Polymer Bulletin 12, 253–260 (1984)

Polymer Bulletin

Functional Polymers and Sequential Copolymers by Phase Transfer Catalysis.

11. Synthesis of α,ω-Di(chloroallyl)- and α,ω-Di(bromobenzyl) Aromatic Polyether Sulfones

Virgil Percec and Brian C. Auman

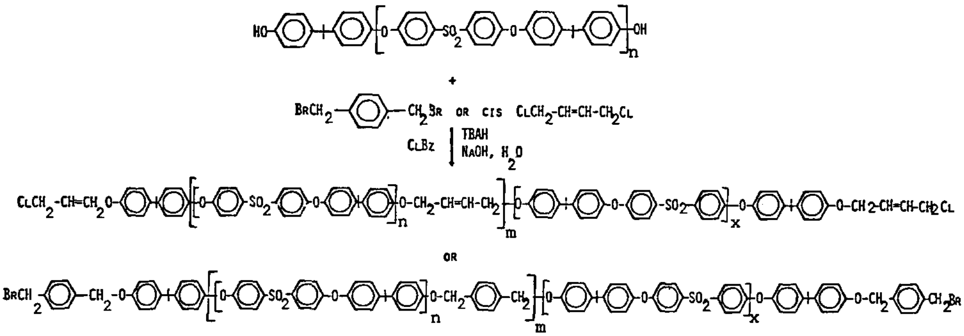
Department of Macromolecular Science Case Western Reserve University Cleveland,
OH 44106, USA

SUMMARY

The phase transfer catalyzed polyetherification of α,ω-di(phenol)aromatic polyether sulfones (PSU) with cis-dichloro-2-butene and α,α'-dibromo-p-xylene in two phase reaction conditions (monochlorobenzene-aqueous NaOH) gives α,ω-di(chloroallyl)PSU and α,ω-di(bromobenzyl)PSU. Reaction conditions which lead to perfectly bifunctional α,ω-di(electrophilic)PSU are presented.

INTRODUCTION

Previously, we have demonstrated that phase transfer catalyzed etherification and polyetherification provide convenient methods for the synthesis of macromonomers (1-4), regular copolymers (5,6) including liquid crystalline polyethers (7), alternating block copolymers (5,8,9) and ABA triblock copolymers (10). α,ω-Di(electrophilic) oligomers are suitable starting materials for the synthesis of several classes of macromonomers (4), and for the preparation of both alternating (5,8,9), as well as, triblock copolymers (10). They are also useful as macroinitiators for cationic ring opening polymerization, and consequently, can be exploited for the preparation of ABA triblock copolymers. This paper presents the synthesis and characterization of α,ω-di(chloroallyl)- and α,ω-di(bromobenzyl) aromatic polyether sulfones. Scheme 1 outlines the synthetic routes used for their preparation.



Scheme 1: Synthesis of α,ω-di(electrophilic) aromatic polyether sulfones

EXPERIMENTAL

A. Materials

Bisphenol-A (Aldrich) (BPA) was recrystallized from aqueous methanol, 4,4'-dichlorodiphenyl sulfone (DCPS) (Aldrich) from toluene, and α,α'-dibromo-p-xylene (DBX) (Aldrich) from carbon tetrachloride. Cis-1,4-dichloro-2-butene (c-DCB, 95% cis, 5% trans), tetrabutylammonium hydrogen sulfate (TBAH) and all the other reagents (all from Aldrich) were used as received.

B. Techniques

200 MHz ^{1}H- and 50 MHz ^{13}C-NMR spectra were recorded on a Varian XL-200 spectrometer ($CDCl_3$, TMS). A Digilab FTIR spectrometer was used to record IR spectra of polymer films on KBr plates. Tg values were determined by a Perkin-Elmer DSC-2 differential scanning calorimeter. Indium was used as calibration standard. GPC analyses were carried out with RI and UV detectors, using micro-styragel columns of 10^4, 10^3 Å , and a calibration plot constructed with polystyrene standards.

C. Synthesis of α,ω-Di(phenol)PSU

The α,ω-di(phenol)PSU oligomers were synthesized and characterized as previously reported (5). PSU-2 was synthesized by using a molar ratio of BPA/DCPS=1.2/1.0, while PSU-5 by using a molar ratio of 2.0/1.0. Table 1 summarizes several characteristics of these oligomers.

D. Synthesis of α,ω-Di(chloroallyl)PSU (PSU-CA)

A typical procedure is presented in the following example. PSU-5 (5.0g, 4.14 mmole) was dissolved in 45ml monochlorobenzene. An aqueous solution of 12% NaOH (25ml, 75mmole) was added to the stirring solution, and the sodium salt of the PSU precipitated immediately. After the addition of 2.8114g (8.28 mmole) of TBAH, the reaction returned to a clear solution. c-DCB (2.6 g, 20.8 mmole) was added, and the mixture was allowed to stir at 70°C for the reaction times given in Table 1. After cooling, the reaction mixture was acidified with dilute HCl. The organic layer was separated, washed several times with water, and the polymer was separated by precipitation with methanol. The resulting polymer was always purified through two more precipitations with methanol from chloroform solution.

E. Synthesis of α,ω-Di(bromobenzyl)PSU (PSU-BX)

The synthesis of PSU-BX was carried out under similar experimental conditions as those presented for PSU-CA except that c-DCB was replaced with DBX.

Table 1:Synthesis and Characterization of α,ω-Di(electrophilic)PSU

Sample	α,ω-Di(phenol) PSU*		Dielectrophilic Monomer		ClBz	NaOH 12%,	Reaction	α,ω-Di(electrophilic)PSU				
								$\overline{Mn}$	$\overline{Mn}$	$\overline{Mw}$	$\overline{Mw}/\overline{Mn}$	Tg
	Sample	mmole	Type	mmole	ml	ml	Time, hr	NMR	GPC			°C
PSU-BX1	PSU-5	3.31	DBX	33.1	40	11	2.7	1,850	1,900	2,400	1.3	82
PSU-CA1	PSU-5	4.14	c-DCB	20.8	45	25	1.8	1,930	2,300	3,200	1.4	67
PSU-CA2	PSU-5	1.49	c-DCB	3.0	15	8	6.5	3,800	4,000	7,500	1.9	103
PSU-CA3	PSU-5	4.47	c-DCB	9.0	45	24	2.0	4,800	3,900	7,200	1.9	105
PSU-CA4	PSU-2	1.64	c-DCB	3.28	42	10	2.0	11,300	7,300	16,700	2.3	149

*PSU-5, $\overline{Mn}$=1,210, Tg=87°C;PSU-2, $\overline{Mn}$=3,050, Tg=138°C

F. Determination of $\overline{Mn}$ of PSU-CA and PSU-BX

The number average molecular weights ($\overline{Mn}$) of the PSU-CA and PSU-BX were determined by 200 MHz ^{1}H-NMR spectroscopy, based on the following polymer structures:

$$\mathrm{ClCH_2\text{-}CH{=}CH\text{-}CH_2\left[OPSU\text{-}OCH_2\text{-}CH{=}CH\text{-}CH_2\right]_n\text{-}OPSU\text{-}OCH_2\text{-}CH{=}CH\text{-}CH_2Cl}$$

$$\mathrm{BrCH_2\text{-}Ph\text{-}CH_2\left[OPSU\text{-}OCH_2\text{-}Ph\text{-}CH_2\right]_n\text{-}OPSU\text{-}OCH_2\text{-}Ph\text{-}CH_2Br}$$

and using the following relationships:

$$\bar{n}=[A_{-CH=CH-}/2]/[A_{-CH_2Cl}/4]-2=[A_{-CH_2O-}/4]/[A_{-CH_2Cl}/4]-1 \quad \text{for PSU-CA, and}$$

$$\bar{n}=[A_{-Ph-}/4]/[A_{-CH_2Br}/4]-2=[A_{-CH_2O-}/4]/[A_{-CH_2Br}/4]-1 \quad \text{for PSU-BX}$$

RESULTS AND DISCUSSION

Phase transfer catalyzed Williamson polyetherification of c-DCB with BPA yields amorphous polyethers (5,8,13), while polyetherification of t-DCB with BPA provides crystalline polyethers (5). In both cases, the resulting polymers are soluble in the organic phase of the reaction medium (in these cases, toluene). Several particularities of this reaction which are not yet completely elucidated, make this polyetherification a simple synthetic method for the preparation of α,ω-di(chloroallyl)polyethers.

In contrast to the above, the polyetherification of α,α'-dichloro(bromo)-p-xylene (DCX, DBX) with BPA produces polymers which are insoluble in the organic phase of the reaction medium (14). Under these reaction conditions (14) and depending on the nature of the solvent used, the use of DCX or DBX leads to several side reactions which affect both the polymer's microstructure and the nature of its chain ends. For example, in non-polar aprotic solvents, DCX or DBX behave both as nucleophile and electrophile.Because of this, and because of their high concentration in the organic phase (versus that of the onium bisphenate), they can react with themselves (15), i.e.,:

$BrCH_2PhCH_2Br + OH^- \longrightarrow BrCH_2PhCH^-Br$

$BrCH_2PhCH^-Br + BrCH_2PhCH_2Br \longrightarrow BrCH_2[PhCHBrCH_2]_nPhCH_2Br$

$BrCH_2[PhCHBrCH_2]_nPhCH_2Br + OH^- \longrightarrow BrCH_2[PhCH{=}CH]_nPhCH_2Br$

The poly(p-xylylidene) units, thus formed, decrease the solubility of the resulting polyether. Once the polyether precipitates from solution, the displacement of the chloro- or bromobenzylic chain ends by OH^- occurs. i.e.,

$\sim\sim PhCH_2Br + OH^- \longrightarrow \sim\sim PhCH_2OH$

The reaction performed in this manner typically gives low molecular weight polyethers with low electrophilic chain end functionality.

To increase the molecular weight of the obtained polyethers, Yamazaki and Imai (16) used a mixture of dipolar aprotic solvents (e.g., DMSO, DMF, etc) and nonpolar aprotic solvents (e.g., toluene, etc) as the organic phase of the reaction. Under these conditions, high molecular weight polyethers could be obtained;however, the resulting polymers do not contain only electrophilic chain ends. This is basically because the extraction constant (and the nucleophilicity) of anions like OH^- is very high in dipolar aprotic solvents. Once the concentration of the stronger nucleophile (onium phenolate) is very low (4,10), this reaction particularity causes the displacement of the electrophilic end groups by OH^-.

In order to avoid these side reactions, the polymerization should be performed under conditions in which the extraction constant for OH^- into the organic phase is very low, but the extraction constant of the onium bisphenate is very high. The organic phase must also be a good solvent for the resulting polymer. The use of aromatic solvents (like chlorobenzene) which are typically poor solvents for phase transfer catalyzed reactions, lead to a very low extraction constant for OH^-. On the other hand, the use of oligomeric bisphenols which are very lipophilic, will enhance their extraction constant into these solvents, and will yield a high concentration of the nucleophile in the organic phase. Consequently, phase transfer catalyzed etherification and polyetherification are particularly effective for performing quantitative reactions with polymeric chain ends. This reaction particularity was exploited by us in the preparation of α,ω-di(electrophilic)PSU.

FTIR, 200 MHz ^1H- and 50 MHz ^{13}C-NMR spectroscopies were used to demonstrate the quantitative functionalization of the α,ω-di(phenol)PSU chain ends with chloroallyl and bromobenzyl electrophilic groups. The absence of the absorption at 3448 cm^{-1} (ν-OH) in the FTIR spectra of α,ω-di(electrophilic)PSU offers the first evidence for the complete conversion of the phenol chain ends in these two products. Figures 1,2 and 3 present typical ^{13}C-NMR spectra of the α,ω-di(phenol)PSU and of the α,ω-di(electrophilic)PSU, together with their carbon resonance assignments. The resonence of carbon 6 (the quaternary carbon of the isopropylidene group from the terminal BPA unit of α,ω-di(phenol)PSU) is downfield versus the resonance of carbon 17 (same carbon but from internal BPA units) in α,ω-di(phenol)PSU (Fig.1). After the terminal BPA unit was completely etherified with either c-DCB or DBX, the chemical shift of carbon 6 was shifted upfield in comparison with that of carbon 17 (Fig.1-3). In addition, both PSU-CA2 (Fig.2) and PSU-BX1 (Fig.3) exhibit the expected resonances for the chloroallyl and bromobenzyl chain ends. Even more representative is the evidence from the 200 MHz ^{1}H-NMR spectra of α,ω-di(phenol)PSU (Fig.4), α,ω-di(chloroallyl)PSU (Fig.5) and α,ω-di(bromobenzyl)PSU (Fig.6). It is important to notice the following two particularities of these spectra. α,ω-Di(phenol)PSU presents two resonances for the methyl protons of the isopropylidene groups from BPA units.

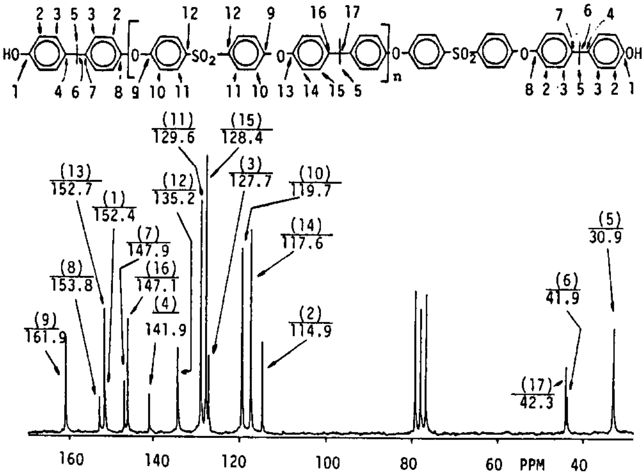
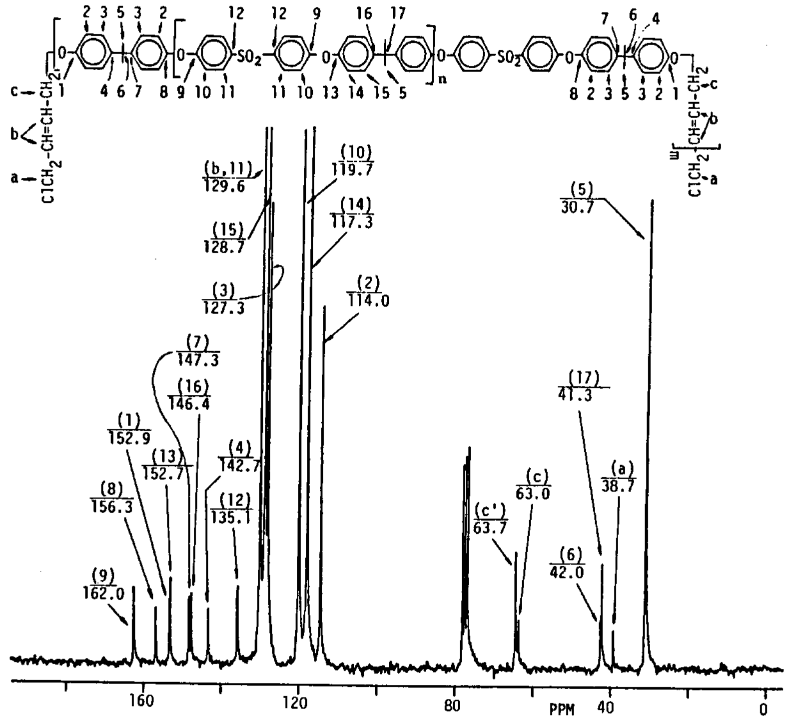


Figure 1: ^{13}C-NMR spectrum of α,ω-di(phenol) PSU-5 from Table 1

Figure 2: ^{13}C-NMR spectrum of α,ω-di(chloroallyl)PSU (PSU-CA1 from Table 1)



One is situated at 1.63 ppm (signal 8) and is due to internal BPA units, and the other at 1.60 ppm (signal 3) and is due to terminal BPA units (5). The second representative resonance is that of the meta aromatic protons (versus

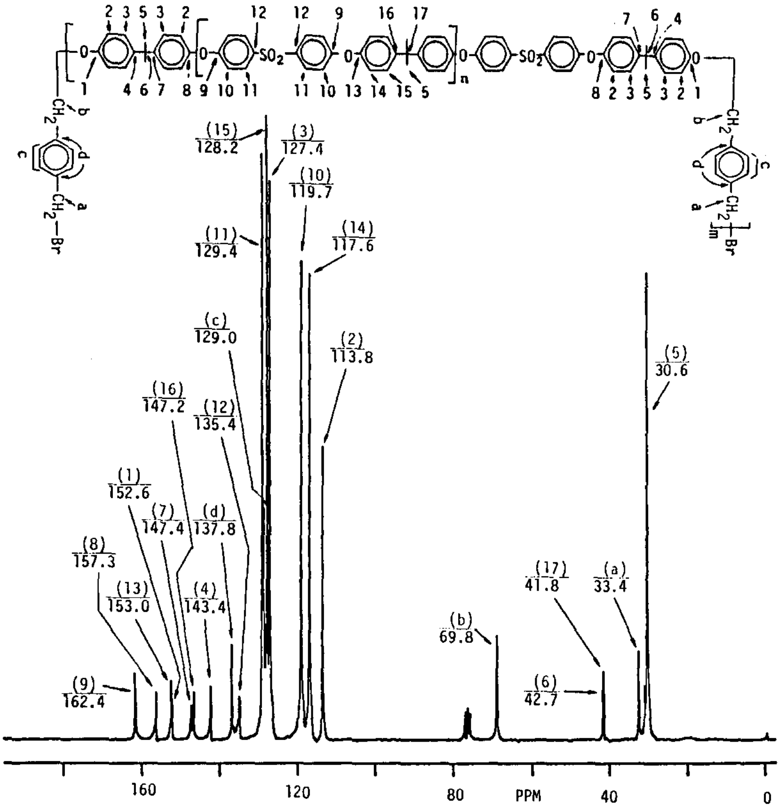


Figure 3: ^{13}C-NMR spectrum of α,ω-di(bromobenzyl)PSU(PSU-BX1, Table 1)

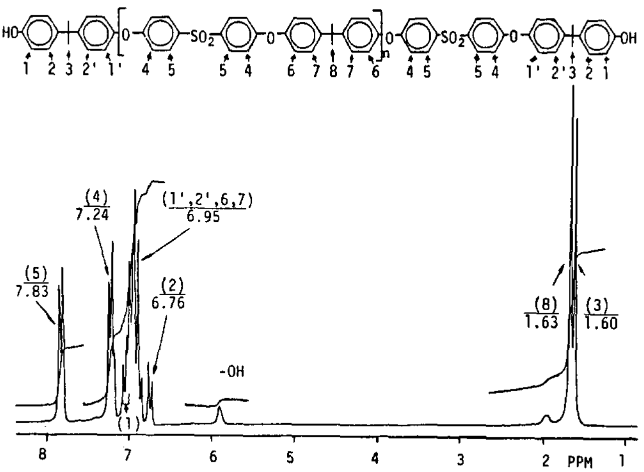


Figure 4: 200 MHz ^{1}H-NMR spectrum of α,ω-di-(phenol)-PSU (PSU-5 from Table 1)

-OH) from terminal BPA units. This signal (2) appears at 6.76 ppm, while the corresponding internal protons (meta versus the ether linkage, signals 2' and 7) are shifted downfield (6.95 ppm). As was already demonstrated (4, 5,10), the etherification of the phenol groups from α,ω-di(phenol)PSU, shifts downfield both the resonance of the methyl and of the aromatic protons meta to the -OH group. Figures 5 and 6 provide this evidence for the case of α,ω-di(chloroallyl)PSU and α,ω-di(bromobenzyl)PSU respectively. In both cases the $-CH_3$ signal from 1.60 ppm is shifted to 1.66 ppm, while the signal (2) which was initially present at 6.76 ppm (Figure 4) appears together with the other aromatic signals at about 6.95 ppm. In addition to this, the signals of the $-C\underline{H}=C\underline{H}-$ (6.0 ppm), $-C\underline{H}_2O-$ (4.7 ppm) and $-C\underline{H}_2Cl$ (4.2 ppm) of the α,ω-di(chloroallyl)PSU and those of the $-CH_2-\underline{Ph}-CH_2-$ (7.5 ppm), $-C\underline{H}_2O-$ (5.0 ppm) and $-C\underline{H}_2Br$ (4.5 ppm) allow, as was shown in the experimental part (Section F), an accurate determination of the $\bar{M}n$ of these two α,ω-di(electrophilic)PSU's.

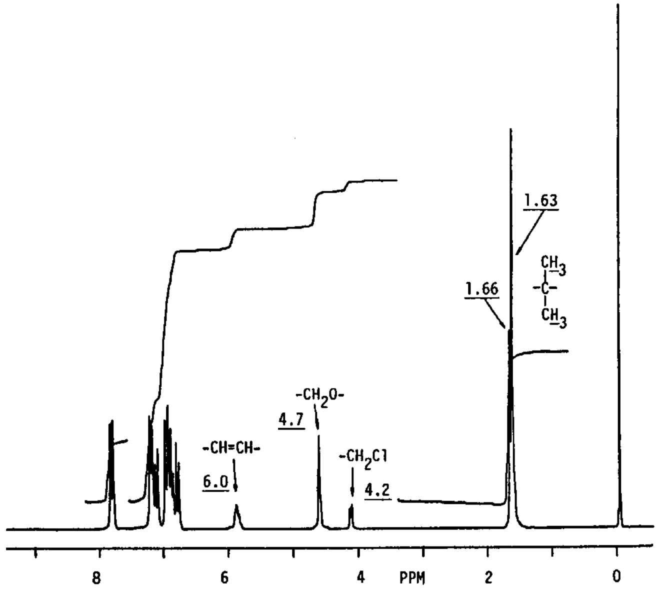


Figure 5: 200 MHz ^1H-NMR spectrum of α,ω-di(chloroallyl)PSU (PSU-CA2 from Table 1)

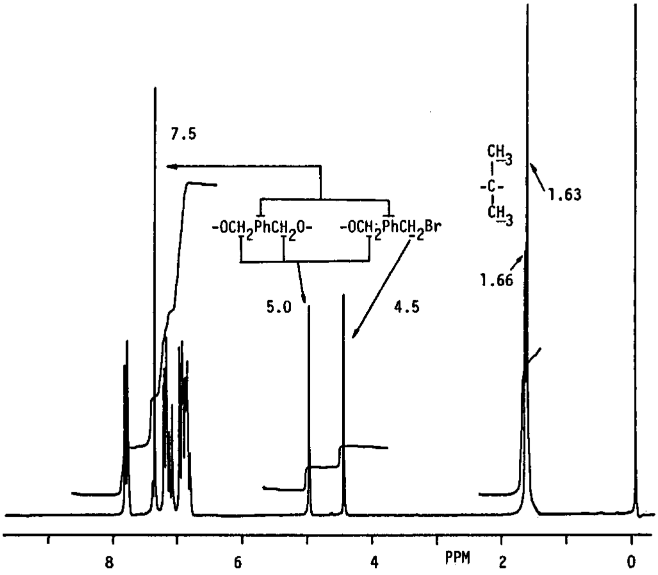


Figure 6: 200 MHz ^1H-NMR spectrum of α,ω-di(bromobenzyl)PSU (PSU-BX1 from Table 1)

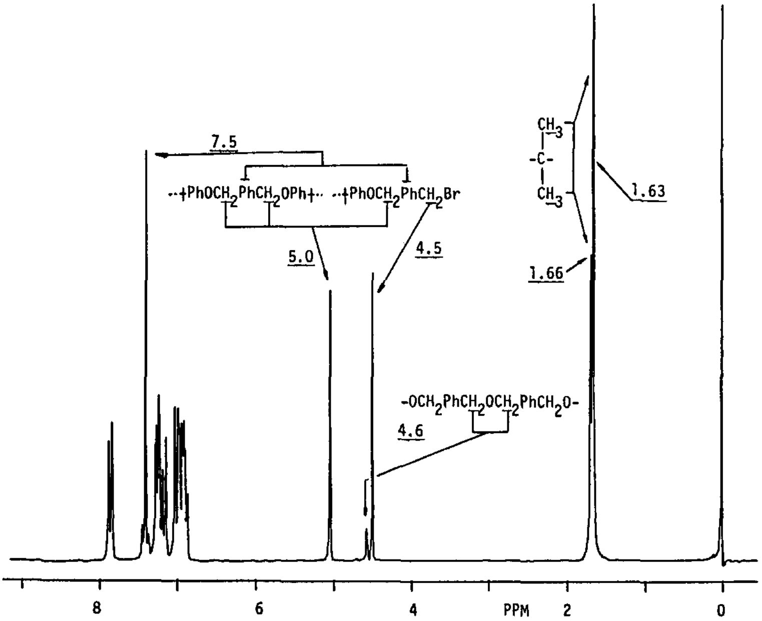


Figure 7: 200 MHz ^{1}H-NMR spectrum of the α,ω-di(bromobenzyl)PSU synthesynthesized in the presence of 50% aqueous NaOH

Figure 7 presents the ^{1}H-NMR spectrum of an α,ω-di(bromobenzyl)PSU prepared under similar experimental conditions as those discussed in the experimental part (D and E), except that the 12% aqueous NaOH solution was replaced by a 50% aqueous NaOH solution. As can be seen from the proton resonance assignments given on this figure, the displacement of the bromine by OH^-, followed by etherification, creates in this case, a side reaction which produces benzyl ether groups. This particular behavior is a result of the transfer of OH^- into the organic phase via a salting out effect (saturated solution of NaOH in water). Consequently, although very concentrated solutions of NaOH still yield quantitative functionalization of the α,ω-di(phenol)PSU with electrophilic chain ends, the reaction is accompanied by the aforementioned side reactions, which result in changes in the microstructure of the polymers. The quantitative data from the synthesis and characterization of these α,ω-di(electrophilic)PSU is summarized in Table 1.

In conclusion, the phase transfer catalyzed polyetherification of α,ω-di(phenol)PSU with c-DCB and DBX represents a simple method for the preparation of α,ω-di(electrophilic)PSU. Quantitative functionalization of the polymer chain ends occurs when the reaction is carried out in aromatic solvents, in the presence of stoichiometric amount of the phase transfer catalyst versus the phenol chain ends and in the presence of relatively dilute NaOH aqueous solution. This method can be easily applied to the quantitative functionalization of other α,ω-di(phenol)oligomers.

ACKNOWLEDGEMENT

This work was supported by the Center for Applied Polymer Research of Case Western Reserve University and by the National Science Foundation. The manuscript was prepared during the time V. P. was visiting professor and B. C. A. visiting graduate student at the Institute of Macromolecular Chemistry, University of Freiburg, Germany. A visiting professorship from the Deutsche Forschungsgemeinschaft and a NATO grant to V. P. are gratefully acknowledged.

REFERENCES

1. V. Percec, P. L. Rinaldi and B. C. Auman, Polym. Bull., 10, 215(1983)
2. V. Percec, P. L. Rinaldi and B. C. Auman, Polym. Bull., 10, 397(1983)
3. V. Percec and B. C. Auman, Makromol. Chem., in press
4. V. Percec, H. Nava and J. M. Rodriguez-Parada, J. Polym. Sci. Polym. Lett. Ed., in press
5. V. Percec and B. C. Auman, Makromol. Chem., 185, 617(1984)
6. V. Percec and B. C. Auman, Polym. Bull., 10, 385(1983)
7. V. Percec, T. D. Shaffer and H. Nava, J. Polym. Sci. Polym. Lett. Ed., in press
8. V. Percec, B. C. Auman and P. L. Rinaldi, Polym. Bull., 10, 391(1983)
9. V. Percec, H. Nava and B. C. Auman, Polym. J., in press
10. V. Percec and H. Nava, Makromol. Chem. Rapid Commun., 5, 319(1984)
11. F. J. Burgess, A. V. Cunliffe, J. R. Mac Callum and D. H. Richards, Polymer, 18, 719(1977)
12. F. J. Burgess, A. V. Cunliffe, J. R. Mac Callum and D. H. Richards, Polymer, 18, 726(1977)
13. T. D. N'Guyen and S. Boileau, Polym. Bull., 1, 817(1979)
14. G. Gordon Cameron and K. S. Law, Makromol. Chem. Rapid Commun., 3, 99 (1982)
15. N. Yamazaki and Y. Imai, Polym. J., 15, 905(1983)
16. N. Yamazaki and Y. Imai, Polym. J., 15, 603(1983)

Accepted August 8, 1984