

## RAPID COMMUNICATION

# Synthesis of poly(arylene ether sulfone): 18-Crown-6 catalyzed phase-transfer polycondensation of bisphenol A with 4,4'-dichlorodiphenyl sulfone

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Poly(arylene ether sulfone) (PSF) derived from 4,4'-dichlorodiphenyl sulfone (DCDPS) and bisphenol A is a typical engineering thermoplastic and widely used in industries due to its high glass transition temperature, high thermal stability, good mechanical properties and excellent resistance to hydrolysis and oxidation. Thus, PSF has been widely used in gas and water separations, and in household, electric and automotive parts. PSF is generally prepared by a two-step method, that is, the formation of the anhydrous dipotassium salt of bisphenol A by the reaction of bisphenol A with potassium carbonate in a polar aprotic solvent/toluene and careful removal of the water as an azeotrope with toluene, and the polycondensation of dipotassium salt with DCDPS at 160–180 °C. Water needs to be removed from the system to avoid hydrolysis of DCDPS, since hydrolysis reduces the reaction rate and upsets the stoichiometry of the monomers.<sup>1,2</sup> However, the azeotropic process is tedious and would be eliminated during the synthesis of PSF. Although PSF is an important class of materials and has a broad range of applications as already described, few advances in the synthetic method have been realized in the past decades. We were interested in the facile synthesis of PSF from bisphenol A and DCDPS.

Although the dipotassium salt of bisphenol A is relatively soluble in a polar aprotic solvent, the polycondensation basically proceeds under a solid-liquid two-phase condition, in which a phase-transfer catalyst, such as quaternary ammonium and phosphonium salts, and crown ethers are effective for organic synthesis and polymer synthesis, particularly, nucleophilic substitutions.<sup>3,4</sup> Williams and coworkers reported the synthesis of poly

(perfluorinated arylene ether)s by the solid-liquid phase-transfer catalyzed aromatic nucleophilic substitutions of perfluorobiphenyl and perfluorobenzophenone with bisphenols using 18-crown-6 (18-C-6).<sup>5</sup> Lue *et al.*<sup>6</sup> investigated the effects of various crown ethers on the polycondensation of bisphenol A with DCDPS in the presence of alkaline salts, such as NaNH<sub>2</sub>, NaOH and KOH in DMSO, and found that crown ethers, that is, monobenzo-15-crown-5 and 15-crown-5, were good phase-transfer catalysts for the polycondensation in the presence of NaNH<sub>2</sub> in DMSO at 95 °C for 4 h, producing PSF with high molecular weights ( $M_n$ : around 25 000, polystyrene as a standard). In our previous paper,<sup>7</sup> we reported the successful synthesis of PSF by the solid-liquid two-phase polycondensation of ethyl cyanoacetate with  $\alpha,\alpha'$ -dichloro-*p*-xylene without hydrolysis of the ester group in the presence of potassium carbonate and a crown ether (18-C-6) in 1-methyl-2-pyrrolidinone at 100 °C in which 18-C-6 affected the attained inherent viscosity of the polymer.

On the basis of these findings, we examined the 18-C-6-catalyzed phase-transfer polycondensation of bisphenol A with DCDPS in the presence of potassium carbonate in non-dehydrated grade *N,N*-dimethylacetamide (DMAc) without using azeotropic distillation. As a result, PSF with a high molecular weight (the number-average molecular weight ( $M_n$ ) up to 46 800) was obtained in a quantitative yield (Scheme 1).

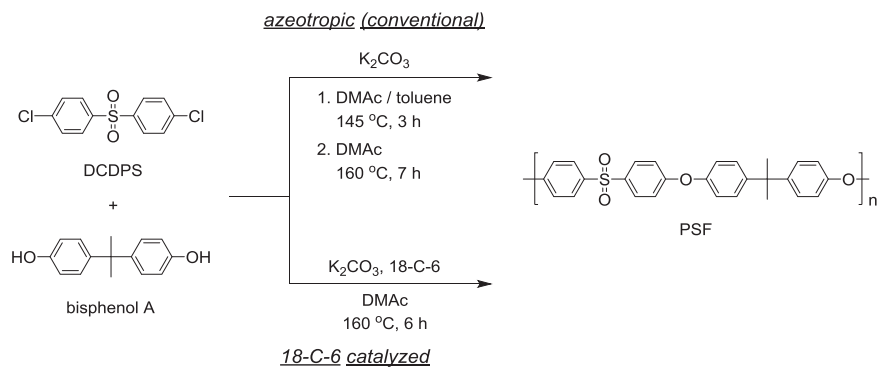
To clarify the effect of dehydration on the synthesis of PSF from bisphenol A and DCDPS, the following two polymerizations were studied: (i) the synthesis of PSF using azeotropic distillation<sup>8</sup> and (ii) the synthesis of PSF in non-dehydrated grade DMAc

(Scheme 1). The polycondensation was carried out with 1 mmol of each monomer in DMAc at 160 °C for 7 h under a nitrogen atmosphere. Table 1 lists the results of the polycondensations.

Although the polycondensation in non-dehydrated grade DMAc yields PSF with the  $M_n$  and weight-average molecular weight ( $M_w$ ) of 19 000 and 33 000 (Run 1), respectively, PSF with a much higher molecular weight ( $M_n = 32 800$  and  $M_w = 63 100$ ) can be obtained by applying an azeotropic distillation (Run 2). These results clearly indicate the effect of dehydration on the synthesis of PSF.

On the basis of these results, the 18-C-6-catalyzed polycondensation of bisphenol A with DCDPS in the presence of potassium carbonate in non-dehydrated grade DMAc without using azeotropic distillation was investigated. 18-C-6 was selected as a phase-transfer catalyst because 18-C-6 has cavity dimensions of the same magnitude as the diameter of the potassium ion and widely used for nucleophilic substitution reactions and solid-liquid phase-transfer polymerizations.<sup>3,4</sup> Moreover, to clarify the effect of 18-C-6 on the polycondensation, non-dehydrated grade DMAc was used as the solvent. The results are summarized in Table 2. The structure of PSF was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and IR spectroscopy (see Supplementary Information).

The addition of 1 mol% 18-C-6 is effective and improves the  $M_n$  of PSF from 19 000 to 26 000 (Run 3). By increasing the amount of 18-C-6, the  $M_n$  and  $M_w$  of PSF increase and PSF with the  $M_n$  and  $M_w$  of 46 800 and 140 000, respectively, is obtained in the presence of 5.0 mol% 18-C-6 in 5 h (Run 5). Even in the presence of 2.5 mol% 18-C-6, PSF with a high molecular weight is obtained and the  $M_n$



**Scheme 1** PSF synthesis via 18-C-6-catalyzed polycondensation.

**Table 1** The effect of azeotropic distillation on the synthesis of PSF<sup>a</sup>

Run	Azeotropic distillation <sup>b</sup> (h)	Yield (%)	$M_n^c$	$M_w^c$	$M_w/M_n^c$
1	0	98	19 000	33 000	1.74
2	3	95	32 800	63 100	1.92

Abbreviations: DCDPS, 4,4'-dichlorodiphenyl sulfone; PSF, poly(arylene ether sulfone).

<sup>a</sup>Polymerization was conducted using DCDPS (1 mmol), bisphenol A (1 mmol) and  $K_2CO_3$  (1.25 mmol) in DMAc (1.2 ml) at 160 °C for 7 h under nitrogen.

<sup>b</sup>Conducted using toluene (5 ml) at 145 °C under nitrogen.

<sup>c</sup>Determined by gel permeation chromatography (GPC) eluted with *N,N*-dimethylformamide (DMF) using polystyrene standards.

**Table 2** Synthesis of PSF catalyzed with 18-C-6

Run	18-C-6 (mol%)	Time (h)	Yield (%)	$M_n^b$	$M_w^b$	$M_w/M_n^b$
3	1.0	6	95	26 000	50 000	1.92
4	2.5	6	99	34 100	63 200	1.85
5	5.0	5	96	46 800	140 000	3.00

Abbreviations: DCDPS, 4,4'-dichlorodiphenyl sulfone; DMAc, *N,N*-dimethylacetamide; PSF, poly(arylene ether sulfone); 18-crown-6, 18-C-6.

<sup>a</sup>Polymerization was conducted using DCDPS (1 mmol), bisphenol A (1 mmol),  $K_2CO_3$  (1.25 mmol) and 18-C-6 in DMAc (1.2 ml) at 160 °C under nitrogen.

<sup>b</sup>Determined by GPC eluted with DMF using polystyrene standards.

and  $M_w$  values are very similar to those of PSF obtained by azeotropic distillation (Run 4). The presence of 18-C-6 as the solid-liquid phase-transfer catalyst significantly affects the attained  $M_n$ s of PSF and shortens the reaction time. These results suggest that 18-C-6 prevents the hydrolysis of DCDPS by acceleration of the aromatic nucleophilic substitution between the dipotassium salts of bisphenol A with DCDPS

through the formation of free phenolate ions which have been termed 'naked' anions.<sup>9</sup> Namely, the polycondensation rate is much faster than the hydrolysis of DCDPS, resulting in that the hydrolysis is relatively suppressed.

In summary, we demonstrated that PSF with a high molecular weight could be prepared by a one-step method, that is, the 18-C-6-catalyzed phase-transfer polycondensation of bisphenol A with DCDPS in the

presence of potassium carbonate in non-dehydrated grade DMAc without azeotropic distillation. To obtain the optimal polycondensation conditions, we are now investigating the effects of various phase-transfer catalysts, reaction temperatures, reaction times and concentrations of the monomers.

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- Guo, R. & McGrath, J. E. in *Polymer Science: A Comprehensive Reference* (eds Schmidt H-W., Ueda M.) Vol. 5: Ch. 17, 377–430 (Elsevier, Amsterdam, Netherlands, 2012).
- Wang, S. & McGrath, J. E. in *Synthetic Methods in Step-Growth Polymers* (eds Rogers M. E., Long T. E.) Ch. 6, 327–374 (Wiley-Interscience, New Jersey, NJ, USA, 2003).
- Starks, C. M. & Liotta, C. *Phase Transfer Catalysis* (ed. Liotta C.) (Academic, New York, NY, USA, 1978).
- Imai, Y. Syntheses of condensation polymers by phase transfer catalyzed method. *J. Syn. Org. Chem. Jpn.* **42**, 1095–1106 (1984).
- Lellman, R., Williams, R., Dimotris, G., Gerbi, D. J. & Williams, J. in *Phase-Transfer Catalysis: New Chemistry, Catalysts, and Applications* (ed. Starks C. M. ACS Symposium series 326) Ch. 11, 128–142 (American Chemical Society, Washington DC, USA, 1987).
- Lue, L.-C. & Shih, J.-S. Crown ether phase transfer catalysts for an ionic polymerization of bisphenol A and 4,4'-dichlorodiphenyl Sulfone. *J. Chinese Chem. Soc.* **49**, 69–75 (2002).
- Ueda, M., Sato, K. & Sato, M. Polymer synthesis by solid-liquid two-phase polycondensation of ethyl cyanoacetate with  $\alpha,\alpha$  dichloro-*p*-xylene in the presence of potassium carbonate and crown ether. *Makromol. Chem. Rapid Commun.* **4**, 613–615 (1983).
- Viswanathan, R., Johnson, B. C. & McGrath, J. E. Synthesis, kinetic observations and characteristics of polyarylene ether sulfones prepared via a potassium carbonate DMAc process. *Polymer* **25**, 1827–1836 (1984).
- Liotta, C., Grisdate, E. E. & Hopkins, H. P. Jr. Relative nucleophilicities of naked anions. *Tetrahedron Lett.* 4205–4208 (1975).

Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)