The Gel Permeation Chromatography of Poly(tetramethylene Terephthalate)

Poly(tetramethylene terephthalate) (PTMT), a semicrystalline polymer, is soluble in relatively few solvents. The solvents commonly used to measure dilute solution properties of PTMT are a 60/40 weight ratio of phenol/1,1,2,2-tetrachloroethane and *o*-chlorophenol/1,1,2,2-tetrachloroethane.[1] Hobbs and Pratt[2,3] have used hexafluoroisopropanol (HFIP) to measure the intrinsic viscosity of PTMT resins, while Waters Associates[4] have used this solvent for gel permeation chromatography of poly(ethylene terephthalate) polymers. We wish to report our initial results on the GPC of PTMT using HFIP as the carrier solvent.

EXPERIMENTAL

The PTMT resins used for the GPC analysis were commercial polymers manufactured by Goodyear Tire and Rubber Co. under the trade name of VFR 4716 and 4884. PTMT resins of molecular weight higher than those commercially available were made by heating the VFR 4716 under vacuum at 200°C. Two higher molecular weight materials were made and are designated as PTMT-1 and PTMT-2. The intrinsic viscosities of these samples were measured in a Cannon Ubbelohde viscometer at 30°C using a 60/40 weight ratio of phenol/1,1,2,2-tetrachloroethane and are reported in Table I.

The GPC used in this study was a Waters Associates Model 502 instrument equipped with a Model 6000 solvent delivery system, a U6K sample injection valve, a R401 differential refractometer, and four micro-Styragel columns (Waters Associates) of 10^6, 10^5, 10^4, and 10^3 Å porosity, operated at a flow rate of 1 ml/min using HFIP as the carrier solvent.

The HFIP was purchased from du Pont (from Division) and was used as received. HFIP can cause serious burns (skin and eyes) and should be used with extreme caution.

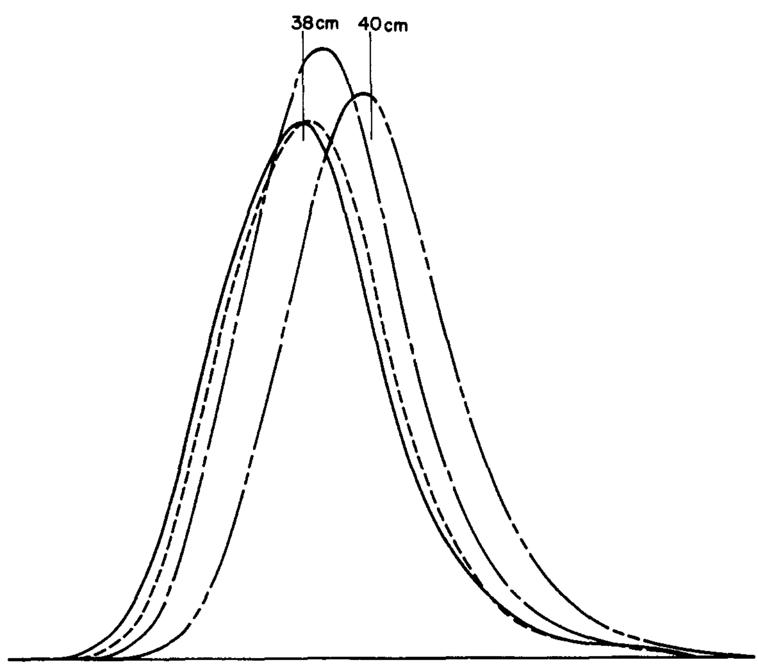

Fig. 1. GPC differential molecular weight distribution for PTMT polymers: (— - -) VFR 4716; (— -) VFR 4884; (- -) PTMT-1; (—) PTMT-2.

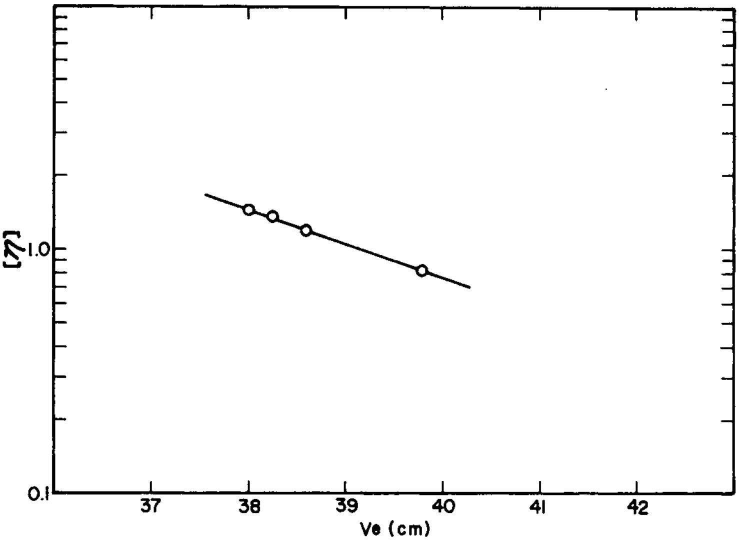

Fig. 2. GPC calibration curve of [η] (60/40 phenol/1,1,2,2-tetrachloroethane) vs V_e. Distance values taken at apex of differential distribution curve.

RESULTS

The GPC traces of the four different molecular weight PTMT resins are shown in Figure 1. The elution volumes are measured as distance values from the point of injection, and the time for a typical GPC run in HFIP is approximately 1 hr.

Unfortunately, polystyrene is not soluble in HFIP, which eliminates the use of narrow-distribution polystyrene standards for calibrating the GPC columns in this solvent. A calibration curve utilizing the measured intrinsic viscosity value as a function of the elution volume (V_e) measured at the apex of the GPC differential distribution curve for each resin is shown in Figure 2, and a linear relationship between the log of [η] versus V_e is observed. The V_e values are listed in Table I. In order to convert these GPC traces to molecular weight values, the more recent calibration techniques involving whole polymers probably need to be applied.[5,6,7] However, this note is intended to report our success of obtaining reasonable chromatograms of PTMT via GPC using the solvent HFIP.

The authors wish to thank Mr. J. A. Pawlak for providing the PTMT-1 and PTMT-2 samples.

TABLE I
Intrinsic Viscosity Value of PTMT Resins

Sample description	[η], dl/g	V_e, cm
VFR 4716	0.81	39.8
VFR 4884	1.20	38.6
PTMT-1	1.38	38.3
PTMT-2	1.46	38.0

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Received November 1, 1976
Revised November 23, 1976