should compensate for the titer of the reactants, since the diesters are probably only 95–98% pure. Care should be taken to precipitate polymer to remove impurities such as hydroquinone. Solutions should be filtered before precipitation to remove PbO. Polymer should be dried overnight on the vacuum line with a cold trap.

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Gel Permeation Chromatography of Nominally Linear Aliphatic Polyesters

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In the course of studies[1–4] on structure–property relations in essentially linear aliphatic polyesters, we have examined the molecular weight distribution of some of these condensation polymers by gel permeation chromatography (gpc). Flory[5] has shown that, when made under equilibrium conditions and of sufficiently high molecular weight, these polymers should have the so-called "most probable" distribution of molecular weights, an important characteristic of which is that the breadth parameter $\bar{M}_w/\bar{M}_n = 2.0$. In our previous work,[3] we assumed this to be true for polyesters we synthesized by the direct esterification technique of Carothers.[6] The purpose of this paper is to point out that, probably as a result of side reactions during synthesis,[7] values of $\bar{M}_w/\bar{M}_n$ significantly higher than 2.0 are sometimes obtained in aliphatic polyesters made with nominally bifunctional reagents.

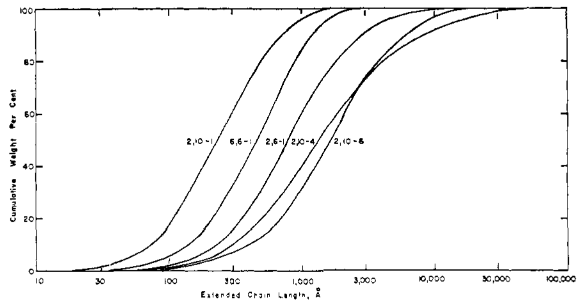

Figure 1. Cumulative molecular size distributions of nominally linear aliphatic polyesters by gel permeation chromatography.

Experimental Section

The synthesis of the polyesters of the 2,6; 2,8; 2,10; 4,6; and 6,6 types[8] used in this work has been described elsewhere.[3]

Gel permeation chromatography[9,10] was performed in a Waters Model 100 gel permeation chromatograph[11] using tetrahydrofuran as solvent at 37°. Columns with Waters designations 10^6, 10^5, 3×10^4, and 9×10^2 Å were used at a standard flow rate of 1 cc/min. Although tetrahydrofuran is not a good solvent for these polyesters, all of the samples were completely soluble at the operating temperature.

The column system had a plate count of 720 plates/foot. The system was calibrated with narrow-distribution polystyrenes,[12] and the convention of expressing results in terms of equivalent fully extended chain lengths was adopted. No corrections for axial dispersion (zone broadening) were made; it is not expected to have a major effect on the results with the relatively broad distribution samples studied. Cumulative and differential molecular weight distributions and weight- and number-average chain lengths were calculated on a digital computer, using the scheme described in the Waters instruction manual and by Cazes.[10]

For some of the samples, number-average molecular weights were determined by vapor phase osmometry[13] using a "Mechrolab" Model 302 vapor pressure osmometer.[14] Chloroform was used as solvent at 37°, and calibration was made with benzil.

Intrinsic viscosities were measured for a few of the polyesters in chloroform solution at 25°, using a Cannon–Ubbelohde viscometer, size 25.

Results

Table I summarizes the experimental results, expressed as number-average and weight-average chain lengths, $\bar{A}_n$ and $\bar{A}_w$, respectively. Values of $\bar{M}_n$, by vapor phase osmometry, and of the intrinsic viscosity are reported in Table II. A few typical cumulative molecular weight distributions are shown in Figure 1.

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(10) J. Cazes, *J. Chem. Educ.*, **43**, A567, A625 (1966).

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(12) Pressure Chemicals Co., Pittsburgh, Pa., ArRo Laboratories, Joliet, Ill., or Waters Associates, Framingham, Mass.

(13) J. Van Dam, *Rec. Trav. Chim. Pays-Bas*, **83**, 129 (1964).

(14) F & M Scientific Division, Hewlett-Packard Corp., Avondale, Pa.

TABLE I
NUMBER- AND WEIGHT-AVERAGE MOLECULAR SIZES OF NOMINALLY LINEAR ALIPHATIC POLYESTERS

Polymer type	Sample	$\bar{A}_n$, Å	$\bar{A}_w$, Å	$\bar{A}_w/\bar{A}_n$
Poly(ethylene adipate)	2,6-1	340	690	2.0
	2,6-2	360	710	2.0
	2,6-3	430	1190	2.7
	2,6-4	690	1590	2.3
	2,6-5	950	2170	2.3
Poly(ethylene suberate)	2,8-1	440	1000	2.3
	2,8-2	480	1030	2.1
	2,8-3	610	1500	2.5
	2,8-4	690	1580	2.3
Poly(ethylene sebacate)	2,10-1	175	390	2.2
	2,10-2	460	1440	3.1
	2,10-3	530	1300	2.5
	2,10-4	830	4050	4.9
	2,10-5	850	4000	4.7
	2,10-6	1000	3050	3.1
Poly(tetramethylene adipate)	4,6-1	520	1190	2.3
	4,6-2	580	1540	2.7
Poly(hexamethylene adipate)	6,6-1	570	1560	2.7
	6,6-2	1140	4500	4.0

TABLE II
NUMBER-AVERAGE MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES OF NOMINALLY LINEAR ALIPHATIC POLYESTERS

	This work		Ref 4	
Sample	M_n	$[\eta]$, dl/g	M_n	$[\eta]$, dl/g
2,6-1	7,000	0.335	16,300	0.548
2,6-2	7,600	0.340	12,600	0.440
2,6-3	9,400	0.443	34,500	1.140
2,8-2	14,400		18,800	0.646
2,8-3	18,200	0.536	50,000	0.914
2,8-4	19,500		22,300	0.790
2,10-1	5,500		5,700	0.256
2,10-2	18,800		17,900	0.719
4,6-1	9,800	0.460	21,200	0.800
4,6-2	12,800	0.530	58,000	0.932
6,6-1	8,100	0.521	23,000	0.560
6,6-2	16,300	1.018	45,000	1.050

TABLE III
EXPERIMENTAL AND THEORETICAL GPC *Q* VALUES FOR NOMINALLY LINEAR ALIPHATIC POLYESTERS

Sample	$\bar{M}_n$	Experimental *Q*	Theoretical *Q*
2,6-1	7,000	20.6	14.6
2,6-3	9,400	21.8	14.6
2,8-2	14,400	30.0	14.0
2,8-3	18,200	29.8	14.0
2,8-4	19,500	28.2	14.0
2,10-1	5,500	31.4	13.5
2,10-2	18,800	40.8	13.5
4,6-1	9,800	18.8	14.0
4,6-2	12,800	18.8	14.0
6,6-1	8,100	14.2	14.6
6,6-2	16,300	14.3	14.6

It is pertinent to note that the broadened molecular weight distributions found in some of these polyesters do not appear to result from the presence of high or low molecular weight "tails," but instead from a general expansion of the range of molecular weights covered in the sample, as indicated by differences in the slope of the cumulative distribution curve in the center portion (say 30–70% of the sample) as well as at the extremes.

Strictly speaking, the above statements refer to molecular size rather than weight, since this has been amply demonstrated to be the basis of the gpc separation. If one were to assume that there are no branched species present, the ratio $\bar{A}_w/\bar{A}_n$ could be taken equal to $\bar{M}_w/\bar{M}_n$. Values of $\bar{A}_w$ and $\bar{A}_n$ can be related to $\bar{M}_w$ and $\bar{M}_n$, respectively, by multiplication by the so-called "*Q*" factor, the mole weight per unit extended-chain length. If specific chemical effects were absent in the gpc separation and if all the species present were linear, experimental and theoretical values of *Q* should be in good agreement; often, this is not the case.

For these polyesters, theoretical values of *Q* were calculated using X-ray diffraction data[15] on the crystal unit cell *c* axis length (16.9 Å) of poly(ethylene sebacate), the 2,10 polyester. In the crystal, the molecular chain is essentially fully extended. For the other polyesters, 2.54 Å was subtracted for each pair of $-CH_2-$ groups removed to give the 2,8 and 2,6 polymers. It was assumed that the 2,8 and 4,6 polymers had the same fully extended length, and similarly the 2,10 and 6,6.

These theoretical values of *Q* are compared in Table III with experimental *Q*'s obtained by dividing values of $\bar{M}_n$ from vapor phase osmometry by corresponding $\bar{A}_n$'s. Although experimental *Q*'s for different samples of any single polyester are reasonably consistent, the large and erratic differences between experimental and theoretical *Q*'s furnish strong evidence of the unsatisfactory nature of the *Q*-factor approach to gpc calibration.

Where possible, values of $\bar{M}_n$ and $[\eta]$ were checked against those reported earlier[4] for the same samples. In many cases, large discrepancies were found, suggesting molecular weight degradation of the samples in the 3–4-year period between the two determinations. The data, summarized in Table II, led us to study alternate synthesis conditions for these polyesters.[7] The new data are too fragmentary to allow reevaluation of the viscosity–molecular weight relationships published previously,[4] but they should be used with caution.

We conjecture that the most likely cause for the discrepant results observed in this work is small amounts of chain branching introduced in the synthesis step, by the presence of traces of polyfunctional impurities or by mechanisms not yet elucidated. In one instance, in fact, we saw evidence of gel formation toward the end of the polycondensation.

The competing effects of broadened molecular weight distribution and the reduction of hydrodynamic volume accompanying branching at constant molecular weight

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[15] C. S. Fuller, *Chem. Rev.*, **26**, 143 (1940).

would alter the apparent value of $\bar{A}_w/\bar{A}_n$ obtained by gpc in opposite directions. It is not possible to predict which effect would predominate from the data at hand. Branching might also be expected to lead to species more susceptible to degradation, but we have no specific evidence on this point.[16]

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(16) See also V. V. Korshak, *Dokl. Akad. Nauk SSSR*, **64**, 525 (1949).

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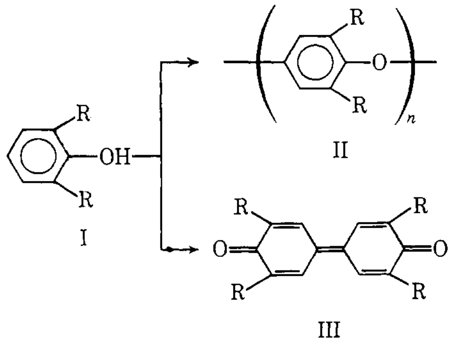
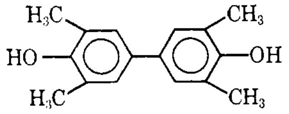
Communications to the Editor

Poly(2,6-diphenyl-1,4-phenylene oxide)

The oxidative polymerization of 2,6-disubstituted phenols with oxygen in the presence of amine complexes of copper(I) salts as catalysts has been shown to yield aromatic polyethers (II) or diphenoquinones (III) as products.[1,2] It has also been shown that by increasing the size of the substituents, R, diphenoquinone formation is favored.[3] It has been further demonstrated in the oxidation of 2,6-dimethylphenol that increasing the temperature of the reaction also increases the amount of diphenoquinone formed.[4] In fact by raising the reaction temperature from 25 to 100° the reaction changes from one that gives predominantly C–O coupling to one that gives predominantly C–C coupling. Endres[4] has suggested that this behavior may be due to the presence of at least two catalytic species in the reaction, one of which favors C–O coupling and the other C–C coupling and that the latter predominates at high temperatures.

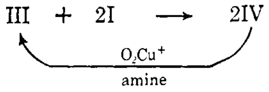


We subsequently found that tetramethyldiphenoquinone reacts very rapidly with 2,6-dimethylphenol at 100° in the presence of amines to give predominantly (85%) the C–C coupled product (IV).[5] Hence, in the



IV

polymerization of 2,6-dimethylphenol at elevated temperatures the predominant reaction becomes



Oxidation of 2,6-diphenylphenol[6] with oxygen in pyridine solution at room temperature using copper(I) chloride as catalyst yields as product only low molecular weight polymer as well as substantial amounts (~50%) of the diphenoquinone. An examination of molecular models indicated that it should be feasible to prepare high molecular weight poly(2,6-diphenyl-1,4-phenylene oxide) (II, R = phenyl); therefore this problem was examined further.

We have found that the most active catalysts for oxidative coupling reactions are obtained by using bidentate amines such as N,N,N′,N′-tetramethylethylenediamine (TMEDA) as ligands for the catalyst;[2,7] hence, this class of catalysts was examined for the oxidative polymerization of 2,6-diphenylphenol.

At 30° with a catalyst consisting of equimolar amounts of copper(I) chloride or copper(I) bromide and TMEDA as catalyst only polymers with low intrinsic viscosities (~0.1 dec/g in $CHCl_3$ at 25°) were obtained. Surprisingly, in contrast to our experience with oxidative polymerization of 2,6-dimethylphenol, as the temperature of the reaction mixture was raised polymers with higher intrinsic viscosities were obtained and above 60° high molecular weight polymers were readily obtained with only small amounts of the diphenoquinone as a by-product. An example of the polymerization of 2,6-diphenylphenol follows.

To a 250-ml wide-mouthed erlenmeyer flask equipped

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