## The separation of some poly(ethylene terephthalate) oligomers

During the trans-esterification of dimethyl terephthalate by ethylene glycol and the subsequent polymerization of the product to form poly(ethylene terephthalate) a variety of oligomeric materials are formed. In order to study the reaction kinetics of the interchange reaction, it is desirable to be able to detect the products formed and to measure the amounts of each formed. Also, for continuous production, it is desirable to have a method of detecting any unreacted methyl groups prior to polymerization.

The oligomers formed can be listed as three series of compounds:

(1) Those terminated with methyl groups at both ends;
(2) those terminated with hydroxyl groups at both ends, and
(3) those terminated with one methyl and one hydroxyl group.

These series can be seen in the following scheme:

Dimethyl terminated series

Monomethyl monohydroxyl terminated series

Dihydroxyl terminated series
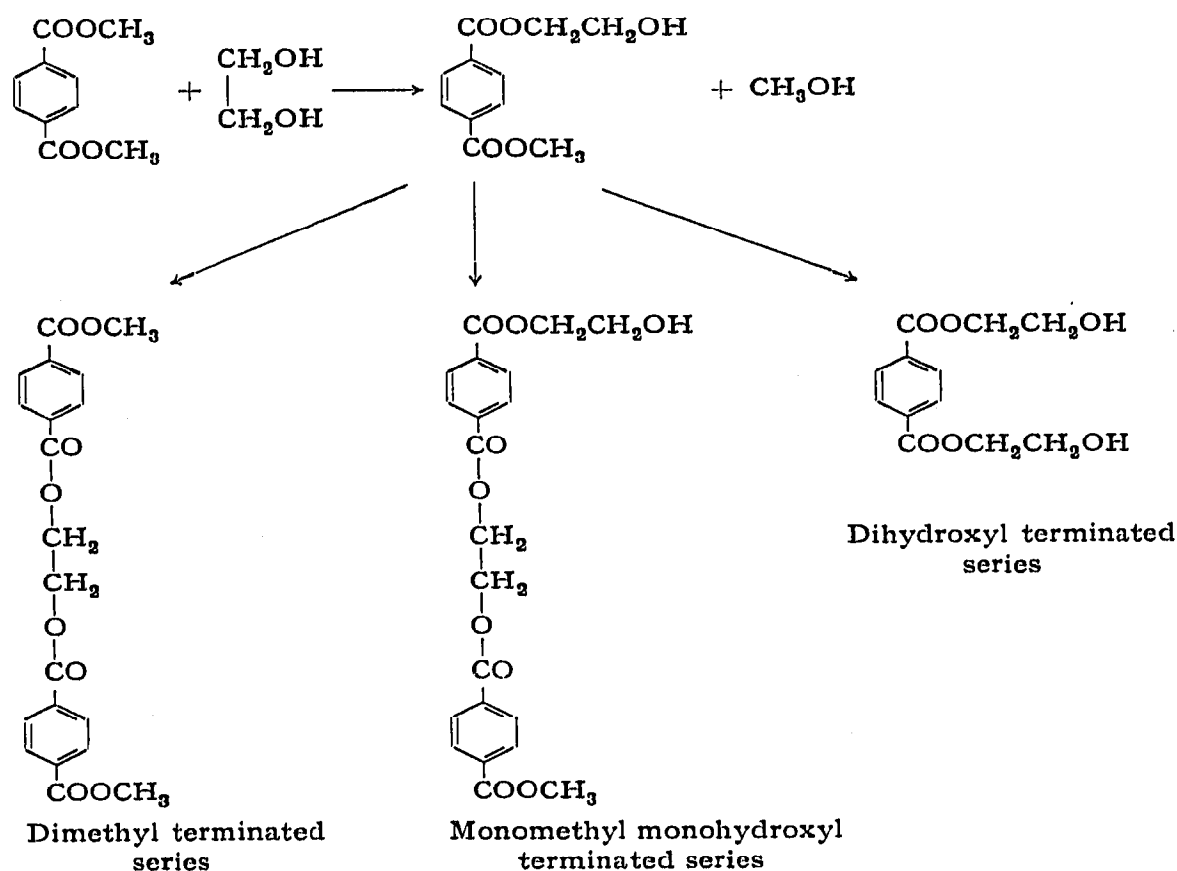
The dihydroxyl terminated series is the most important since these compounds can be polymerized by the removal of ethylene glycol whereas methyl terminated compounds will not polymerize without prior esterification. .

Experimental

For calibration and identification purposes, our polymer research group synthesized monohydroxyethylenemonomethyl terephthalate, bishydroxyethylene terephthalate, dimethyl dimer and dimethyl trimer.

Thin-layer chromatographic layers were made up 200 μ thick of Silica Gel G containing 13 % calcium sulfate. The layers were activated at 120° for 30 min, cooled in a desiccator, spotted and developed for 15 cm in a closed, saturated chamber using one of three developers: (a) an 85:15 benzene–ethyl acetate mixture[1] which gives good separation of the dimethyl species; (b) a 55:45 benzene–ethyl acetate mixture which gives reasonable separation of all species with some overlap of the dimethyl species, or (c) ethyl acetate which does not separate the dimethyl species but which will separate the others.

Standards and unknowns were dissolved (about 1 % concentration) in dioxane and 5 μl spotted on the TLC layer. After development and subsequent evaporation of the solvent, the plates were sprayed with a mixture of 0.2 g methyl red, 0.2 g bromo-thymol blue, 100 ml 35 % formaldehyde and 400 ml 95 % ethanol[2]. About 10 min after spraying, the background had faded sufficiently for the spots to be identified, usually a pale rose color.

Table I shows the R_F values of the species in the different solvents.

TABLE I

| Compound | Solvent mixture | | |
	Benzene–ethyl acetate (85:15)	Benzene–ethyl acetate (55:45)	Ethyl acetate
Dimethyl terephthalate	0.70	0.88	1.0
Dimethyl dimer	0.62	0.87	1.0
Dimethyl trimer	0.50	0.85	1.0
Monohydroxyethylene monomethyl terephthalate	0.12	0.44	0.72
Bishydroxyethylene terephthalate	0.00	0.12	0.36
Secondary front	0.72	0.88	—

If a quantitative estimation of the compounds present is required, this can be obtained by lifting the spots and surrounding support from the plate, dissolving the organic matter in methanol, and, after filtration, measuring the absorption of the solution at 240 mμ in the U.V. Previous calibration of absorption vs. concentration for each specie at 240 mμ then provides a measure of the amount of material present. Studies indicate that absorption is proportional to concentration up to at least 1.2 mg/100 ml.

Conclusion

The method described is fast and can be used either quantitatively or qualitatively. With practice the method is reproducible to ± 5 %.

Fibers Division Technical Center,   Victor A. Dorman-Smith
Allied Chemical Corporation, P.O. Box 31,
Petersburg, Va. 23804 (U.S.A.)

1 J. W. C. Peereboom, *J. Chromatog.*, 4 (1960) 323.
2 E. Stahl, *Thin Layer Chromatography*, Academic Press, New York, 1965, p. 495.