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Reaction Mechanisms

Comb-Like Polymers and Graft Copolymers from Macromers

2. Synthesis, Characterization and Homopolymerization of a Styrene Macromer of Poly(2,6-Dimethyl-1,4-Phenylene Oxide)

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SUMMARY

A poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) macromer containing styrene (PPO-St) as a polymerizable group was prepared from a PPO containing phenol and p-bromophenoxy groups as the two chain ends. The main reaction consists of the quantitative etherification of the phenol chain end with chloromethylstyrene in the presence of tetrabutylammonium hydrogen sulfate as a phase transfer catalyst. Preliminary data on radical polymerization of PPO-St demonstrates that under suitable polymerization conditions comb-like PPO can be obtained with 46% yield and polymerization degree of about 34.

INTRODUCTION

The previous paper in this series presented the synthesis and characterization of methacrylate- and styrene-type macromers of aromatic polyether sulfones (1). We have chosen aromatic polyether sulfone and poly(2,6-dimethyl-1,4-phenylene oxide) type macromers because of their unique physical properties, and the ease of their spectroscopic characterization. Two convenient methods are available for the preparation of low molecular weight PPO. These are the polymerization of 4-bromo-2,6-dimethylphenolate in the presence of an oxidizing agent (2), and the separation of low molecular weight PPO during the redistribution reaction of PPO oligomers (3). Despite the narrow molecular weight distribution of PPO produced in the second procedure, the first method was selected for this preliminary study because the resulting polymer contains one p-bromophenoxy group and one phenol group as chain ends. High resolution 200 MHz ^{1}H- and 50 MHz ^{13}C-NMR spectroscopy is useful for the quantitative characterization of both the concentration of chain ends and the conversion of phenol end groups by Williamson etherification with chloromethylstyrene (CMS). Radical homopolymerization of PPO-St produced comb-like PPO with a degree of polymerization of about 34 in 45% yield.

EXPERIMENTAL

Materials

4-Bromo-2,6-dimethylphenol (Aldrich), lead dioxide (Alfa), chloromethylstyrene (40% p, 60% m, from Dow Chemical Co.,) (CMS), tetrabutylammonium hydrogen sulfate (TBAH) (Aldrich) and all solvents were used as received. Toluene used as polymerization solvent was refluxed over sodium and then distilled under argon. 2,2'-Azo-bis(isobutyronitrile) (AIBN) (Polysciences) was freshly recrystallized from methanol (at 40°C) and dried under vacuum at room temperature.

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-OH)

A solution of KOH (13.2 g in 1.15 l of water) and lead dioxide (0.565g, 1 mole %) were added to a solution of 47.3 g of 2,6-dimethyl-4-bromophenol in 1.15 l of benzene. The mixture was stirred for 44 hr at room temperature. The benzene layer was separated, washed with water until it became colorless and concentrated to 200 ml. The polymer was precipitated with methanol. A second precipitation with methanol from benzene solution yielded 22.4 g (78%) of PPO-OH with $\bar{M}n$ = 3973 (determined by 200 MHz ^{1}H-NMR).

Styrene Macromer of Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-St)

A 50% aqueous solution of NaOH (4 ml) was added to a stirred solution of PPO-OH (4g, 0.0012 moles) in 40 ml benzene at room temperature, followed by addition of 0.4 g (0.0012 moles) TBAH and 0.9 g (0.006 moles) CMS. The addition of CMS created a dark green colored reaction mixture. After stirring 2 hr at room temperature, the color of the reaction mixture turned to dark brown and shortly thereafter to light brown. NMR analysis indicated complete reaction at this point, but usually the reaction was continued for one more hr. The reaction mixture was then diluted with benzene, and washed with water. The macromer was precipitated with methanol. The final purification was carried out by precipitation of the product from benzene solution with methanol. The filtered macromer was dried in vacuum at room temperature.

Polymerizations

The polymerization of PPO-St was carried out in toluene solution in the presence of AIBN in sealed glass tubes under argon. After the required reaction time, the reaction mixture was diluted with $CHCl_3$ and the polymacromer was precipitated with methanol. The conversion of the macromer to polymacromer was determined from the area under the GPC trace of the reacted and unreacted material.

Techniques

200 MHz ^{1}H- and 50 MHz ^{13}C-NMR spectra were recorded using a Varian XL 200 spectrometer (CCl_4 solution). Chemical shifts are reported relative to internal TMS. Glass transition temperatures (Tg) were determined with a Perkin-Elmer Differential Scanning Calorimeter (model DSC-2) with Indium used as a calibration standard. The Tg value was recorded during the third heating cycle. GPC analyses were carried out with RI and UV detectors using µ-Styragel columns of 10^5, 10^4, 10^3, 500 Å and a calibration plot constructed with polystyrene standards.

RESULTS AND DISCUSSION

PPO-OH was synthesized using a method developed by Staffin and Price (2). They calculated the molecular weight from elemental analysis, assuming only one bromine and one phenol group per molecule. Titration of the phenolic end groups then provided evidence for the presence of equal concentrations of bromine and phenolic chain ends. Our 200 MHz ^{1}H-NMR analysis of the PPO-OH confirmed these findings. A typical spectrum is presented in Fig.1 together with an expansion of its aromatic region and the resonance assignments. Several solvents were tested for the analysis of the PPO-OH chain ends by ^{1}H-NMR spectroscopy. The most suitable solvent for dispersing the resonances is CCl_4. The areas under the resonances for the aromatic protons from the 4-bromo-2,6-dimethylphenoxy- (signal C at δ=7.2 ppm) and 2,6-dimethylphenol (signal B at δ=6.43 ppm) chain ends are equal. This analysis demonstrates that indeed PPO-OH contains only one phenol chain end per polymer molecule. Additionally, the PPO-OH degree of polymerization was determined from its ^{1}H-NMR spectrum by using the relationship $\overline{DP}=[(A_A+A_B)/2]/ /(A_C/2) - 1$. In our case $\overline{DP}$ = 26 with the $\bar{M}n$ = 3473 corresponding to this value. ^{13}C-NMR spectroscopy was also used to characterize the microstructure of PPO-OH. A typical spectrum is presented in Fig.2, with an expansion of its aromatic region shown in Fig.3. The assignments of the main chain

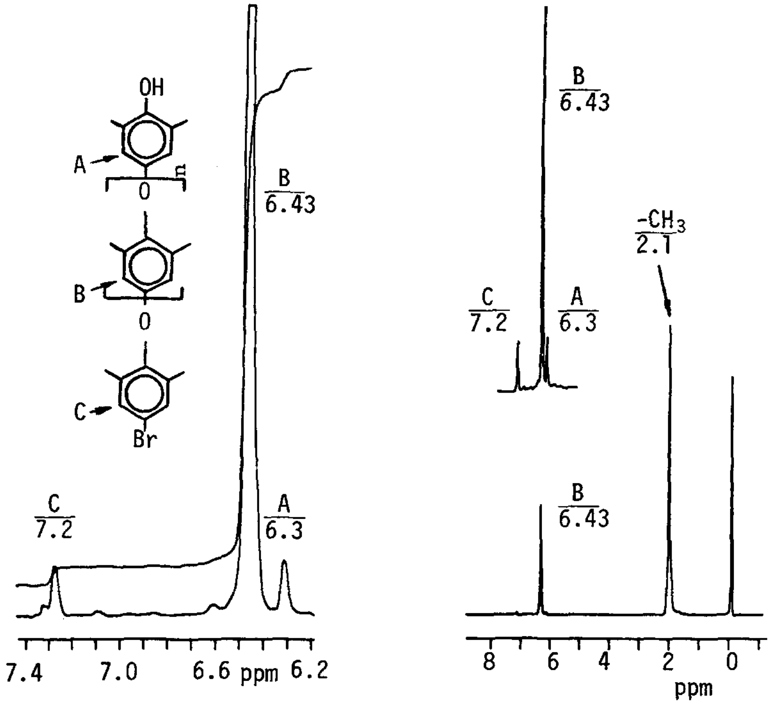

Figure 1: ^{1}H-NMR spectrum of PPO-OH (CCl_4, TMS)

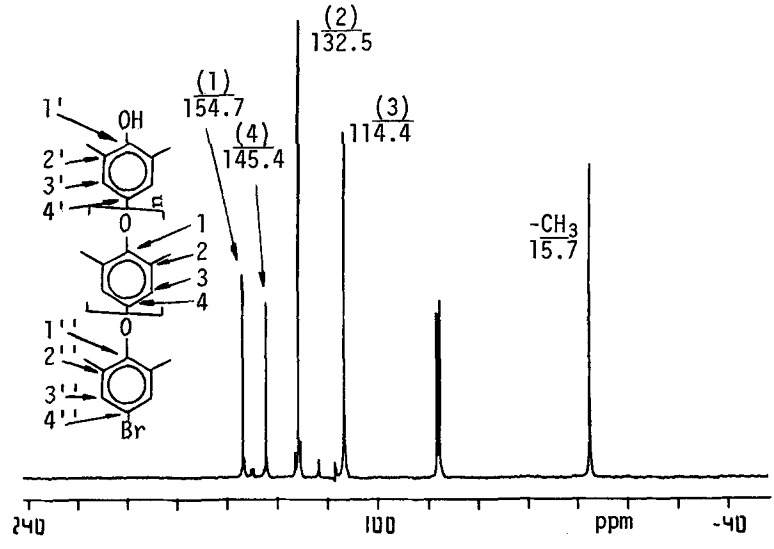

Figure 2: ^{13}C-NMR spectrum of PPO-OH ($CDCl_3$)

carbon resonances (shown in Fig.2) were made using chemical shift additivity rules (4), and are consistent with those previously proposed in the literature(5). The assignments of the chain end carbon resonances are presented in Fig.3. The ratio of the signal intensities due to carbon 1'' and 2'

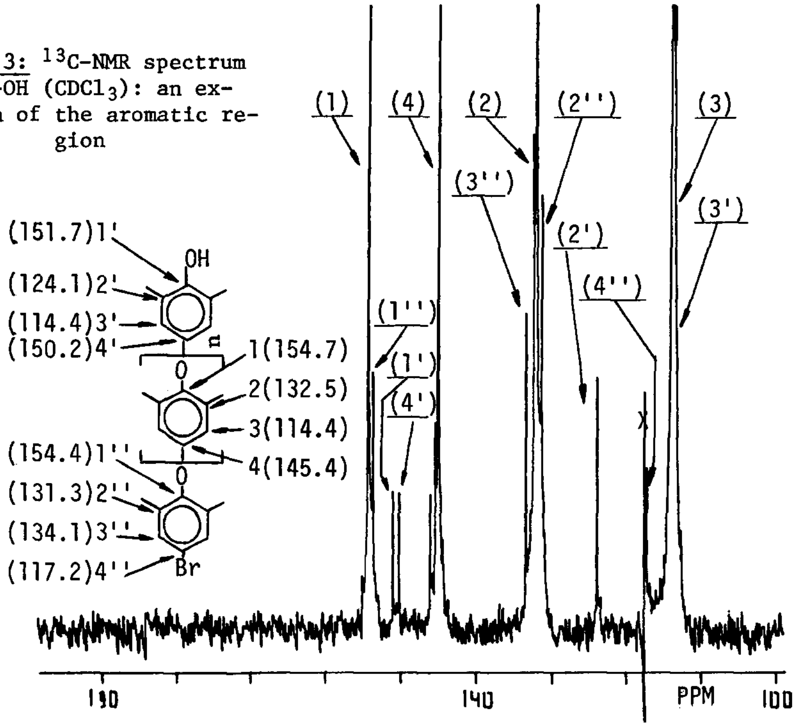

Figure 3: ^{13}C-NMR spectrum of PPO-OH ($CDCl_3$): an expansion of the aromatic region

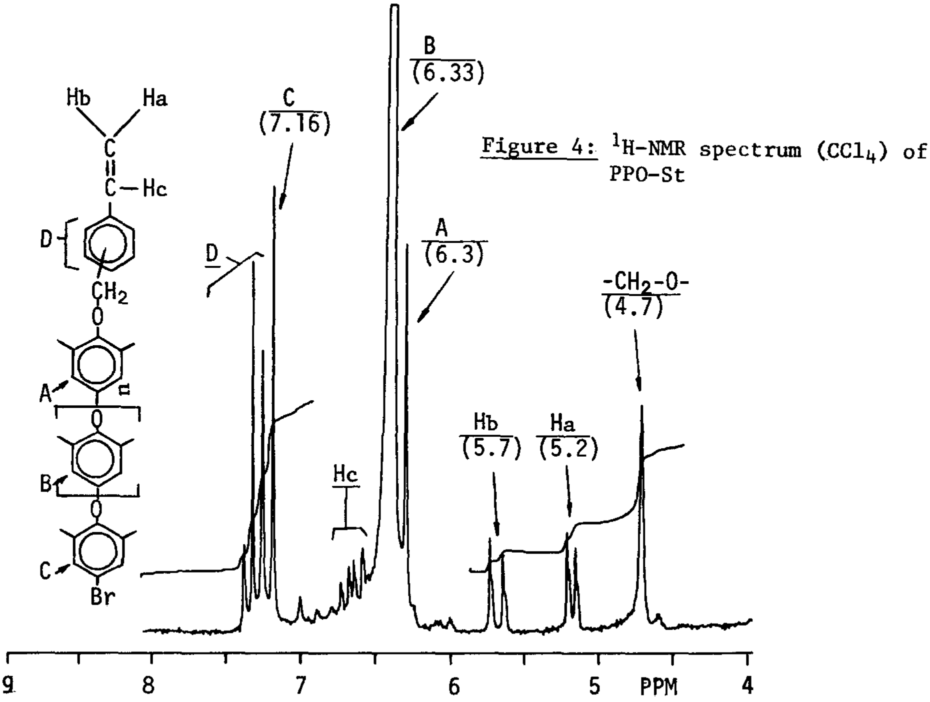

Figure 4: ^{1}H-NMR spectrum (CCl_4) of PPO-St

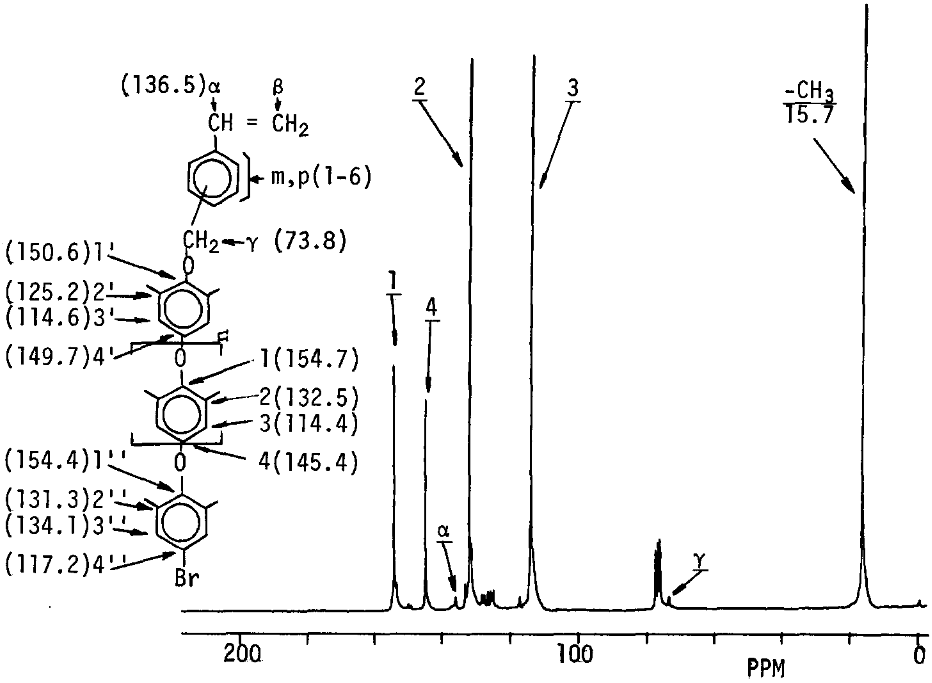

Figure 5: ^{13}C-NMR spectrum ($CDCl_3$) of PPO-St

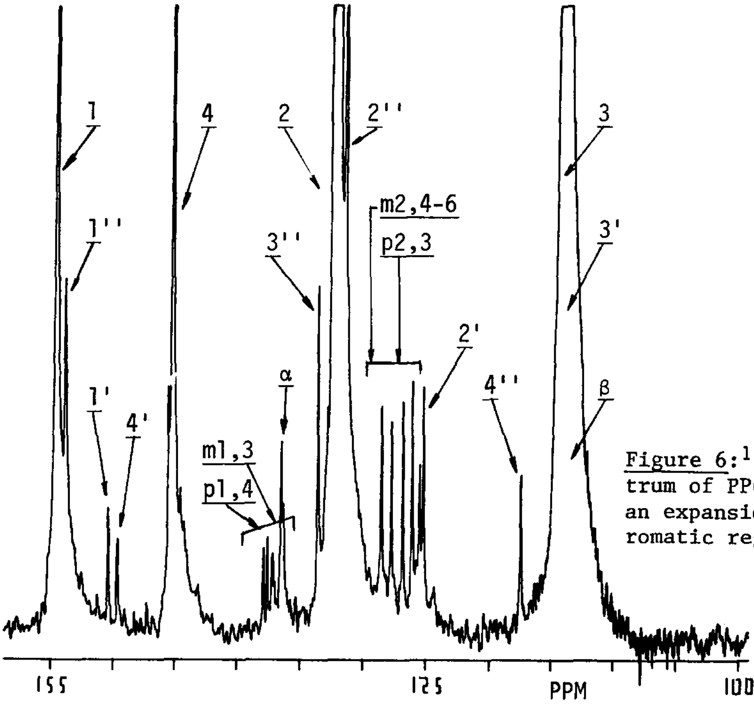

Figure 6: ^{13}C-NMR spectrum of PPO-St ($CDCl_3$): an expansion of the aromatic region

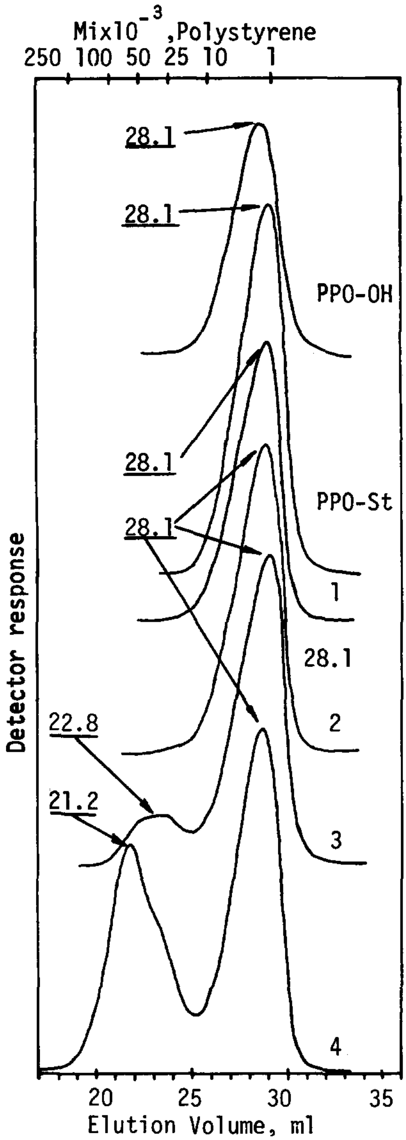

Figure 7:Gel Permeation Chromatograms of: PPO-OH, PPO-St and polymacromers 1-4 from Table 1

or 1', 4' and 4'' again demonstrates that PPO-OH contains only one phenol chain end per molecule.

We have already demonstrated (1,6) that Williamson etherification of the phenolic type chain ends of different polymers can be performed quantitatively with TBAH as phase transfer catalyst. The major difference between our reaction conditions (1, 6) and the conventional phase transfer catalyzed Williamson etherification (7) is the use of stoichiometric amounts of phase transfer catalyst versus the nucleophilic chain ends in the former case. Under these reaction conditions, both the nucleophilic and electrophilic groups are present in the organic phase. Consequently the etherification takes place in solution, the reaction is very fast at room temperature, and the reaction course can be followed by the disappearance of the green colour of the phenolate anion.

The analysis of the styrene, 2,6-dimethylphenol, and 4-bromo-2,6-dimethylphenoxy chain ends was performed by 200 MHz ^{1}H-NMR. An expansion of the aromatic region of the PPO-St ^{1}H-NMR spectrum is presented in Fig.4. The ratio of the signals (D+C): Ha:Hb:-CH$_2$O- demonstrates the incorporation of one styrene group per PPO molecule. The structure of the PPO-St was also analysed by ^{13}C-NMR spectroscopy. These spectra along with the carbon resonance assignments are presented in Fig.5 and 6. Due to the different relaxation times of the backbone carbons versus the styrene chain end carbons, this method is less reliable for a quantitative analysis.

PPO-St has a Tg=170°C. Preliminary data on the radical polymerization of PPO-St are presented in Table 1.

Table 1

Radical Polymerization of PPO-St (polymerization temperature, 60°C; reaction time, 24 hr; polymerization solvent, toluene)

	PPO-St		Toluene	AIBN				Conversion
No	(g)	(moles)x10^5	(ml)	(g)x10^3	(moles)x10^6	wt%	moles%	%
1.	0.2	5.75	0.5	0.4	2.4	0.2	4.17	0
2.	0.2	5.75	0.5	0.2	1.2	0.1	2.09	0
3.	0.2	5.75	1.0	0.4	2.4	0.2	4.17	19
4.	0.2	5.75	0.5	1.8	10.9	0.9	18.96	46

The conversion of PPO-St into polymacromer was determined by GPC (Fig.7). This conversion does not correspond with the number of vinylic double bonds consumed (determined by NMR) as was also found by other authors (8,9,10). The macromer polymerization under high initial macromer concentration is diffusion controlled even from the very early stages of the reaction. The major difference between conventional radical polymerization in the diffusion controlled regime (11) and macromer polymerization, is that in the latter case the termination, chain transfer to macromer, propagation and initiation are perhaps all diffusion controlled. This is due to the fact that we are dealing with high weight concentrations and very low molar concentrations of the macromer. Experiments No. 1 and 3 from Table 1 provide evidence that the rates of initiation and/or propagation are affected by diffusion. Solely by increasing the amount of solvent used (exp. No. 3), the rate of propagation in comparison with those of chain transfer and termination reactions increases. At higher initiator concentration (molar ratio macromer//AIBN = 5.3/1, exp. No.4) high conversion and degree of polymerization was obtained. The degree of polymerization of this polymacromer was determined by GPC calibrated with polystyrene (Ev = 28.1, Mi =2,450, for PPO-St; and Ev = 21.2, Mi = 83,000 , for polymacromer) (Fig. 7), and was found to be about 34.

CONCLUSIONS

PPO-St macromer was prepared by quantitative etherification of the phenol end groups of PPO-OH with CMS in the presence of TBAH as a phase transfer catalyst. Preliminary data on its radical homopolymerization demonstrates that high molecular weight comb-like PPO can be prepared with high conversion. Radical homopolymerization and copolymerization of macromers represent special and very particular cases of radical polymerizations, and PPO-St is a suitable model for their study. Kinetic studies on its polymerization and copolymerization are in progress and will be reported soon.

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