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Fractionation of linear saturated (co)polyesters by differential precipitation

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Summary

Samples of poly(ethylene terephthalate) (PET), poly(ethylene terephthalate-co-naphthalene-2,6-dicarboxylate) (PENT) and poly(ethylene naphthalene-2,6-dicarboxylate) (PEN), materials which find application in textile and packaging industry, have been investigated, with the aim to obtain narrow molecular weight fractions suitable for further characterization. Preliminary results concerning with the fractionation of gram-quantities of the polyesters are reported, using a method based on the fractional precipitation from a phenol/1,2,4-thrichlorobenzene solution of the polymer, using n-heptane as non-solvent. Obtained fractions have been characterized by intrinsic viscosity measurements and Gel Permeation Chromatography analysis.

Introduction

Very little has been published about the attainment of narrow molecular weight fractions of linear saturated polyesters (1-6), although these materials find wide applications. The limited and difficult solubility of PET in common organic solvents (7-13) leads to serious difficulties on its characterization in solution, especially for determination of molecular weights (Mw) and their distribution (MWD). For the polyesters studied in this work, the phenol/1,2,4-thrichlorobenzene (50:50 v/v) (PTCB) mixture was chosen as solvent, and with the aim to obtain narrow fractions, studies of fractionation of such polymers were started. A method have been set up based on the fractional precipitation from a PTCB solution of the sample, of a series of fractions, induced by a stepwise decrease of the solvent power of the system, through addition of n-heptane (HE) as non-solvent.

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Experimental

Materials - PET, with intrinsic viscosity (IV) of 1.03 dl/g was supplied by Montefibre (Italy); PENT and PEN were synthesized by bulk polycondensation from dimethyl esters and ethylene glycol using manganese tetraacetate and antimony trioxide as catalysts, following a previously reported procedure (14). In PENT the molar ratio of terephthalate/naphthalene-2,6-dicarboxylate units was 94:6. Solvents used for fractionation and characterization were all "spectrograde" (purity > 98%) and were used without further purification.

Fractionation - A solution of the sample in PTCB was obtained at 80°C in a separatory flask. In order to obtain each fraction, different amounts of HE as non-solvent were added at 30°C until a slight turbidity developed. To assure achievement of equilibrium between the two phases, solutions were warmed to homogeneity and the precipitation was allowed to take place by gradually cooling to the temperature of fractionation bath. Each fraction was allowed to settle for a night, filtered and then dried. Seven, six or eight fractions were obtained from fractionations of PENT, PEN and PET respectively, with a total recovery of over 96% in all cases.

Characterization - Intrinsic viscosity measurements were performed on each fraction in PTCB at 30°C with a Desreux-Bishoff capillary viscosimeter. In order to determine the MWD and the average Mw, Gel Permeation Chromatography (GPC) analyses were performed in PTCB at 85°C. A Waters 150C instrument, equipped with four Styragel HT columns, was used; universal calibration was applied, using polystyrene standards of sharp MWD, as discussed in the following. Values of number average molecular weight (Mn) were obtained through a Gonotech Membrane Osmometer mounting a cellulose regenerated membrane of cut-off=10000.

Results and discussion

Two different calibration methods of GPC were used. In the case of PENT, due to the presence of low quantity of the comonomer (6% of naphthalene-2,6-dicarboxylic units) and PET, universal calibration according Benoit theory (15) was followed, with the support of ten monodisperse polystyrene standards and the following two couples of Mark-Houwink constants: $a_1=0.68$; $k_1=1.55\cdot10^{-4}$ for polystyrene and $a_2=0.81$; $k_2=1.48\cdot10^{-4}$ for PET. The latter couple of values was calculated by us, investigating six standards of known different molecular weight.

For PEN, in absence of calculated Mark-Houwink constants, molecular weights were calculated through the Q theory (16), taking into account the size of naphthalene-2,6-dicarboxylate unit: such method leads to a higher level of approximation of molecular weights with respect to the previous one. Average molecular weights obtained by GPC were partially confirmed by

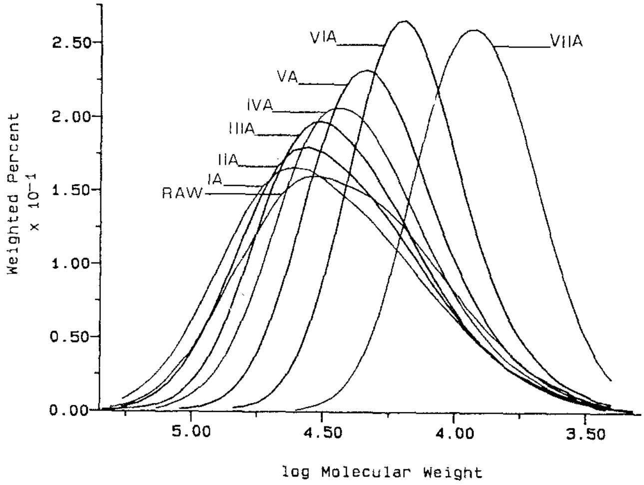

Figure 1. GPC chromatograms of PENT fractions

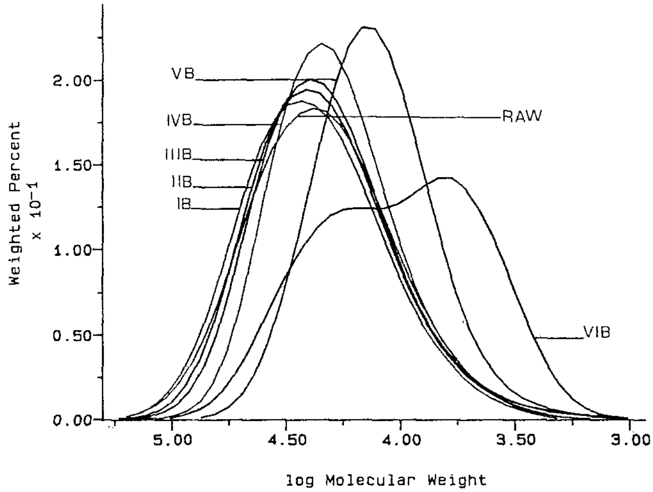

Figure 2. GPC chromatograms of PEN fractions

osmometric measurements of Mn, performed on the raw sample. Values of 22000, 15000 and 31000 for PENT, PEN and PET, respectively, were obtained. It is important to underline that such values could be overstimated, due to the use of a membrane permeable to low molecular weight species which, passing through the membrane, failed to contribute to the final averages.

In Figs. 1 and 2, GPC chromatograms of raw materials and of the two series of fractions are reported, showing a substantial overlapping; they clearly show the decreasing value of molecular weight of the successive fractions gathered, testifying the efficiency of the fractionation method. Also MWD decreases for the successive fractions; the bimodality of the last fraction of PEN sample, suggests the presence of very low molecular weight oligomers (17).

Viscosity measurements are in good agreement with the progressive values of molecular weight obtained from GPC, as shown in Tabs. 1 and 2.

A plot of the logarithm of molecular weights from GPC vs.

TABLE 1: FRACTIONATION DATA OF PENT

sample	HE add. prog.(ml)	prog.weight (g)	$[\eta]$ (dl/g)	Mw 10^{-3}	Mn 10^{-3}	MWD
IA	65.0	0.1338	0.71	40	22	1.85
IIA	68.0	1.2530	0.66	36	21	1.72
IIIA	71.0	1.9648	0.57	31	17	1.81
IVA	71.5	2.1758	0.55	29	15	1.80
VA	80.0	2.4730	0.41	22	14	1.69
VIA	90.0	2.7944	0.36	16	12	1.41
VIIA	150.0	3.0740	0.20	9	7	1.33
raw			0.60	34	18	1.79

TABLE 2: FRACTIONATION DATA OF PEN

sample	HE add. prog.(ml)	prog.weight (g)	$[\eta]$ (dl/g)	Mw 10^{-3}	Mn 10^{-3}	MWD
IB	76.0	1.2370	0.59	28	14	2.00
IIB	79.0	1.6985	0.49	26	13	2.00
IIIB	81.5	2.2589	0.47	25	13	1.92
IVB	87.0	2.9558	0.42	21	12	1.75
VB	100.0	3.9452	0.33	14	9	1.55
VIB	200.0	4.1698	0.29	13	6	2.16
raw			0.51	26	12	2.16

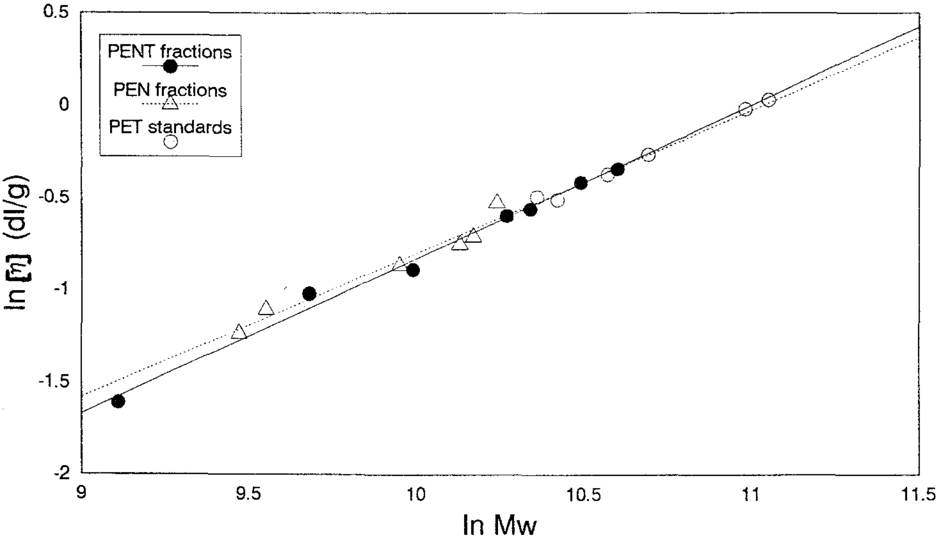

Figure 3. Viscosity-Mw relationship for fractions of PENT, PEN and PET standards

logarithm of the intrinsic viscosities is given in Fig. 3 for the investigated polymers and for PET standards. Values of 0.83, 0.78 and 0.81, respectively, of the **a** constants in the Mark-Houwink relation ($[\eta] = k \cdot Mw^a$) were obtained.

Fractionation of PET presented different aspects due to its higher molecular weight in comparison with the others.

TABLE 3: FRACTIONATION DATA OF PET

sample	HE add. prog.(ml)	prog.weight (g)	$[\eta]$ (dl/g)	Mw 10^{-3}
IC	175.0	2.3694	1.05	57
IIC	185.0	5.1052	0.99	53
IIIC	187.0	5.9807	0.97	51
IVC	191.0	7.5770	0.94	49
VC	196.0	8.0890	0.90	47
VIC	206.0	8.7598	0.75	37
VIIC	226.0	9.2584	0.63	30
VIIIC	350.0	9.6681	0.52	24
raw			1.03	57

Note: Mw calculated from $[\eta]=1.48 \cdot 10^{-5} \cdot Mw^{0.81}$

The time required for a clear separation of the two phases which form after HE addition, and the very slow precipitation rate made the experiment duration very long. Separation of fractions of higher molecular weight were more influenced than other ones; as shown in Tab. 3, the first fractions are barely separated. These problems depends on the high degree of cristallinity (> 40%) of such PET sample (18). Near the separation point, in fact, the more concentrated phase (from which the fraction will be separated) results partially crystalline and can carry chains at low molecular weight, which influenced the neat separation of a determined fraction. Therefore, such fractionation method seems not the most convenient for highly crystalline polymers.

Conclusion

Efficient fractionation of (co)polyesters was obtained with the proposed method. Fractionation of PET resulted the most difficult, probably due to its high molecular weight and cristallinity degree.

Mark-Houwink constants for PEN have been determined, resulting slightly different from those of PET and PENT, because of the different structure; on the other hand, the presence of the 6% naphthalene-2,6-dicarboxylate comonomer in PENT seemed not to influence the solution behaviour respect to PET.

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