. Z. Ciuta, *J. Appl. Polym. Sci.*, **6**, 683 (1962).

18. S. A. Berkowitz, *J. Appl. Polym. Sci.*, **29**, 4353 (1984).

19. H. A. Pohl, *Anal. Chem.*, **26**, 1614 (1954).

20. H. Zimmermann and C. Kolbig, *Faserforsch. Textiltech.*, **18**, 536 (1967).

21. K. Weisskopf, *J. Polym. Sci. Polym. Chem. Ed.*, **26**, 1919 (1988).

22. G. Challa, *Makromol. Chem.*, **38**, 105 (1960).

23. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.