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Short communication

Study of an appropriate procedure for the chromatographic analysis of poly(ethylene terephthalate), after melt processing with triphenyl phosphite

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Abstract

The performance of a chromatographic technique for polyester analysis at a moderate temperature was investigated. Sample dissolution at room temperature in phenol–1,1,2,2-tetrachloroethane (TCE) and analysis at 70°C in *m*-cresol, despite the efficiency for pure polyesters, proved to be inadequate for molecular mass determination of polyester/phosphite systems since it causes a rapid degradation of bonds created by the phosphite in the molten state. Furthermore, the presence of three different solvents makes the technique highly complex. Large modifications of the chromatographic conditions result, partly irreversibly, from the injection of samples dissolved in phenol–TCE. A new procedure, working close to room temperature with phenol–TCE eluent, was therefore developed, thus avoiding any polymer degradation and allowing for the study of polyester/phosphite samples by size exclusion chromatography.

Keywords: Poly(ethylene terephthalate); Triphenyl phosphite; Polyesters; Poly(butylene terephthalate)

1. Introduction

Poly(ethylene terephthalate) (PET) is an industrial polymer produced worldwide on a large scale. Its intrinsic properties have allowed the development of numerous applications in fibres, films, bottles and reinforced plastics. In particular, its solvent resistance is appreciated, but conversely, this leads to difficulties in accurate molecular characterisation using size exclusion chromatography (SEC). Weis-

skopf [1] reviewed the different approaches already followed to find appropriate conditions for the chromatographic analyses of such polyesters.

The use of *m*-cresol as the high temperature SEC solvent was observed to induce polyester degradation during the dissolution and analysis steps [2,3]. As a matter of fact, it must be considered that ester bond stability in this solvent is only adequate for moderate conditions. Our preliminary experiments showed that excessive treatments, such as 20 min at 180°C or 24 h at 115°C, dramatically reduced the polyester molecular masses [4]. Degradation by acid-catalysed hydrolysis occurs and interchange reactions, between the hydroxyl end-groups and ester linkages along the chain, lead to a reequilibration of the molecular mass

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distribution [5,6]. However, degradation was not observed at temperatures below 70°C [4].

Mixtures of solvents such as *o*-chlorophenol–chloroform [7,8] or 1,1,2,2-tetrachloroethane (TCE)–nitrobenzene [5,6,9] have also been proposed in the literature. These allow analysis to be carried out at room temperature but they require heating for the dissolution step. The choice of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) as the SEC solvent [1] has the advantage that there is an absence of degradation due to the solubility and analysis being performed at room temperature. Furthermore, because of the low refractive index of HFIP, UV detection can be carried out and this gives rise to the greater sensitivity of the method. The insolubility of polystyrene standards (PS) in pure HFIP leads, however, to experimentally different mixtures of solvents, such as chloroform–HFIP being used. Nevertheless, despite many improvements, this method still has some disadvantages that are linked to the low boiling point of chloroform but, mainly, to the high cost of HFIP.

The aim of the present work is to explore the performance of a new SEC technique at a moderate temperature. The need for such “soft” analysis conditions became apparent during research work that was carried out on the molecular mass increase of PET and/or PET–poly(butylene terephthalate) (PBT) blends, by the addition of triphenyl phosphite (TPP). This research, on selective reactions involving TPP and polyester hydroxyl and carboxyl chain ends, is described in detail elsewhere [10–12].

To avoid any exposure of the polyesters to high temperatures, dissolution was performed at room temperature in a phenol–TCE (60:40, v/v) mixture. SEC measurements were conducted at 70°C with *m*-cresol as the eluent solvent. The occurrence of polyester degradation during the analyses was investigated.

2. Experimental conditions and materials

The PET used was B73L supplied by ICI. The PBT used was Celanese 2000 supplied by Hoechst/Celanese. PET–PBT (75:25, w/w) blends were prepared in a Brabender plastograph at 275–280°C. Different quantities of TPP (0, 2 or 5%) were added in polyester blends [11].

Phenol (Janssen, 99%) was used as received. 1,1,2,2-Tetrachloroethane (TCE) (Aldrich, 99%) and *m*-cresol (Merck, P.S.) were distilled before use.

Size exclusion chromatography was performed by using a Waters 150C high temperature chromatograph with a refractive index detector. Two Shodex columns from Showa Denko (Ref: AT-80M/S) and one Ultrastaygel column (500 Å from Waters) were used in series. *m*-Cresol was used as the eluent solvent, at 70°C, and the flow-rate was 0.4 ml/min.

As described elsewhere, samples reacted with phosphite were purified from the by-products of the reaction by an extraction with refluxing acetone [11]. After drying, 8–10 mg of polyesters were dissolved, at room temperature, in 2 ml of a phenol–TCE mixture (60:40, w/w). Approximately 120 μl were injected. The results were analysed on a Digital Micro Vax 2000 computer using Waters “Expert Ease Chromatography” software (version 2.3). Chromatograms obtained from 70-min runs were divided in 150 slices for integration. The chromatograph was calibrated with twelve polystyrene standards supplied by Waters and ranging from 2700 to 2 700 000 g mol⁻¹. These were dissolved in *m*-cresol. Since blends are analysed, molecular mass values are expressed in polystyrene equivalents (PS g mol⁻¹). The precision inherent to chromatographic measurements is estimated to 10%. In order to check the stability of the system, calibration by polystyrene standards was done immediately before analysis of the polyester blends.

3. Results and discussion

3.1. Sample molecular mass stability

Following the method studied, polyesters were dissolved at room temperature in phenol–TCE and analysed in *m*-cresol at 70°C. The reliability of the chromatographic procedure can thus be checked by following the weight-average molecular mass (\bar{M}_w) evolution of PET–PBT blends versus holding time of the samples in solution at 70°C, as presented in Fig. 1.

Polyesters free of phosphite show stable molecular mass values, even after 38 h at 70°C. This clearly proves that these conditions do not degrade neat

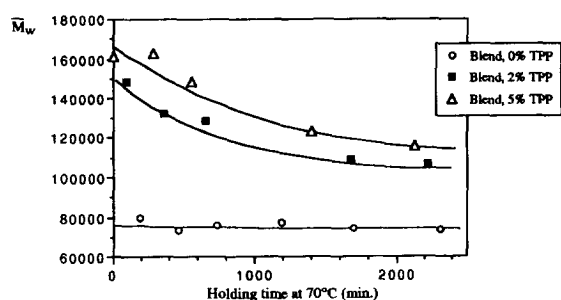


Fig. 1. Weight-average molecular mass versus holding time at 70°C in a phenol–TCE solution (60:40, v/v) for PET–PBT (75:25, v/v) samples following the addition of 0, 2 or 5% phosphite, respectively.

PET–PBT blends and therefore are suitable for polyester analysis. Polyester samples can thus be dissolved and analysed in *m*-cresol without degradation occurring, provided that the temperature does not exceed 70°C.

On the contrary, polyester blends reacted with 2 or 5% phosphite are known to be very sensitive to degradation by phenols at high temperature [11]. Their molecular mass values are influenced significantly by the holding time of the samples at 70°C in solution. A large decrease is observed initially, followed by stabilisation at longer times. Since these analytical conditions do not modify ester bonds, the large molecular mass decrease observed strongly suggests the presence of other links induced by the polyester/phosphite reactions.

3.2. System stability

The use of phenol–TCE for dissolution and of *m*-cresol as eluent solvent needs further control of the stability of the SEC system. Therefore, in this work, the molecular mass values of PET–PBT blends are obtained by reference to a calibration curve deduced from PS injected immediately before the polyester analysis. Such a procedure allows the determination of accurate values; since calibrations are done regularly, the measurements are not disturbed by changes developing in the system.

Retention times of the PS dissolved in *m*-cresol are observed to change from run to run. The variations are much larger than normally expected from

the chromatographic system. As the procedure involves the presence of three different solvents during the chromatographic analyses, the evolution is attributed to the injection of samples dissolved in phenol–TCE. Polystyrene standards dissolved either in *m*-cresol or in phenol–TCE were then used to precisely identify the cause of the changes.

To carry out relevant comparisons, *m*-cresol was first eluted through the columns until “clean” conditions were reached, i.e. until successive analyses of polystyrene standards dissolved in *m*-cresol showed identical retention time values. Fig. 2 shows the influence of phenol–TCE injection on the stationary phase of the chromatographic columns. It also shows the retention times of PS dissolved in *m*-cresol, analysed either under “clean” conditions or following the injection of several samples dissolved in phenol–TCE. It is clear that the presence of phenol–TCE induces a reduction of the retention times for PS, especially for low molecular masses.

Subsequent elution with *m*-cresol allows the system to return to “clean” conditions and restores the retention times. That points out the partially reversible character of the observed evolution. The values do not, however, return to those observed before phenol–TCE injection. This is clearly seen in Fig. 3 where the retention times of PS measured under “clean” conditions, are represented. Between the three series of measurements, numerous samples dissolved in phenol–TCE were injected. It is obvious that the analysis of such samples causes an appreciable permanent decrease in the retention times. A

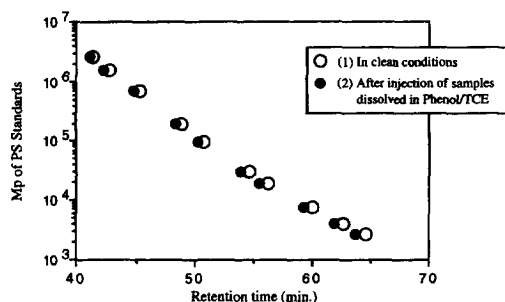


Fig. 2. Retention times for PS with different peak molecular masses (M_p), dissolved in *m*-cresol and measured either under “clean” conditions (1) or after analysis of the samples dissolved in phenol–TCE (2).

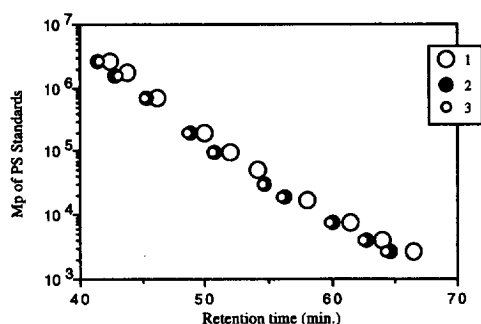


Fig. 3. Retention times for PS with different peak molecular masses (M_p), dissolved in *m*-cresol and measured under “clean” conditions. Between the three series of measurements (1, 2 and 3), repeated injections of polyester samples dissolved in phenol–TCE were carried out.

slow, but irreversible, modification of the chromatographic system therefore results from the addition of phenol–TCE to the eluent solvent.

The influence of the solvent on the polymer hydrodynamic volume was also studied. Under “clean” conditions, PS dissolved in *m*-cresol and phenol–TCE were successively analysed. In this way, the stationary phase of the chromatographic columns is not significantly altered during a single experiment involving phenol–TCE and the influence of the solvent on the hydrodynamic volume can be isolated. In Fig. 4, it can be seen that polystyrene standards dissolved in phenol–TCE show shorter retention times than those dissolved in *m*-cresol. This shows that the polymer dissolved in phenol–TCE has a higher hydrodynamic volume.

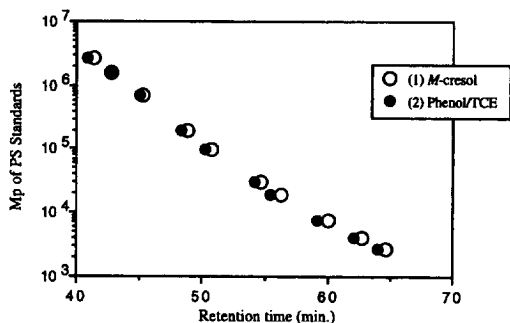


Fig. 4. Retention times for PS with different peak molecular masses (M_p), dissolved in *m*-cresol and measured under “clean” conditions (1), or dissolved in phenol–TCE and measured immediately after analysis of the former samples (2).

The drift in retention times means that the dissolution of polyester samples in phenol–TCE and calibration with polystyrene standards in *m*-cresol are not optimum analytical conditions to use in an extensive SEC study of the polyester molecular masses.

3.3. Proposed procedure for highly sensitive samples

To avoid the problems inherent in the current analytical method, a new procedure, suitable even for polyester/phosphite systems, was developed. Phenol–TCE is used as the only solvent. Samples are dissolved at room temperature and analysed at 50°C. Since TCE normally contains, and forms, decomposition products harmful to polymer and chromatographic components, extended purification and stabilisation of this solvent is necessary [9]. TCE was distilled carefully immediately before use to ensure consistently high quality.

Consistent results can be obtained with this system, i.e. successive polystyrene standards show similar retention times. Moreover, no degradation is observed when polyester/phosphite systems are held at 50°C and no molecular mass modification with the holding time in solution is observed. Finally, good reproducibility of results, with time, is also noticed. Detailed results of the SEC study on polyester/phosphite systems with this new procedure are described elsewhere [12].

4. Conclusion

Sample dissolution at room temperature in phenol–TCE followed by SEC analysis at 70°C in *m*-cresol, despite the efficiency for pure polyesters, proved to be inadequate for molecular mass determination of polyester/phosphite systems. This procedure causes a rapid degradation of bonds created by TPP in the molten state [11]. Furthermore use of three different solvents makes the technique highly complex. Large modifications of the chromatographic conditions result, partly irreversibly, from the injection of samples dissolved in phenol–TCE. A new procedure, working close to room temperature with phenol–TCE eluent, was therefore

developed, thus avoiding any polymer degradation and allowing the study of polyester/phosphite samples by SEC.

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References

- [1] K. Weisskopf, *J. Polym. Sci., Part A - Polym. Chem.*, 26 (1988) 1919 and references therein.
- [2] J.R. Overton, J. Rush and L.D. Moore, Jr., *Sixth International GPC Seminar Proceedings*, Miami Beach, FL, 1968.
- [3] G. Shaw, *Seventh International GPC Seminar Proceedings*, Monte Carlo, 1969.
- [4] B. Jacques, unpublished results.
- [5] E.E. Paschke, B.A. Bidlingmeyer and J.G. Bergmann, *ACS Polym. Prepr.*, 17 (1976) 440;
- [6] E.E. Paschke, B.A. Bidlingmeyer and J.G. Bergmann, *J. Polym. Sci., Polym. Chem. Ed.*, 15 (1977) 983.
- [7] M.M. Sang, N.N. Jin and E.F. Jiang, *J. Liquid Chromatogr.*, 5 (1982) 1665.
- [8] S.A. Jabarin and D.C. Balduff, *J. Liquid Chromatogr.*, 5 (1982) 1825.
- [9] L.H. Ponder, *Polym. Prepr.*, 21 (1980) 169.
- [10] S.M. Aharoni, C.E. Forbes, W.B. Hammond, D.M. Hindenlang, F. Mares, K. O'Brien and R.D. Sedgwick, *J. Polym. Sci., Part A - Polym. Chem.*, 24 (1986) 1281.
- [11] B. Jacques, J. Devaux, R. Legras and E. Nield, submitted to *Polymer*.
- [12] B. Jacques, J. Devaux, R. Legras and E. Nield, submitted to *Polymer*.