Comparative Gel Permeation Chromatography Calibration Techniques in Oxidative Coupling Polymerization

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Synopsis

Gel permeation chromatography was utilized in measuring the kinetics of the oxidative coupling polymerization of 2,6-dimethylphenol. The elution curves at the early stages of reaction were analyzed by two methods of calibration, specifically by comparison to the elution times of oligomers up to the 6-mer level, and by the classical counts method. The two methods give similar results, both indicating a polymerization pattern of the general condensation type and increasing dispersity of molecular weight with degree of polymerization.

INTRODUCTION

Gel permeation chromatography (GPC), has been widely used to determine molecular weight distributions and also to study mixtures of molecules.[1] With this technique it is possible to analyze the whole reaction mixture in a polymerization at various times and thus determine the composition from the GPC elution curves. This method presents an obvious advantage in that it avoids the problems and errors associated with the recovery and separation of polymeric species. We have used this technique in analyzing a number of polymerizations and have checked its reproducibility.

In the presence of a copper complex catalyst and an amine, under oxygen flow, 2,6-dimethylphenol is converted by oxidative coupling to polyphenylene ether.[2] To date neither the kinetics nor catalytic activity descriptions have been complete. Generally, the oxygen consumption during the polymerization is followed volumetrically and the viscosities of various samples of the reaction mixture, obtained at various times, are determined.[3] The kinetic pattern is then based on these viscosities. In the oxidative coupling of 2,6-dimethylphenol, a pattern of molecular weight growth analogous to condensation polymerization has been observed and a scheme rationalizing it has been suggested by Hay.[4]

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Obviously the viscosity data are of limited value in the early stages of polymerization. In the light of this, gas phase chromatography has been utilized to follow monomer disappearance and to measure the concentrations of the very low molecular weight species.[5]

Since GPC is capable of defining the species present at both early and late stages of reaction,[1] support for a given mechanism can be forthcoming from such analyzes. Moreover, since the growth of polymer from 2,6-dimethylphenol is by a stepwise coupling, a unique opportunity exists to test a number averaging rather than a time-size averaging to GPC analysis. The value of such a comparison has been emphasized by Tung.[6]

This paper reports our observations on polymer growth by GPC. In a future report we will elaborate on the kinetics and mechanism of polymerization.

EXPERIMENTAL

2,6-Dimethylphenol monomer was purified by recrystallization several times from n-hexane and then filtered through alumina or decolorizing carbon.

Pyridine, decane, and chloroform were used as received.

The catalyst was methanol green: cuprous chloride obtained by reduction of cupric chloride by ascorbic acid[7] was stirred 20 hr in methanol under oxygen in the presence of pyridine. The solid formed was filtered, washed, and dried. It is a green powder having the formula $(C_5H_5NCuClOCH_3)_2$.

The polymerization reactions were carried out at atmospheric pressure and generally at room temperature under stirring and O_2 flow with $MgSO_4$ as the drying agent. A typical reaction mixture contained 1 g of monomer in 30 ml $CHCl_3$ with 40 mg of catalyst, 200 mg of pyridine, 200 mg of decane as an internal standard, and O_2 at 550 ml/min. Small samples were removed every minute and the catalyst was killed by 2,2'-bipyridine. The role of the latter is to stop the continuous interchange between the two forms of Cu(I) and Cu(II) complexes. In some cases, N,O-bis(trimethylsilyl) acetamide was added to silylate the OH endgroups, thus avoiding further reaction, such as redistribution,[8] during heating for GPC analysis.[9] It was not possible to calculate the number of OH groups present by the quantity of Si reagent consumed, since this measure is too sensitive to moisture.

In the GPC analyses, 50 μl of the solution in 2 ml tetrahydrofuran was injected (2 min, flow rate 1 ml/min) into a Waters Associates Model 200 GPC apparatus using tetrahydrofuran (THF) as solvent and equipped with three columns of crosslinked polystyrene gel of pore diameters 100, 250, and 400 Å, respectively. Since the behavior of higher oligomers in the GPC is unknown, we used calibration curves based on polystyrene and poly(propyleneglycol) standards, and chose average values given either by plotting log-extended chain length or molecular weight versus elution volume. For the low molecular weight components the calibration was made directly with pure materials. It was found that the silylated com-

pounds fell on the general curve if one assigned to them an increase in molecular weight of 75 and an increase in length of 2 Å. In assigning a length to the repeating unit in the polymer, various values found in the literature for the dimensions of small compounds with phenyl rings were considered,[10,11] but the best agreement was obtained with the value of 5.34 Å given by Barrales-Rienda and Pepper.[12]

The resolution of the columns, determined classically with orthodichlorobenzene, was 835 plates/ft, i.e., a total of 10,000 theoretical plates. The efficiency of various sets of columns was checked with different polymers and various small molecules. For instance, with a nominal 100 Å column the separation was effective for low molecular weight species but decreased very sharply for polymers of chain length higher than 120 Å. With the set 100–250–400 Å we were able to get satisfactory analyses of the oligomers and polymers from the beginning of polymerization up to a large extent of reaction.

RESULTS AND DISCUSSION

The elution curves of the total polymerization mixture for both "killed catalyst" and silylated samples at reaction times of 2, 9, and 14 min are shown in Figure 1.
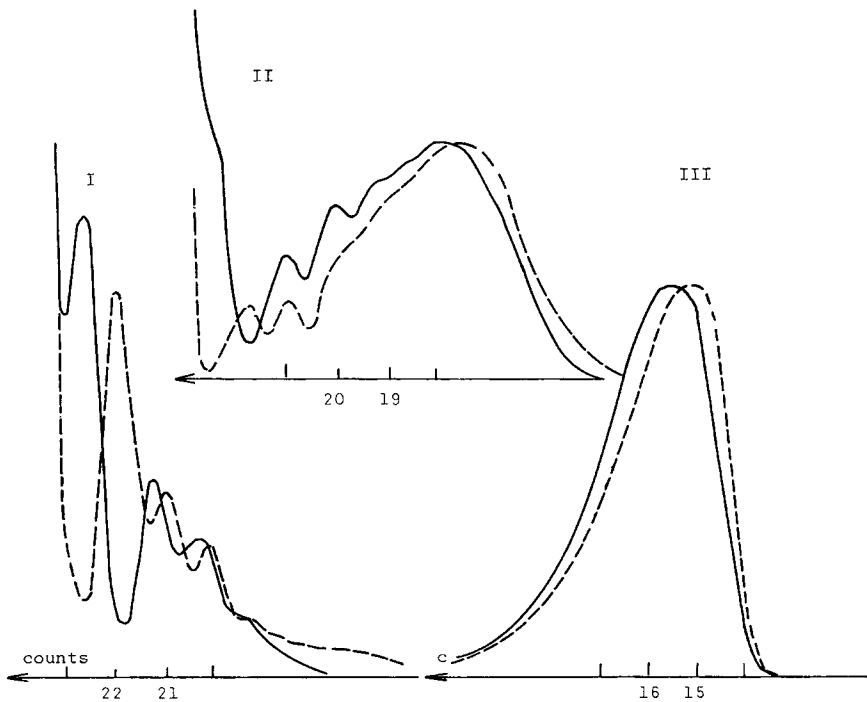

Fig. 1. Elution curve at different times: (I) 2 min; (II) 9 min; (III) 14 min (—) before silylation; (– – – –) after silylation.

TABLE I

Description of the 6-Minute Elution Chromatogram. Analysis by n-Mer vs. Counts Methods[a]

	Native					Silylated				
	H	H/A	$H \cdot A$	H/M	$H \cdot M$	H	H/A	$H \cdot A$	H/M	$H \cdot M$
$n = 1$ (monomer)	150	28	800	1.230	18 300	61	8.25	451	0.314	11 900
2	56	5.20	600	0.231	13 600	35	2.69	465	0.111	11 000
3	49	3.04	785	0.135	17 700	24	1.40	445	0.055	10 450
4	28	1.30	602	0.058	13 500	16	0.67	380	0.029	8 900
5	24	0.92	640	0.040	14 400	11	0.39	306	0.016	7 420
6	16	0.50	512	0.021	11 500	8	0.23	272	0.010	6 350
7	11	0.30	400	0.013	9 250	5	0.13	192	0.005	5 000
x	4.5	0.06	315	0.002	9 500	2	0.03	150	0.001	4 000
y	3	0.03	270	0.001	9 600	1	0.01	100	—	3 000
$\sum$ Without monomer	191.5	11.37	3 824	0.501	99 050	102	5.55	2 761	0.227	56 120
$\sum$ With monomer	341.5	39.37	4 624	1.731	117.350	163	13.80	3 212	0.531	68 120
$c = 22$	17	2.42	119	0.100	3 740	60	8.60	420	0.35	10 200
21	63	5.72	692	0.242	16 400	36	3.30	395	0.14	9 350
20	63	3.70	1 070	0.165	23 900	19	1.11	323	0.05	7 220
19	50	2.18	1 150	0.093	27 000	21	0.91	483	0.04	11 350
18	32	1.06	1 000	0.043	24 000	16	0.53	480	0.02	12 000
17	13	0.09	585	0.010	16 900	9	0.20	405	—	11 700
16	3	0.04	225	0.001	7 800	2	0.26	152	—	5 200
$\sum$ Without monomer	241	15.01	4 841	0.654	119 740	103	6.31	2 538	0.25	56 820

[a] n = number of mers of the polymer chain; c = number of counts of the elution curve at a count or a n-mer; H = height in the elution curve; A and M = corresponding size and weight.

TABLE II
Different Values of the Degree of Polymerization at 6 Minutes, Based on n-Mer and Counts Calculations[a]

Way of calculation	Counts method	n-Mer method		Counts method	n-Mer Method	Polydispersity
Native						
$\bar{M}_n$	368	383	$\bar{M}_w$	497	517	1.35
$\bar{X}_n$	3.06	3.16	$\bar{X}_w$	4.15	4.3	
$\bar{A}_n$	16.05	16.9	$\bar{A}_w$	20	20	
$\bar{X}_n$	3	3.16	$\bar{X}_w$	3.75	3.75	1.22
Silylated $\bar{M}_n$	412	450	$\bar{M}_w$	550	550	
$\bar{X}_n$ after correction[b]	3.43	3.75	$\bar{X}_w$	4.15	4.3	1.35
$\bar{A}_n$	2.81	3.13	A_w	3.81	4.24	
$\bar{X}_n$	16.3	18.3	$\bar{X}_w$	24.6	22.6	
after correction	3.05	3.43		4.6	4.22	
	2.68	3.06		3.27	3.73	1.22

[a] A_n = Number-average size; A_w = weight-average size.
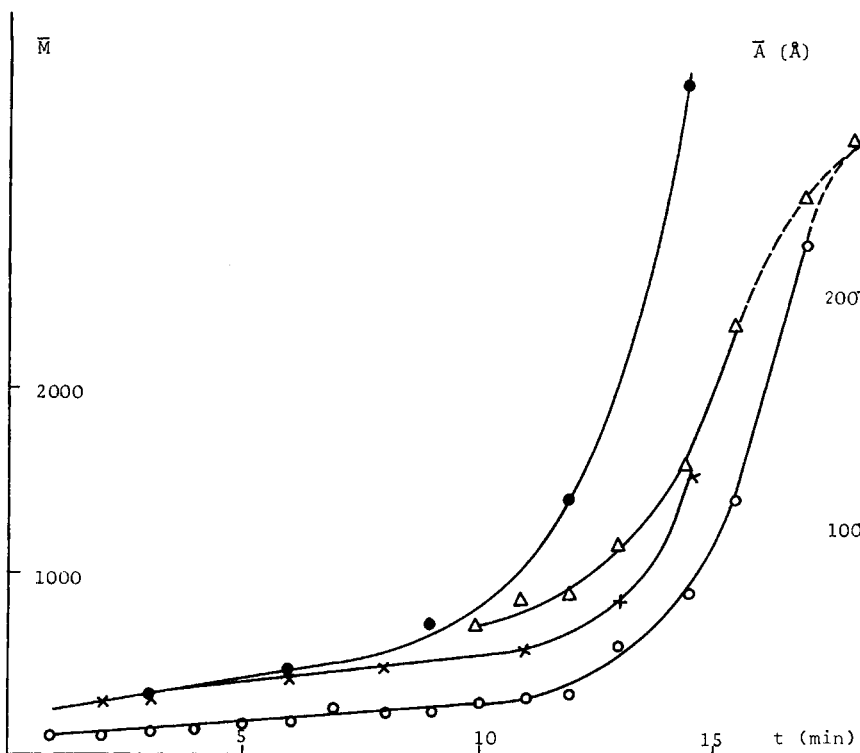[b] Correction for silylation.

Fig. 2. Evolution of average molecular weight vs. time: (×) unsilylated samples $\bar{M}_n$; (●) unsilylated sample M_w; (○) silylated sample $\bar{A}_n$; (△) silylated sample $\bar{A}_w$.

The maxima in the chromatogram are due to monomer and to low molecular weight compounds (oligomers) present in the early stages of the reaction. Intermediate molecular weight species appear after some minutes. With time, the ultimate maximum in the elution curve appears and is moved progressively toward high molecular weights and finally polymer. The last position of the curve, I–III, is limited by the maximum pore size of the columns.

Two methods have been used to evaluate these curves. The first was that generally applied,[13] wherein heights at each count were measured and were related to a chain length A or a weight M as determined by the calibration of the columns. This method as used here is called the count method and is referred to as c in the tables. It gave good results only when the chromatograms had sufficiently definite maxima.

The second method was possible since, at the beginning of the reaction, the elution curve is polynodal in nature. We assumed Gaussian shapes for these peaks[6] of the different low components of the reaction mixture and decomposed the total curve in a sum of independent peaks. We then measured their heights H. Since the polymerization in its early stages is a stepwise process, each of these low molecular weight peaks represents a discrete degree of polymerization. Verification was made with pure com-

TABLE III

Evolution of the Degree of Polymerization with Time, Based on n-Mer and Counts Calculations[a]

	Method		Time, min								
			2	3	6	8	9	11	12	13	14.5
$\bar{X}_n$, Native	L	c	2.02	2.2	3	4.3	4.6	5.1	6	6.4	11.2
		n	2.5	2.7	3.16	3.55	4	4.4	5.9	7	10.5
	W	c	2.12	2.31	3.06	3.94	4.65	6.6	7.9	9.1	15.9
		n	2.5	2.6	3.19	4	4.45	4.8	6.8	8	13
		n^x	1.2	1.25	1.65	2.2	2.6	3.7	5.2	6.8	13
$\bar{X}_n$, Silylated	L	c	2.5	2.5	2.7	3.4	3.9	4.6	4.9	8.3	13
		c^x	1.25	1.3	1.66	2.48	2.95	3.5	4	7.6	13
	W	c^x	2.08	2.54	2.7	3.6	3.8	5.5	6	7.3	10.2
		n	1.15	1.21	1.65	2.2	2.43				
		n^x	2.37	2.64	3.14	4.65	4.9	5.9	6.8	8.5	12.8
$\bar{X}_w$, Native		n^x	1.27	1.41	2.16	2.75	3.4	4.6	6.2	8	12.8
		n	2.6	2.7	3.75	5	5.6	6.7	7.8	8.7	15.5
$\bar{A}_w$, Å	L	c	2.34	2.62	3.75	5.23	5.8	8.6	10.5	12.9	16.1
		c	12.5	14	20	28	31	46	56	69	86
$\bar{A}_w$, Silylated		c	16	17.7	24.6	29.2	33.6	65	67	90	125

[a] L and W = Calibration by length and weight; x = monomer included in the calculation at counts c or n-mers n.
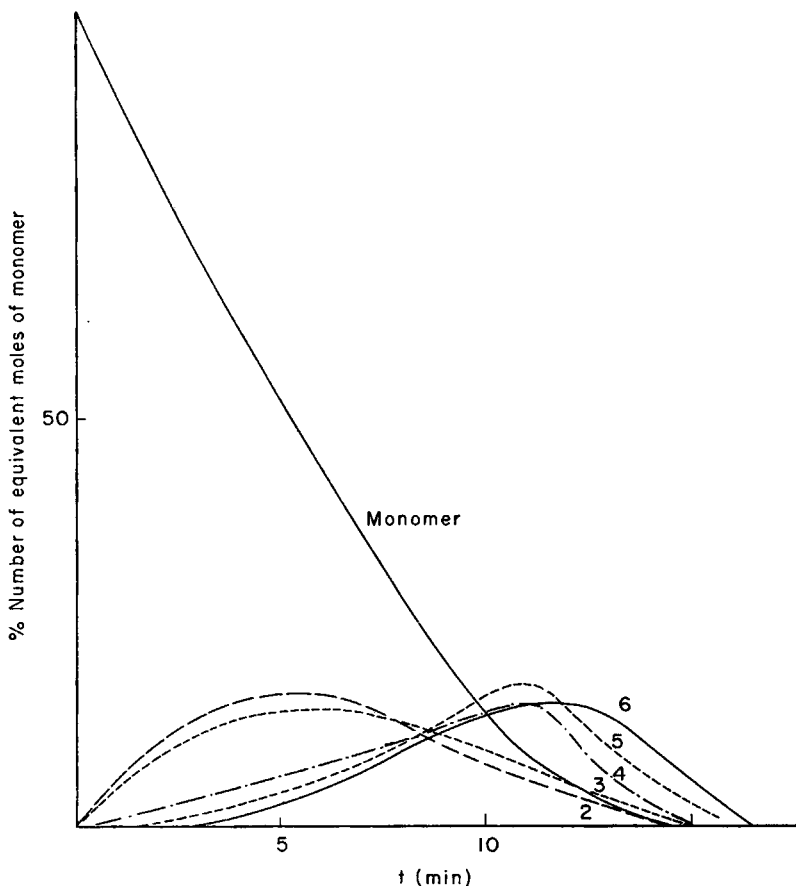
Fig. 3. Evolution of the first oligomers vs. time.   Concentrations calculated in equivalent number of moles of monomer $H/\Sigma H$ of the GPC analysis of native samples.

pounds.   For the highest components, where the columns are incapable of separating the components into their unique compounds, the curves were considered in the classical way.   This method is called the n-mer method and is defined by n in the tables.

Measurements made on a 6-min chromatogram of the type shown in Figure 1 and the calculations based on them are shown in Table I.   Summation of the total mixture is made with and without monomer, and the degree of polymerization is calculated for both cases.   The first summation is used to obtain a complete balance of reaction species.   This technique is only possible with precision with the n-mer method since height at a given position on the chromatogram by the count method c does not generally correspond to a definite compound.

The results for $\bar{A}_n$, $\bar{A}_w$, $\bar{M}_n$, and $\bar{M}_w$ at $t = 6$ min are shown in Table II. Here the comparison of degrees of polymerization allows the comparison of the two methods (c and n).   The values for silylated samples are corrected in the following manner.   By definition, $\bar{M}_n = (\Sigma n_i M_i)/(\Sigma n_i)$;

when silylated $SM_i = M_i + 73$, the corrected $\bar{M}_n$ is $[(\Sigma n_i SM_i)/(\Sigma n_i)]$ — 73. The same correction was applied for $\bar{A}_n$.

The evolution of polymer growth obtained by these independent methods, counts and n-mers, for both native and silylated samples, is shown in Table III and Figure 2. If the monomer is included in the calculation of the number of molecules of the reaction mixture, the $\bar{X}_n$ values (the number-average degree of polymerization) are naturally lower at the beginning of the reaction. From the table it is seen that the polydispersity of the oligomers increases slowly from 1 to 1.5 at times 2 min and 14.5 min, respectively. These same results are found again for the polymers where dispersity increases with increasing molecular weight. As can be seen from Figure 2, the evolution of $\bar{X}_n$ with time follows the pattern generally found in condensation polymerization and thus supports previous observations.[4]

Comparison of the data in Tables II and III shows the two methods of analysis to be in increasingly good agreement as the molecular weight rises. Even at the low trimer and hexamer stages the agreement is very good.

By the n-mer method a very detailed analysis of the low polymers is possible and consequently considerable insight into mechanisms can be had. Discrete species can be followed from minute to minute during a polymerization. In the present case the mole-% concentrations of the species, up to $n = 6$, were followed during the early stages of polymerization and are shown in Figure 3.

With a still greater selection of columns, there is no doubt that this level of analysis could be followed to still higher molecular weights.

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