European Polymer Journal Vol. 17, pp. 31 to 34
© Pergamon Press Ltd 1981. Printed in Great Britain

0014-3057/81/0101-0031$02.00/0

INTRODUCTION OF PHOSPHORUS INTO THE POLYETHYLENETEREPHTHALATE MOLECULE VIA DISODIUM 1,2-DICARBOMETHOXYETHYL-PHOSPHONATE—II

A STUDY ON THE INFLUENCE OF THE MODIFIER ON THE PROPERTIES OF POLYETHYLENETEREPHTHALATE

K. TROEV, AT. GROZEVA and G. BORISOV
Central Laboratory on Polymers, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

(*Received* 30 *May* 1980)

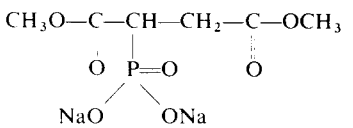
Abstract—The effect of disodium 1,2-dicarbomethoxyethylphosphonate on the polycondensation stage is studied. It is found that the polycondensation stage proceeds normally at 1–9% (by weight) of the combined dimethylterephthalate and ethylene glycol weights. The phosphorus-containing polyethylene-terephthalate obtained showed improved resistance to combustion and better thermal stability.

The results from a study on the influence of the modifier on the properties of the pre-condensate were reported in an earlier paper [1]. The present work refers to the effect of the modifier and its concentration on the polycondensation stage of polyethylene terephthalate formation. Diethylene glycol content, carboxylic groups content, viscosity and temperature of melting of the resin were studied as a function of the concentration of the modifier.

EXPERIMENTAL

Starting compounds

Pre-condensates prepared in the presence of disodium 1,2-dicarbomethoxyethylphosphonate



containing 0.40, 0.74, 1.20 and 1.50% of phosphorus [1].

The polycondensation was conducted in apparatus described earlier [2]. The process took place in a test tube containing 5 g of pre-condensate, the temperature being brought to 200 over 1 hr. Pressure was then reduced gradually to 2 Torr and the temperature increased to 275–280 ; the reaction was maintained at that temperature for 5 hr.

Characteristics of the resin

Viscosity—determined in a mixture of phenol/carbon tetrachloride (1:1 by weight) as solvent at a concentration of 0.5% at 20 .

Diethyleneglycol—determined gas-chromatographically [3].

Carboxylic groups—a known amount of the resin dissolved in benzyl alcohol was titrated with 0.02 M NaOH in glycol.

Thermogravimetric analysis—the curves were recorded on a Paulik–Erdey derivatograph in air at a rate of heating of 5 /min.

Determination of the resistance to combustion—1 g of the powdered sample was placed in a wire-net receptacle (50 mesh) with a conical angle of 100 . A microburner was kept for 20 sec. at the bottom of the receptacle and withdrawn as soon as the sample ignited. A record was made of the time required for ignition, duration of combustion, time necessary for complete burning out and weight of the residue.

Fractional precipitation

Polymer of the following characteristics was subjected to fractionation: 0.80% of phosphorus; temperature of melting 258 ; relative viscosity 1.164; carboxylic groups 39.14×10^{-6} g-equiv./g; diethyleneglycol content 0.55%.

Fractionation conditions

Solvent—phenol/carbon tetrachloride (1:1 by weight); precipitant—*n*-heptane [5]; concentration of the solution—1%; temperature of fractionation 25 ± 0.3 . The fractionation was conducted in apparatus described by Shattenstein *et al.* [4].

RESULTS AND DISCUSSION

The polycondensation stage in the synthesis of polyethyleneterephthalate is known to last between 4 and 5 hr [6, 7] at 275–280 . For this reason the influence of the modifier was studied under the same conditions.

The polycondensation of polyethyleneterephthalate modified with disodium 1,2-dicarbomethoxyethyl-phosphonate pre-condensates leads to a resin of the following structure:

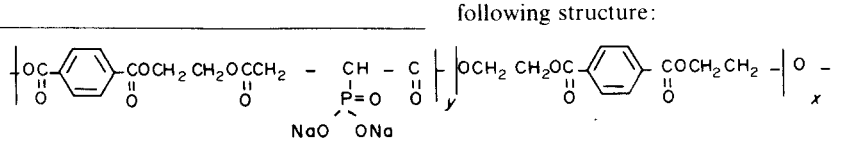


Table 1. Characteristics of polyethyleneterephthalate modified with disodium 1,2-dicarbomethoxyethylphosphonate

Temperature of polycondensation		280°			
Duration of the polycondensation process, hr		5			
Phosphorus content	In the pre-condensate	0.40	0.74	1.20	1.50
found, %	In the resin	0.45	0.80	1.35	1.62
Diethyleneglycol content, %		0.48	0.55	0.52	0.70
Temperature of melting, C		259	258	258	255
Relative viscosity		1.342	1.331	1.315	1.283

The physical and chemical properties of polyethyleneterephthalate are strongly influenced by side-reactions during its synthesis. The main among these was found to be the formation of diethyleneglycol units of which disturb the regular structure of the macromolecular chain thus resulting in decreases in the temperature of melting [8], thermal stability [9] and stability to light [10] of the resin.

The results from the synthesis (Table 1) indicate that the polyethyleneterephthalate samples obtained with various phosphorus content have a low diethyleneglycol content.

According to Buxbaum [11] diethyleneglycol is formed as a result of the thermal destruction of hydroxyl-group containing intermediates. It is known that blocking the thermal hydroxyl groups, which are the most sensitive to thermal destruction, results in a thermostable resin [12]. Various phosphorus acid esters are being used as thermostabilizers of polyethyleneterephthalate [13–15]. A comparison of the diethyleneglycol content in unmodified polyethyleneterephthalate (ranging between 1.5 and 2%) and that in the modified material shows that the modifier suppresses the diethyleneglycol-forming reactions. An indirect indication that these processes are inhibited is the temperature of melting of the samples. For unmodified polyethyleneterephthalate, this temperature is in the range 258–260°. As can be seen from Table 1, the temperatures of melting of the modified samples range between 258 and 259° and is 255° only for the sample containing 1.62% of phosphorus. This indicates that the polyethyleneterephthalate modified macromolecules do not include diethyleneglycol units i.e. the modifier acts as a thermostabilizer. The low content of carboxyl groups in the resin supports the assumption that disodium 1,2-dicarbomethoxyethylphosphonate acts as a thermostabilizer (Fig. 1). The content of carboxyl groups in the resin is between 117×10^{-6} and 107×10^{-6} g-equiv./g in the absence of a thermostabilizing additive [16]. It is known that thermal destruction in polyethyleneterephthalate leads to a decrease in the molecular mass and an increase in carboxyl group content, i.e. the carboxyl group content can be used as a measure of thermodestruction undergone by the polymer. In the synthesis of polyethyleneterephthalate, triphenyl phosphite is often used as a thermostabilizer [13, 14]. Terehova *et al.* [16] have studied the thermostabilizing influence of triphenyl phosphite as a function of the catalyst employed. They found that the carboxyl group content went down to 62×10^{-6} g-equiv./g. Triphenyl phosphite was used as thermostabilizer in the synthesis of polyethyleneterephthalate in the presence of disodium 1,2-dicarbomethoxyethylphosphonate; the carboxyl group content was in the range 35×10^{-6} to 44×10^{-6} g-equiv./g indicating the thermostabilizing effect of the modifier also.

Some polymer characteristics such as viscosity and temperature of melting are known to be closely related with the molecular mass which in turn depends on the degree of completeness of the main reaction and the interference of side processes [18]. These factors influence to a considerable degree the

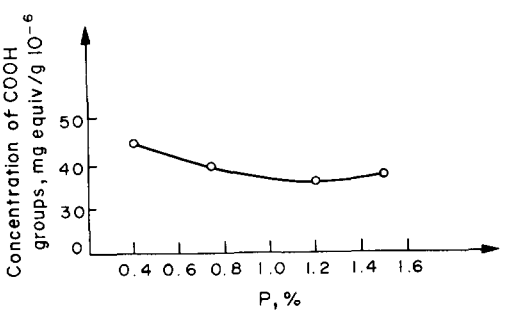


Fig. 1. Carboxyl group concentration vs phosphorus content.

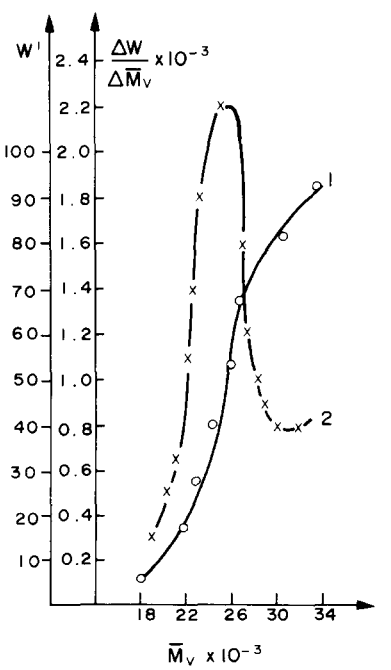


Fig. 2. Molecular mass distribution curves of a modified polyethyleneterephthalate sample containing 0.80% of phosphorus; integral curve (curve 1); differential curve (curve 2).

Table 2. Results from combustion of polyethyleneterephthalate samples modified with disodium 1,2-dicarbomethoxyethylphosphonate, using the basket procedure

Phosphorus content, %	0	0.45	0.80	1.35	1.62
Weight of sample, g	1.0182	1.0342	1.0290	1.0328	1.0423
Time for ignition, sec	6	8	12	15	15
Duration of combustion, sec	181	Stops	Stops	Stops	Stops
Time for burning out, sec	181	202	229	227	240
Weight of residue, %	8	25	50	52	50

polydispersity of the polymer and so the properties of fibres [19]. It can be assumed that the presence of the modifier in the reaction system affects the molecular mass and the dispersity of the resin. The molecular mass distribution provides an answer to these questions. An earlier paper referred to the determination of the characteristic viscosity, the molecular mass and the building of the integral distribution curve [2]. The molecular mass distribution (Fig. 2, curve 2) shows that the modified polyethyleneterephthalate is quite uniform, supporting the assumption that the disodium salt of 1,2-dicarbomethoxyethylphosphonic acid does not hinder the normal course of the reaction leading to polyethyleneterephthalate.

Differential thermal analysis was used for investigation of the thermal behaviour of the modified polyethyleneterephthalate. The derivatograms (Fig. 3) indicate that the modified samples (Fig. 3, curve 1, P,% = 0.45; curve 2, P,% = 1.35; curve 3, P,% = 1.62 and curve 4 pure polyethyleneterephthalate) begin to undergo destruction at about 300–320° and at 425° lose 40% of their weight, and at 700° lose 72–74%; above this temperature no changes occur. A comparison of the weight loss curves of the modified samples with that for unmodified polyethyleneterephthalate (curve 4) shows that a difference exists above 425°. The unmodified material loses 85% up to 500° while the modified samples lose 72–74% of their weight up to 700 . This difference can be explained on the assumption that the destructions of the modified and unmodified samples proceed differently. Obviously, the presence of the modifier suppresses the destruction processes accompanied by evolution of volatile products and stimulates the formation of a solid residue.

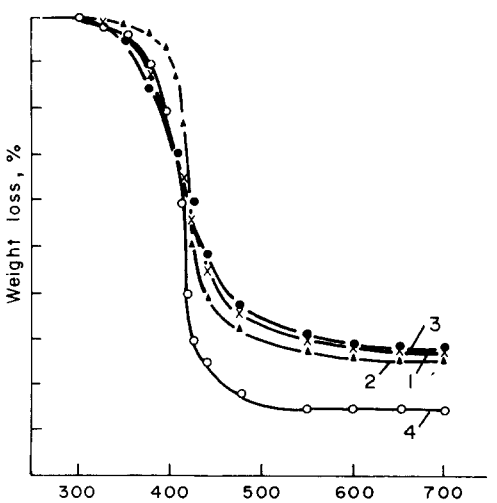


Fig. 3. Thermogravimetric curves of modified polyethyleneterephthalate samples: curve 1—P% = 0.45; curve 2—P% = 1.35; curve 3—P% = 1.62; curve 4—pure polyethyleneterephthalate.

It is established that phosphorus-containing antipyrenes affect the combustion process by preventing heating to high temperatures, cause dehydrations leasing to carbonation and thus accelerating coking [20]. In this way a protective layer is formed on the surface of the material; this layer of polyphosphoric acid hinders the supply of air to the burning region.

The basket procedure was employed in the evaluation of the efficiency of the modifier as an antipyrene. The efficiency in this connection is indicated by the following parameters—time required for ignition, duration of combustion, time required for burning out and weight of residue after burning. The results show (Table 2) that the samples containing phosphorus ignite with greater difficulty, the time required for ignition lengthening with increase in phosphorus content. The modified samples stop burning on withdrawal from the flame; the duration of combustion increases from 181 sec for the unmodified polyethyleneterephthalate to 240 sec for the material containing 1.62% of phosphorus. The assumption that coking is accelerated by phosphorus-containing antipyrenes is corroborated by the weight of the residue after burning. The results indicate that the weight of the residue increases 6-fold at a phosphorus content of 0.80% with respect to the unmodified sample.

It can be concluded that the introduction of phosphorus into the polyethyleneterephthalate molecule via disodium 1,2-dicarbomethoxyethylphosphonate does not prevent the normal course of the transesterification and polycondensation stages. The phosphorus-containing polyethyleneterephthalate thus synthesized has good characteristics and exhibits improved resistance to combustion and good thermal stability.

REFERENCES

1. K. Troev, At. Grozeva and G. Borisov, *Eur. Polym. J.* **17**, 27 (1981).
2. K. Troev, At. Grozeva and G. Borisov, *Eur. Polym. J.* **15**, 1143 (1979).
3. G. Hartwing and W. Furgen, *Faserforsch. TextTech.* **25**, 86 (1974).
4. A. I. Shattenstein, Y. P. Vyrskii, N. A. Pravikova, P. P. Alihanov, K. I. Zhdanova and A. L. Iziumnikova, *Opredel. molek. polim. Chim.* **M-L**, 145 (1964).
5. K. Gehrke and G. Reinisch, *Faserforsch. TextTech.* **17**, 201 (1966).
6. J. Mleziva, V. Hanzlik, J. Kinzl and Z. Miklas, *Poliest. Tekh.* 117 (1969).

7. N. K. Moshtenskaia, L. I. Zhupiev and V. S. Olifer, *Chim. volokna* **3,** 11 (1961).
8. R. Ianssen, H. Ruysshacrt and R. Vroom, *Makromolek. Chem.* **77,** 153 (1964).
9. H. A. Pohl, *J. Am. chem. Soc.* **73,** 5660 (1951).
10. D. Coleman, *J. Polym. Sci.* **14,** 15 (1954).
11. L. H. Buxman, *Angew. Chem.* **6,** 225 (1968).
12. G. M. Terehova and B. V. Petuhov, *Chim. volonkna* **4,** 8 (1960).
13. Br. Pat., 791283 (1958); *R. Z. Chim.* 24628 (1960).
14. Br. Pat., 770531 (1957); *R. Z. Chim.* 66415 P (1959).
15. Br. Pat., 802921 (1958); *R. Z. Chim.* 37023 P (1960).
16. G. M. Terehova, N. V. Mihailov and L. G. Tokareva, *Chim. volokna* **4,** 28, 33 (1964).
17. E. L. Gudins, *Chim. techn. polim.* **3,** 104 (1961).
18. V. I. Kodolov and S. S. Spaskii, *Usp. Khim.* **33,** 12 (1964).
19. Z. H. Rogovin, *Osnov. chim. techn. proizv. chim. volokna* (1957).
20. C. E. Hoke, *S.P.E. Jl,* 29, 5, 36 (1973).