High Molecular Weight Aromatic Polyformals Free of Macrocyclic Oligomers. A Condensative Chain Polymerization Reaction

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Introduction

High molecular weight aromatic polyformals have been previously synthesized by the reaction of salts of bisphenols with methylene chloride or bromide in aprotic dipolar solvents such as *N*-methylpyrrolidinone or in the presence of phase transfer catalysts in nonpolar solvents.[1−5] Aromatic polyformals have property profiles similar to aromatic polycarbonates except that the glass transition temperatures are generally 40−60 °C lower.[4]

It was observed in the polymerization of bisphenol A **1** at room temperature to produce polyformal **2** that large amounts of macrocyclic oligomers **3** ($n = 2-25$) were formed.[1,4] During the initial stages of the reaction, the bisphenol reacted with the sodium or potassium hydroxide to give a copious precipitate of the salt which hindered stirring of the reaction mixture. The solids went slowly into solution, and the polymer **2a** was isolated after several hours. By raising the reaction temperature to about 80 °C, polymer **2b** was obtained containing a decreased amount of cyclics. However, we were never able to carry out a reaction with less than 3.5% of cyclic oligomers forming. When the reaction with the methylene halide was carried out using the preformed anhydrous salts, the formation of as much as 66% of cyclic oligomers was observed.[6] The conclusion that we reached was that cyclic oligomers were formed because of the slow dissolution of the salt that created high dilution conditions in the reaction mixture. In other systems that involved a nucleophilic displacement reaction, e.g., the formation of macrocyclic poly(aryl ether) sulfones, high dilution conditions have been shown to favor the formation of cyclic oligomers.[7] Other bisphenols behave in a similar fashion.

Results and Discussion

We have now found that if these polymerization reactions are carried out under high-intensity mixing conditions,[8] very high molecular weight polymers with very low molecular weight distributions (~1.3) can be obtained in a very short time. Using a blender as a reactor,[8] a reaction mixture which consisted of potassium hydroxide pellets, 4,4′-isopropylidenediphenol **1,** and excess methylene bromide in *N*-methylpyrrolidinone (NMP) very rapidly heated to about 100 °C. The viscosity of the reaction mixture very rapidly increased, and the reaction was complete in a few minutes! Only almost imperceptible amounts of macrocyclic oligomers were formed under these conditions. This implies that the rate-controlling step in the reaction is the dissolution of the salt and that the high-intensity mixing increased the surface area of the salt, hence aiding its dissolution.

Condensative chain polymerization reactions[9] have been recently described by Yokozawa,[10−12] and Voit[13] has reviewed their findings. An alkoxy-substituted poly(benzyl ester) was formed under phase transfer conditions from a solid monomer to give polymers with very low molecular weight distributions. To convert a step-growth polymerization reaction to a controlled chain-growth reaction, the monomers must not react with each other, and they must add almost exclusively to the growing chain.

The formation of formals is an irreversible reaction so that no equilibrium exists in this polymerization reaction. In the polyformal reaction the first intermediate formed, the bromomethyl ether **5**, is much more reactive than the monomer, methylene dibromide, which is also used as a partial solvent for the reaction (Scheme 2). Therefore, as the bisphenol salt **4** dissolves, it preferentially reacts with the very reactive bromomethyl ether groups in preference to reaction with methylene bromide. The intermediate **5** then reacts with the salt **4** to give **7** or with another molecule of **5** to give **6**. Under normal stirring conditions where **4** very slowly goes into solution, its concentration is low so that the intermediate **6** could react with itself to give a cyclomer **8**. Higher analogues of **6** could also give cyclomers when the concentration of **4** in solution is low, thus contributing to a broad molecular weight distribution. Under high-intensity mixing conditions the concentration of **4** is high so that **6** and higher analogues would preferentially react with **4**. The soluble intermediate **9** that formed and **7** can react with methylene bromide to give reactive halomethyl intermediates, and the cycle then continues to give high molecular weight polymer.

A typical procedure follows. Into a blender[8] were charged 7 g (30.66 mmol) of **1**, 4 g (71.29 mmol) of KOH, and 28 mL of NMP. The mixture was vigorously stirred for 2 min. The temperature reached 65 °C, and at this point there was added 10 mL of CH_2Br_2. The ensuing reaction was very exothermic, and after 1 min the temperature rose to 80 °C. After about 3 min the temperature rose to 95 °C (without external heating), and stirring was continued with difficulty because the reaction mixture became very thick. After 5 min the polymer was isolated by precipitation in methanol. It was dissolved in chloroform, filtered through a bed of Celite, and reprecipitated in methanol in a Waring blender. The polymer **2c** was dried overnight in vacuo to give a 99% yield of **2c**.

Alternatively, the reaction can be carried out by first forming the salt in the blender in NMP as solvent and then transferring it under nitrogen to a test tube equipped with a high-intensity mixer[8] in an oil bath at 80 °C. Excess methylene dibromide was then added. After about 10 s the reaction mixture became very viscous. The polymer **2d** was isolated as above in 92% yield. The detailed properties of the polymers formed are summarized in Table 1.

Figure 1 shows the GPC curves for BPA polyformal polymer synthesized under different conditions. When the polymerization was carried out at room temperature with magnetic stirring, the reaction mixture rapidly became very difficult to stir because of dipotassium salts

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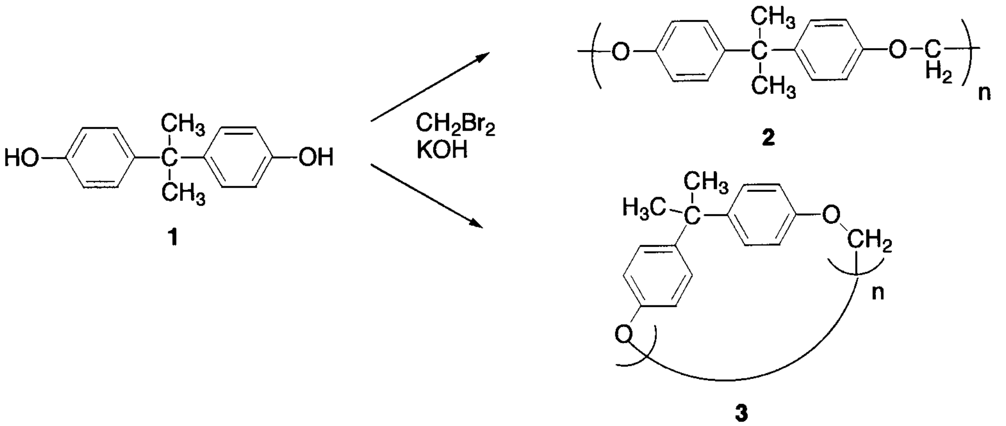
Scheme 1. Synthesis of Polyformal of BPA



Scheme 2. Formation of Aromatic Formals from Phenols and Methylene Halides

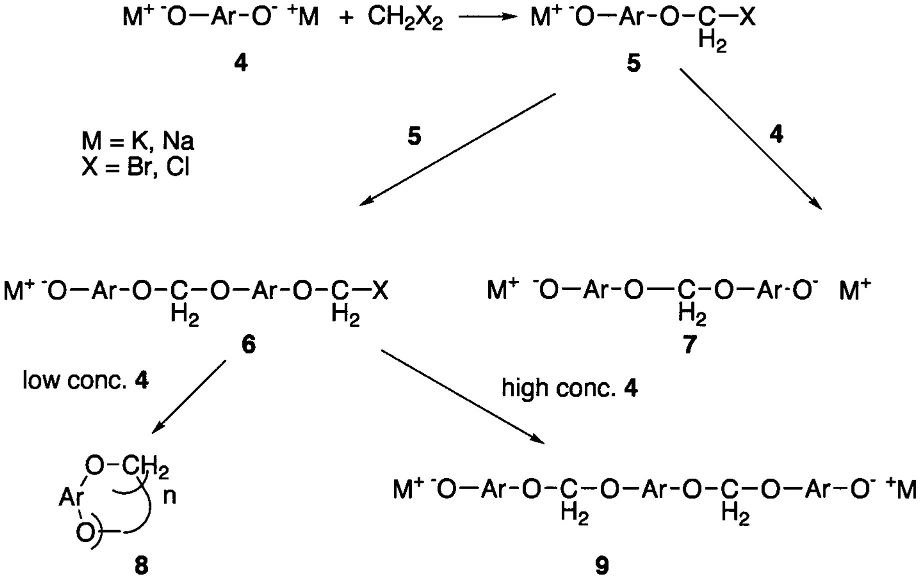


Table 1. Properties of BPA Polyformals Prepared under Different Mixing Conditions

polymer	η_{inh} (dL/g)	T_g[a] (°C)	$\bar{M}_w$[b] ($\times 10^3$)	$\bar{M}_n$[b] ($\times 10^3$)	$\bar{M}_w/\bar{M}_n$	% yield[c]	% cyclics[d]
2a	0.38	87	149.7	46.9	3.1	65	23
2b	0.7	91.4	140.5	81.2	1.8	73	7
2c	1.4	94.4	333.8	250.1	1.3	99	
2d	1.1	92	123.2	71.9	1.7	92	

[a] The glass transition temperatures were determined on a Seiko 220 DSC instrument at heating rate of 20 °C/min under N_2 (flow rate 160 mL/min). [b] Gel permeation chromatography (GPC) analyses were carried out on reprecipitated samples on a Waters 510 HPLC equipped with 5 μm phenogel columns (linear, 3 × 200 Å) arranged in series with chloroform as solvent and UV detector at 254 nm. [c] Isolated yield after purification. [d] Determined from GPC on reaction mixture.

of BPA that separated. The salt slowly went into solution over several hours to give polymer **2a** that had a bimodal distribution. In addition, **2a** contained large amounts of low molecular weight materials that were almost exclusively macrocyclic oligomers, as identified by Maldi-TOF MS analysis.[14] When the same reaction was carried out at 80 °C, the reaction was greatly improved; however, large amounts of cyclic oligomers were still present, and polymer **2b** had a wide MW distribution. When carried out under high-intensity mixing conditions, as described above, polymer **2c** with a number-average molecular weight of 250 000 and a molecular weight distribution of 1.3 was obtained.[15] Only miniscule amounts of cyclic oligomers were present which were identified by Maldi-TOF MS.

Aromatic Polyformal from Hydroquinone. We previously found that the polyformal **11** obtained from hydroquinone **10** was highly crystalline and insoluble in solvents at room temperature[5] (Scheme 3). The hydroquinone salt was also insoluble in the reaction mixture, and in addition, the highly crystalline polymer was insoluble in solvents at room temperature. Only very low molecular weight materials were obtained at that time.

Under high-intensity mixing conditions, we have now obtained high molecular weight polyformals from hydroquinone (Scheme 3). The polymerization reaction was complete within a few minutes so that high molecular weight polymer was formed before it crystallized and precipitated out of the reaction mixture. The polymer was soluble in halogenated hydrocarbons such as 1,1,2,2-tetrachloroethane, chlorobenzene, and 1-chloronaphthalene above 100 °C. The molecular weight of the polymer obtained was $M_w = 771\,000$ and $M_n = 135\,000$, deter-

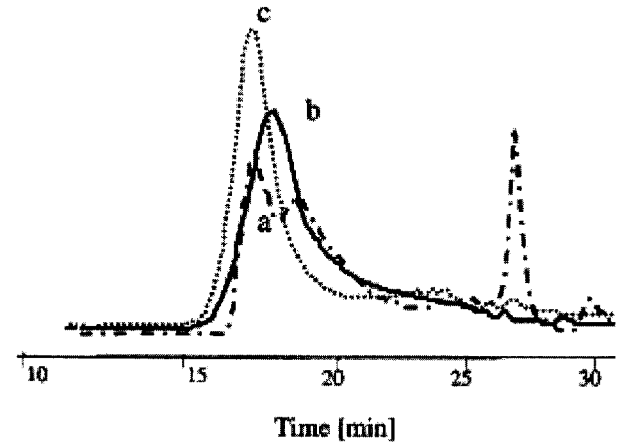
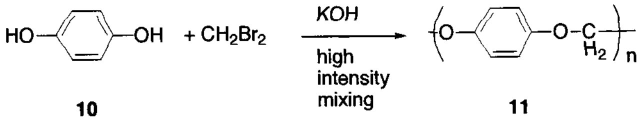


Figure 1. GPC curves for polymers **2a**−**c**.

Scheme 3. Synthesis of Polyformal of Hydroquinone



mined by GPC at 210 °C. In contrast to the BPA polyformal which is amorphous, HQ polyformal showed a clear T_m at 193 °C (heat of fusion: $\Delta H = 40$ J/g), detected by DSC. In the first DSC scan, no T_g was observed. The second scan after quenching from the melt gave a T_g of 36 °C and a T_c of 57.5 °C ($\Delta H = 22.1$ J/g). Tough, flexible films of the polymer were obtained from the melt. The preliminary wide-angle X-ray diffraction (WAXD)[16] measurements showed that the polymer was semicrystalline with sharp diffractions peaked at $2\theta = 16.1°$, 20.8°, 21.5°, 23.8°, 24.7°, and 25.0°. The assignment of the peaks to determine the crystal structure is under investigation and will be reported elsewhere.

Conclusions

High molecular weight aromatic polyformals have been synthesized in very high yield that have very low molecular weight distributions (~1.3) in a condensative chain polymerization reaction. The reaction of the bisphenol with methylene bromide in the presence of potassium hydroxide in a solvent like NMP was carried out under high-intensity mixing conditions at about 100 °C. The reactions are complete in a few minutes. The resulting polymers contain almost no macrocyclic oligomers. The procedure is general and can also be used for the synthesis of the corresponding polythioformals from dithiols. This work is in progress, and further details will be reported in the near future.

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References and Notes

(1) Hay, A. S.; Williams, F. J.; Relles, H. M.; Boulette, B. M.; Donahue, P. E.; Johnson, D. E.; Loucks, G. R. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1982**, *23*, 117.
(2) Hay, A. S.; Williams, F. J.; Relles, H. M.; Boulette, B. M.; Donahue, P. E.; Johnson, D. E. *Polym. Lett.* **1983**, *21*, 449.
(3) Hay, A. S. US 4374974, General Electric Co., 1993.
(4) Williams, F. J.; Hay, A. S.; Carnahan, J. G.; Loucks, G. R.; Boulette, B. M.; Donahue, P. E.; Johnson, D. E. In *New Monomers and Polymers*; Plenum Publishing: New York, 1984; p 67.
(5) Hay, A. S.; Williams, F. J.; Relles, H. M.; Boulette, B. M. *J. Macromol. Sci., Chem.* **1984**, *A21*, 1065.
(6) Williams, F. J. III.; Donahue, P. E. U.S. 4136087, General Electric Co., 1979.
(7) Wang, Y.-F.; Chan, K. P.; Hay, A. S. *React. Funct. Polym.* **1996**, *30*, 205.
(8) The reactions were carried out with a semi-micro-stainless steel blender assembly from Eberbach with a cloverleaf design with 25−250 mL capacity or in an ULTRA-TURRAX T25 blender from Janke & Kunkel.
(9) Mita, I.; Stepto, R. F. T.; Suter, U. W. *Pure Appl. Chem.* **1994**, *66*, 2483.
(10) Yokozawa, T.; Suzuki, H. *J. Am. Chem. Soc.* **1999**, *121*, 11573.
(11) Yokozawa, T.; Asai, T. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40*, 587.
(12) Yokozawa, T.; Shimura, H. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2607.
(13) Voit, B. *Angew. Chem., Int. Ed.* **2000**, *39*, 3407.
(14) MALDI-TOF mass spectra were recorded on a Kratos Kompact MALDI-TOF-III mass spectrometer with the instrument set in the positive reflectron mode. 1,8,9-Anthracenetriol (dithranol) was used as the matrix.
(15) GPC analyses were carried out on a Waters 510 HPLC equipped with 5 mm phenogel columns (linear, 3 × 200 Å) arranged in series with chloroform as solvent and UV detector at 254 nm using polystyrene standards. High-temperature GPC was carried out at 210 °C using a Senshu Kagaku VHT-GPC SSC7000 system equipped with a UV detector set at 365 nm. 1-Chloronaphthalene was used as eluent.
(16) WAXD patterns were obtained on a powder sample employing a Bruker axs DfAdvance diffractometer with a curved crystal, graphite monochromator and counting equipment. Measurements were made with Ni-filtered Cu Kα radiation. With the goniometer operated at 35 kV and 20 mA, the intensities of 1 s counts were taken every 0.02° (2θ) over the angular range 10−60° and recorded.

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