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Functional Polymers and Sequential Copolymers by Phase Transfer Catalysis.

6. On the Phase Transfer Catalyzed Williamson Polyetherification as a New Method for the Preparation of Alternating Block Copolymers

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SUMMARY

α,ω-di(Chloroallylic)polyethers and α,ω-di(phenol)aromatic polyether sulfones were purified from cyclic oligomers. Their characterization by ^{1}H- and ^{13}C-NMR spectroscopy demonstrates perfect bifunctionality of their chain ends. Phase transfer catalyzed polyetherification of stoichiometric amounts of these telechelics in the presence of tetrabutylammonium hydrogen sulfate, produced alternating block copolymers free of unreacted starting materials.

INTRODUCTION

In the first paper from this series we have proposed phase transfer catalyzed Williamson polyetherification as a new and convenient method for the preparation of alternating block copolymers (1). This method consists of the phase transfer catalyzed polyetherification of telechelic polymers containing α,ω-di(nucleophilic)- and α,ω-di(electrophilic) chain ends. The etherification reaction is performed in solution despite the fact that a liquid-liquid (organic solvent-water) type etherification is used. This is accomplished by using stoichiometric amounts of phase transfer catalyst versus the nucleophilic chain ends. Unsaturated polyethers containing chloroallylic end groups (prepared from cis- or trans-1,4-dichloro-2-butene and bisphenol A) as the electrophilic chain ends, and aromatic polyether sulfones containing terminal phenol groups (prepared from 4,4'-dichlorodiphenyl sulfone and bisphenol A) as the nucleophilic chain ends, were used to demonstrate the utility of this method (1). Alternating block copolymers with high molecular weight could be easily prepared by this method. In all cases a certain amount of unreacted starting materials limited the use of this new and simple synthetic procedure. It is the aim of this paper to demonstrate that when electrophilic or nucleophilic chain ended polymers free of cyclic compounds are used as starting materials, the phase transfer catalyzed Williamson polyetherification produces alternating block copolymers free of unreacted materials in less than one hr reaction time.

EXPERIMENTAL

Materials

Bisphenol-A (Aldrich) was recrystallized from aqueous methanol. 4,4'-Dichlorodiphenyl sulfone (Aldrich) was recrystallized twice from toluene. Cis-1,4-dichloro-2-butene (95% cis, 5% trans), tetrabutylammonium hydrogen sulfate (TBAH), toluene, chlorobenzene, DMSO, methylene chloride, methanol (all from Aldrich) were used as received.

Synthesis of α,ω-di(phenol)aromatic polyether sulfone (PS)

An α,ω-di(phenol)aromatic polyether sulfone was prepared by condensation

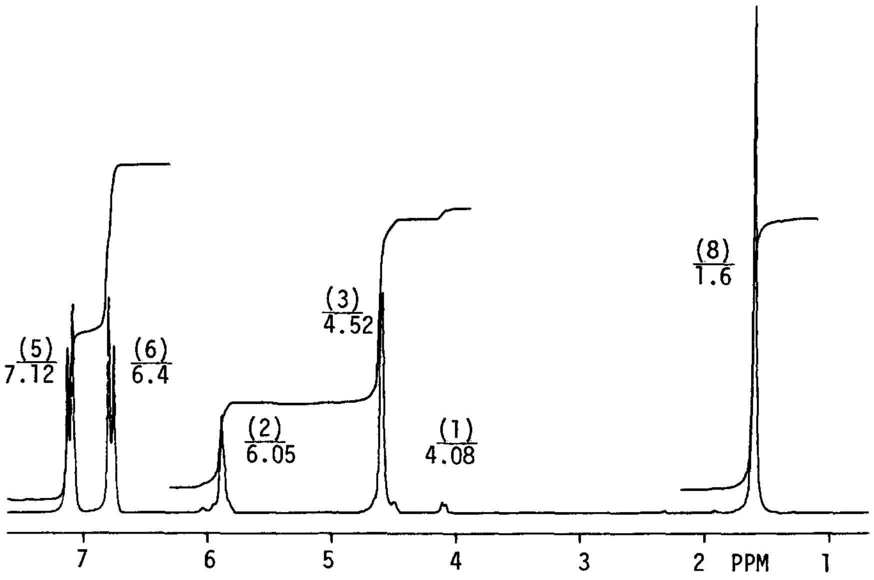


Figure 1: ^{1}H-NMR spectrum of α,ω-di(chloroallyl)PE (CDCl$_3$, TMS) (all notations correspond to those in Figure 3)

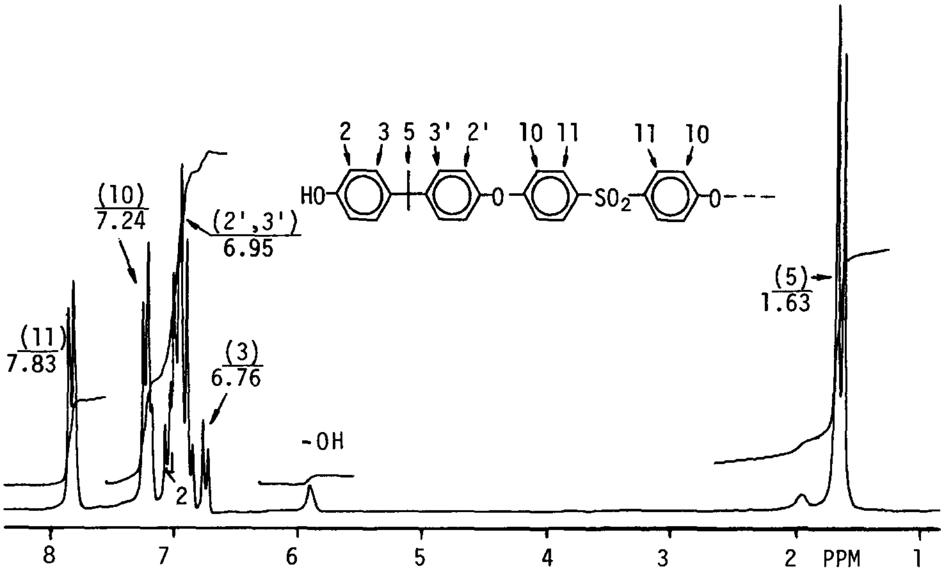


Figure 2: ^{1}H-NMR spectrum of α,ω-di(phenol)PS (CDCl$_3$, TMS)

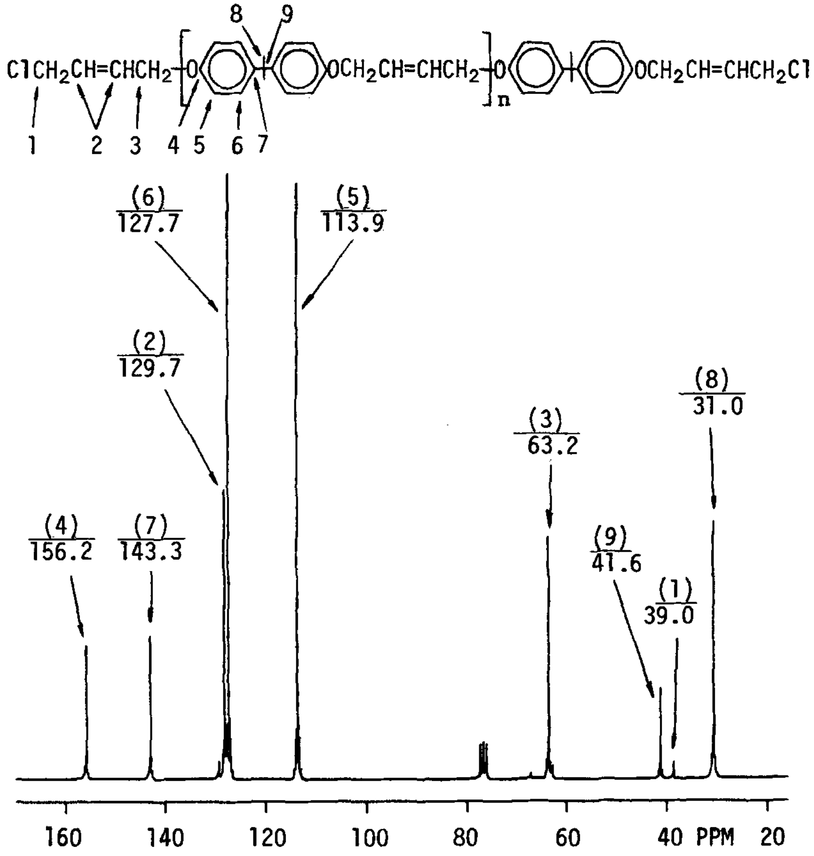


Figure 3: ^{13}C-NMR spectrum of α,ω-di(chloroallyl)PE ($CDCl_3$)

polymerization of 4,4'-dichlorodiphenyl sulfone with an excess of bisphenol A sodium salt (1.0 / 1.5 molar ratio) in DMSO as previously reported (1). Cyclic oligomers and eventual chlorophenyl terminated aromatic polyether sulfones were removed by precipitation of PS sodium salt from a methylene chloride solution. The synthetic procedure is as follows. 5g of PS were dissolved in 30 ml methylene chloride. Aqueous NaOH (5 ml, 50%) was added to this solution to precipitate the sodium salt of polysulfone. The organic phase was removed with a pipete, and the precipitated PS was washed several times with methylene chloride. Enough dilute HCl was added to a suspension of PS sodium salt in methylene chloride to bring the PS into solution. The methylene chloride solution was washed with water and the PS was precipitated with methanol and analyzed by GPC. Three precipitations from methylene chloride solution with NaOH were enough to produce a PS with $\bar{M}n$ = 2220 (determined by ^{1}H-NMR as previously reported (1)) free of cyclic compounds.

Synthesis of α,ω-di(chloroallyl)polyether (PE)

An α,ω-di(chloroallyl)polyether was prepared by condensation polymerization of bisphenol-A with excess cis-1,4-dichloro-2-butene (1/1.1 molar ratio) in a toluene - 3N aqueous NaOH reaction mixture , in the presence of TBAH (10 moles % versus bisphenol-A) at 70°C (1,2). Cyclic oligomers were

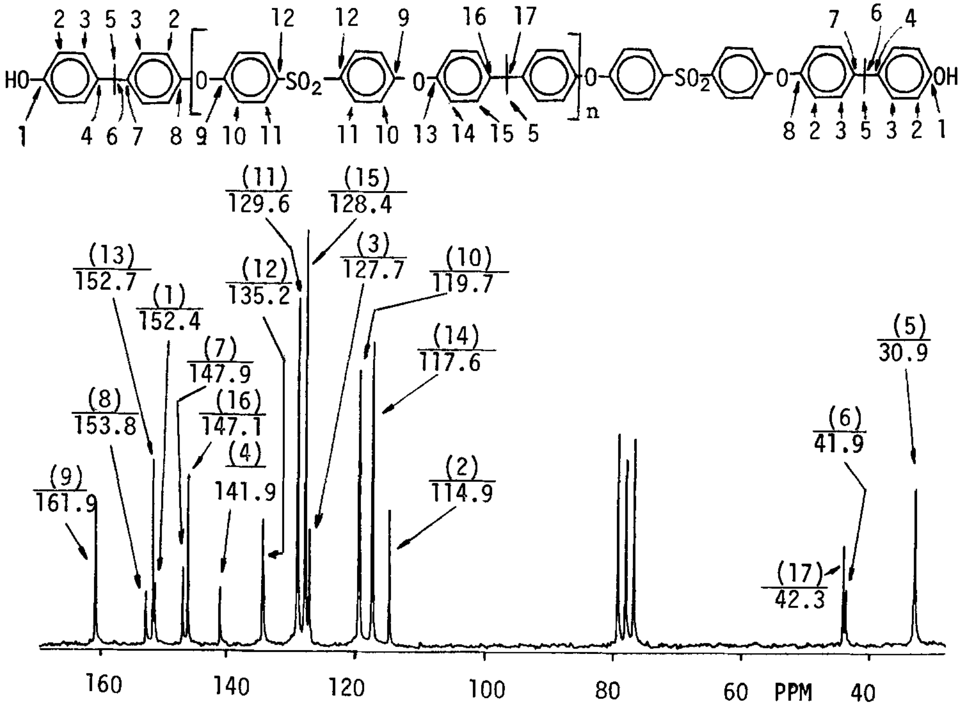


Figure 4: ^{13}C-NMR spectrum of α,ω-di(phenol)PS ($CDCl_3$)

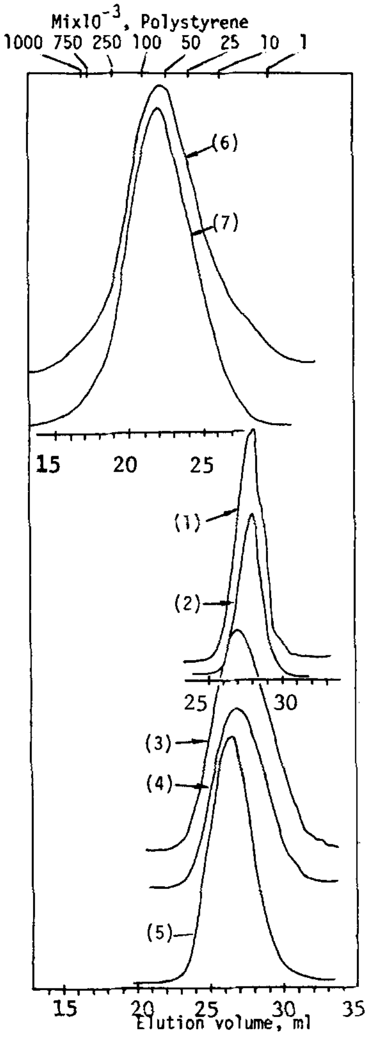
removed from this PE by two succesive precipitations from chloroform solutions. The first one was done with a 50/50 (V/V) methanol/acetone mixture and the second one with a 25/75 (V/V) methanol/acetone mixture. A PE with $\bar{M}n$ = 4900 (determined by ^1H-NMR as previously reported (1)) was obtained.

Alternating block copolymerizations

Solutions of PS ($8x10^{-5}$ moles in 3 ml chlorobenzene) and 3N aqueous NaOH (1 ml) were stirred together vigorously. The sodium salt of PS precipitated, but redissolved upon addition of TBAH ($1.6x10^{-4}$ moles) to produce a homogeneous solution. At this point a solution of PE ($8x10^{-5}$ moles) in 2 ml chlorobenzene were added and the reaction mixture was stirred at 70°C for 5 hr. The reaction mixture was cooled to room temperature. The organic phase was washed with water, dilute HCl was added to change the pH to acid, and the organic phase was diluted with chloroform. The alternating block copolymer was precipitated from the resulting chloroform solution using methanol

Techniques

200 MHz ^1H- and 50 MHz ^{13}C-NMR spectra were recorded using a Varian XL-200 spectrometer from $CDCl_3$ solution. Chemical shifts are reported relative to internal TMS. A Digilab FTIR spectrometer was used to record IR spectra of polymer films on KBr plates. GPC analysis 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.



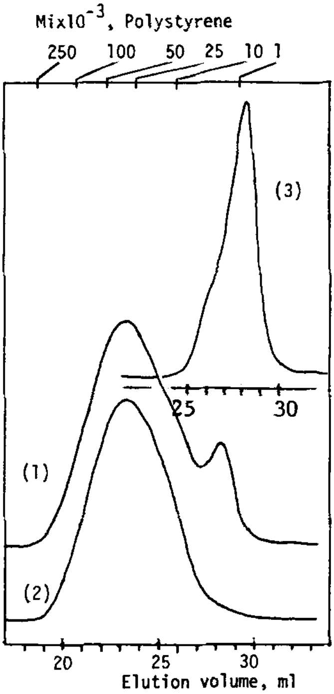


Figure 6 : (1) alt. block copolymer (PE/PS=1.6/1); (2) purif. alt. block copolymer; (3) unreacted PS removed by precipitation.

Figure 5 : (1) PS; (2) linear PS; (3) PE; (4) purified PE (acetone/methanol=50/50); (5) purified PE (acetone/methanol=75/50); (6) alternating block copolymer (PE/PS=1/1);(7) alt. block copolymer precipitated with acetone/methanol (90/10,V/V) from chloroform solution.

RESULTS AND DISCUSSION

Both α,ω-di(chloroallyl)PE and α,ω-di(phenol)PS free of cyclic oligomers were characterized by 200 MHz ^{1}H- and 50 MHz ^{13}C-NMR spectroscopy as well as by GPC. ^{1}H-NMR spectra of these compounds are presented in Fig.1 and Fig. 2 together with their proton resonance assignments. These spectra are of a perfectly bifunctional telechelic polymer as was already demonstrated in a previous paper (1). The ^{13}C-NMR spectra of these two polymers are presented in Fig. 3 and Fig. 4. The assignments of the main chain and chain ends carbon resonances were made using chemical shift additivity rules (3) and in the case of PS are consistent with those previously proposed in the literature (4).

No resonance at about 153 ppm due to bisphenol chain end was detected in the ^{13}C-NMR spectrum of the PE (Fig. 3) (3). At the same time the PS spectrum does not exhibit a resonance at 140.22 ppm due to chlorophenyl chain ends (4). Additionally, the FTIR spectrum of PE does not contain an -OH absorption due to phenol end groups. Consequently, both PE and PS are perfectly bifunctional telechelic polymers.

The GPC traces of the unpurified and purified PE and PS are shown in Fig. 5. After purification the shoulders at higher elution volumes were removed from both PE and PS by precipitation. A typical GPC curve for an alternating polymer is also presented in Fig. 5. It does not exhibit any evidence for unreacted PE or PS. After one more precipitation from chloroform solution with acetone-methanol (90/10, V/V) mixture the very small shoulder at higher elution volumes was removed. Consequently, perfectly pure alternating block copolymers can be prepared when 1:1 molar ratio between the dinucleophilic and dielectrophilic telechelics is used. In order to follow the reaction course, samples were removed at different reaction times and analyzed by GPC. In this way it was demonstrated that both the molecular weight as well as the yield of the alternating block copolymer does not increase after 50 minutes of reaction at 70°C.

Several experiments were performed with a slight molar excess of PS versus PE (1.1/1.0 -1.6/1.0). In all cases the alternating block copolymer obtained exhibits a bimodal distribution of the molecular weight. The product from higher elution volume could be removed by precipitation from chloroform solution with acetone/methanol (90/10, V/V). Figure 6 shows a typical example of crude block copolymer, purified block copolymer, and for the acetone/methanol removed fraction. Pure alternating block copolymers can be prepared in this way too. The removed fraction exhibits the same maximum as that of the starting PS. Consequently, only the excess PS did not react.

We assume that the alternating block copolymer prepared in the presence of excess of PS should have phenolic chain ends. If this is so, this method could be extended to the preparation of alternating multiblock copolymers. Research is in progress to demonstrate this. A large variety of alternating block copolymers prepared by this method are being studied in our laboratory.

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REFERENCES

1. V. Percec and B. C. Auman, Makromol. Chem., in press
2. T. D. N'Guyen and S. Boileau, Polym. Bull., 1, 817(1979)
3. G. C. Levy, R. L. Lichter and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd Ed., John Wiley, New York, 1980
4. A. Kh. Bulai, Yu. G. Urman, I. Ya. Slonim, L. M. Bolotina, L. Ye. Reitburd, M. M. Gol'der, A. N. Shapovalova and R. N. Sivakova, Polym. Sci. U.S.S.R., 24, 1183(1983)

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