

Estimation and Characterization of Polyester Oligomers

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ABSTRACT: Oligomers were obtained from polyester samples by solvent extraction and dissolution methods. Dioxane, chloroform, and chlorobenzene were used for the extraction method, whereas dimethyl formamide and phenol : tetrachloroethane (1 : 1 mixture) were used for the dissolution method. The oligomers were separated and analyzed by a thin-layer chromatographic technique. It was observed that extraction with chloroform and dissolution with phenol : tetrachloroethane gave higher oligomer contents. Also, the values were higher for as-spun fibers. Thin-layer chromatographic analysis showed that in all the cases lower oligomers were obtained with a maximum of the cyclic trimer, whereas the efficiencies of solvents varied for removal of higher oligomers. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1987–1991, 1999

INTRODUCTION

In common with a wide range of polymers prepared by condensation polymerization or ring-to-chain equilibration reactions, polyethylene terephthalate (PET) also contains cyclic molecules along with the linear ones.¹ Linear oligomers are formed when ethylene glycol is condensed with terephthalic acid methyl ester. Because of their polar end groups, linear oligomers are partially water soluble, and hence, they do not produce much of a problem during the wet processing of polyester fibers.² The cyclic oligomers, consisting mainly of cyclic trimer, on the other hand, create problems during PET fiber processing.

The cyclic trimer affects the spinnability of fibers. In knitting, trimer causes high and nonuniform yarn tensions and needle wear, as well as general maintenance problems. Most commonly, it shows up as a white dust or a gummy deposit on the guides and other contact surfaces of knitting and coning machines. During dyeing, oligomer

deposition occurs on the yarn or on the nonaccessible parts of the dyeing machines, for example, pipes, valves, pumps, heat exchanger, etc. It decreases the pump efficiency due to higher resistance to the flow. Uneven dyeing often results from congested pipes and valves where the heavy deposits restrict the proper liquor flow. Oligomer precipitates bring down the dye molecules with them, thereby causing shade variations in the high-temperature dyeing.

All commercial samples of PET fibers contain approximately 1–3% cyclic oligomers. They are characterized by a high crystallization rate and extremely difficult water solubility, even at a high temperature beyond 100°C. The oligomeric particles inside the fiber migrate to its surface during the heat treatment at 150–230°C and grow there as crystals. Maximum oligomer migration occurs at 170–190°C.³

Addition of auxiliaries in the dyeing liquor does not principally prevent the emergence of oligomers. By bonding the oligomers to the fiber surface, they do prevent dust, but may interfere with dye adsorption characteristics as well as fastness of the dyeings. Carriers promote oligomer emergence, as they do dye adsorption. Dispersing agents for dyes are found ineffective with

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the cyclic trimer. Hot draining of the exhausted dyebath is ineffective because the oligomer portion dissolved in the dye bath is negligibly small. Only the loosely deposited portion can be removed by aftertreatment. Even a solvent pretreatment does not prevent its emergence.⁴ Reducing agents have no effect on surface content. An intensive alkali treatment may peel the fiber surface along with the oligomers.

The separation and isolation of a few members of the most of the PET oligomer series have been reported since Ross and coworkers⁵ first isolated the cyclic trimer from PET. Zahn and Krzikalla⁶ were the first to separate a linear polyethylene terephthalate oligomer series by paper chromatography. The other techniques used for isolation and characterization of number of oligomers from polyethylene terephthalate were column chromatography,⁷ thin-layer chromatography,⁸ silica gel column chromatography,⁹ and gas chromatography.¹⁰ Gueris and Meybeck¹¹ have reported on preparative gel-permeation chromatography of linear oligomers. Dugal et al.¹² analyzed the cyclic trimer by HPLC in 1973. Luttringer et al.¹³ reported a spectrophotometric method for determination of total oligomers. The kinetics of formation of oligomers was reported by Ha and Choun.¹⁴ Bryant and Semlyen¹⁵ prepared cyclic oligomers from solution ring chain reaction and analyzed them using a ¹H-NMR spectrophotometer, fast atomic bombardment mass spectrometry (f.a.b.m.s.), and liquid chromatography tandem mass spectrometry (l.c.m.s.). They reported two series of cyclic compounds.

The present article reports the results on oligomer content of as-spun and drawn varieties of PET by extraction and dissolution methods. The qualitative estimation was carried out using a thin-layer chromatography technique.

MATERIALS AND EXPERIMENTAL PROCEDURES

Materials

The polyethylene terephthalate samples obtained from Reliance Co. Ltd., India, had following specifications: Staple fibers (1.44 d × 44 mm) with a draw ratio of about 3. As-spun fibers (Spun tow).

Chemicals

All the chemicals used were of Analytical Reagent grade. Auxipon NP (Auxichem Ltd., Mumbai) was used as a nonionic detergent.

Scouring of Polyester Fibers

Polyester fibers were scoured using 2-g/L nonionic detergent solution at boil for 1 h, washed thoroughly, and air dried to remove any surface finish present on the fibers.

Oligomer Removal from Samples

Oligomers were removed from polyester samples by two methods—extraction of oligomers and dissolution of oligomers.

Extraction of Oligomers

For extraction of oligomers, a standard Soxhlet apparatus was used. Accurately weighed (about 5 g) dried polyester samples were extracted for 12 h using 1,4-dioxane and chloroform, and for 24 h using chlorobenzene. Fibers were enclosed in a filter paper bag and inserted in the Soxhlet apparatus for the extraction. A number of samples were extracted from each variety. After completion of extraction, bulk of the solvent was recovered by distillation and the concentrated solution was subjected to evaporation in air to obtain a solid residue. The residue was then dried in an oven at 60°C for 4 h. The oligomer extracted was determined gravimetrically.

Dissolution Method

For the dissolution method a dimethyl formamide and phenol : tetrachloroethane mixture [1 : 1 (w/w)] was used as the solvent to remove the oligomers. Freshly distilled 150 mL of dimethyl formamide and a 2 g polyester sample were placed in a 500-mL round-bottom flask. The flask was fitted with a mechanical stirrer and a water condenser, and heated carefully with constant stirring until a clear solution was obtained. It was then cooled to room temperature so that the polymer was precipitated. The precipitate was filtered and given washings with 100 mL chloroform. The filtrate with washings was concentrated by removing the bulk of the solvent by distillation. The concentrated solution was then evaporated to dryness to obtain a solid residue. The residue was dried in an oven at 60°C for 4 h to get the oligomers.

In another method, 2 g polyester sample was dissolved in 30 mL of 1 : 1 (w/w) phenol : tetrachloroethane mixture. The solution was cooled and then added to 50 mL of freshly distilled dioxane under constant stirring when the poly-

Table I Oligomer Content of Polyester Samples by the Extraction Method

Sample	Extracting Solvent	Oligomer, %
Staple fibers	1,4-Dioxane	1.66
	Chloroform	2.35
	Chlorobenzene	2.19
As-spun fibers	1,4-Dioxane	2.58
	Chloroform	3.27
	Chlorobenzene	2.49

mer precipitated out. The solution was filtered off and evaporated to a dry residue of oligomers.

Qualitative Analysis of Oligomers

A thin-layer chromatographic technique was used to separate and identify the oligomer components. The dried extracts were dissolved in 1 : 1 (w/w) phenol : tetrachloroethane mixture to make 5% (w/v) solution. The solution was spotted onto the TLC plates made of silica gel. The spotted plates were dried at 100°C until complete removal of phenol odor, cooled, and then developed to 15 cm using the eluents chloroform : ethyl ether (90 : 10) for cyclic oligomers.¹⁴ The chromatograms were observed by exposing the plates into a chamber saturated with iodine vapors. R_f values were calculated by the formula,

$$R_f = \frac{\text{Distance travelled by solute}}{\text{Distance travelled by solvent front}}$$

During preparation of polyethylene terephthalate by condensation polymerization, low molecular weight constituents of same chemical composition, the oligomers are also formed. These essentially are different among themselves and from the main polymer as far as molecular weight, chain length, and other physical properties are concerned. Although they are confined to as low as 2–3%, they are most prob-

lematic, especially during dyeing. A number of extraction and dissolution solvents as well as the characterization techniques have been reported for the removal of oligomers.

The results in Table I show that, for staple fibers as well as for as-spun fibers, chloroform gave the maximum oligomer extraction, the values being 2.35 and 3.27% (owf), respectively. With all the three solvents used for extraction, as-spun fibers gave a higher level of oligomer content.

Table II gives the % oligomer content values for the two types of polyester samples using the dissolution method. In this method also, the as-spun fibers gave higher values of oligomer content than for the staple fibers. The phenol : tetrachloroethane solvent mixture gave somewhat higher values of oligomer content than with dimethyl formamide. Thus, dimethyl formamide gave 2.52% oligomer content while phenol : tetrachloroethane gave a value of 2.75% in the case of staple fibers. For as-spun fibers, the values were 2.90 and 3.21% (owf), respectively.

The process of extraction may involve either diffusion of oligomers from interior to the polymer surface, where they are dissolved away by the solvent, or penetration of the solvent molecules well within the polymer structure to dissolve the oligomers followed by diffusion of the solution to the bulk solvent phase. Therefore, the analytical results are expected to show variation from solvents, extraction time, and accessibility of polymer.

Cooper and Semlyen¹ pointed out that the extraction method removes almost all the cyclic trimer, but very little of higher oligomers are obtained by this method, which is in relation to the ease of diffusion of the different oligomeric components from the interior to the surface of the fiber. Solvent extraction method is more conventional. However, it has several disadvantages, such as incomplete removal of the larger cyclic oligomers; although all cyclic dimer and trimer are practically completely removed, the

Table II Oligomer Content of Polyester Samples by the Dissolution Method

Sample	Dissolving Solvent	Oligomer, %
Staple fibers	A: Dimethyl formamide	2.52
	B: Phenol : tetrachloroethane (1 : 1)	2.75
As-spun fibers	A: Dimethyl formamide	2.90
	B: Phenol : tetrachloroethane (1 : 1)	3.21

Table III R_f Values of Oligomers

Method	R_f Values					
Chloroform extraction	0.79	0.64	0.56	—	0.40	0.29
Chlorobenzene extraction	0.79	0.65	0.58	0.49	—	0.30
Dioxane extraction	0.76	0.66	0.56	0.47	—	0.28
Dissolution A	0.74	0.64	0.57	0.47	—	—
Dissolution B	0.73	0.67	—	0.48	0.43	0.32

tendency of fresh linear oligomer chains to polymerize and that of aged polymer to depolymerize during extraction, and the tendency of low boiling solvents to decompose on prolonged treatment of fibers.

In the present studies, chloroform gave higher oligomer content by the extraction method, which may be attributed to its smaller size compared to chlorobenzene or dioxane containing aromatic ring structures. The smaller molecular dimensions enable better penetration of chloroform within the fiber structure leading to maximum possible extraction of the oligomers. The somewhat higher values of oligomer content for the as-spun fibers are due to the fact that the structure of these fibers is much more open compared to that of the staple fibers, in which the development of crystalline portions is caused by virtue of the drawing process. This is evident from the birefringence values (0.009 for the as-spun fibers against 0.180 for the staple fibers). These compact crystalline portions in the fiber structure do not allow easy penetration of the solvent molecules to extract the oligomeric components to the maximum possible extent.

In dissolution method, on the other hand, all the chemical units, whether linear polymeric, linear oligomeric, cyclic oligomeric, or unutilized primary reactant species, are dissolved fully in the solvent. This is followed by selective precipitation of the higher molecular weight species, leaving behind the oligomeric components in solution. This method, therefore, is likely to lead to different amounts and compositions of the oligomeric components, depending upon the precipitation mechanism.

It is, thus, obvious that the values for oligomer content of same sample will be higher when obtained by the dissolution method than by the extraction method, or at least comparable with those obtained with the best extracting solvent, as is evident from the data given in Tables I and II.

Thin-layer chromatography (TLC) is the simplest technique used for oligomer characterization. The oligomer mixtures obtained in the present work were subjected to TLC analysis in the chloroform : ether (9 : 1) as the eluent used on silica gel-coated glass plates. The plates were developed in iodine vapors.

Table III gives the R_f values for different oligomers in mixtures derived by the two different techniques. Comparison of these values with the reported R_f values in the literature^{9,14} indicates that both cyclic dimer and cyclic trimer were obtained in all the cases, as shown by their respective R_f values of 0.77 and 0.65. Cyclic trimer showed its prominent presence, with higher proportions compared to the other types of oligomers, in all the mixtures. Regarding higher oligomers like cyclic tetramer (R_f 0.56), cyclic pentamer with DEG (R_f 0.48), cyclic pentamer alone (R_f 0.40) and still larger components, the method and solvent employed behaved differently.

It may be concluded, therefore, that the amount and composition of the oligomers obtained from a polymer sample differs considerably, depending on various factors such as the fiber structure, nature, and molecular weight of the solvent as well as the method adopted.

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