Notes

Ring−Chain Interconversion in High-Performance Polymer Systems. 2. Ring-Opening Polymerization−Copolyetherification in the Synthesis of Aromatic Poly(ether sulfones)

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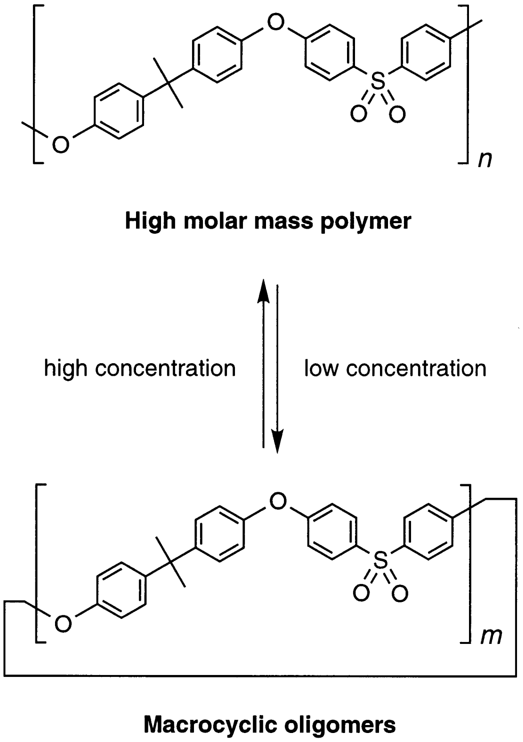
Introduction

It has recently been demonstrated that the activated-ether linkages in aromatic poly(ether sulfone)s can be reversibly cleaved by fluoride ion in dipolar aprotic solvents and that, at low polymer concentrations, such reactions lead to formation of macrocyclic oligomers via ring-closing depolymerization.[1] High conversions of polymer to macrocycles can be achieved at relatively modest dilutions (1−2 wt % of polymer),[2] but the reaction can be driven in the opposite direction at high concentration—for example in the melt—where ring-opening polymerization is entropically favored (Scheme 1).[2,3] Macrocyclic aromatic ether−sulfones, ether−ketones and ether−imides have also been obtained by cyclo-condensation reactions under pseudo-high-dilution conditions, and the products have been shown to undergo ring-opening polymerization (initiated by nucleophilic attack at an ether linkage), both in the melt and in solution.[3,4]

It has been proposed that the combination of ring-closing depolymerization and ring-opening polymerization could provide a possible means of recovering and recycling high-cost, high-performance aromatic polymers.[5] Here we report that macrocyclic homologues of the commercial engineering thermoplastic bisphenol A polysulfone, **2**, trademarked by Solvay as Udel and by BASF as Ultrason-S, can be recycled not only into the standard nucleophilic synthesis of the parent polymer **2** but also into the synthesis of a *co*-poly(ether sulfone) (**3**) based on 4,4′-biphenol. In such reactions, an aryloxide anion can either (i) condense with a 4-chlorophenyl sulfone unit, (ii) attack the sulfone-activated ether linkages of a macrocycle, opening the ring and generating a new phenoxide end group (Scheme 2), or (iii) attack a sulfone-activated ether linkage within an existing polymer chain. Since cyclic dimer **1**, together with a range of higher macrocycles, can readily be obtained by fluoride-catalyzed cyclodepolymerization of high molar mass polysulfone,[2,6] this work represents a new depolymerization/repolymerization approach to the recycling of aromatic poly(ether sulfone)s.

Scheme 1. Fluoride-Catalyzed Cyclodepolymerization and Ring-Opening Polymerization Processes in Bisphenol-A Polysulfone



Results and Discussion

In an exploratory experiment (Scheme 2), polycondensation of the disodium salt of bisphenol A with 4,4′-dichlorodiphenyl sulfone was carried out in the presence of the macrocyclic dimer **1** (9.1 mol**%** of total polymer repeat-units), under conditions analogous to those used in the original synthesis of this polysulfone,[7] i.e., 160 °C in dimethyl sulfoxide (DMSO) solution, at a polymer concentration of 48 wt %. The resulting polymer **2a**, obtained in 95% yield, had an inherent viscosity (η_{inh}) of 0.56 dL g^{-1}, and GPC showed $M_{\mathrm{w}} = 123\ 000$ and $M_{\mathrm{n}} = 63\ 000$, values which are in fact somewhat higher than those of the commercial material. Analysis of polymer **2a** by GPC showed residual cyclic dimer in the polysulfone at a level of 2.9 wt %, indicating 68% incorporation of the added macrocycle. However, we find that commercial polymers of this type can contain up to 1.4 wt % of cyclic dimer **1**, (presumably representing an equilibrium macrocycle concentration) so that the level of incorporation in polymer **2a** on this basis rises to ca. 84%. of the theoretical value.

A second experiment involved *copolymerization* of macrocycle **1** with 4,4-biphenol and 4,4′-dichlorodiphenyl sulfone (Scheme 3). This was intended to allow the level of macrocycle incorporation in the polymerization to be determined *directly* (rather than by difference as in the first experiment) using a combination of prepara-

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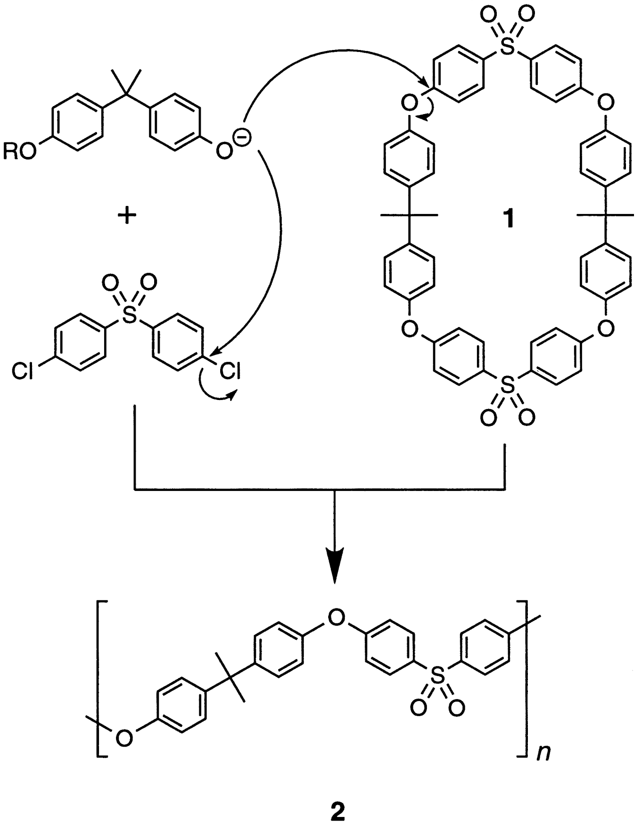
Scheme 2. Incorporation of Cyclic Dimer 1 into the Synthesis of Bisphenol-A Polysulfone (R = H or a Growing Polysulfone Chain)[a]



[a] An additional reaction occurring in this synthesis (but not shown) involves reversible nucleophilic cleavage of a sulfone-activated ether linkage within an existing polymer chain by the phenoxide end-group. Since this produces a new phenoxide group and a further polymer chain, the reaction is essentially degenerate.

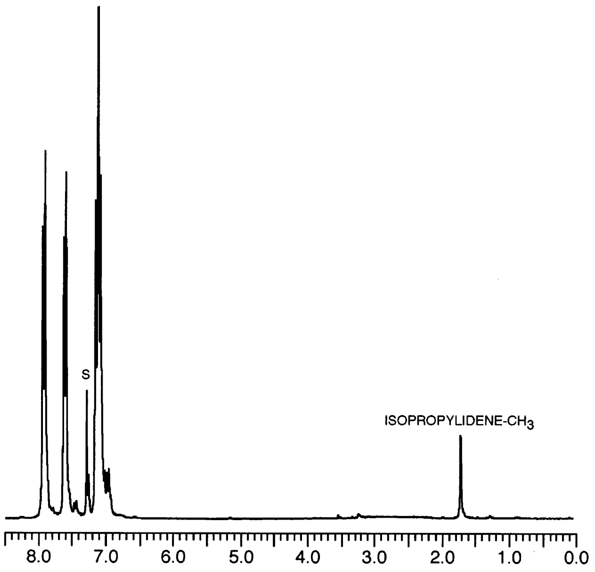


Figure 1. ^{1}H NMR spectrum (CDCl$_3$) of copolymer **3a**. Integration of the isopropylidene resonance against the aromatic signals indicates >98% incorporation of the macrocyclic dimer 1. (*S* = residual solvent resonance.)

tive GPC and ^{1}H NMR spectroscopy, since any isopropylidene resonances in the ^{1}H NMR spectrum of a high molar mass polymer-fraction could *only* arise from incorporation of macrocyclic monomer-residues. The polycondensation was carried out in *N*-methylpyrrolidone (NMP) at 200 °C,[8] using the same proportion of macrocycle (9.1 mol % of polymer repeat units) as in the first experiment. The resulting polymer **3a** proved fully soluble in NMP, DMAc and THF, and analysis by GPC gave M_w = 14 800, M_n = 7300. The ^{1}H NMR spectrum of this polymer (Figure 1) showed a single isopropylidene methyl resonance at 1.73 ppm, integration of which against the remaining signals was consistent with essentially quantitative incorporation of the macrocycle into the polycondensation reaction.

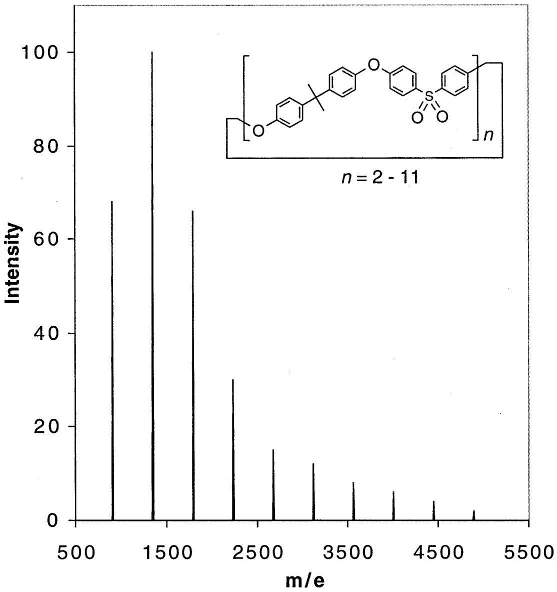


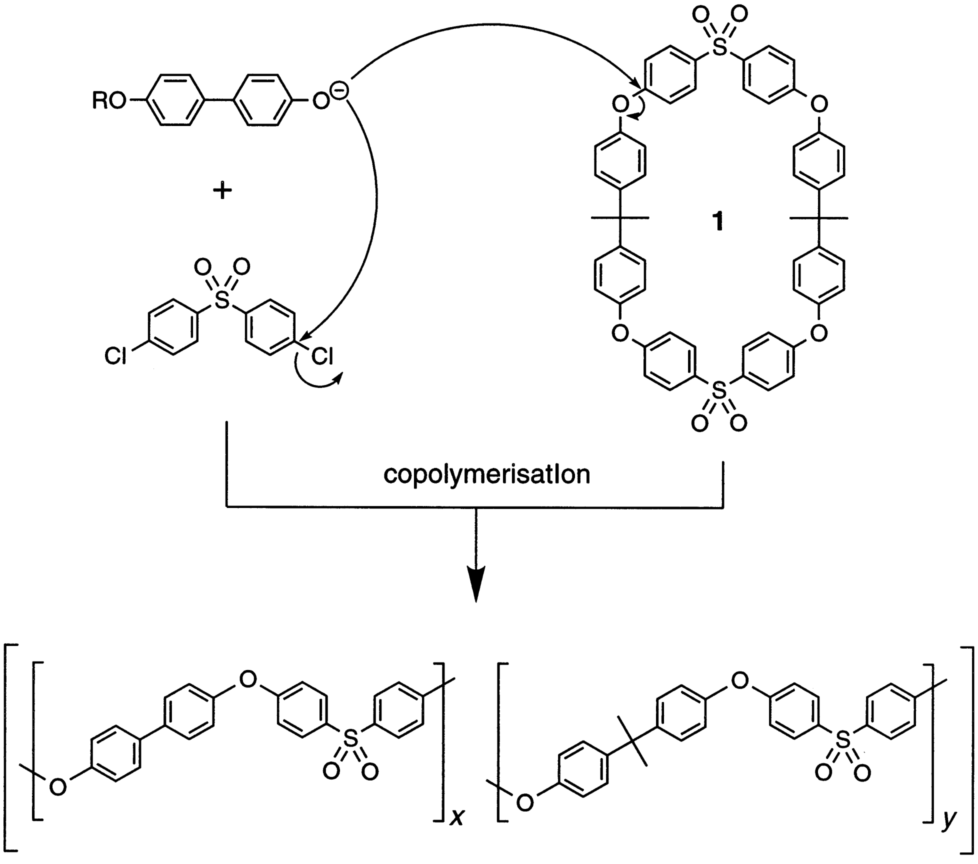
Figure 2. MALDI–TOF mass spectrum of the mixed macrocyclic oligomer sample used for copolymerization with bisphenol A and 4,4′-dichlorodiphenyl sulfone.

To determine the distribution of ring-opened residues as a function of molar mass, we next undertook preparative fractionation of copolymer **3a** by GPC. Four fractions were obtained, with a total recovery of 92%. These had average molar masses (M_w) of 24 700 (24% recovery), 14 500 (39%), 12 000 (24%), and 5900 (5%). Analysis of each fraction by ^{1}H NMR spectroscopy showed that the level of incorporation of (macrocycle-derived) isopropylidene-containing residues was, if anything, slightly greater than theoretical for the two highest molar mass fractions and slightly less than theoretical for the lower molar mass materials, although the differences were not large (ca. ±10% variation from theory).

Next, the proportion of macrocycle **1** in a copolymerization with 4,4-biphenol and 4,4′-dichlorodiphenyl sulfone was increased from 9.1 to 50 mol %, and the higher-boiling sulfolane rather than NMP was used as solvent. The resulting copolymer **3b** was obtained in 93% yield, implying a *minimum* level of incoporation of macrocyclic oligomers of 86%. Analysis of copolymer **3** by GPC gave M_w = 15 200, M_n = 8100, values very close to those observed in the earlier experiment. Only small amounts (2.4 wt %) of residual oligomeric material were evident by GPC, and once again, ^{1}H NMR analysis confirmed that the composition of the final copolymer closely reflected the stoichiometry of the reactants.

Finally, the polycondensation of bisphenol A with 4,4′-dichlorodiphenyl sulfone was carried out in the presence of 50 mol % of a *mixture* of the macrocyclic oligomers homologous with bisphenol A polysulfone (from cyclic dimer to cyclic undecamer; see Figures 2 and 3),

Scheme 3. Incorporation of Macrocycle 1 into the Synthesis of 4,4′-Biphenol Polysulfone (R = H or a Growing Polysulfone Chain)[a]



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[a] Here, reversible nucleophilic cleavage of sulfone-activated ether linkages within the growing polymer chain by phenoxide end-groups will lead to an essentially random sequence-distribution of the two different repeat units.

obtained by cyclopolycondensation under pseudo-high-dilution conditions.[2] The incorporation of a mixed-macrocyclic fraction was designed to model recycling the products of cyclodepolymerization back to the production process for the parent polymer. The resulting polymer (**2b**) was isolated in 93% yield, indicating a minimum 86% incorporation of the cyclic oligomers. The polymer had an inherent viscosity of 0.41 dL g^{-1} and, by GPC, showed M_w = 73 000 and M_n = 23 900 (Figure 3). The residual cyclic dimer, trimer, and tetramer evident in Figure 3a comprised 1.5, 0.5, and 0.3 wt %, respectively, of the total mass.

It is noticeable that the highest molar mass polymers formed in this work by ring-opening polymerization *co*-polyetherification (**2a** and **2b**) were obtained using hydroxide as base rather than carbonate, and it is therefore possible that residual hydroxide ion in trace amounts can act as a particularly effective initiator of ring-opening polymerization. However, even with carbonate as base, it is clear that macrocyclic aromatic ether sulfones may be successfully used as comonomers in conventional nucleophilic polyetherification reactions, affording both homopolymers and copolymers. Given the relative ease with which poly(ether sulfone)s undergo cyclodepolymerization,[1,2] the present work goes some considerable way toward demonstrating a new technique for the recycling of these materials.

Experimental Section

General Methods and Instrumentation. All commercial reagents were analytical grade and were used, unless stated otherwise, without further purification. Instrumentation and analytical methods were as previously described.[2] Cyclic dimer **1** was obtained from commercial bisphenol A polysulfone as discussed in a previous publication,[9] and mixed cyclic oligomers homologous with this polymer were synthesized by cyclocondensation under pseudo-high-dilution conditions as described below. All reactions were conducted under a dry nitrogen atmosphere. Preparative GPC was carried out using a Waters 590 pump, chloroform eluent, flow rate 10 mL min^{-1}, Styragel 500 Å preparative column, and Waters R403 differential refractometer.

Copolymerization of Macrocycle 1 with Bisphenol A and 4,4′-Dichlorodiphenyl Sulfone. Bisphenol A (13.41 g, 58.7 mmol), chlorobenzene (87 g), DMSO (30.3 g), and 50% (w/w) aqueous sodium hydroxide (9.4 g, 117.5 mmol) were heated with mechanical stirring to 120 °C, and water and chlorobenzene were removed by azeotropic distillation until the temperature had risen to 160 °C (ca. 4 h). Cyclic dimer **1** (2.60 g, 2.94 mmol, i.e., 5.88 mmol of polymer repeat units) and 4,4′-dichlorodiphenyl sulfone (17.01 g, 59.2 mmol) were added, and reaction was continued at the same temperature for a further 2 h. The resulting viscous paste was diluted with chlorobenzene (200 mL), cooled to room temperature, added to stirring ethanol (800 mL), and the solid filtered off. The granular polymer **2** was extracted with refluxing ethanol (3 × 200 mL) and then with boiling water (3 × 200 mL) before being dried under vacuum at 135 °C. Yield: 27.8 g (95%). Inherent viscosity (0.1% in DMAc): 0.56 dL g^{-1}.

Copolymerizations of Macrocycle 1 with 4,4′-Biphenol and 4,4′-Dichlorodiphenyl Sulfone. Anhydrous potassium carbonate (9.33 g, 67.5 mmol), 4,4′-biphenol (9.31 g, 50.0 mmol), 4,4′-dichlorodiphenyl sulfone (14.65 g, 51.0 mml), cyclic dimer **1** (2.21 g, 2.50 mmol), NMP (100 mL), and toluene (50

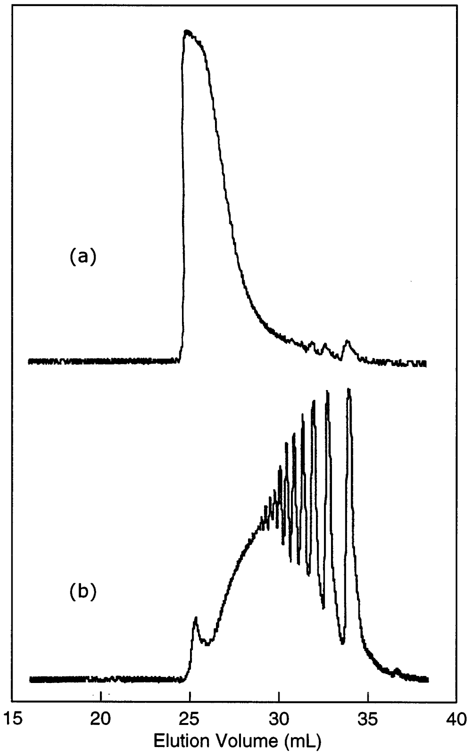

Figure 3. (a) GPC trace for bisphenol A polysulfone obtained by copolymerization of 4,4′-dichlorodiphenyl sulfone and bisphenol A with 50 mol % of mixed macrocyclic oligomers homologous with this polymer (oligomer column, chloroform as eluent). (b) Original GPC trace for the macrocyclic oligomers used in this polymerization.

mL) were stirred and heated to 140 °C and then held at this temperature for 2 h as water was removed by azeotropic distillation. Toluene was then progressively distilled off over about 4 h, allowing the temperature to rise to 200 °C. The solution was stirred at this temperature for a further 3 h and then cooled to room temperature, diluted with NMP (100 mL), and added dropwise to 1 M hydrochloric acid (2.5 L). After the resulting suspension was stirred for 4 h, it was filtered and the solid copolymer **3a** was extracted with hot water (50 °C, 3 × 300 mL) before being dried at 90 °C under vacuum. Yield: 21.1 g (94%). Inherent viscosity (0.1% in DMAc): 0.32 dL g^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.73$ (s, 6H), 6.98 (d, $J = 8.7$ Hz, 4H), 7.05 (d, $J = 8.9$ Hz, 4H), 7.11 (d, $J = 8.8$ Hz, 40H), 7.15 (d, $J = 8.5$ Hz, 40H), 7.28 (d, $J = 8.4$ Hz, 4H), 7.62 (d, $J = 8.4$ Hz, 40H), 7.93 (d, $J = 8.8$ Hz, 44H). A sample of this copolymer (0.502 g) was fractionated by preparative GPC to give 0.120 g of material with $M_w = 24\,700$, 0.195 g with $M_w = 14\,500$, 0.120 g with $M_w = 12\,000$, and 0.025 g with $M_w = 5900$ (92% total recovery).

In a second polymerization of this type, cyclic dimer **1** (2.31 g, 2.61 mmol), anhydrous potassium carbonate (1.20 g, 8.7 mmol), 4,4′-dichlorodiphenyl sulfone (1.50 g, 5.22 mmol), and 4,4′-biphenol (0.97 g, 5.22 mmol) in sulfolane (17 mL) were heated at 210 °C and stirred for 6 h. The solution was cooled to room temperature, diluted with DMAc (20 mL), and poured into methanol (150 mL) with stirring. The precipitated copolymer **3b** was filtered off, washed with water (3 × 100 mL) and methanol (3 × 50 mL), and dried under vacuum at 60 °C. Yield: 4.10 g (93%). Inherent viscosity (0.1% in DMAc): 0.35 dL g^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.73$ (s, 6H), 7.10 (m, 16H), 7.28 (d, $J = 8.4$ Hz, 4H), 7.62 (d, $J = 8.4$ Hz, 4H), 7.93 (m, 8H).

Macrocyclic Oligomers by Cyclocondensation of Bisphenol A with 4,4′-Dichlorodiphenyl Sulfone. A solution of bisphenol A (4.74 g, 20.8 mmol) and 4,4′-dichlorodiphenyl sulfone (5.97 g, 20.8 mmol) in dimethylacetamide (250 mL) was added, over 5 h, to a stirred, refluxing suspension of potassium carbonate (2.89 g, 21.0 mmol) in dimethylacetamide (400 mL) and toluene (80 mL). Water was removed by azeotropic distillation via a Dean−Stark trap, and after the addition was complete, toluene was distilled out until the reflux temperature reached 150 °C and the reaction was continued for a further 15 h. After cooling and filtering of the solution, solvent was removed under reduced pressure to give ca. 50 mL of concentrate, which was added to 0.1 M hydrochoric acid (700 mL) to precipitate the product. The resulting white solid was filtered off, washed with water, and then extracted with methanol (500 mL) at 60 °C for 1 h before filtering and drying under vacuum (8.51 g, 93% yield). Analysis by MALDI−TOF MS, with sodium trifluoroaceate as cationising agent), gave peaks at 907, 1349, 1793, 2235, 2678, 3121, 3563, 4006, 4449, and 4885, corresponding to cyclic oligomers $[M + Na]^+$ from dimer to undecamer. From GPC analysis (Figure 3b) the proportions (w/w) of the different macrocycles were estimated as follows: dimer, 17%; trimer, 14%; tetramer, 11%; pentamer, 10%; hexamer, 9%; heptamer, 7%; higher homologues plus a small amount of polymer, 32%.

Copolymerization of Bisphenol A and 4,4′-Dichlorodiphenyl Sulfone with Mixed Macrocyclic Oligomers of Bisphenol A Polysulfone. Bisphenol A (2.00 g, 8.76 mmol), chlorobenzene (15 g), DMSO (15 g), and 50% (w/w) aqueous sodium hydroxide (2.08 g, 26.1 mmol) were heated with mechanical stirring to 130 °C, and water was removed by azeotropic distillation with chlorobenzene until the temperature had risen to 160 °C (ca. 3 h). The cyclic oligomer mixture (3.84 g, 8.69 mmol) and 4,4′-dichlorodiphenyl sulfone (2.51 g, 8.71 mmol) were added, and reaction was continued at the same temperature for a further 3 h. The cooled solution was diluted with DMF (20 mL) and precipitated in methanol (200 mL). The polymer was extracted with refluxing methanol (3 × 50 mL) and then with boiling water (3 × 50 mL) before drying under vacuum at 60 °C to give polymer **2b**. Yield: 7.10 g (93%). Inherent viscosity (0.1% in DMAc): 0.41 dL g^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.73$ (s, 6H), 6.97 (d, $J = 8.7$ Hz, 4H), 7.04 (d, $J = 8.8$ Hz, 4H), 7.28 (d, $J = 8.7$ Hz, 4H), 7.88 (d, $J = 8.8$ Hz, 4H).

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