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Syntheses

Comb-Like Polymers and Graft Copolymers from Macromers

1. Synthesis and Characterization of Methacrylate and Styrene Macromers of Aromatic Polyether Sulfones

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Dedicated to Professor J. P. Kennedy on his 55th birthday

SUMMARY

The synthesis of aromatic polyether sulfone macromers containing methacrylate and styrene as polymerizable groups is presented. Their characterization by 200 MHz ^{1}H- and 50 MHz ^{13}C-NMR, and FTIR spectroscopies demonstrated the presence of one polymerizable chain end per aromatic polyether sulfone molecule.

INTRODUCTION

One of the most interesting techniques for the preparation of comb-like polymers and graft copolymers consists of the homopolymerization or copolymerization of a macromer. The macromer concept (macromoleculer monomer) was developed by Milkovich (1-3) and represents a polymer containing a polymerizable group at one chain end. The interest in this novel strategy for the preparation of graft copolymers developed only after Vogl reviewed this concept (4). Since then, several research groups have become actively engaged in the use of the macromer technique for the synthesis of novel graft copolymers (5-11). This paper presents the synthesis and characterization of methacrylate- (PS-MM) and styrene-type (PS-St) macromers of aromatic polyether sulfones. The first step of the synthetic procedure is the synthesis of an aromatic polyether sulfone containing one phenol end group (PS-OH). PS-MM was obtained by esterification of PS-OH phenol chain ends with methacryloyl chloride in the presence of 4-N,N-dimethylaminopyridine. PS-St was synthesized by Williamson etherification of the PS-OH phenol end groups with a commercial mixture of m- and p-chloromethylstyrene in the presence of tetrabutylammonium hydrogen sulfate phase transfer catalyst. In both cases 200 MHz ^{1}H- and 50 MHz ^{13}C-NMR, and FTIR spectroscopies were used to demonstrate the quantitative functionalization of PS-OH phenol end groups.

EXPERIMENTAL

Materials

4,4'-Dichlorodiphenyl sulfone (DCPS) (Aldrich) was recrystallized twice from toluene. Sulfolane (Aldrich) was purified and dried by conventional methods (12) and kept over BaO. Chloromethylstyrene (40%p, 60%m, from Dow Chemical Co.,) (CMS), tetrabutylammonium hydrogen sulfate (TBAH), 4-N,N-dimethylaminopyridine (DMAP), methacryloyl chloride (MC) and triethylamine (TEA) (all from Aldrich), were used as received.

4-Chloro-4'-hydroxydiphenyl sulfone (CHPS)

CHPS was prepared by the hydrolysis of DCPS with 50% aqueous KOH (2 moles KOH for one mole of DCPS) in DMSO according to a literature method (12, 13). The product obtained was recrystallized from a methanol/toluene (50/50, V/V) and then from toluene (mp 147.5-149°C).

Potassium salt of 4-chloro-4'-hydroxydiphenyl sulfone

This compound was prepared from a 4N potassium hydroxide solution in aqueous methanol and methanolic CHPS by using the same procedure reported earlier (14). The potassium salt was vacuum dried for 24 hr at 120°C before use.

Synthesis of PS-OH

PS-OH was prepared by condensation polymerization of the potassium salt of CHPS in sulfolane (40% phenoxide) under nitrogen at 230°C (14). The reaction time was 20 hr. The solution obtained was cooled and diluted with DMSO. The product was precipitated from solution with acidified water, then twice dissolved in CH_2Cl_2 and precipitated with methanol. $\bar{M}n$ = 2085 (calculated from 200 MHz ^{1}H-NMR spectrum in DMSO, Fig. 1).

Synthesis of PS-MM

A solution of methacryloyl chloride (0.9 ml, 0.009 moles) in 3 ml of CH_2Cl_2 was added dropwise to a stirred CH_2Cl_2 solution (30 ml) of PS-OH (0.0029 moles of -OH), DMAP (0.35 g, 0.0029 moles), and TEA (0.8 ml, 0.006 moles) cooled in ice-water. After stirring one hr at the ice-water temperature and 5 hr at room temperature, the reaction mixture was washed with dilute HCl solution, then water. The solution was dried over $CaCl_2$ and the product was precipitated with methanol.

Synthesis of PS-St

A 50% aqueous solution of NaOH (7 ml) was added to a stirred solution of PS-OH (6 g, 0.0029 moles -OH) in 40 ml CH_2Cl_2 at room temperature. The sodium salt of PS-OH precipitated immediately. After the addition of TBAH 0.99 g, 0.0029 moles), the reaction mixture became homogeneous once more. The addition of CMS (1.5 ml, 0.015 moles) created a dark blue colored reaction mixture. After stirring 1 hr at room temperature, the color of the reaction mixture turned to light green and shortly thereafter to yellow. 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 CH_2Cl_2, washed twice with water, dried over $CaCl_2$ 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 ^{1}H- and 50 MHz ^{13}C-NMR spectra were recorded on a Varian XL 200 spectrometer in different solvents ($DMSOd_6$, $CDCl_3$, CH_2Cl_2). Chemical shifts are reported relative to internal TMS. IR spectra of polymer films on KBr plates were recorded on a Digilab FTIR spectrometer.

RESULTS AND DISCUSSION

Aromatic polyether sulfones exhibit interesting physical properties. To the best of our knowledge no graft copolymers of this polymer have been reported in the literature. Since both chain end groups of PS-OH can be easily characterized by ^{1}H- and ^{13}C-NMR spectroscopy, the functionalization of the phenol chain end can be followed spectroscopically without difficulties.

An important advantage to the use of PS-OH in the synthesis of glassy macromers is its insolubility in $CHCl_3$. After the -OH end group is reacted, the macromer becomes soluble in $CHCl_3$. Additionally, PS-OH can be easily precipitated from its CH_2Cl_2 solution in the form of Na or K salt. Both of these features can be used as necesary for the purification of either PS-OH or its derivatives.

Figure 1 presents the ^{1}H-NMR spectra of DCPS (left), CHPS (middle) and PS-OH (right). The chemical shifts of the first two compounds were used as

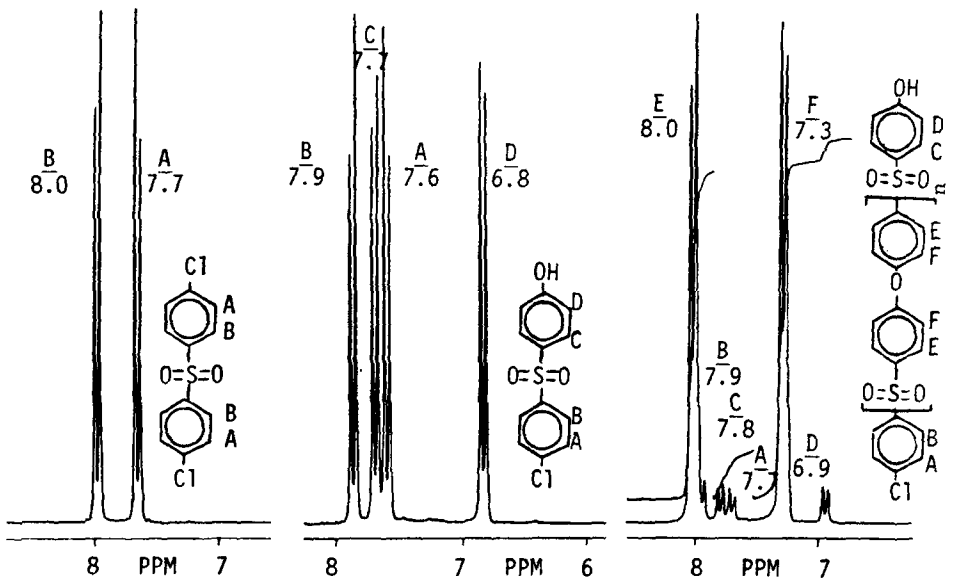

Figure 1. ^{1}H-NMR spectra ($DMSOd_6$) of: DCPS (left spectrum); CHPS (middle spectrum); PS-OH (right spectrum)

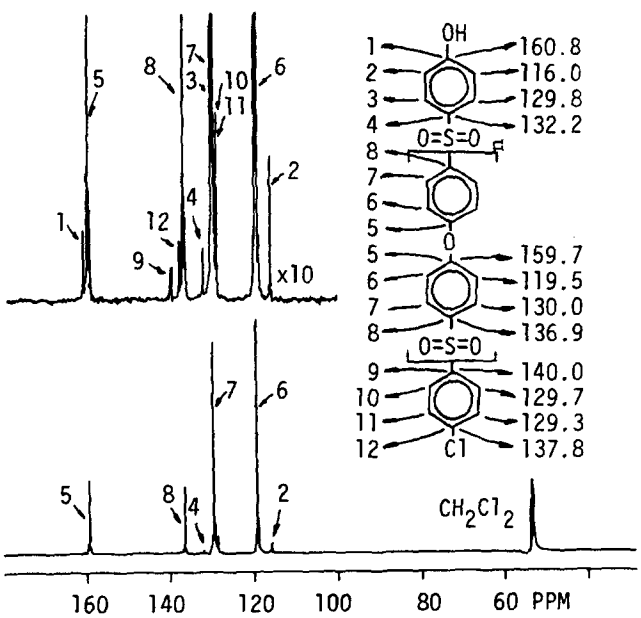

Figure 2. ^{13}C-NMR spectrum (CH_2Cl_2) of PS-OH

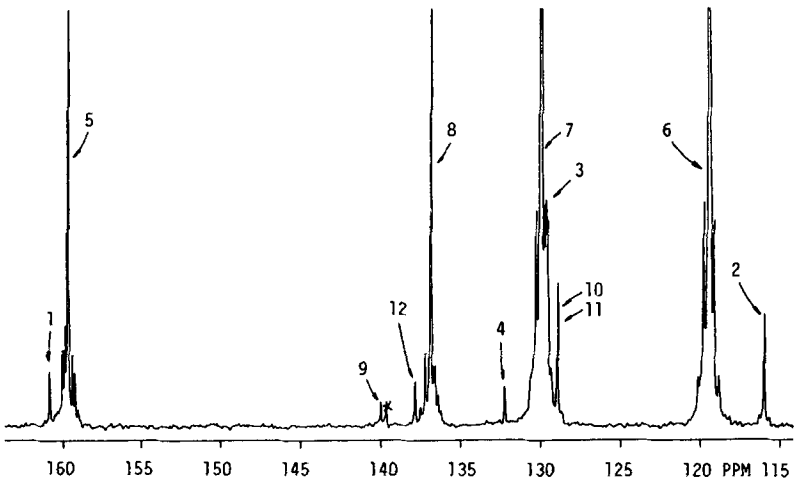

Figure 3. ^{13}C-NMR spectrum (CH_2Cl_2) of PS-OH: an expansion of the aromatic region

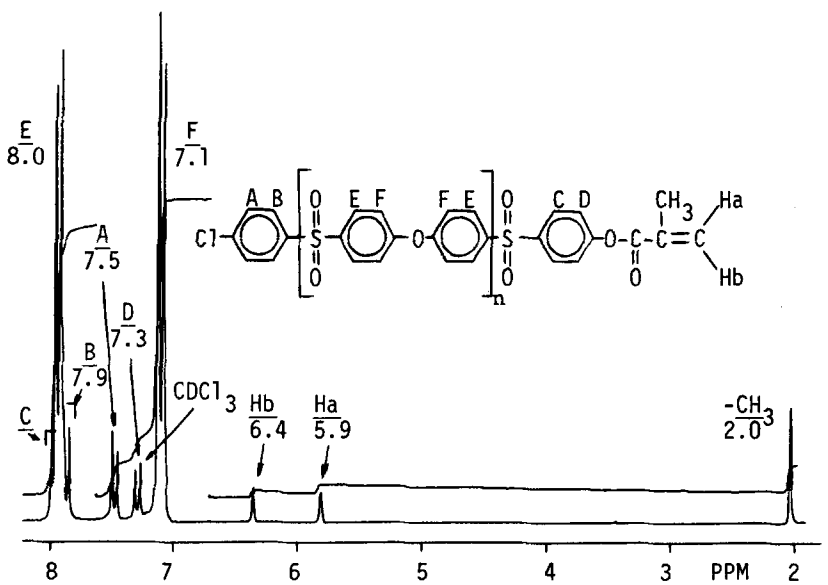

Figure 4. ^{1}H-NMR spectrum ($CDCl_3$) of PS-MM

models for the ^{1}H-NMR resonance assignments of the PS-OH chain ends. The areas under signals D, A and C in the PS-OH spectrum are equal. This demonstrates that the concentrations of phenol and chlorophenyl end groups are equal (i.e., each polymer chain contains one phenol chain end). The degree of polymerization of PS-OH was calculated from the formula: $\overline{DP}=F/2D=F/(A+C)$. The ^{13}C-NMR spectrum of PS-OH is shown in Figure 2, and an expansion of the aromatic region of this spectrum is shown in Figure 3.

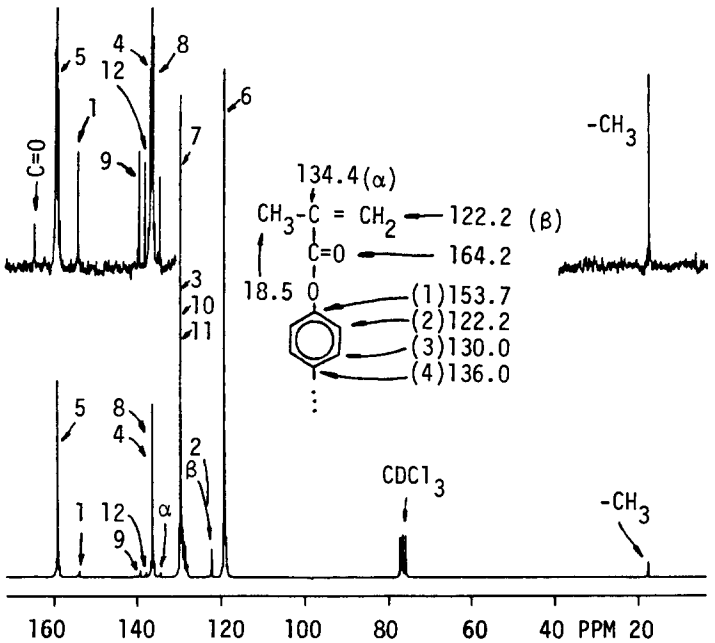

Figure 5. ^{13}C-NMR spectrum ($CDCl_3$) of PS-St

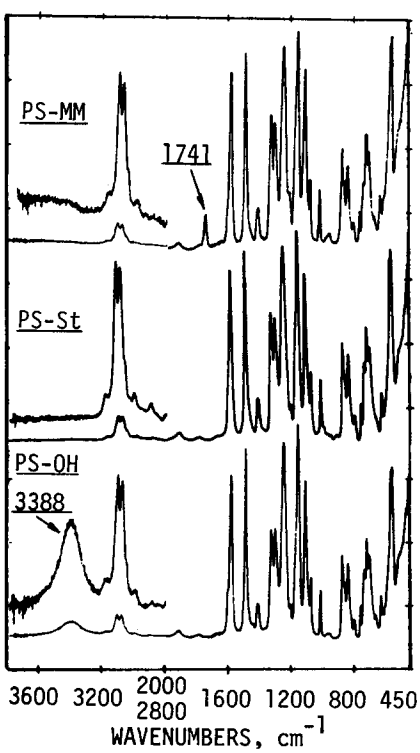

Figure 6. FTIR spectra of: PS-MM, PS-St, PS-OH

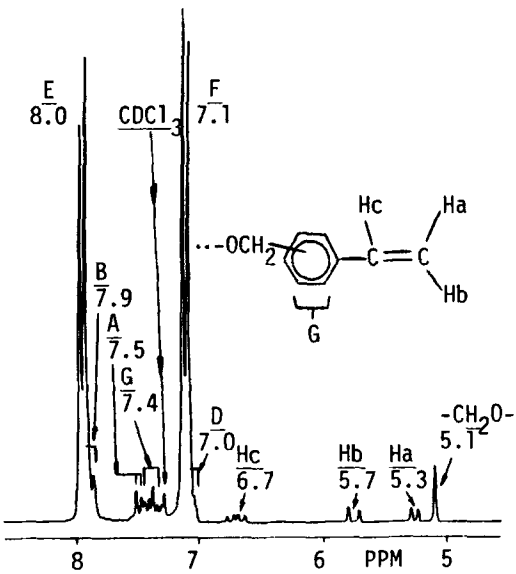

Figure 7. ^{1}H-NMR spectrum ($CDCl_3$) of PS-St

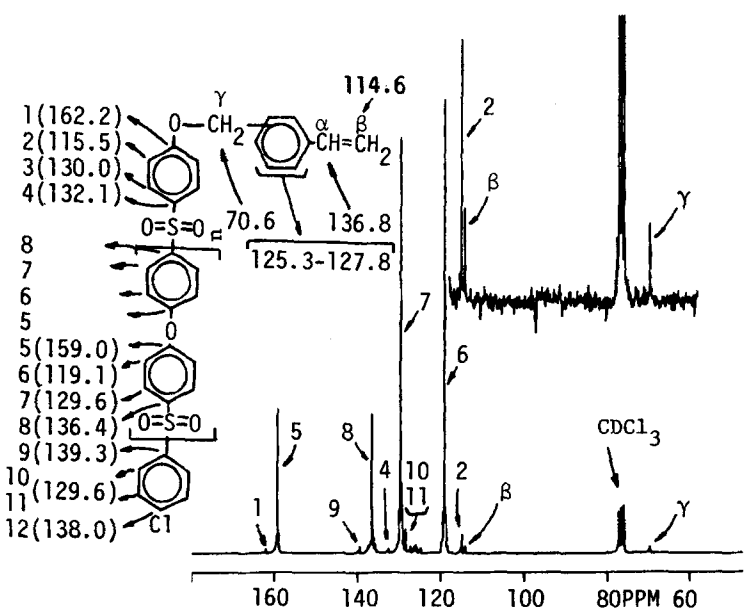

Figure 8. ^{13}C-NMR spectrum ($CDCl_3$) of PS-St

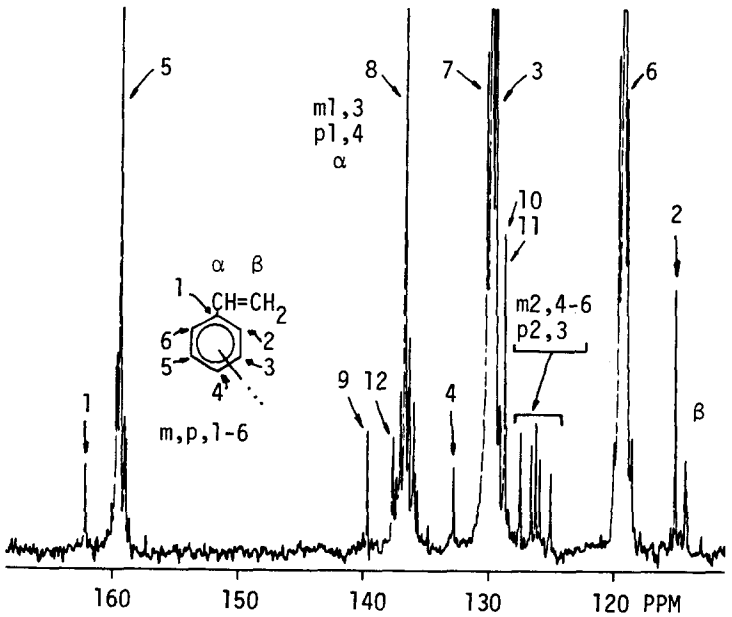

Figure 9. ^{13}C-NMR spectrum of PS-St ($CDCl_3$): an expansion of the aromatic region

Resonance assignments were made by comparison with shifts calculated using ^{13}C chemical shift additivity rules for substituted benzenes (15). The ^{13}C-NMR chemical shifts of DCPS were used to calculate substituent additivity parameters for the $PhSO_2$- group (+13.5, -0.1, +0.4, and +2.0 ppm for C_1, C_o, C_m and C_p, respectively). The degree of polymerization can also be calculated from the ^{13}C-NMR spectrum, but it is less accurate than that obtained from the ^1H-NMR data. This is primarily due to the higher signal to noise levels achieved in the ^1H-NMR spectra which makes integration more reliable than in the ^{13}C spectra.

Both the esterification in the presence of DMAP and Williamson etherification in the presence of TBAH phase transfer catalyst (16) were shown by FTIR, ^1H- and ^{13}C-NMR spectroscopies to give quantitative reaction of the phenolic chain ends. Figure 4 presents the ^1H-NMR spectrum of the PS-MM. Signals D and C are shifted after esterification (compare Fig. 1 and 4). At the same time the area of the signals D or A is equal to the area of (Ha+Hb). The ^{13}C-NMR spectra of PS-OH and PS-MM (compare Fig. 2 and 5) also demonstrate this. Resonances 1, 2, 3 and 4 corresponding to phenol chain end carbons are shifted after esterification, and in addition, PS-MM also exhibits carbon resonances due to methacrylate group (Fig. 5). Additional evidence for complete esterification is obtained from FTIR spectra (Fig. 6). The -OH absorption (3388 cm^{-1}) of the phenol end in PS-OH disappears completely after esterification (PS-MM) and a new absorption due to the C=O appears at 1741 cm^{-1}.

Complete etherification of the phenol groups with CMS was demonstrated by using the same techniques. In the FTIR spectrum of the PS-St the -OH absorption at 3388 cm^{-1} disappears (Fig. 6). The ^1H-NMR spectrum of PP-St (Fig. 7) exhibits a shift of the signals C and D, and at the same time the relative areas of signals Hc, Hb, Ha and $-\underline{CH_2}O-$ compared with the area of the signals (A+G) show that quantitative etherification has taken place. A

^{13}C-NMR spectrum of PS-St is presented in Fig. 8, with an expansion of the aromatic region of this spectrum shown in Fig. 9. The differences between the chemical shifts of carbons 1-4 from PS-OH and PS-St are not as great as in the case of the PS-MM derivative. Assignment of the resonances from carbons 1-6 on the vinylbenzyl chain end is difficult because of the presence of both m- and p-isomers (Fig. 9).

In conclussion, methacrylate- and styrene-type aromatic polyether sulfone macromers can be prepared without difficulties. Their spectroscopic characterization demonstrates the presence of one polymerizable end group per aromatic polyether sulfone molecule. The homopolymerization and copolymerization of these macromers with methacrylate type monomers and styrene are being studied and will be reported elsewhere.

ACKNOWLEDGEMENTS

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