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TECHNICAL PAPER presented at Cryogenic
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Synthesis of Ultrahigh Molecular Weight
Poly(Ethylene Terephthalate)

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Abstract

Poly(ethylene terephthalate) of number average molecular weight of the order of 120 000 was prepared from commercial grade material in the solid state with a gas chromatograph apparatus. Parameters studied were the catalyst, particle size, the molecular weight of the starting material, the reaction temperature and time, and the nature and flow rate of the carrier gas.

INTRODUCTION

Poly(ethylene terephthalate), hereafter called PET, possesses physical and mechanical properties that are of considerable interest for special aerospace applications at cryogenic temperatures (refs. 1, 2, and 3). The relation between these properties and molecular weight has not been studied. Mark (ref. 4) has stated that for all polymers certain mechanical properties depend on the average degree of polymerization (DP) or average molecular weight and approach a limiting value of strength at DP's above 600. To study the effect of molecular weight on the cryogenic properties of PET, it was necessary to synthesize PET having a number-average molecular weight of the order of 120 000 (DP $\simeq$ 600). This report covers the research on the method of synthesizing ultrahigh molecular weight material.

PET is ordinarily prepared by reacting dimethyl terephthalate and ethylene glycol in the melt state and distilling off methanol and the excess of ethylene glycol in two stages (refs. 5, 6, and 7). However, the number-average molecular weight of PET obtained by this method does not normally exceed 30 000 (ref. 8), primarily because of some side ester interchange reactions involved (refs. 9 and 10). The method of solid state polymerization was therefore examined as a means of increasing the molecular weight of the material produced by the melt method. In the solid state method, the removal of ethylene glycol can be effected by either employing a high vacuum technique or by flushing with an inert or carrier gas. It was noted that gas chromatograph apparatus is unusually well suited for performing the desorption of the ethylene glycol from the PET molecules. Thus, the gas chromatograph apparatus was investigated as a tool for performing the solid state polymerization. The column of the chromatograph was packed with PET particles instead of the normal absorbent materials.

This report contains a description of the use of a gas chromatograph to perform the solid state polymerization process and presents the results of attempts to produce ultrahigh molecular weight PET. Parameters studied were the catalyst, particle size, the molecular weight of the starting material, the reaction temperature and time, and the nature and flow rate of the carrier gas.

REACTION MECHANISMS INVOLVED IN POLYMERIZING PET

In the melt state, PET molecules bearing terminal hydroxyl groups are capable of carrying out interchange reactions between the hydroxyl groups and ester linkages (ref. 9). Another type of interchange between two ester linkages, namely esterolysis, is also possible (ref. 10). These two types of interchange reactions, hydroxyl-ester and ester-ester, may take place either intramolecularly (refs. 10 and 11) or intermolcularly. In addition, the interchange products in most cases depend upon the position of the reacting ester linkages along the polymer chain. Free ethylene glycol cannot be formed if the reacting ester linkage is in an in-chain position. It can be split off from PET molecules only if a terminal ester linkage is involved. Here terminal ester linkages refer to those nearest the ends of the polymer chains. In certain cases of intramolecular reactions, the products formed from the in-chain ester linkages on the same side of the repeating phenylene units as the attacking hydroxyl groups may be different from those on the opposite side. The same is true if the attacking group is another ester linkage.

In table I, the possible interchange reactions and their respective products have been listed. No. I is the only reaction which gives the product an increase of number-average molecular weight. All other reactions result either in no change or in a decrease of the number-average molecular weight. The decrease in number-average molecular weight is due to the formation of cyclic compounds which are in turn the consequence of certain intramolecular ester interchange reactions. In the melt polymerization of PET, intramolecular reaction has much less chance to take place than intermolecular reactions (ref. 8).

As the polymer chain grows longer, the number of terminal ester linkages becomes less. In other words, at the final stage of melt polymerization, reactions No. II and VI become predominant. In either of these two ester interchange reactions, there is no net change in the number of interunit linkages before and after the reaction, and therefore no increase in the number-average molecular weight of the product. This explains why the number-average molecular weight of PET prepared by the melt method normally does not exceed 30 000.

If a polymerization condition could be found such that only the terminal ester linkages, but not the in-chain ones, are activated, intermolecular reactions No. II and VI would be nearly eliminated. Thus, reaction No. I, as previously stated, remains as the only interchange reaction capable of increasing the molecular weight. This condition can be fulfilled if further polymerization of PET is carried out in the solid state. In the solid state polymerization, the reaction temperature is kept below the melt temperature of PET, but still high enough to activate the terminal ester linkages, so that interchange reactions between the hydroxyl groups of one PET molecule and the terminal ester linkages of another molecule can still take place. In this type of ester interchange reaction, ethylene glycol is split off and the number-average molecular weight is increased.

EXPERIMENTAL PROCEDURES

Materials

Reagent grade ethylene glycol was purified by passing through a column of 60 mesh refrigeration grade silica gel at room temperature or by distilling under reduced pressure below 100° C (373° K) with a spinning band column. Dimethyl terephthalate was purified by crystallization from ethyl alcohol and sublimed at 0.1 mm, mp 141-142° C (414-415° K). Practical grade tetraisopropyl orthotitanate; reagent grade, zinc acetate dihydrate, antimony trioxide, cobaltous acetate tetrahydrate, methylene chloride, and trifluoroacetic acid were used as received. Pet samples and carrier gases used are listed in tables II and III.

Melt Polymerization of PET

Purified dimethyl terephthalate (4 moles) and ethylene glycol (5 to 10 moles) were charged with catalyst (0.01 to 0.05 percent based on dimethyl terephthalate) into a 2-liter 3-neck flask. The melt polymerization procedure is similar to that described in references 5, 6, and 7 and will not be discussed further in this report.

Solid-State Polymerization of PET

The PET samples were ground with a Wiley mill and separated by conventional sieves into ranges of 4 to 6, 18 to 20, 60 to 80, and 80 to 200 mesh (NBS series). The ground particles were packed into the gas chromatograph column with gentle tapping. The column was 16 feet long (4.9 m) and 3/4-inch O.D. (1.9 cm) and held approximately 300 grams of sample. The melt temperature of each sample was checked with a hot-stage polarized light microscope before starting polymerization.

The general procedure of solid state polymerization with a preparative gas chromatograph (ref. 12) is relatively simple. The column packed with PET sample was installed in the chromatograph oven. After the flow of carrier gas was adjusted to the desired rate, the oven was heated and maintained at the reaction temperature for a specified time. Detector and collection trap may be used but are not necessary. The product was allowed to cool with a minimal flow of the carrier gas. It was then stored in a gas-tight container to avoid moisture absorption.

Number-Average Molecular Weight Determination

The intrinsic viscosity $[\eta]$ measurements of PET were carried out in a solvent mixture of trifluoroacetic acid and methylene chloride (1:1 by volume) with a Ubbelohde viscometer at 25° C (298° K). Dr. C. J. Heffelfinger of DuPont Company recommended the solvent mixture. Number-average molecular weights ($\overline{M}_n$) were calculated from Mark-Houwink equation: $[\eta] = K\overline{M}_n^a$. K and a were determined by employing a set of PET samples of known number-average molecular weights from 14 000 up to 28 000. Their values were found to be 9.2×10^{-4} and 0.70, respectively.

RESULTS AND DISCUSSION

Effect of Catalyst

Coover, Joyner, and Shearer (ref. 13) indicate that an organotitanium compound has to be used as the catalyst in a solid phase polymerization process for preparing linear superpolyesters. The results summarized in table IV, however, show that other commonly used ester interchange catalysts such as zinc acetate-antimony trioxide, and cobaltous acetate are capable of increasing the molecular weights of PET as well. This suggests that polymerization of PET in the solid state is essentially the elimination or minimization of undesired interchange reactions involving the in-chain ester linkages. Any type of catalyst which affects the polymerization of PET in the melt state should be also effective in the solid state as long as the reaction temperature is high enough to activate the terminal hydroxyl groups and those ester linkages nearest the ends of the chains. It is well known that the nature and amount of catalyst used in polyesterification can affect the molecular weight of the product. However, as a great deal of research has been done on catalysts (refs. 14 and 15) for melt polymerization of PET, the knowledge may be applied to the solid-state polymerization as well.

Effect of Initial Molecular Weight

The results summarized in table IV show that the final molecular weight of the product is very much dependent upon the molecular weight of the starting material. Apparently, in solid-state polymerization the chances for the reacting groups to come together are very much limited and the removal of ethylene glycol is also restrained because of solid phase diffusion problems. Within the same interval of reaction time, the higher the molecular weights of the starting materials, the higher the molecular weights of the products that should be expected.

Effect of Reaction Temperature

Figure 1 shows the relation between the reaction temperature and the molecular weight of the final product. The starting material had a number-average molecular weight of 16 500. There is no appreciable degree of further polymerization below 150° C (423° K) for the period of time studied. The reaction starts around 175° C (448° K) and the molecular weight of the product increases with temperature up to 250° C (523° K) which is close to the melt temperature of the PET sample (254 to 256° C) (527 to 529° K). However, it does not mean that in the solid state polymerization, PET of ultrahigh molecular weight has to be obtained at the highest allowable reaction temperature. Theoretically, the sample would eventually reach the same molecular weight as long as the reaction temperature is kept above 175° C (448° K).

Effect of Reaction Time

As shown in figure 2, the solid-state polymerization was carried out at 250° C (523° K) and the number-average molecular weights of the final products were plotted against the reaction time. There is an optimum time (about 40 hours in this case) for the process to reach the stage of maximum molecular weight, 120 000. Beyond this point the curve falls instead of remaining flat. Since under the condition of solid-state polymerization, cyclic compounds can hardly be formed, the decrease in molecular weight apparently is due to chain degradations which become predominant as the reaction time gets longer. The most probable degradation is the thermal type (ref. 8) which may be minimized by adopting a relatively lower reaction temperature. Oxidative and hydrolytic degradations (refs. 16 and 17) due to the small amount of oxygen and moisture content in the carrier gas, cannot be ruled out. These side reactions can be eliminated by passing the inert gas through a train of absorption columns containing copper filings heated to above 500° C (773° K) and molecular sieves or silica gel.

Effect of PET Particle Size

Figure 3 indicates that increased molecular weight is obtained by decreasing the PET particle size. Since decreasing the particle size not only increases the reaction sites of polymerization but also facilitates the removal of ethylene glycol, the result of the effect of particle size is expected.

Effect of Gas Flow Rate

Figure 4 shows the variation of molecular weight with the nitrogen gas flow rate. It can be seen that there is an optimum value of the flow rate above which only a modest increase in molecular weight is obtained. The optimum value was found in this study to be 500 ml/min.

Effect of Nature of Carrier Gas

The effectiveness of carrier gas on the molecular weight increase is given in table V. The increasing order of N_2, CO_2, and He is rather interesting. If the carrier gas simply functioned as the carrier for ethylene glycol vapor, there should have been no significant difference in the final molecular weights. In other words, their influence on the molecular weight increase should be nearly equal. If the desorption of the ethylene glycol molecules from PET were affected only by the diffusion of the gas through the solid phase, their effectiveness should be inversely proportional to their molecular sizes and would be in the increasing order of $CO_2 < N_2 <$ He. The discrepancy could arise from the intermolecular forces of attraction between ethylene glycol and the gases, which are expected to be He $\leq N_2 < CO_2$. Because of these two main factors, diffusion and intermolecular forces, the experimental findings, $N_2 < CO_2 <$ He, appears reasonable.

Extensions of Solid-State Polymerization Using A Gas Chromatograph Apparatus

Following the program discussed in this report, additional PET was polymerized on a larger scale by using the 4-inch O.D. (0.1 m) columns, up to 20 pounds per operation (about 10 kg) could be processed in this fashion. A number-average molecular weight of 68 000 was obtained from a 20 pound (about 10 kg) sample of Celanese PET polymerized at 250° C (523° K) for 48 hours and with a helium flow rate of 1 l/min.

It is my opinion that with selection of the proper polymerization variables, this larger scale process could be used to synthesize PET with a number-average molecular weight in the order of 120 000.

In addition to using the gas chromatograph apparatus for the solid state polymerization of PET, it is noted that the process should also be suitable for synthesizing ultra-high molecular weight products of other condensation type polymers such as other polyesters, polyamides, polymides, etc.

CONCLUSION

The results of the investigation of the solid-state polymerization of PET performed with a gas chromatograph show that the final product of number-average molecular weight in excess of 120 000 may be obtained from commercial grade materials by adopting the most favorable combination of the parameters studied. Ester interchange catalysts such as tetraisopropyl titanate, zinc acetate-antimony trioxide, and cobaltous acetate are all capable of increasing the molecular weight of PET. Smaller particle size and higher molecular weight of the starting material are essential for achieving the ultra-high molecular weight product. The preferable reaction temperature is between 200° C and 250° C (473° K and 523° K). The optimum reaction time depends upon other polymerization variables including the column size of the gas chromatograph. Molecular weights are also increased by increasing the gas flow rate up to optimum value which varies with other polymerization conditions. The effectiveness of the inert gas on the molecular weight increase is $N_2 < CO_2 < He$. It was found that the process for solid state polymerization could be readily scaled up to prepare relatively large quantities (up to at least 20 pounds per operation (about 10 kg) of ultra high molecular weight PET by using 4-inch O.D. (0.1 m) columns.

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TABLE I. - ESTER INTERCHANGE REACTIONS OF PET BEARING TERMINAL HYDROXYL GROUPS DURING MELT POLYMERIZATION

No.	Reacting groups	Molecular reaction	Position of ester linkage	Products	Change of $\overline{M}_n$
I	$-\text{OH},\ -\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-$	Inter	Terminal	Linear PET, ethylene glycol	Increase
II	$-\text{OH},\ -\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-$	Inter	In-chain	Linear PET	No
III	$-\text{OH},\ -\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-$	Intra	In-chain, on the same side of the repeating phenylene units as the OH group	Linear PET	No
IV	$-\text{OH},\ -\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-$	Intra	In-chain, on the opposite side of the repeating phenylene units as the OH group	Linear PET, cyclic PET	Decrease
V	$-\text{OH},\ -\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-$	Intra	Terminal	Cyclic PET, ethylene glycol	Not significant
VI	$-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O},\ -\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-$	Inter	Both terminal, both in-chain, terminal and in-chain	Linear PET	No
VII	$-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O},\ -\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-$	Intra	Both in-chain, on the same side of the repeating phenylene units	Linear PET cyclic PET	Decrease
VIII	$-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O},\ -\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-$	Intra	Both in-chain, on the opposite side of the repeating phenylene units	Linear PET	No
IX	$-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O},\ -\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-$	Intra	Terminal and in-chain, on the same side of the repeating phenylene units	Linear PET, cyclic PET	Decrease
X	$-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O},\ -\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}$	Intra	Terminal and in-chain, on the opposite side of the repeating phenylene units	Linear PET	No
XI	$-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O},\ -\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}$	Intra	Both terminal	Linear PET	No

TABLE II. - PET SAMPLES

Source	Form	Catalyst	m.p.°C (°K)	$\bar{M}_n$
Dupont	Flake	Unknown	254-256(527-529)	15 300
Celanese Plastic	Chip	Unknown	256-258(529-531)	16 500
NASA-Lewis	Lump	$Ti[O\ CH(CH_3)_2]_4$	256-258(529-531)	2 400
NASA-Lewis	Lump	$Zn(OAc)_2$-Sb_2O_3	254-256(527-529)	8 400
NASA-Lewis	Lump	$Co(OAc)_2$	248-250(521-523)	20 000

TABLE III. - CARRIER GAS

Carrier gas	Purity, Mole %	O_2 Content, ppm	H_2O content, ppm
N_2	99.9	7-8	2
CO_2	99.5	*146	*127
He	>99.99	<1	2

*Analyzed at NASA-Lewis Research Center.

TABLE IV. - EFFECT OF CATALYST ON SOLID STATE POLYMERIZATION[a] OF PET[b] USING GAS CHROMATOGRAPHIC APPARATUS[c]

PET Sample	Catalyst	Number average molecular weight	
		Initial	Final
III[d]	Unknown	15 300	80 000
IV[e]	Unknown	16 500	104 000
I[f]	Tetraisopropyltitanate	2 400	18 000
II[f]	Zinc acetate and antimony trioxide	8 400	65 000
V[f,g]	Cobaltous acetate	20 000	[h]120 000

[a] 250° C (523° K); 24 hours.

[b] Particle diameter 0.18 - 0.25 mm.

[c] Column size 16' × 3/4" O.D. (4.9 m × 1.9 cm O.D.); Nitrogen gas flow rate, 350 ml/min.

[d] Obtained from Du Pont Co.

[e] Obtained from Celanese Plastic Company.

[f] Prepared at NASA Lewis Research Center.

[g] 230° C (503° K); Nitrogen for 24 hours and helium for 12 hours.

[h] Not completely soluble in the solvent mixture of trifluoroacetic acid and methylene chloride (1:1 by volume).

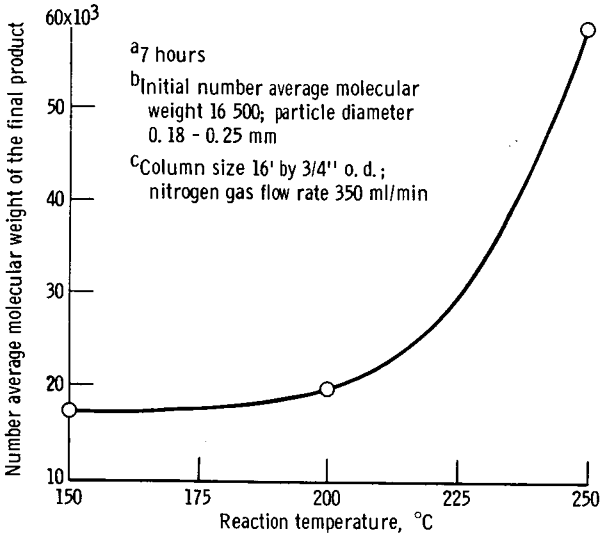
TABLE V. - EFFECT OF CARRIER GAS ON SOLID STATE POLYMERIZATION[a] OF PET[b] USING GAS CHROMATOGRAPHIC APPARATUS[c]

Carrier gas	Number average molecular weight
Nitrogen	58 000
Carbon Dioxide	81 000
Helium	90 000

[a] 250° C (523° K); 7 hours.

[b] Obtained from Celanese Plastic Company; Initial number average molecular weight 16 500; Particle diameter 0.18 - 0.25 mm.

[c] Column size 16' × 3/4" O.D. (4.9 m × 1.9 cm O.D.); Gas flow rate 350 ml/min.

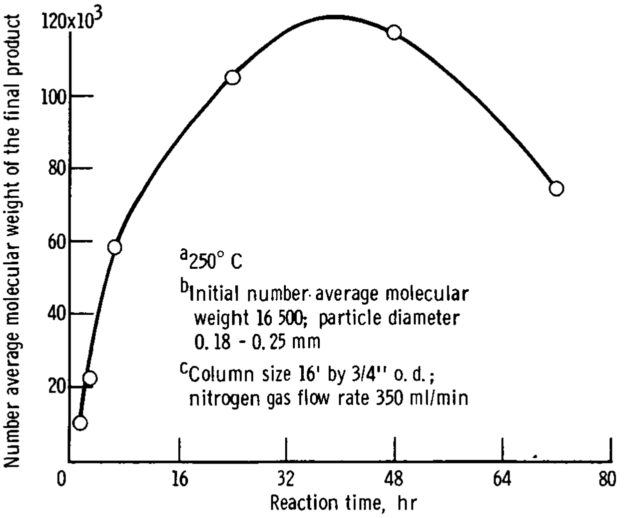


[a] 7 hours

[b] Initial number average molecular weight 16 500; particle diameter 0.18 - 0.25 mm

[c] Column size 16' by 3/4" o. d.; nitrogen gas flow rate 350 ml/min

Figure 1. - Effect of reaction temperature on solid state polymerization[a] of PET[b] using gas chromatograph apparatus[c].



[a] 250° C

[b] Initial number-average molecular weight 16 500; particle diameter 0.18 - 0.25 mm

[c] Column size 16' by 3/4" o. d.; nitrogen gas flow rate 350 ml/min

Figure 2. - Effect of reaction time on solid state polymerization[a] of PET[b] using gas chromatograph apparatus[c].

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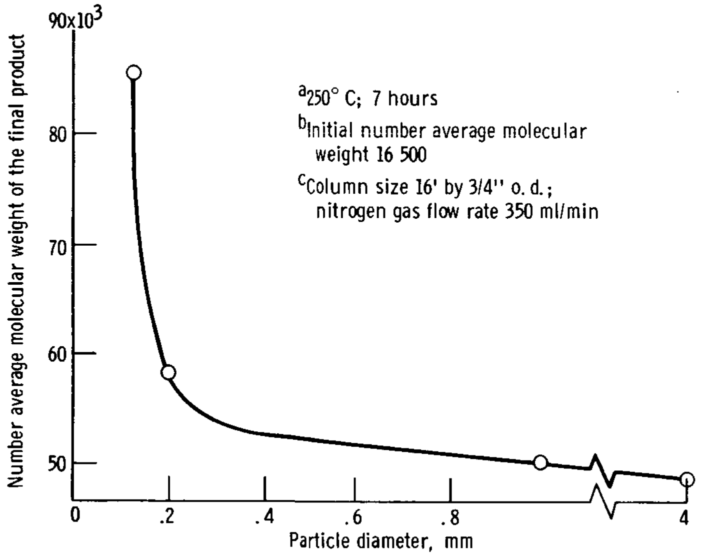

Figure 3. - Effect of particle size on solid state polymerization[a] of PET[b] using gas chromatograph apparatus[c].

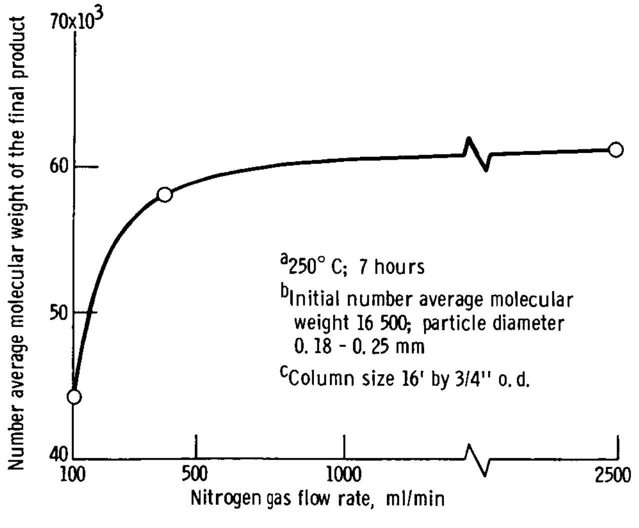

Figure 4. - Effect of nitrogen gas flow rate on solid state polymerization[a] of PET[b] using gas chromatograph apparatus[c].

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