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Phase Transfer Catalysis

Functional Polymers and Sequential Copolymers by Phase Transfer Catalysis.

5. Synthesis and Characterization of Polyformals of Aromatic Polyether Sulfones

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SUMMARY

Polyformals of aromatic polyether sulfones (PS) were prepared by phase transfer catalyzed Williamson etherification of α,ω-di(phenol)PS with methylene chloride used both as reactant and solvent. Degrees of chain extension of up to 73 were obtained in less than 1 hr reaction time. The influence of the reaction conditions on the polymerization degree of these polyformals and on their Tg is presented.

INTRODUCTION

In the first paper from this series we have developed a simple and convenient method for the preparation of alternating block copolymers and regular copolymers (1). This method consists of the phase transfer catalyzed Williamson polyetherification of α,ω-di(phenol)- with α,ω-di(chloroallyl)-terminated polymers in the case of the alternating block copolymers preparation. The polyetherification of one of the above mentioned telechelic polymers with either a bifunctional electrophilic monomer (i.e., cis or trans 1,4-dichloro-2-butene, α,α'-dibromo-p-xylene, etc.) or a bisphenol, gives rise to regular copolymers. In both cases, high molecular weight alternating block copolymers or regular copolymers could be prepared by this technique. In addition, we have also demonstrated (2,3) that Williamson etherification of the phenolic type chain ends of different polymers can be performed quantitatively in the presence of a phase transfer catalyst. This last strategy was used for the preparation of aromatic polyether sulfone (2) and poly(2,6-dimethyl-1,4-phenylene oxide) (3) macromers containing vinylbenzyl type polymerizable groups. The major difference between our reaction conditions (1-3) and the conventional phase transfer catalyzed Williamson etherification (4) is the use of stoichiometric amounts of phase transfer catalyst versus the nucleophilic chain ends in the former case. Under this reaction conditions, both the nucleophilic and electrophilic groups are present in the organic phase, and the etherification takes place in solution.

This paper presents the synthesis and characterization of polyformals of aromatic polyether sulfones through phase transfer catalyzed Williamson polyetherification of α,ω-di(phenol)aromatic polyether sulfones with methylene chloride.

EXPERIMANTAL

Materials

α,ω-di(Phenol)aromatic polyether sulfones (PS) (prepared from Bisphenol-A and 4,4'-dichlorodiphenyl sulfone) used in this work were prepared and characterized as was previously reported (1). Their molecular weight and Tg values are presented in Table 1. Tetrabutylammonium hydrogen sulfate (TBAH) (Aldrich), methylene chloride, methylene bromide, chlorobenzene (ClBz)

TABLE 1: Preparation of Polyformals of Aromatic Polyether Sulfones

No.	PS (1g)				Solvent	NaOH	Time	Polyformal		
	Mn (NMR)	Mi (GPC)	Ev (GPC,ml)	Tg (°C)	CH_2Cl_2/ClBz (V/V,ml)	(ml)	(hr)	Mi (GPC)	Ev (GPC,ml)	Tg (°C)
1.	1,210	1,000	29.1	87	4.5/10.5	2	5.5	55,000	22.1	158
2.	2,550	2,350	28.1	135	3/7	1	2.0			
					1.5/3.5*	-	22.5	170,000	19.6	177
3.	3,050	3,900	27.5	138	4.5/10.5	2	7.0	46,000	22.5	172
4.	3,050	3,900	27.5	138	3/7	1	13.0	53,000	22.2	178
5.	3,410	5,400	27.0	148	3/7	1	24.0	34,000	23.2	174
6.	2,200	2,200	28.3	134	5/11.6	1.7	27.7	42,000	22.7	168
7.	3,875	5,700	26.9	146	4.5/10.5	1	0.8	39,000	22.9	174
							21.5	39,000	22.9	174
8.	3,410	5,400	27.0	148	3/7	1	1.0	120,000	20,5	185
					0.7/1.5	-	3.0	120,000	20.5	185
					0.7/1.5	1	1.5	120,000	20.5	185
9.	2,550	2,350	28.1	135	3/3.5	1	2.0	58,000	22.0	163
					1.5/3.5	-	1.0	58,000	22.0	163
10.	3,410	5,400	27.0	148	5/0	1	0.4	-	-	-
					2.5/0	-	3.7	115,000	20.5	184
11.	3,410	5,400	27.0	148	5/0 (CH_2Br_2)	1	3 min	-	-	-
					3/0 (CH_2Br_2)	-	2.5	113,000	20.6	184

*i.e., 1.5/3.5 CH_2Cl_2/ClBz (V/V, ml) were added after 2.0 hr reaction time and the reaction was continued for other 22.5 hr

and methanol (all from Aldrich) were used as received.

Polymerizations

The phase transfer catalyzed polyetherification of PS was carried out by using methylene chloride both as electrophilic monomer as well as solvent. The amount of PS, methylene chloride, NaOH (50% water solution), reaction temperature, and reaction time are presented in Table 1. The general procedure is as follows. The aqueous solution of NaOH was added to a stirred solution of PS in CH_2Cl_2 or in a CH_2Cl_2 and ClBz mixture. The sodium salt of PS precipitated immediately. After the addition of a stoichiometric (versus the phenol groups) amount of TBAH, the reaction mixture became homogeneous once more. The reaction mixture was then stirred at the polymerization temperature (reflux temperature) for the required period of time. Then it was cooled at room temperature, diluted with dilute HCl, washed with water and the product was precipitated with methanol. A final purification was carried out by precipitation of the product from chloroform solution with methanol.

Techniques

200 MHz ^1H-NMR spectra were recorded using a Varian XL-200 spectrometer ($CDCl_3$ solutions). 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 calibra-

tion standard. The Tg values were 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

Methylene chloride was already used for the synthesis of dialkyl and diaryl formals by Williamson etherification in the presence of a phase transfer catalyst (5,6). Recently, Hay et al (7) reported the preparation of the polyformal of Bisphenol-A. They performed the polyetherification of Bisphenol-A with methylene chloride, both in DMSO (by using the sodium salt of Bisphenol-A) and in ClBz. In the second case the etherification was carried out in the presence of a large variety of phase transfer catalysts. The only phase transfer catalyst which was not used by them is TBAH. It was already demonstrated that TBAH is perhaps the most suitable phase transfer catalyst for liquid-liquid type etherification (1-3,4,8,9).

The most interesting feature of CH_2Cl_2 is that it can be used as an inert solvent when the etherification uses a more powerful electrophilic monomer than CH_2Cl_2 (5,9) and the reaction is performed at room temperature. The most advantageous feature of CH_2Cl_2 as a bifunctional electrophilic monomer is that the reactivity of its two chlorine atoms is different in the SN_2 type reactions.

$$\text{Ph-OH} + CH_2Cl_2 \xrightarrow[OH^-]{k_1} \text{Ph-}OCH_2Cl$$

$$PhOCH_2Cl + PhOH \xrightarrow[OH^-]{k_2} PhOCH_2OPh$$

and : $k_2 \gg k_1$

This is due to the much higher reactivity of the $ClCH_2O$- group in comparisson with that of the $ClCH_2Cl$ in nucleophilic substitutions. Consequently, $k_2 \gg k_1$, and in etherification reactions methylene chloride can be used both as reactant and solvent.

The chain extension reaction of α,ω-di(phenol)aromatic polyether sulfones with CH_2Cl_2 was carried out with a stoichiometric amount of TBAH versus the phenol chain ends. Consequently, the polyetherification reaction occurs in solution. A large variety of reaction conditions were used for this synthesis. The experimental data are presented in Table 1. A first set of experiments (No. 1-9) was carried out in CH_2Cl_2/ClBz mixture. ClBz was used as a cosolvent to increase the boiling point of the reaction mixture, and consequently the reaction temperature to 60°C. The amount of PS was constant (1g in all experiments), but the quantity of the polymerization solvent was changed. Also the reaction time and the amount of NaOH (50% water solution) were varied. In several experiments (No. 2,3,9) a second and even a third amount of solvent (and of course reactant) was introduced to decrease the reaction medium viscosity. The conclusion of these experiments is as follows. Unusually high degrees of chain extension (up to 73 for example in the experiment No. 2) were obtained by this reaction. According to our knowledge, these degrees of chain extension seem to be the highest ever reported in the step polymerization literature. Also, the molecular weights of the obtained polyformals are in the range of unusual high molecular weights for step polymerization type polymers. The degree of polymerization of the polyformal is strongly affected by the initial concentration of the nucleophilic telechelic polymer. The higher the initial concentration of PS, the higher is the polyformal degree of polymerization. The second or the third addition

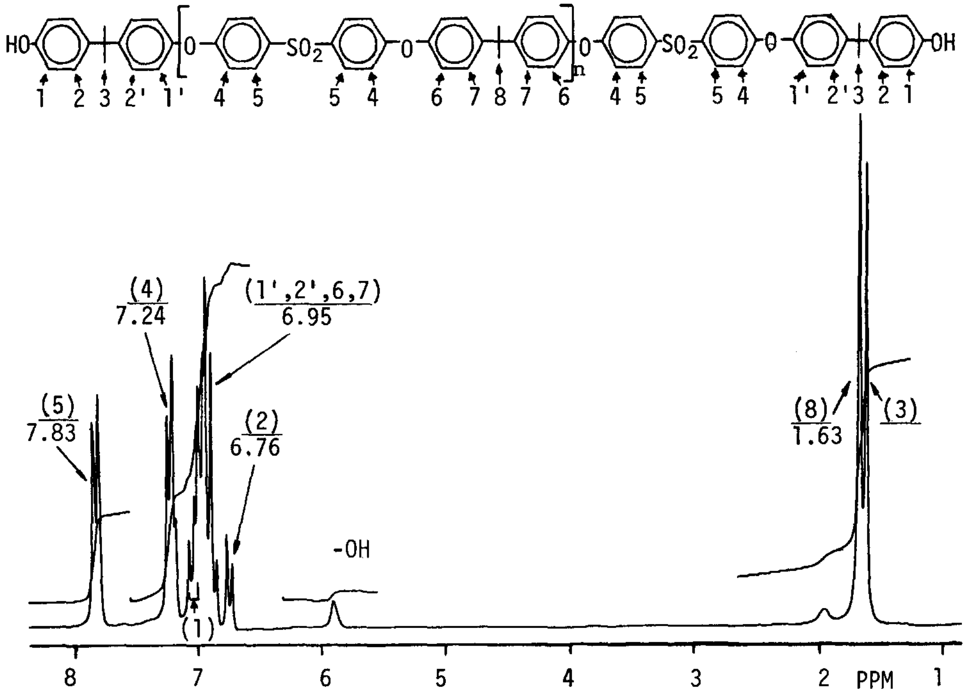

Figure 1: ^{1}H-NMR spectrum of PS used in exp. No.1 from Table 1

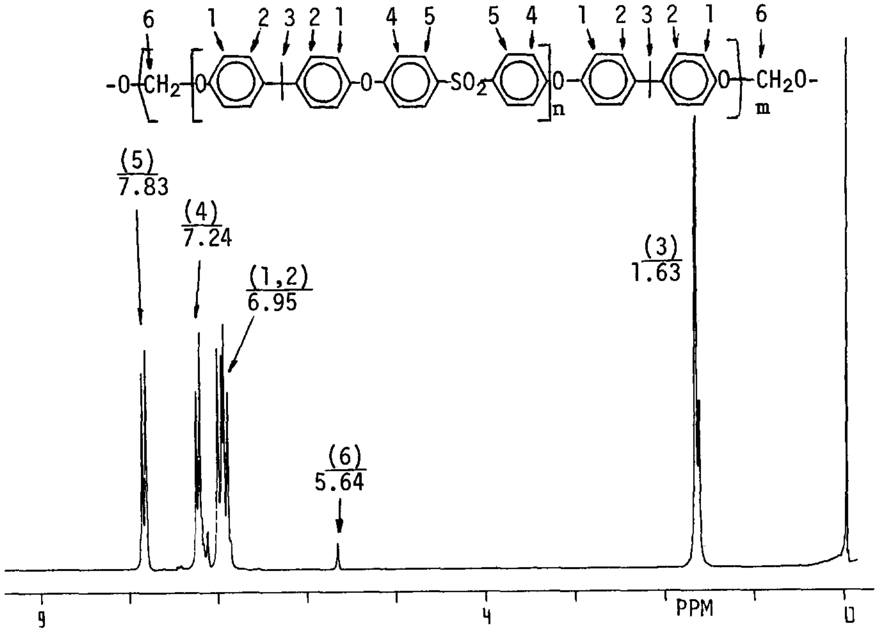

Figure 2: ^{1}H-NMR spectrum of polyformal No.5 from Table 1

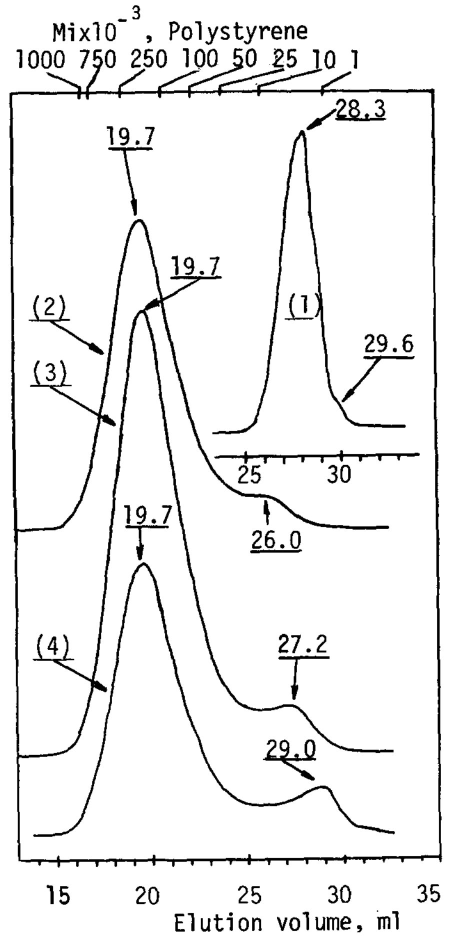

Figure 3: Gel Permeation Chromatograms of: (1) PS used in exp. No.2; (4) polyformal obtained in exp. No. 2; (3) polyformal No.2 precipitated with methanol/acetone (50/50, V/V) from chloroform solution; (2) polyformal (3) from this figure precipitated with methanol/acetone (10/90, V/V) from chloroform sol.

of methylene chloride does not affect the polyformal molecular weight (exp. No. 8, 9). The amount of NaOH used in polyetherification also does not affect the degree of polymerization of the polyformal. In one experiment (No. 7), samples were removed at different reaction times and analyzed by GPC. The conclussion is that the reaction is over after only 50 minutes. This was demonstrated by the fact that the molecular weight did not change after an other 21 hr of reaction.

The experiment No. 10 was done in methylene chloride. Consequently, the reaction was carried out at 40°C only. Even in this case the molecular weight of the polyformal was very high. A last experiment was performed in methylene bromide (No. 11) also at reflux temperature (96-98°C). In this case after only 3 minutes of reaction at reflux temperature, the mixture turned to a gel. This required more solvent to continue the reaction in solution. A high molecular weight polyformal was obtained in this case too.

All the obtained polyformals present higher Tg values than those of the starting PS (Table 1). For much higher molecular weights than those of the conventional aromatic polyether sulfones prepared from bisphenol-A and 4,4'-dichlorodiphenyl sulfones ($\bar{M}_n$ = 20,000, Tg = 195°C), these polyformals have Tg values which are with about 15 - 35°C lower than those of PS. This is due to the increased polymer chain flexibility. The Tg value does depend both on the polyformal molecular weight, as well, as on the molecular weight of the initial PS.

The obtained polyformals were characterized by 200 MHz ^{1}H-NMR. Typical NMR spectra of the α,ω-di(phenol)PS (the PS sample used in exp. No. 1) and of the polyformal (obtained in exp. No. 5) are presented in Fig. 1 and Fig. 2 together with their protonic resonance assignments. Complete reaction of the PS chain ends is assumed according to these spectra. The signal due to protons 2 (Fig. 1) is shifted in Fig. 2 proving complete chain ends reaction. Because of the high molecular weight of the polyformal, we could not yet determine the nature of these polymers chain ends. Presently we assume they should be of the chloromethoxy type, and if this is true, then these polymers could be useful as electrophilic chain ended telechelics for the preparation of alternating block copolymers by our previously described technique (1).

In spite of the fact that quantitative chain extension occurs (by NMR), all GPC curves of these polyformals present a shoulder in the region of the elution volumes (Ev) of the starting PS (Fig. 3). Besides the presence of cyclic aromatic polyether sulfones in the starting PS (Fig. 3, Ev = 29.6 ml) (1), the only explanation for this bimodal molecular weight distribution could be due to the formation of cyclic polyformals. Sample No. 2 from Table 1 was purified by succesive precipitations (Fig. 3). By this treatment the Ev of this shoulder decreased below that of the starting PS demonstrating that cyclic polyformals formation could not be excluded. A 3°C increase in the Tg value was observed after this purification.

CONCLUSIONS

Williamson liquid-liquid phase transfer catalyzed polyetherification of α,ω-di(phenol)aromatic polyether sulfones with methylene chloride used both as reactant and solvent provides a convenient synthetic procedure for the preparation of polyformals of aromatic polyether sulfones. The main factor controlling the molecular weight of these polyformals is the initial concentration of the polysulfone in the reaction mixture. Unusual high degrees of chain extension are obtained by this simple method. The physical properties of these polyformals can be varied both through the molecular weight of the starting polysulfone as well as through the polyformal molecular weight.

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