Notes

Poly(2,6-dimethyl-1,4-phenylene oxide) with Narrow Molecular Weight Distribution via Methylene Chloride Complexation

D. M. WHITE

General Electric Company, Corporate Research and Development, Schenectady, New York 12301.

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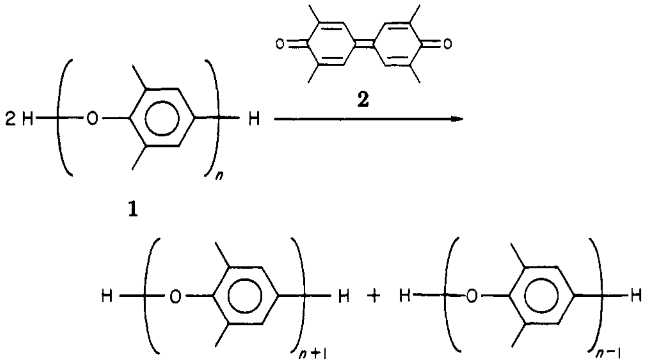
Narrow molecular weight distribution (MWD) poly(2,6-dimethyl-1,4-phenylene oxide)s, 1, are not readily attainable by normal fractionation methods due to a redistribution reaction[1] that broadens the MWD during fractionation. Traces of oxidizing agents such as 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (2) initiate this disproportionation, as in the following example:



We have found that a polymer with very narrow molecular weight distribution can be prepared by utilizing the redistribution reaction. When low oligomers (e.g., the trimer) redistribute slowly in methylene chloride, a solvent known[2] to interact with 1 forms a complex which then precipitates from the methylene chloride solution. In this preparation, trimer redistributes to dimer and tetramer. These oligomers redistribute further to form lower and higher oligomers. Eventually, a sufficient quantity of oligomer with molecular weight required to form a methylene chloride complex is generated. Removal of the high oligomers as the insoluble complex induces formation of additional high oligomers as the system seeks to attain equilibrium, and the newly formed high oligomers also precipitate. The process can be represented by the scheme:

$$\text{trimer} \rightleftarrows \text{monomer} + \text{dimer} + \text{tetramer} + \ldots + 1 \xrightarrow{CH_2Cl_2} [\text{insoluble complex}]$$

The molecular weight of the isolated, dried (methylene chloride free) polymer is ca. 1700, and the dispersivity is low ($\bar{M}_w/\bar{M}_n < 1.10$). The molecular weight represents a value slightly above the minimum value required for complexation with methylene chloride. The narrow MWD suggests that the rate of precipitation is sufficiently rapid under the prevailing reaction conditions to prevent a buildup of even higher oligomers.

The redistribution of the trimer with 2 as initiator resulted in 1 with a very narrow MWD. Incipient precipitation of the methylene chloride complex from a solution of 2 g of pure trimer in 20 mL of methylene chloride at 0 °C was noted within 1 week. Isolation of the complex on the 12th day by filtering, washing (methylene chloride, then methanol), and drying afforded 0.25 g of 1. Molecular weight measurement by gel permeation chromatography (GPC) showed values of $\bar{M}_w$ and $\bar{M}_n$ to be 1800 and 1680, respectively. Light scattering and osmometric measurements on samples of 1 and the acetate of 1 (described below) confirmed the GPC measurements. Spectral analyses (^1H and ^{13}C NMR, and IR hydroxyl end group analysis) were consistent with a linear product with structure 1 and $\bar{M}_n$ 1680. An additional quantity of 1 with properties similar to the first crop was isolated when the filtrate from the first isolation step had been stored at 0 °C for 1 week.

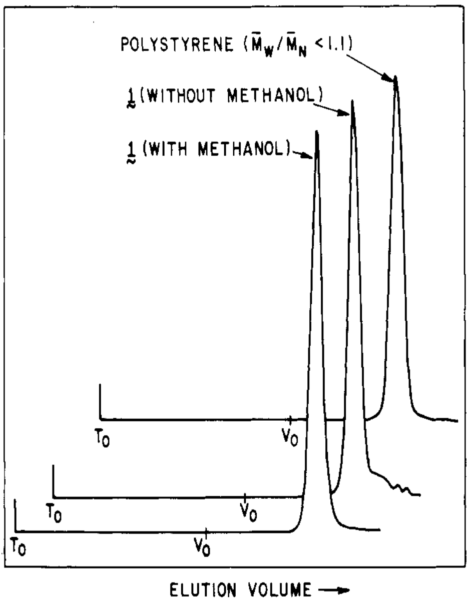


Figure 1. Gel permeation chromatograph of narrow MWD 1 with and without a methanol washing step during isolation and of a commercial standard narrow MWD polystyrene with a molecular weight of 2100, using a Waters Associates, Inc., LC, Model ALC/GPC 244, equipped with μ-styragel columns (10^5, 10^4, 10^3, 500 Å) in tetrahydrofuran. T_0 is time zero; V_0 is the exclusion limit of the columns.

The product 1 was stable toward redistribution at 25 °C in the dark in the solid state but tended to redistribute upon dissolution in many organic liquids. Addition of triethylamine to the solvent retarded the rate of redistribution and allowed satisfactory analysis by GPC.[3]

Omission of the methanol washing step during isolation left a deposit of low oligomers on the product due to evaporation of traces of residual methylene chloride solution. The GPC curves after both workups (Figure 1) have main product peaks of identical sharpness and molecular weight, but when methanol was omitted, there were residual lows which increased the dispersivity ($\bar{M}_w/\bar{M}_n$ is 1.12). For comparison, the GPC curve of a polystyrene standard (molecular weight 2100; $\bar{M}_w/\bar{M}_n < 1.10$) is also presented.

Acetylation of a portion of the first crop of 1 with acetic anhydride in pyridine followed by precipitation with methanol produced the acetate 3: $\bar{M}_n$ (GPC) 1720, $\bar{M}_w$

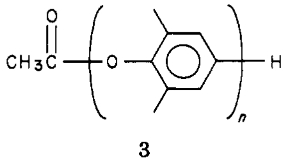


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Table I
Narrow Molecular Weight Distribution Polymers from Low Oligomers

fraction no.	wt, g	$\overline{M}_n$[a]	dispersivity $\overline{M}_w/\overline{M}_n$	T_g, °C[b]
1	45	1850 (1825)	1.18	152
2	12	1570	1.11	
3	10	1650 (1675)	1.08	149
4	11	1640	1.09	
5	5	1590	1.11	
6	12	1670	1.11	
7	9	1660	1.10	
8	1.4	1570	1.12	

[a] $\overline{M}_n$ via GPC, and (in parenthesis) via vapor pressure osmometry $\overline{M}_n$ for acetylated 1: fraction 1, 1890 (1800); fraction 3, 1650 (1650). $\overline{M}_w$ by laser light scattering GPC for fraction 3 (acetylated; 1767 (±2% deviation)).
[b] Measured by DSC; for acetylated 1: (fraction 1) T_g 135 °C; (fraction 3) T_g 132 °C.

(GPC) 1840, T_g (by DSC) 154 °C. The acetate was stable toward redistribution both in solution and in the solid state.

Greater recoveries of 1 resulted with higher concentrations of trimer in methylene chloride. With 2 g of trimer in 10 mL, 0.6 g of 1 (in two crops) was isolated, and with 2 g in 5 mL, 0.8 g of 1 (first crop) was isolated. The MWD's of the products were broader than those with the 2 g in 20 mL system ($\overline{M}_w/\overline{M}_n$ 1.11 vs. 1.07).

The dimer, 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol,[4,5] produced 1 when the solution (2 g in 10 mL of methylene chloride) was cooled to −10 °C. The product weighed 0.32 g: $\overline{M}_n$ 1740; M_n/M_w, 1.10.

Methylene bromide, which also complexes with 1,[2] required longer times and afforded less product than did methylene chloride. The first crop of 1 from 2 g of trimer in 20 mL of methylene bromide after 6 days at 25 °C (to accelerate redistribution; no precipitation occurred) then 25 days at 0 °C weighed 0.13 g: $\overline{M}_n$ 1990; $\overline{M}_w/\overline{M}_n$ 1.15.

A mixture of oligomers with an average molecular weight of ca. 600 also produced 1 with narrow MWD. 2,6-Dimethylphenol was oxidatively coupled[6] with a copper–amine catalyst using only 80% of the quantity of oxygen required to produce high polymer. After removal of polymerization catalyst and solvent, the oily product was dissolved in methylene chloride (400 g into 4 L) and cooled to 0 °C. The addition of an initiator was not required since **2**, a byproduct of the polymerization, was present in the oligomers at a concentration of 1%.[7] The polymer that formed a complex and then precipitated was removed periodically by filtration and washed with cold methylene chloride and methanol. A total of eight fractions were collected. Prior to collection of each of the last three fractions, the concentration of solids was gradually increased (ca. 30% w/v by fraction 8). Table I lists the yields, molecular weights, and dispersivities of the fractions.

The first fraction was collected after 1 day. The relatively high dispersivity indicates that high molecular weight oligomers were present in the initial reaction mixture. The initial complexation thoroughly removed these highs, however, since successive, later crops (collected after 5 days, 11 days, and then at approximately 2-week intervals) were lower in molecular weight and dispersivity than the first crop but not significantly different from each other or from the product of trimer redistribution except for a slightly greater dispersivity.

Experimental Section

GPC measurements were performed on a Waters Associates, Inc., LC, Model ALC/GPC 244, equipped with μ-styragel columns in tetrahydrofuran. Two combinations of columns were used, (10^5, 10^4, 10^3, 500 Å) and (500, 500, 100, 100, 100 Å), and gave similar values of $\overline{M}_w$ and $\overline{M}_n$. The columns were calibrated with pure standards (1, n = 1, 2, 3; **3**, n = 1, 2, 3, 4; redistribution mixtures of 1 (n = 3)) and characterized narrow MWD 1 ($\overline{M}_n$ 1675)[8] and higher molecular weight fractions of acetate capped 1 (i.e., **3**). Osmometric measurements were made on a Mechrolab vapor pressure osmometer. Light-scattering measurements were made by GPC using a Chromatix low angle laser light scattering apparatus. Infrared measurements were made in carbon disulfide vs. carbon disulfide in a 1.00 cm path length cell between 3000 and 4000 cm^{-1} and calibrated with pure oligomers (1, n = 1, 2, 3).

Conversion of Trimer to 1. A solution of 4-[4-(2,6-dimethylphenoxy)-2,6-dimethylphenoxy]-2,6-dimethylphenol[4,5] (2.00 g, 5.5 mmol) and **2** (1.0 mg, 0.004 mmol) in 20 mL of methylene chloride at 0 ± 2 °C was stored under nitrogen. Additional 1.0-mg quantities of **2** were added on the 2nd, 5th, and 9th days to maintain a bright yellow color in the reaction mixture.[9] Incipient precipitation of the complex was noted on the 7th day. After a total of 12 days, solids were removed by filtration at 0 °C and washed with two 1.0-mL quantities of methylene chloride and then methanol. The white solid product was dried at 25 °C in the dark at reduced pressure: yield, 0.25 g; $\overline{M}_n$ (by GPC, calibrated with narrow MWD 1[8]) 1680; $\overline{M}_w$ (also by GPC) 1800; T_g (by DSC) 154 °C; infrared and ^{13}C and ^{1}H NMR spectra were consistent with structure 1. An additional crop of 1 with properties similar to those of the first crop was collected 7 days later; yield 0.05 g.

Preparation of 1 from an Oligomeric Mixture. A mixture of oligomeric products from the copper–amine catalyzed oxidation[6] of 2,6-dimethylphenol, using only 80% of the quantity of oxygen required to prepare high molecular weight polymer, was extracted with 2 N hydrochloric acid to remove copper salts and amines, concentrated on a rotary evaporator to a viscous oil weighing 400 g, dissolved in 4 L of methylene chloride, and cooled to 0 °C. Formation of the complex was noted within 1 h. The complex was collected on a filter 1 day later. The filtration was carried out by gravity at 0 °C with 8 cm (dia) 10–20 μm fritted glass funnels. A vacuum was applied to remove as much remaining solvent as possible. However, because of the fine particle size of the crystals, residual solvent removal was not complete. At this point, the slurry was triturated with cold methanol, and filtration was resumed. The methanol treatment was repeated, and the polymer was dried at reduced pressure in a vacuum oven. The methylene chloride filtrate was stored at 0 °C and additional crops of crystals were collected in a similar manner periodically. The various crops are described in Table I.

Acetylation of 1. Polymer 1 from fraction 3 in Table I, 3.00 g, in 30 mL of pyridine and 3 mL of acetic anhydride was heated to 80 °C on a steam bath under nitrogen. After 1 h, the solution was cooled to 25 °C and added dropwise to 250 mL of methanol. The solid was collected on a filter, washed with methanol, dried, redissolved in 20 mL of toluene, and precipitated into 200 mL of methanol containing 2 mL of acetic acid. The solid was collected on a filter, washed with methanol, and dried: yield, 2.98 g; IR, no OH absorbance at 3610 cm^{-1}. Other properties are described in Table I.

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References and Notes

(1) H. L. Finkbeiner, A. S. Hay, and D. M. White in "Polymer Processes", C. E. Schildknecht and I. Skeist, Eds., Wiley-Interscience, New York, 1977, p 553.
(2) A. Factor, G. E. Heinsohn, and L. H. Vogt, Jr., *Polym. Lett.*, 7, 205 (1969).
(3) Triethylamine probably retards redistribution by enolizing quinol ether intermediates to phenols thereby terminating the propagation step in the redistribution (see ref 1.).

(4) G. F. Endres and J. Kwiatek, *J. Polym. Sci.*, 58, 593 (1962).
(5) D. M. White, *J. Org. Chem.*, 34, 297 (1969).
(6) A variety of catalyst systems can be used to prepare the low oligomers; see, e.g., ref 1, p 541, or G. C. Cooper and J. G. Bennett, U.S. Patent 3 661 848 (1972).
(7) Initiator **2** is formed as a byproduct in low yield during 2,6-dimethylphenol polymerization.[1]
(8) The use of narrow MWD PPO as a standard for GPC calibration will be described in a later report.
(9) Initiator **2** is slowly reduced to 4,4'-dihydroxy-3,3',5,5'-tetramethylbiphenyl[10] which co-redistributes with **1**.[5] To minimize co-redistribution yet provide initiation, **2** was added in portions.
(10) A. S. Hay, *Tetrahedron Lett.*, 4241 (1965).

Comments on the Kinetics of Cationic Polymerization of Tetrahydrofuran

STANISŁAW PENCZEK

Polish Academy of Sciences, Center of Molecular and Macromolecular Studies, 90-362 Łódź, Poland.

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Recently, Professor Szwarc proposed a new interpretation of the kinetics of polymerization of THF, stemming from the new way of treating the immediate surroundings of the growing macrocations and/or macroion pairs.[1] According to this interpretation, propagation in solvents of low polarity proceeds in clusters constituted of THF (monomer) molecules and polymer segments in the proportion identical with that in the bulk solvent. Solvent molecules, according to this treatment, do not enter the immediate surroundings of the growing macrocations.

Starting from this view, the kinetics of propagation is treated as a process in which the real rate constants of propagation are the same for various THF/solvent mixtures.

This interesting new proposal refers to our work,[2,3] in which we showed that in the polymerization of THF in CCl_4 solvent the rate constant of propagation k_p, expressed as a second-order rate constant, increases with decreasing starting monomer concentration $[THF]_0$. On the other hand, propagation is internally first order on monomer in this solvent as well as in bulk. We interpreted the observed dependence of k_p on $[THF]_0$ in terms of the influence of polarity of the medium on k_p, tacitly assuming that CCl_4 molecules are present in the immediate surroundings of macrocations. By influence of polarity, we understand the change of the electrostatic energy of ions with dielectric constant as well as specific solvating action. We have at present no way to dissect these two effects.

According to Szwarc's proposal, the difference observed by us could come from the formal treatment of the kinetics, namely Szwarc proposes to use the "unimolecular rate constant" k_u, which, at least for the THF/CCl_4 system, does not depend on $[THF]_0$ and is equal to $k_p[THF]_0$, where k_p is the second-order rate constant of propagation determined in our studies and is found to be dependent on $[THF]_0$ for the CCl_4 solvent.

One has to agree that the dependence of k_p on $[THF]_0$ in CCl_4 solvent, taken as an isolated fact, could have been alternatively interpreted in this way.

The simplest proof for the treatment outlined above would be the constancy of k_u. Simple calculations, based on our data already published,[2] give, e.g., $k_u = 0.42\ s^{-1}$ ($[THF]_0 = 12.3\ mol\ L^{-1}$) and $k_u = 0.32\ s^{-1}$ ($[THF]_0 = 8.0\ mol\ L^{-1}$) in CCl_4 solvent. Thus, the difference in k_u is even larger than that between our k_p values (see below) for the same conditions. Thus, either an assumption, treating the ratio [THF]/[polymer segment] in proximity of the growing species, is too rough an approximation or, as we are still inclined to suppose, the solvent molecules are indeed present in the immediate proximity of the growing species.

Table I

solvent	$[THF]_0$, mol L^{-1}	$10^2 k_p$, mol $^{-1}$ L s^{-1}	$\Delta H^{\ddagger}{}_p$,[a] kcal mol $^{-1}$	$\Delta S^{\ddagger}{}_p$, cal mol $^{-1}$ deg $^{-1}$
THF	12.3	3.4	14.0	−17.5
CCl_4	8.0	4.0	9.0	−33.0
CCl_4	7.0	4.3	8.4	−36.0

[a] $\Delta H^{\ddagger}{}_p$ calculated for k_p are equal to $\Delta H^{\ddagger}{}_p$ calculated for k_p because $k_u = k_p[THF]_0$ (by definition).

Moreover, we observed for the THF/CCl_4 system the large change of the activation parameters $\Delta H^{\ddagger}{}_p$ and $\Delta S^{\ddagger}{}_p$ (mostly compensating each other) in spite of only small changes of the corresponding k_p; this is illustrated in Table I. According to Szwarc, the CCl_4 molecules are absent in the immediate proximity of the growing species, and the solvation of macrocations by THF and poly(THF) segments proceeds with equal probability. Thus, one should not expect such a change of $\Delta H^{\ddagger}{}_p$ with the changing starting concentration of THF. Indeed, according to Szwarc's treatment, merely the proportion of THF and poly(THF) would change in the surroundings of the macrocations with changing $[THF]_0$.

We explained the change of $\Delta H^{\ddagger}{}_p$ and $\Delta S^{\ddagger}{}_p$ with the $[THF]/[CCl_4]$ ratio[2,3] by assuming that in the immediate proximity of the active species all of the components of the mixture are present, namely THF, the poly(THF) segments, and CCl_4 molecules. Consequently, the higher the proportion of THF molecules around macroions in the ground state the higher the enthalpy of activation.

More recently, the polymerization of THF was studied in polar solvents, namely in CH_2Cl_2 and CH_3NO_2.[4] In CH_2Cl_2 solvent, the second-order k_p is almost independent of $[THF]_0$ at 25°C. In CH_3NO_2, which is much more polar and polarizable than THF, the dependence of k_p on $[THF]_0$ is opposite to that observed for CCl_4; namely with increasing $[THF]_0$, k_p also increases. Thus, for all of the three systems there is a monotonous trend, and with increasing polarity, expressed by the bulk dielectric constants, the k_p slightly decreases. There is no indication that the mechanism of propagation changes when passing to CCl_4 as the solvent.

As mentioned above, it is difficult at present to discuss separately the influence of the electrostatic energy of ions on the rate parameters influenced mostly by the dielectric constant at the proximity of ions and of solvation of ions, related to the solvating power of the components of the system. Apparently, for systems with lower dielectric constants, the influence of changes of the electrostatic energy may prevail.

There are a number of systems known in physical organic chemistry behaving very similarly to the cationic polymerization of THF discussed above, and they all belong to the group of reactions between ions and polar molecules. The ground states in these reactions have more ionic character than the corresponding transition state,[5] and the values of the activation parameters are usually directly related to the solvation–desolvation phenomena when passing from the ground state to the transition state.

Thus, the data available at present do not allow us to adopt for the polymerization of THF the idea of the monomer–polymer clusters around the growing species. However, this original approach, stressing the importance of the noncontinuity of ionic solutions in the ionic po-

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