Molecular Weight Distribution of an Unsaturated Polyester

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Synopsis

A precipitation fractionation was carried out by the nonsolvent addition method of 60 g of an unsaturated polyester. The polyester was prepared by the generally known melt condensation of maleic anhydride, phtalic anhydride, ethylene glycol, and cyclohexanol. Number-average molecular weights of fractions were determined by vapor pressure osmometry in acetone at 36°C. Polydispersities of fractions were evaluated by gelpermeation chromatography (GPC) measurements with tetrahydrofuran as solvent. They seem to be wider for fractions of higher molecular weights. By infrared spectroscopy the fractions were found not to have marked differences in chemical compositions. The obtained molecular weight distribution curve of the unsaturated polyester was found to be in good agreement with that expected from the theory of polycondensation kinetics. The small differences appear only in the low molecular weight range.

INTRODUCTION

Physical properties of a polymer of fixed chemical composition are markedly influenced by its molecular weight and molecular weight distribution. One of the ways of obtaining the required greater quantities of fractions for studying physical properties of a polyester is preparation of fractions by precipitation fractionation.[1–10] Their polydispersities can be estimated by using the GPC method,[11–14] and precipitation fractionation efficiency can be determined. Also, combination of precipitation fractionation with the GPC method allows the molecular weight distribution of an unfractionated polyester to be determined.

Assuming equal reactivity of all functional groups during polycondensation of linear polyesters, Flory[15] derived the "most probable distribution" of molecular weights. A fractionation of saturated polyesters proved the validity of this molecular weight distribution in a number of cases.[16–18] Also fractionation results of an unsaturated polyester prepared by condensation of isophtalic acid, maleic anhydride, and propylene glycol shows the "most probable distribution."[19] In our case, an unsaturated polyester prepared by condensation of maleic anhydride, phtalic anhydride, and ethylene glycol and terminated by cyclohexanol at the final stage of condensation was used for fractionation. Comparison of the real distribution with the "most probable distribution" is important also from the point of view of mechanism and kinetics of polycondensation of the unsaturated polyester.

EXPERIMENTAL PROCEDURE

A. Preparation of the Polyester

Unsaturated polyester (UP) was prepared by melt condensation of ethylene glycol (740 g), maleic anhydride (472.5 g), and phtalic anhydride (1044 g) in atmosphere of nitrogen at 220°C. When the acid value 62.2 mg KOH/g had been reached, cyclohexanol (160 g) was added dropwise for 15 min. At last, vacuation was carried out (15 min).

Analytical Values of Polyester UP

Acid value [the amount (mg) of KOH needed for neutralization of carboxyl groups and anhydrides in 1 g of a polyester] is 35.5 mg KOH/g.

Hydroxyl value [the amount (mg) of KOH needed for neutralization of acetic acid bonded by acetylation in 1 g of a polyester is 42 mg KOH/g.

Saponification value [the amount (mg) of KOH needed for neutralization of carboxyl groups, anhydrides, and hydrolysis of ester linkages in 1 g of a polyester] is 604.8 mg KOH/g.

Weight fraction of cyclohexanol in the polyester is 0.036.

B. Precipitation Fractionation

Polyester UP was fractionated by the nonsolvent addition method by using acetone as a solvent and petrolether as a nonsolvent. The original concentration of acetone solution was 4 g UP/100 mL; the amount of the solution was 1500 mL. Fractionation was carried out in 5-L pear-shaped flasks in a water thermostat. The nonsolvent was added gradually to the vigorously agitated solution at constant temperature 25°C. After the nonsolvent had been added, the fractionated system was warmed until a great deal of the precipitated polyester dissolved. Then the solution was cooled gradually with agitation to the original temperature. After the phases had separated completely (96 h), the supernatant phase was drawn off by syphoning. The precipitated phase was collected by dissolving it in a small amount of solvent. Then a great deal of solvent and nonsolvent was removed by evaporating the solution. The whole procedure was repeated till all but one fraction was obtained. The final fraction was obtained by evaporating the last supernatant liquid. Ten fractions were obtained which are designed as $A-K$ in Table I.

The original fractions were refractionated. Each fraction was dissolved in acetone (4 g/100 mL) and the solution was precipitated by petrolether. Twenty new fractions were obtained, which are designated as A_1, A_2-K_1, K_2 in Table I.

The fractions were dried under vacuum ca. 100 Pa at 74°C to constant weight. Before vacuation gas nitrogen was blown through a drying-box. The fractions were stored with P_2O_5 in a dessiccator. Weight fractions w of all the fractions are given in Table I.

TABLE I
Results of Polyester Fractionation

Fraction	$w \times 10^2$	$\overline{M}_n$	Fraction	$w \times 10^2$	$\overline{M}_n$
A	4.631	3270	A_1	2.152	5020
			A_2	2.479	2510
B	12.572	2760	B_1	5.088	4390
			B_2	7.483	2200
C	8.480	1890	C_1	3.350	2930
			C_2	5.130	1530
D	10.111	1940	D_1	4.340	2700
			D_2	5.771	1600
E	11.677	1470	E_1	5.854	2200
			E_2	5.823	1100
F	10.618	1300	F_1	4.491	2040
			F_2	6.127	1030
G	10.727	920	G_1	6.190	1260
			G_2	4.537	680
H	13.044	820	H_1	8.281	1070
			H_2	4.763	590
I	8.726	530	I_1	4.176	650
			I_2	4.559	450
K	9.416	430	K_1	4.256	500
			K_2	5.160	390

C. Molecular Weight Determination

To determine the number-average molecular weights $\overline{M}_n$, a commercial apparatus was used (a Hewlett-Packard Model 302B VPO) which is based on the Hill–Blades vapor tension apparatus.[20] The measurements were carried out in acetone at 36°C. Four to six solutions of varying concentrations (0.01–0.1 mol/L) were measured. The apparatus was calibrated by pentaacetyl glucose.

The number-average molecular weights $\overline{M}_n$ of all the fractions are given in Table I.

D. GPC Measurements

For our measurements, a gel-permeation chromatograph consisting of four columns packed by Styragel of different permeability was used. The flow rate of tetrahydrofuran was maintained at 0.5 mL/min. All samples (0.4% concentration) were injected for 45 s. A UV analyzer (a Water Associates Model 440 absorbing at wavelengths 254 nm and 280 nm) was made use of for identification of the eluated polyester.

As an example the dependences of the UV-analyzer signal at wavelength 254 nm on the elution volume for fractions A, A_1, A_2–C, C_1, C_2 and polyester UP are shown in Figure 1.

E. Infrared Measurements

A Perkin-Elmer Model 283 infrared spectrophotometer was used for our measurements. The samples were milled down in liquid nitrogen and homogenized with KBr into tablets (3 g of sample/1000 mg of KBr). Absorbancy A
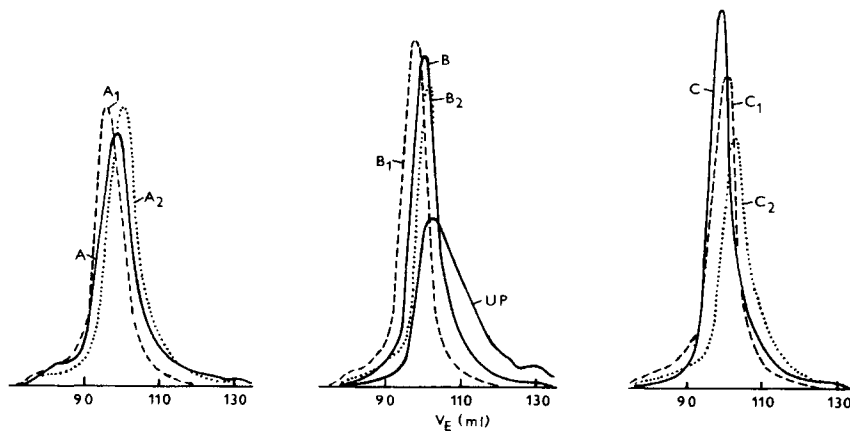
Fig. 1. Dependence of UV-analyzer signal at wave length 254 nm on elution volume.

was measured at wavenumbers 1610 cm^{-1} and 1640 cm^{-1} during quantitative conditions. The absorbancy ratio A_{1640}/A_{1610} is a measure of a fumaric acid-phtalic acid ratio in a sample.

RESULTS

A. Polydispersities of the Fractions

The marked points in Figure 2 are given by elution volumes at the tops of elution curves and number-average molecular weights $\overline{M}_n$ for fractions A, A_1, A_2–G, G_1, G_2. The best agreement between experimental number-average molecular weights $\overline{M}_n$ and number-average molecular weights $\overline{P}_n$ calculated from distribution curves of fractions is, however, reached if the relationship log M – V_E is given by a full line and not a dotted line lying within the marked points in
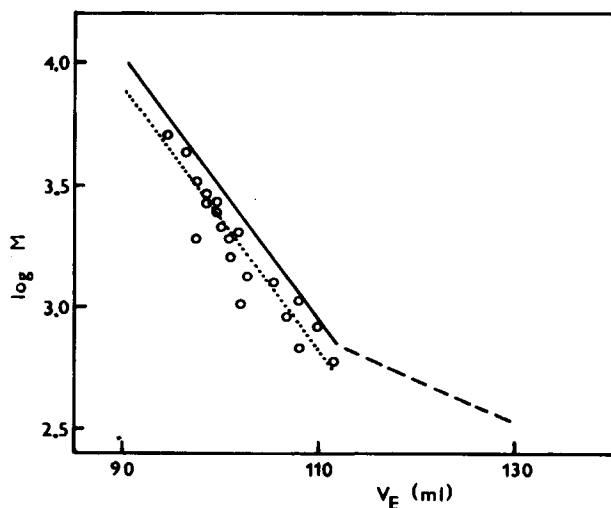

Fig. 2. Dependence of log M on V_E: (O, ·····) $\overline{M}_n$ is put for M at the top of elution curve, (——, - - -) the best agreement between $\overline{M}_n$ and $\overline{P}_n$.

Figure 2. In the region of elution volumes higher than 112 mL the relationship $\log M - V_E$ is given by a dashed line in Figure 2. The unequal course of the relationship $\log M - V_E$ for the whole elution volume range corresponds to the permeabilities of the gel used packing in columns of the chromatograph.

The number-average molecular weights $\overline{P}_n$ and the weight-average molecular weights $\overline{P}_w$ corresponding to the distribution curves of fractions, the coefficients of polydispersity $\mu = \overline{P}_w/\overline{P}_n$, and number-average molecular weights $\overline{M}_n$ determined by vapor pressure osmometry are given for several fractions of polyester UP in Table II.

It appears from the values given in Table II that the calculated number-average molecular weights $\overline{P}_n$ are in good agreement with the experimental number-average molecular weights $\overline{M}_n$. The polydispersities seem to be wider for fractions of higher molecular weights.

Absorbancy ratios A_{1640}/A_{1610} corresponding to fumaric acid-phtalic acid compositions do not show marked and regular differences for successively precipitated fractions ($A_{1640}/A_{1610} = 0.8$–1.0).

B. Molecular Weight Distribution of Polyester UP

Figure 3 shows a plot of $I(M)$ as a function of M. The cumulative weight fraction $I(M)$ denotes the weight fraction of a polyester containing all molecular weights lower than molecular weight M.

The marked points shown in Figure 3 were calculated of the values w and $\overline{M}_n$ of fractions given in Table I according to the procedure given by Mark and Raff.[21]

The dashed curve in Figure 3 represents the "most probable distribution." It was calculated on the basis of acid, hydroxyl, saponification values, and the weight fraction of cyclohexanol for polyester UP (these values are given in Sec. A). The "most probable distribution" is expressed by

$$I(M) = \frac{(1-p)^2}{p(\ln p)^2}\left\{1 + p^{M/M_0}\left[\left(\frac{M}{M_0}\right)\ln p - 1\right]\right\} \tag{1}$$

where

$$p = 1 - (\overline{x}_n)_{\text{mp}}^{-1} \tag{2}$$

$$(\overline{x}_n)_{mp} = (\overline{M}_n)_{\text{mp}}/M_0 \tag{3}$$

$(\overline{M}_n)_{\text{mp}} = 1150, \qquad (\overline{x}_n)_{\text{mp}} = 13.2$

$M_0 = 87.18, \qquad p = 0.924$

TABLE II
Average Molecular Weights and Coefficients of Polydispersity of Fractions

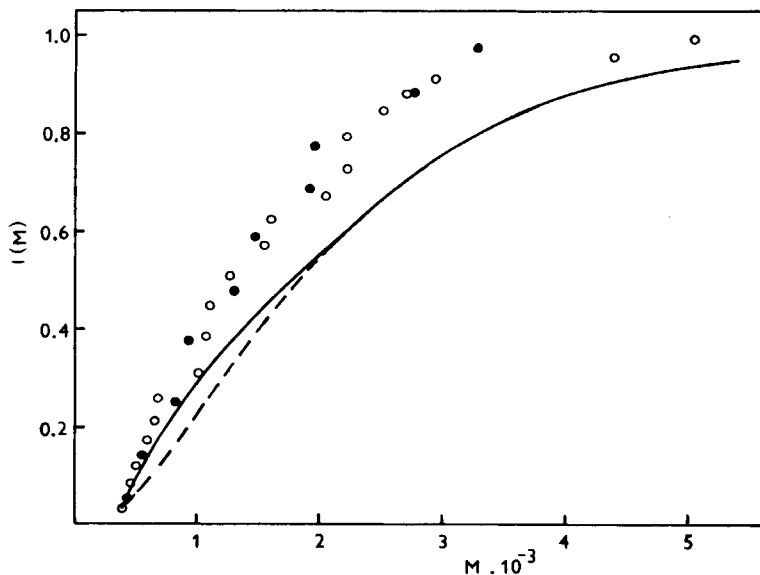| Fraction	$\overline{M}_n$	$\overline{P}_n$	$\overline{P}_w$	$\overline{P}_w/\overline{P}_n$
A_1	5020	4630	7260	1.57
A_2	2510	2600	4690	1.77
B_1	4390	4310	6190	1.44
B_2	2200	2080	3720	1.79
D_1	2700	2530	3720	1.47
D_2	1600	1680	2520	1.50
G_1	1260	1040	1480	1.42
G_2	680	740	990	1.34
I_1	650	670	920	1.37
I_2	450	450	520	1.16

Fig. 3. Dependence of cumulative weight fraction on molecular weight for polyester UP: by procedure of Mark and Raff[21] for number of fractions 10 (●) and 20 (○); (- - -) the "most probable distribution"; (——) the real distribution.

$(\overline{M}_n)_{mp}$ is a number-average molecular weight of linear chains, M_0 is an mean molecular weight of one unit (1 mer), $(\overline{x}_n)_{mp}$ is a number-average polymerization degree of linear chains, and p is a degree of conversion.

The full line in Figure 3 represents a real distribution curve of polyester UP. It was obtained by treatment of the GPC measurement of polyester UP (its elution curve is shown in Fig. 1) by means of the relationship $\log M - V_E$ given in Figure 2.

DISCUSSION

The molecular weight distribution of polyester UP, demonstrated as an integral weight distribution curve in Figure 3 (the solid curve), differs from the "most probable distribution" (the dashed curve) only in the low molecular weight range (under molecular weight 2000). In polyester UP there is a greater part of molecules of the lowest molecular weights. That is why the real integral weight distribution curve is not S-shaped as that of the "most probable distribution." Above molecular weight 2000, both of these distribution curves are practically coincident. Because of considerable polydispersities of the fractions, the distribution corresponding to marked points in Figure 3 would differ in a most pronounced way from the real distribution.

The greater part of molecules of the lowest molecular weights results in a little bit lower number-average molecular weight of polyester UP ($\overline{M}_n = 1030$; $\overline{P}_n = 1080$) compared with that of the "most probable distribution" [$(\overline{M}_n)_{mp} = 1150$]. However, there is no difference in the weight-average molecular weights of both distributions practically [$\overline{P}_w = 2210$; $(\overline{M}_w)_{mp} = 2210$]. That is why the coefficient of polydispersity of the real distribution is somewhat higher than that of the "most probable distribution" ($\mu = 2.05$, $(\mu)_{mp} = 1.92$).

The difference between the real distribution and the "most probable distribution" can be caused by several factors: by incomplete fulfilling of the fundamental condition of the "most probable distribution," to keep the equal reactivity of all functional groups at every stage of polycondensation; by presence of other reactions than those taking place during preparation of saturated linear polyesters; by the very method of preparation of polyester UP; and by formation of cycle molecules.

As far as the principle of equal reactivity of all functional groups is concerned, it should be taken into account that both anhydrides used and carboxyl end groups of formed molecules react with hydroxyl groups during condensation.

Formation of cycle molecules of the lowest molecular weights during polycondensation is probable. Generally, cycle molecules cause the change of the "most probable distribution" curve into a similar shape which has the distribution curve of our polyester. Occurrence of cycle molecules in polyester UP seems to be very probable because of the fact that the molecular weight $\overline{M}_n$ of polyester UP determined by osmometry is rather lower than the molecular weight $(\overline{M}_n)_{mp}$ of linear molecules $(\overline{M}_n = 1030; (\overline{M}_n)_{mp} = 1150)$.

Polyester UP was prepared by condensation of ethylene glycol, maleic anhydride, and phtalic anhydride. Only at the final stage of polycondensation was cyclohexanol added. It is possible that cyclohexanol reacted not only with the carboxyl end groups but caused also partial scission of linkages already earlier formed. This newly formed molecular weight distribution need not correspond to that which could have arisen on reaching the same degree of conversion if all components had been present at the beginning of polycondensation.

CONCLUSION

Precipitation fractionation of the unsaturated polyester allows preparation of greater quantities of fractions which are not sharp enough. It was proved that the refractionations of 10 original fractions did not reduce the polydispersities of the newly obtained fractions too much. The fumaric acid–phtalic acid ratios determined by infrared spectroscopy do not show marked differences in chemical compositions of the fractions.

The molecular weight distribution of polyester UP does not differ markedly from that which was calculated according to the statistical derivations given by Flory.[15] There is a rather greater amount of molecules of the lowest molecular weights in the polyester as comparison with the "most probable distribution." The formation of cycle molecules of the lowest molecular weights is probable.

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