

Molecular Weight Distribution of Poly(ethylene Adipate) and Its Changes Caused by Aging

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Synopsis

Precipitation fractionations of poly(ethylene adipate) were carried out by nonsolvent addition methods using chloroform as solvent and petroleum ether as nonsolvent. Seventy-five grams of the polyester was fractionated into 10 fractions by stepwise method and 35 g of the former was fractionated into nine fractions by triangle method. Number-average molecular weights were determined by ebullioscopic measurements with chloroform as solvent. Acid, hydroxyl, and saponification numbers were determined by analytical methods. It was proved that poly(ethylene adipate) contained considerable quantity of cyclic molecules (ca. 23 mol %). The molecular weight distribution curves of linear molecules constructed from the results of polyester fractionations were found to differ rather from distribution expected from the theory of kinetics of polycondensation and statistical theory. This discrepancy may be explained by higher reactivity of functional groups belonging to shorter molecular chains. It was found out that the aged poly(ethylene adipate) hydrolyzed to a great extent and practically contains no cyclic molecules. Molecular weight distribution of the aged poly(ethylene adipate) determined by GPC is very near to the theoretical "most probable distribution" derived for polycondensates.

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 to obtain the required quantities of fractions for studying physical properties of a polyester is preparation of fractions by precipitation fractionation.¹⁻¹⁰ The most widely used method of fractional precipitation is the addition of nonsolvent to solution of a polymer.¹¹ Fractionation can be carried out either by the simple stepwise method with the possibility of following refractionations of fractions^{12,13} or by using more complicated schemes, especially the triangle method.^{14,15} As to obtain good fractionation results, a number of experimental conditions is required to be maintained.¹⁶

Assuming equal reactivity of all functional groups during polycondensation of linear polyesters, Flory¹⁷ derived "the most probable distribution" of molecular weights. Theoretical molecular weight distribution of cyclic molecules, which are formed during polycondensation too, may be calculated according to the theory given by Jacobson and Stockmayer.¹⁸ Fractionation of saturated polyesters prepared from dicarboxylic acids and glycols proved the validity of "the most probable distribution" for linear chains in a number of cases.¹⁹⁻²² Pope and Williams^{19,20} found that molecular weight distribution of poly(diethylene adipate) of number-average molecular weight higher than 850

is in good agreement with "the most probable distribution." Entelis et al.²³ used GPC for measurement of molecular weight distribution of oligo(diethylene adipate) at molecular weight range 300–1000 and found out that its molecular weight distribution corresponds to "the most probable one." Also Ljubimova et al.²⁴ used GPC for measurements of molecular weight distributions of various samples of oligo(diethylene adipate) and its esters with methacryl acid and found out that their molecular weight distributions of linear molecules correspond to "the most probable ones" as well.

Comparison of molecular weight distribution curves obtained from the results of precipitation fractionations resp. gel permeation chromatography of poly(ethylene adipate) with distributions expected from the theory of kinetics of polycondensation and statistical theory makes it possible to judge efficiencies of used fractionation methods and to analyze the factors governing molecular weight distribution.

EXPERIMENTAL

Preparation of the Polyester

Poly(ethylene adipate) was prepared by melt condensation of ethylene glycol and adipic acid in nitrogen atmosphere at 190–200°C. A ratio of the number of moles of ethylene glycol and the number of moles of adipic acid was 1.04. When number 40 mg KOH/g had been reached (after 12 h), condensation was finished under vacuum (ca. 10^4 Pa for 5 h). The polyester was designated as PEA.

Stepwise Fractionation by Addition of Nonsolvent

Chloroform was used as solvent and petroleum ether as nonsolvent. The original concentration of the chloroform solution of PEA was 7.5 g/100 mL and its amount was 1000 mL. Fractionation was carried out in 2.3-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 precipitated polyester dissolved. Then the solution was cooled gradually with agitation to the original temperature. After the phases had separated completely (1–2 days), 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 evaporation. The whole procedure was repeated until the next to last fraction was then obtained. The final fraction was then prepared by evaporation of the last supernatant liquid. Ten fractions were obtained. The fractions were dried under vacuum ca. 10^2 Pa at 70°C to constant mass.

Triangle Fractionation by Addition of Nonsolvent

The initial concentration of the chloroform solution of PEA was 7 g/100 mL and its amount was 500 mL. Petroleum ether was used as nonsolvent. According to this way of fractionation the solution was divided into two liquid phases by addition of nonsolvent. Each phase was again divided into two new

ones. The dilute phase coming of the original concentrated one was combined with the concentrated phase originating from the original dilute one. Three polyester fractions were obtained. In this way the polyester was further divided and its parts were combined one with another. Nine fractions were finally prepared.

Molecular Weight Determination

To determine the number-average molecular weights \bar{M}_n , a differential ebulliometer was used which is based on the Hill and Brown apparatus.²⁵ The temperature differentials were measured by liquid differential thermometer. Chloroform solutions of varying concentrations (0.5–2.5 g/100 mL) were used for our measurements.

Determination of Acid, Hydroxyl, and Saponification Numbers

Acid Number

Two grams of the sample were dissolved in 25 mL of mixed solvent (2 vol of benzene and 1 vol of ethyl alcohol) at room temperature. The solution was titrated with 0.1*N* alcoholic KOH to a phenolphthalein end point.

Hydroxyl Number

Two grams of the sample were dissolved in 5 mL of pyridine and treated with 5 mL of the mixture of 25 vol % acetic anhydride in toluene at boiling temperature for 1 h. The cooled solution was titrated with 0.5*N* alcoholic KOH to a phenolphthalein end point.

Saponification Number

One half gram of the sample was treated with 25 mL of 0.5*N* alcoholic KOH at boiling temperature. An excess of KOH was titrated with 0.5*N* HCl to a phenolphthalein end point.

GPC Measurement

For our measurement, a commercial liquid chromatograph (a Spectra-Physics Model 8100) consisting of four columns (a column is 25 cm long and its inner diameter is 7.7 mm) packed by Microgel of different permeability (100, 500, 10^3 , and 10^4 Å) was used. Tetrahydrofuran was used as a solvent, temperature of GPC measurement was 40°C, the flow rate was 1 mL/min, volume of injected sample (of concentration 1 g/100 mL) was 10^{-4} L. An RI detector (a Waters Model R 401) was used for identification of the eluted polyester. Plot and evaluation of elution curve were carried out by means of the integrator (a Spectra-Physics Model 4200). The set of used columns was calibrated by polystyrene standards (Waters Assoc.).

RESULTS AND DISCUSSION

Results of both precipitation fractionations are given in Tables I and II. w is a mass fraction of a polyester fraction, \bar{M}_n is a number-average molecular

TABLE I
Results of Triangle Precipitation Fractionation

Fraction	$10^2 \times w$	\bar{M}_n	n_a (mg KOH/g)	n_h (mg KOH/g)	n_s (mg KOH/g)	$\frac{n_h}{n_a}$	$10^5 \times N$	$10^5 \times N_c$	$10^5 \times N_r$	\bar{M}_{nB}	M_0
1	11.319	1030	8.9	59.5	636.4	6.68	10,989	6.900	4.089	1640	84.78
2	6.615	1530	9.4	50.8	636.6	5.40	4.323	3.549	0.774	1865	85.38
3	16.138	1800	8.8	45.6	637.9	5.18	8.965	7.824	1.141	2062	85.48
4	6.164	2100	8.8	36.4	641.9	4.14	2.935	2.483	0.452	2482	85.56
5	15.701	2300	7.2	30.9	636.6	4.29	6.826	5.331	1.495	2945	86.51
6	7.997	2700	7.4	28.8	642.3	3.89	2.962	2.580	0.382	3099	85.91
7	11.380	3000	6.0	22.4	646.7	3.73	3.793	2.880	0.913	3951	85.66
8	12.859	3900	4.8	15.4	647.8	3.21	3.297	2.315	0.982	5555	85.90
9	11.846	5630	3.6	10.2	648.8	2.83	2.104	1.449	0.655	8177	86.03

TABLE II
 Results of Stepwise Precipitation Fractionation

Fraction	$10^2 \times w$	\bar{M}_n	n_a (mg KOH/g)	n_h (mg KOH/g)	$10^5 \times N$	$10^5 \times N_c$	$10^5 \times N_r$	\bar{M}_{nB}
1	5.525	730	56.2	96.8	7.568	7.534	0.034	733
2	7.062	1790	7.6	52.4	3.945	3.776	0.169	1870
3	7.781	2090	6.5	36.7	3.723	2.996	0.727	2597
4	14.715	2340	6.4	31.4	6.288	4.957	1.331	2968
5	12.143	2450	6.4	27.5	4.956	3.668	1.288	3310
6	13.814	2450	6.3	27.4	5.638	4.149	1.489	3330
7	12.794	2560	6.4	26.0	4.998	3.694	1.304	3463
8	10.742	2760	5.4	24.0	3.892	2.815	1.077	3816
9	11.187	3000	5.4	25.0	3.729	3.031	0.698	3690
10	4.235	3180	5.3	24.4	1.332	1.121	0.211	3780

weight of all molecules (determined by ebullioscopic measurement), n_a is an acid number [an amount (mg) of KOH needed for neutralization of carboxyl groups in 1 g of a polyester], n_h is a hydroxyl number (an amount of KOH needed for neutralization of acetic acid bonded by acetylation in 1 g of a polyester), n_s is a saponification number (an amount of KOH needed for the splitting of ester linkages and neutralization of carboxyl groups in 1 g of a polyester), N is the number of moles ($N = w/\bar{M}_n$), N_c is the number of moles of linear molecules ($N_c = w \cdot (n_a + n_h)/1.122 \times 10^5$), N_r is the number of moles of cyclic molecules ($N_r = N - N_c$), \bar{M}_{nB} is a number-average molecular weight of linear molecules calculated on the presumption that the mass of cyclic molecules is negligible ($\bar{M}_{nB} = w/N_c$), and M_0 is the mean molecular weight of a mer unit.

An actual mean molecular weight of a mer unit of a certain number of linear and cyclic molecules consisting of condensed molecules of adipic acid and ethylene glycol at nonequivalent proportions is given by

$$M_0 = \frac{1}{1.782 \times 10^{-5} \cdot (n_s - n_a) + 0.891 \times 10^{-5} \cdot (n_a + n_h)} \quad (1)$$

As is evident from Table I, values of M_0 decrease as the fraction number grows smaller and the value of M_0 of the last fraction is only slightly lower than 86.1 (86.1 is a value of M_0 of linear molecules of $M \rightarrow \infty$). The reason of this decreasing of M_0 is that the presence of two end molecules of ethylene glycol has a higher effect on M_0 in shorter-chain molecules. Not even the increase of influence of end functional groups on the increase of M_0 (as molecular chains become shorter) can sufficiently compensate the above-mentioned influence. It is necessary to realize that fractions consist of both linear and cyclic molecules. That is why the values of M_0 of linear molecules would be still something smaller than those given in Table I. However, the differences between actual values of the mean molecular weights of mer units of linear molecules and 86.1 are small enough, so that the only value of $M_0 = 86.1$ was used for calculations of polymerization degrees x of differently long linear molecules ($x = M/86.1$).

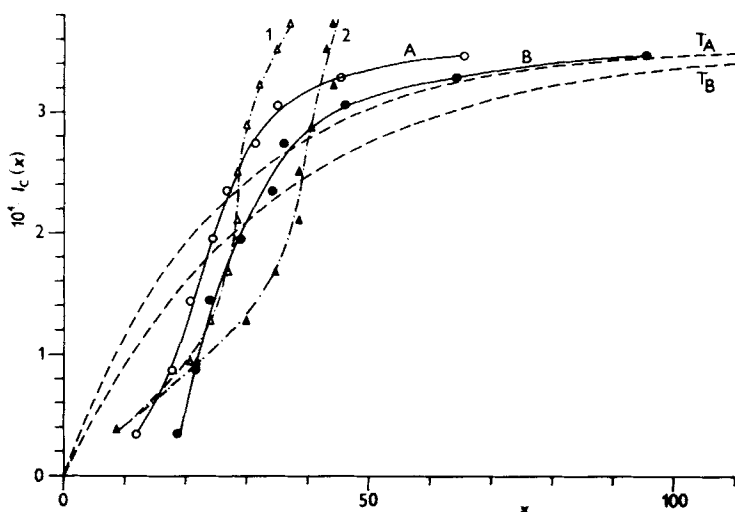


Fig. 1. Dependence $I_c(x)-x$. Stepwise fractionation (---), $\bar{x}_{nAi} = \bar{M}_{ni}/86.1$ (curve 1, Δ), $\bar{x}_{nBi} = \bar{M}_{nBi}/86.1$ (curve 2, \blacktriangle). Triangle fractionation (—), $\bar{x}_{nAi} = \bar{M}_{ni}/86.1$ (curve A, \circ), $\bar{x}_{nBi} = \bar{M}_{nBi}/86.1$ (curve B, \bullet). Theoretical cumulative number distribution curves of linear molecules (- -): $p_A = 0.9866$, $r_A = 0.95$ (curve T_A), $p_B = 0.9897$, $r_B = 0.96$ (curve T_B).

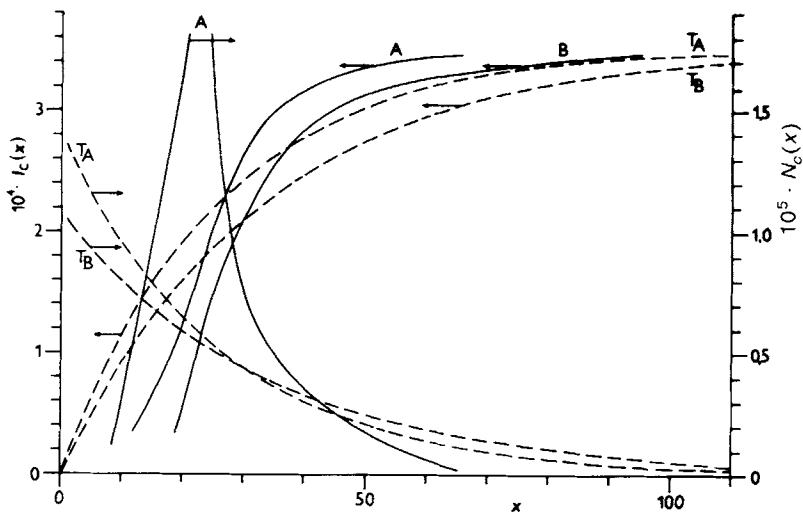


Fig. 2. Dependences $I_c(x)-x$ and $N_c(x)-x$. Triangle fractionation (—): number distribution curve and cumulative number distribution curve (curves A, $\bar{x}_{nAi} = \bar{M}_{ni}/86.1$), cumulative number distribution curve (curve B, $\bar{x}_{nBi} = \bar{M}_{nBi}/86.1$). Theoretical number distribution curves and theoretical cumulative number distribution curves (- -): $p_A = 0.9866$, $r_A = 0.95$ (curves T_A), $p_B = 0.9897$, $r_B = 0.96$ (curves T_B).

Figure 1 (resp. Figure 2) shows a plot of $I_c(x)$ [resp. $N_c(x)$] as a function of x . Each value of $N_c(x)$ represents the number of moles of linear molecules of polymerization degree x ($x = 1, 2, 3, \dots$). Cumulative number of moles $I_c(x)$ means the number of moles of linear molecules of all polymerization degrees lower than polymerization degree $x + 1$. $I_c(\infty)$ is the total number of moles of linear molecules contained in 1 g of a polyester.

The points marked in Figure 1 represent the number-average polymerization degrees \bar{x}_{nAi} (curves 1 and A) resp. \bar{x}_{nBi} (curves 2 and B) of fractions ($\bar{x}_{nAi} = \bar{M}_{ni}/86.1$, where \bar{M}_{ni} is also the number-average molecular weight of linear molecules in i th fraction on the first extreme presumption that number-average molecular weights of linear molecules are equal to number-average molecular weights of cyclic molecules, $\bar{x}_{nBi} = \bar{M}_{nBi}/86.1$, where \bar{M}_{nBi} is the number-average molecular weight of linear molecules in the i th fraction on the second extreme presumption that the masses of cyclic molecules in fractions are negligible). Cumulative numbers of moles $I_c(x)_i$ are given by²⁶

$$I_c(x)_i = \sum_{n=1}^i N_{cn} - N_{ci}/2 \quad (2)$$

where N_{cn} resp. N_{ci} is the number of moles of linear molecules in the n th resp. i th fraction.

Dashed curves designated T_A and T_B (see Figs. 1 and 2) represent distributions calculated according to the theory of kinetics of polycondensation and statistical theory. The relationship $N_c(x)-x$ is given for linear molecules by²⁷

$$N_c(x) = (p_c \cdot r_c^{1/2})^{x-1} \cdot (1 - p_c \cdot r_c^{1/2}) \cdot N_c \quad (3)$$

where p_c is the degree of conversion of carboxyl groups in linear polyester, r_c is the ratio of the number of all carboxyl groups (reacted and unreacted), and the number of all hydroxyl groups in linear polyester, N_c , is the total number of moles of linear molecules in 1 g of PEA ($N_c = 3.5 \times 10^{-4}$).

On the presumption that number-average molecular weight of linear molecules in each fraction is equal to number-average molecular weight of cyclic molecules, the total mass fraction of cyclic molecules in PEA, $w_r = 0.23$ (calculated from the results of triangle fractionation), and degree of conversion, $p_c \equiv p_A = 0.9866$, $r_c \equiv r_A = 0.95$ (curve T_A). On the presumption that mass fraction of cyclic molecules in PEA is negligible ($w_r = 0$), degree of conversion $p_c \equiv p_B = 0.9897$, $r_c \equiv r_B = 0.96$ (curve T_B). The calculations of p_c and r_c were carried out by means of determined values of acid number, hydroxyl number, and saponification number of PEA ($\bar{M}_n = 2180$, $n_a = 6.6$, $n_h = 32.5$, $n_s = 642.3$).

Figure 3 shows two examples of mass distribution curves which were calculated from experimental number distribution curve A and from theoretical number distribution curve T_A that are given in Figure 2. Mass fraction of linear molecules $w_c(x)$ is given by

$$w_c(x) = \frac{N_c(x) \cdot M(x)}{\sum N_c(x) \cdot M(x)} \quad (4)$$

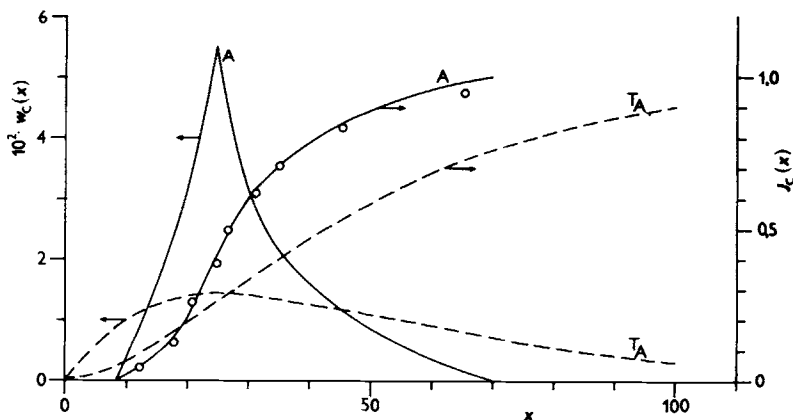


Fig. 3. Dependences $w_c(x)$ - x and $J_c(x)$ - x . Triangle fractionation (—): mass distribution curve and cumulative mass distribution curve (curves A) calculated from number distribution curve A (in Fig. 2). Experimental points (\circ) are determined by \bar{x}_{nA_i} and $J_c(x)_i$ [according to eq. (6)]. Theoretical mass distribution curve and theoretical cumulative mass distribution curve (- - , curves T_A) are calculated from number distribution curve T_A (in Fig. 2).

Cumulative mass fraction of linear molecules $J_c(x)$ is given by

$$J_c(x) = \sum_1^x w_c(x) \quad (5)$$

Experimental points marked in Figure 3 (fractionation according to triangle scheme) are determined by number-average polymerization degrees \bar{x}_{nA_i} and cumulative mass fractions $J_c(x)_i$ are given by²⁶

$$J_c(x)_i = \frac{\sum_{n=1}^i w_{cn} - w_{ci}/2}{1 - w_r} \quad (6)$$

where w_{cn} (resp. w_{ci}) is the mass fraction of linear molecules in the n th resp. i th fraction and w_r is total mass fraction of cyclic molecules.

On the presumption that the number-average molecular weight of linear molecules is equal to the number-average molecular weight of cyclic molecules ($w_r = 0.23$), the number-average molecular weight of linear molecules of PEA is equal to number-average molecular weight of PEA ($\bar{M}_n = 2180$). Number-average molecular weight of linear molecules \bar{M}_{nc} can be also calculated by use of the equation

$$\bar{M}_{nc} = \frac{1.122 \times 10^5 \cdot (1 - w_r)}{(n_a + n_h)} = 2220 \quad (7)$$

(where $w_r = 0.23$, $n_A = 6.6$, $n_h = 32.5$) or by calculation from distribution function $N_c(x)$ - x obtained from the results of fractionation (curve A in Fig. 2) according to Eq. (9) ($\bar{M}_{nc} = 2215$).

The value of number-average molecular weight of linear molecules \bar{M}_{nc} calculated according to equation

$$\bar{M}_{nc} = \frac{86.1}{1 - p_A \cdot r_A^{1/2}} = 2247 \quad (8)$$

(where $p_A \cdot r_A^{1/2} = 0.9617$) is the same as that obtained by calculation (micro-computer HP-85B) from the theoretical distribution curve according to equation

$$\bar{M}_{nc} = \frac{\sum N_c(x) \cdot M(x)}{\sum N_c(x)} \quad (9)$$

where $M(x) = 86.1 \cdot x$ and values of $N_c(x)$ are given by points of the theoretical curve T_A .

The value of the weight-average molecular weight of linear molecules \bar{M}_{wc} calculated from the theoretical distribution curve according to equation

$$\bar{M}_{wc} = \frac{\sum N_c(x) \cdot M(x)^2}{\sum N_c(x) \cdot M(x)} \quad (10)$$

is 4409.

On the presumption that mass of cyclic molecules is negligible ($w_r = 0$), the number-average molecular weight of linear molecules of PEA can be calculated according to equation

$$\bar{M}_{nc} = \frac{1.122 \times 10^5}{n_a + n_h} = 2870 \quad (11)$$

The value of the number-average molecular weight of linear molecules \bar{M}_{nc} calculated according to equation

$$\bar{M}_{nc} = \frac{86.1}{1 - p_B \cdot r_B^{1/2}} = 2896 \quad (12)$$

is the same as that obtained by calculation from the theoretical distribution curve according to eq. (9), where the values of $N_c(x)$ are given by points of the theoretical curve T_B . The value of the weight-average molecular weight of linear molecules \bar{M}_{wc} calculated from theoretical distribution curve according to eq. (10) is 5718.

The values of number-average molecular weights of linear molecules of PEA calculated from results of fractionation of PEA and analytical values of PEA should be the same as those obtained by calculations from theoretical distribution functions. Comparison of the previous results with each other shows that the respective differences are very small. It proves that use of a corrected degree of conversion (expressed as $p_c \cdot r_c^{1/2}$) in eq. (3), which defines the theoretical distribution function, is quite justified. But much greater differences exist between calculated values of weight-average molecular weights of

linear molecules. For instance, on the presumption that $w_7 = 0.23$, the value of the weight-average molecular weight calculated from the experimental distribution function $N_c(x)-x$ (curve A in Fig. 2) according to Eq. (10) is 2600. This is in contrast to the value of $\bar{M}_{wc} = 4409$ calculated from the theoretical distribution function. Possible reasons of this discrepancy will be discussed in the following part.

Using chloroform as solvent and petroleum ether as nonsolvent, the efficiency of stepwise precipitation fractionation is lower than the one of triangle fractionation (as is evident from Fig. 1). The individual fractions did not consist of molecules of only one size but they contained molecules of certain different sizes. Polydispersity of fractions obtained by stepwise fractionation is obviously considerable.¹⁶ That is why the determination of quite precise distribution curves of linear molecules is very difficult and practically impossible. In addition, PEA consisted of both linear and cyclic molecules and actual mass contents (determined experimentally) of both species in fractions and PEA were not known. That is why we have chosen two extreme cases to treat the results of fractionations: On the one hand, the mass contents of cyclic molecules in fractions were neglected; on the other hand, the number-average molecular weights of cyclic molecules in fractions were considered to be equal to the ones of linear molecules. That is why the initial course of experimental curve B is obviously incorrect (the actual mass content of cyclic molecules in the first fraction cannot be negligible). As well, the final course of experimental curve A is obviously incorrect (the actual mass content of cyclic molecules in the last fraction is rather negligible; the position of the last marked point under curve A in Fig. 3 is in favor of it). As it is evident from Fig. 3, however, it makes practically no difference whether the experimental results from fractionation are used for determination of cumulative number distribution curve (and mass distribution functions are then calculated from it) or whether the cumulative mass distribution curve is determined directly from the experimental data (the marked points lie fairly well on curve A in Fig. 3).

However, one important thing is quite obvious. It is evident from Figure 3 and especially from Figure 2 that the real (experimental) distribution, unlike the theoretical "most probable distribution," does not contain linear molecules of the lowest polymerization degrees (ca. $x = 1-8$; polymerization degree $x = 8$ means molecules consisting of four units of adipic acid and four units of ethylene glycol). The number "most probable distribution" comprises the greatest number of molecules of polymerization degree $x = 1$ and the number of molecules decreases as the polymerization degree of the molecule increases. That is why the theoretical curve expressing dependence of $I_c(x)$ resp. $N_c(x)$ on x has a monotonous course over the whole range of x . Possible explanation of the different courses of the theoretical curve and the experimental one is higher reactivity of functional groups belonging to shorter linear molecules. It means that when a certain degree of conversion is reached, first of all, functional groups of shorter molecules have reacted so that the molecules of medium size are created while the reactions of functional groups of medium molecules resulting in formation of long molecules were suppressed for the just-mentioned reason. Then the cumulative number distribution curve can be even S-shaped, which is generally typical for cumulative mass distribution curves of polycondensates.

The formation of a great amount of cyclic molecules is in favor of this opinion. The extensive formation of cyclic molecules can be caused by much higher reactivities of functional groups belonging to shorter molecules.

If the molecules with two terminal hydroxyl groups would occur quite randomly (independent of the length of molecules), then the values of a ratio of the number of hydroxyl groups and the number of carboxyl groups would have to be the same for all fractions and equal to 4.9. As is evident from Table I (see column inscribed with n_h/n_a), the value of this ratio decreases as the figure of fraction increases. Then both side endings of molecules by two hydroxyl groups are obviously more frequent for shorter molecules (considering equal numbers of differently long molecules). Unequal reactivity of functional groups of differently long molecules is possibly responsible for the above-mentioned fact.

As PEA contains both linear and cyclic molecules, the measuring of molecular weight distribution of linear molecules by using GPC could be difficult too. Besides, we did not yet have a liquid chromatograph SP-8100.

PEA was stored in sealed ground glass bottle at laboratory conditions for 20 years. PEA stored by this way was designated as aged PEA. The number-average molecular weight \bar{M}_n of aged PEA was determined by vapor pressure osmometry (a Hewlett-Packard Model 302B VPO) using tetrahydrofuran as solvent: $\bar{M}_n = 1210$. Acid number, hydroxyl number, and saponification number of aged PEA were determined by usual methods (described in experimental part): $n_a = 33.8$, $n_h = 58.9$, $n_s = 627.7$.

Comparing the original acid number (6.6) resp. the original hydroxyl number (32.5) of PEA with the now determined values of respective numbers of aged PEA, it becomes evident that the differences of values of respective numbers are almost equal (27.2 resp. 26.4). Calculation of saponification number of the aged PEA using quantity $r_B = 0.9612$, which characterizes composition of the original PEA (r_B is a ratio of the number of moles of adipic acid and the number of moles of ethylene glycol used for synthesis of PEA), according to equation

$$n_s = \frac{r_B \cdot (n_h - n_a)}{1 - r_B} \quad (13)$$

(where $n_a = 33.8$ and $n_h = 58.9$), results in value 626.2 which is very near to that determined analytically (627.7).

The value of number-average molecular weight \bar{M}_n of aged PEA calculated according to equation

$$\bar{M}_n = \frac{1.122 \times 10^5}{n_a + n_h} \quad (14)$$

(where $n_a = 33.8$ and $n_h = 58.9$) is 1210. This value is practically equal to that determined by vapor pressure osmometric measurement of the aged PEA.

It follows from the above that stored PEA hydrolyzed to a great extent during 20 years, it means that many ester linkages were split off and the number of molecules of poly(ethylene adipate) increased considerably. It

surely results in a changed molecular weight distribution of the aged PEA. As the value of the number-average molecular weight \bar{M}_n of the aged PEA calculated according to eq. (14) does not practically differ from the value of \bar{M}_n determined by vapor pressure osmometric measurement of aged PEA, the aged PEA contains practically no cyclic molecules. On the average, one cleavage occurs for each molecule (both cyclic and linear). As a matter of fact, some original molecules did not hydrolyze at all, while some molecules formed by hydrolysis hydrolyzed again. As evident from Figure 3, the original PEA contained the greatest mass fraction of linear molecules of polymerization degrees ca. 20–30. That is why a great number of molecules of these polymerization degrees should have been split up by hydrolysis.

For determination of molecular weight distribution of aged PEA by GPC measurement, a liquid chromatograph SP-8100 was used. The elution curve (dependence of RI detector signal on elution time) of aged PEA is shown in Figure 4. The system of chromatographic columns used was calibrated by polystyrene standards. Calculation of calibration curve elution volume– M_{pea} valid for poly(ethylene adipate) from calibration curve elution volume– M_{ps} valid for polystyrene by means of constants of Mark–Houwink equation is not possible as constants valid for poly(ethylene adipate) are not known.

Ratios of mean-square end-to-end distance \bar{L}^2 and molecular weight M are designated as $K(M)_{\text{ps}}$ for polystyrene and as $K(M)_{\text{pea}}$ for poly(ethylene adipate):

$$\bar{L}_{\text{ps}}^2/M_{\text{ps}} = K(M)_{\text{ps}} \quad (15)$$

$$\bar{L}_{\text{pea}}^2/M_{\text{pea}} = K(M)_{\text{pea}} \quad (16)$$

Equal values of mean-square end-to-end distances of two different materials should correspond to the equal elution volumes of both materials. Then equation

$$M_{\text{pea}} = M_{\text{ps}} \frac{K(M)_{\text{ps}}}{K(M)_{\text{pea}}} \quad (17)$$

can be written.

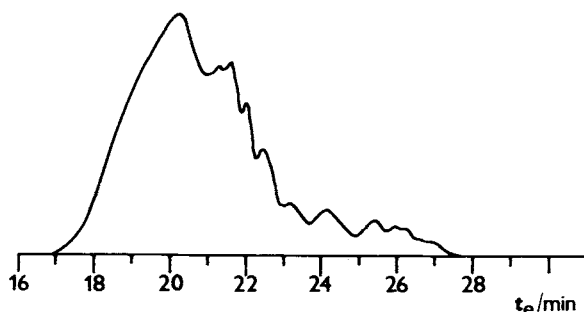


Fig. 4. Dependence of RI detector signal on elution time. Elution curve of aged PEA.

If the values of the ratios of the above-mentioned ratios of two different materials do not change to a great extent as molecular weight changes, the values of the ratios of the unperturbed mean-square end-to-end distance and molecular weight (\bar{L}_0^2/M) of both materials, if they are known, are often used to calculate the calibration GPC curve valid for measured material from the known calibration GPC curve of other material. Anyway, the value of \bar{L}_0^2/M valid for poly(ethylene adipate) is not known. However, the ratio $K(M)_{ps}/K(M)_{pea}$ can be assessed²⁸ as a ratio of the number-average molecular weight \bar{M}_n of aged PEA determined by VPO ($\bar{M}_n = 1210$) and the apparent number-average molecular weight \bar{M}_{na} of aged PEA calculated from the results of GPC measurement of aged PEA by using the GPC calibration curve valid for polystyrene ($\bar{M}_{na} = 1520$). Calculated value of the ratio $K(M)_{ps}/K(M)_{pea} = 0.79$. It means that the value of the ratio \bar{L}_0^2/M valid for poly(ethylene adipate) is rather higher than that valid for polystyrene. It corresponds to the general trend that the values of ratios \bar{L}_0^2/M valid for various polyesters are something higher than that stated for polystyrene.²⁹

Figure 5 shows the cumulative mass distribution curve of aged PEA determined from results of GPC measurement of aged PEA and the theoretical cumulative mass distribution curve calculated according to equations²⁷

$$w(x) = x \cdot (1 - p \cdot r^{1/2})^2 \cdot (p \cdot r^{1/2})^{x-1} \quad (18)$$

$$J(x) = \sum_1^x w(x) \quad (19)$$

The corrected degree of conversion $p \cdot r^{1/2}$ of aged PEA was calculated by means of the equation

$$\bar{x}_n = \frac{1}{1 - p \cdot r^{1/2}} \quad (20)$$

where $\bar{x}_n = \bar{M}_n/86.1$. As $\bar{M}_n = 1210$, $p \cdot r^{1/2} = 0.928$.

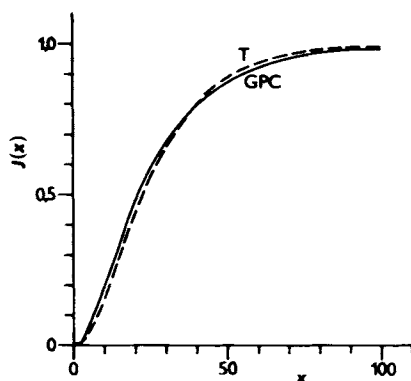


Fig. 5. Dependence $J(x)$ - x for aged PEA. Cumulative mass distribution curves determined from GPC measurement (—) and from theory according to eqs. (18) and (19) (- -).

As evident from Figure 5, both distribution curves differ only a little. As well, the values of weight-average molecular weights calculated from distribution curves given in Figure 5 differ only a little [\bar{M}_w (GPC) = 2270, $\bar{M}_w(T)$ = 2300]. So, it can be said that molecular weight distribution of aged PEA is very near to the theoretical "most probable distribution" of molecular weights.

CONCLUSION

Precipitation fractionations of PEA by addition of nonsolvent according to stepwise and triangle schemes enabled preparation of greater quantities (ca. 5 g) of polyester fractions. The efficiency of stepwise precipitation fractionation using chloroform as solvent and petroleum ether as nonsolvent and obtaining 10 fractions is lower than the efficiency of triangle fractionation. It was found out that PEA contained 23 mol % of cyclic molecules. The molecular weight distribution curves of linear molecules determined from results of fractionations of PEA were found to differ rather from distribution calculated according to the theory of kinetics of polycondensation and statistical theory. The theoretical "most probable molecular weight distribution" appears to be wider than those determined experimentally from results of fractionations of PEA. Possible explanation of an essential reason of this discrepancy can be higher reactivity of functional groups belonging to shorter molecules.

It was found out that stored PEA hydrolyzed to a great extent. The aged PEA contains practically no more cyclic molecules and its number-average molecular weight (1210) is much lower than the one of original PEA (2180). Molecular weight distribution of aged PEA determined by GPC is very near to the theoretical "most probable distribution" of molecular weights.

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