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Preparation of Polysulfone/Poly(ethylene oxide) Block Copolymers

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Introduction

Poly(ethylene glycol)s are widely employed in the synthesis of segmented block copolymers via polycondensation (e.g. polyurethanes, polyesters, and poly(ether imide)s[1]). Results reported herein demonstrate that monomethylpoly(ethylene glycol) (Me-PEG) can be directly employed in aromatic nucleophilic substitution polymerization to form diblock/triblock copolymers of polysulfone and poly(ethylene oxide) (PEO-*b*-PSF). Previously, Butuc et al.[2] showed that α-hydroxy-ω-allyl-PEO could be reacted with a chlorophenyl sulfone terminated polysulfone oligomer in a two-step process to form poly(ethylene oxide)-modified polysulfones. In related work, Aksenov et al.[3] have previously prepared poly(ethylene oxide)/polysulfone block copolymers. However, they employed diisocyanate chemistry to link hydroxy-terminated polysulfone oligomers and poly(ethylene glycol).

Apart from general interest in the polymerizability of Me-PEG, materials incorporating PEO are of widespread interest for biotechnical and biomedical applications.[4] Polysulfone is often used for the manufacture of ultrafiltration and microporous membranes. PEO-*b*-PSF is of unique interest as a material for membrane manufacture, especially membranes for biomedical applications (dialysis, plasmapharesis, etc.). A forthcoming article will report on the utility of PEO-*b*-PSF for the fabrication of membranes.[5]

Results and Discussion

Monomethylpoly(ethylene glycol) is effective as an end-capping reagent in the polymerization of polysulfone. The nucleophilic substitution polymerization employs a weak base in a polar aprotic solvent (Scheme 1) as is common for the preparation of poly(aryl ether)s.[1] Monomethylpoly(ethylene glycol) (M_n = 5000) is wholly compatible with the polymerization conditions and may be charged directly to the reaction with Bisphenol A and 4,4′-chlorophenyl sulfone. The solvent system for the polymerization is *N*-methylpyrrolidinone/toluene and the base is K_2CO_3. The mixture is initially heated to 150−160 °C to effect reaction of K_2CO_3 with the hydroxylic monomers. Water distills from the reaction mixture at this temperature as an azeotrope with toluene. A Dean−Stark trap removes water from the polymerization mixture. Polymerization occurs at 180−190 °C. PEO-*b*-PSF materials precipitate in water either as a hard, porous white particle or as a soft, water-swollen gel depending on the PEO content.

^{1}H NMR easily quantitates PEO content of the product materials (Figure 1). Exhaustive extraction of the product materials with methanol, a selective solvent for PEO demonstrates block copolymer formation. Table 1 compares the composition of product materials charged at 20 and 30% Me-PEG with a physical mixture of Me-PEG(5K) and polysulfone. PEO persists in the PEO-*b*-PSF samples following extraction with methanol. In contrast, nearly all of the PEO extracts from a simple physical mixture of PEO and PSF. In aggregate, the results demonstrate that PEO is covalently linked with PSF to form a block copolymer.

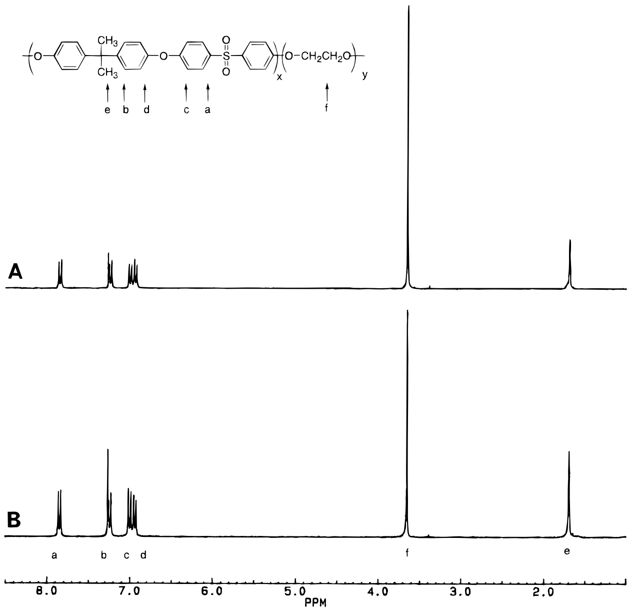

Figure 1. ^{1}H NMR of PEO-*b*-PSF: (A) run 6, 26.9% PEO; (B) run 2, 15.7% PEO.

Table 1. Composition of PEO-*b*-PSF on Extraction with Methanol Compared with a Physical Mixture of Me-PEG(M_n=5000) and PSF

	composition by ^{1}H NMR (wt % PEO)			
sample	initial	H_2O ppt	24 h MeOH	48 h MeOH
run 2	20[a]	15.7	12.4	12.5
run 6	30[a]	26.9	24.0	24.5
Me-PEG + PSF	30[b]	4.6	0.5	0.4

[a] Polymerization charge. [b] Formulation as an NMP solution.

Table 2 reports PEO-*b*-PSF yield and composition as a function of reactant feed, polymerization stoichiometry, and polymerization temperature. The feed composition and the polymerization stoichiometry effectively control the product molecular weight as expected from polycondensation statistics. The molecular weight and weight fraction of Me-PEG charged to the reaction fix the number of monofunctional, chain-terminating units. Comparing run 2 (20% PEO_{feed}) and run 6 (30% PEO_{feed}), the molecular weight of the product PEO-*b*-PSF is depressed as the weight fraction of PEO is increased in the polymerization feed.

Polymerization stoichiometry can be manipulated to maximize the limiting molecular weight defined by the monofunctional reagent. Simply adding Me-PEG to a polymerization with molar equivalents of Bisphenol A and 4,4′-chlorophenyl sulfone (stoichiometry A) creates one chain end arising from the unreactive end of the monofunctional and a second chain end as now there is an excess of hydroxyl functional groups in the polymerization. Stoichiometry B compensates for the excess hydroxyl groups with a proportionate increase in 4,4′-chlorophenyl sulfone. Experimentally, stoichiometry B results in a higher molecular weight product in each pair of similar polymerization conditions (Table 2, runs 1 and 2, 3 and 4, and 5 and 6. In addition, as the polymerization approaches complete reaction, one would

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Scheme 1

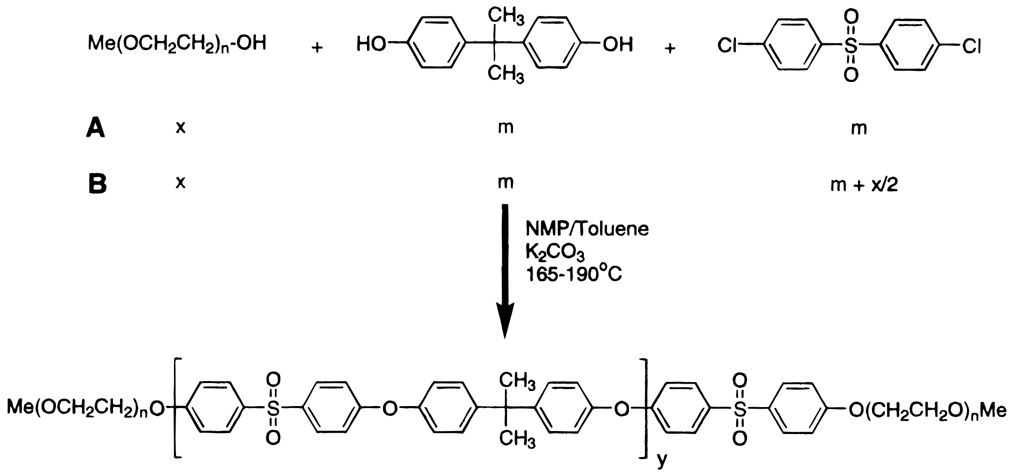

Table 2. PEO-*b*-PSF Characteristics as a Function of Polymerization Conditions[a]

polymerization conditions						PEO-*b*-PSF characteristics				
run	stoich[a]	% PEO_{feed}	T (°C)	*t* (h)	$M_{n,max}$[b] ($\times 10^{-3}$)	yield (%)	% PEO_{prod}[c]	M_n[d] ($\times 10^{-3}$)	M_w[d] ($\times 10^{-3}$)	M_w/M_n[d]
1	A	20	190	6	50	92.9	13.5	43.9	69.9	1.59
2	B	20	190	6	90	95.3	15.9	54.4	81.0	1.49
3	A	30	180	6	34	83.7	15.9	42.0	59.6	1.42
4	B	30	180	6	58	84.2	16.8	45.0	65.6	1.46
5	A	30	190	6	34	92.9	26.0	25.9	36.3	1.40
6	B	30	190	6	58	96.5	26.8	34.6	47.4	1.37
7	B	30	190	12	58	99.1	28.2	29.3	42.3	1.44

[a] Stoichiometries A and B are defined in Scheme 1. [b] $M_{n,max}$ calculated using the Carothers equation: $X_n = (1 + r)/(1 + r - 2rp)$, where $r = N_a/(N_b + 2N_b')$ and assuming $p = 1$ (complete reaction). [c] % PEO determined from ^1H NMR (Bruker, 300 MHz). [d] M_n and M_w determined by GPC using a Hewlett-Packard 1090 system equipped with 3 Phenomenex columns and eluted at 1.0 mL/min with THF at 40 °C. M_n and M_w are based on PMMA narrow molecular weight standards.

expect stoichiometry B to yield triblock, whereas stoichiometry A would yield some mixture of diblock and triblock.

Polymerization time and temperature also affects the molecular weight and composition of the product block copolymer. At 180 °C the reaction is incomplete; yields are low as is the incorporation of PEO. Interestingly, the product molecular weight is high. This is apparently the result of a fractionation of the product block copolymer during the aqueous precipitation. Further increases in block copolymer yield and PEO incorporation occur as the polymerization time increases from 6 to 12 h and the reaction approaches completion.

Incorporation of PEO into the product material follows the weight fraction of PEO charged to the polymerization. The deficit of PEO in the product reflects losses of low molecular weight copolymer into the aqueous precipitation bath. Either more vigorous polymerization conditions (runs 4 and 6 or 6 and 7) or stoichiometry B results in greater incorporation of PEO. Both result in higher molecular weight materials which do not extract as easily into the aqueous precipitant. Similarly, the polydispersity (M_w/M_n) for each run is relatively low for a condensation polymerization, also suggesting fractionation during precipitation.

Table 3 reports preliminary DSC thermal analysis of representative samples of PEO-*b*-PSF. Materials are apparently homogeneous as a single-T_g intermediate of the two components is observed. The observed transitions were broad, occurring over 20–40 °C. Reasonable qualitative agreement is found between the observed T_g's and that calculated using the Fox equation. There was no evidence of a glass transition characteristic of a pure PSF phase nor was there any evidence of a PEO melting endotherm. This result concurs with that of Swinyard et al.,[7] who demonstrated that a 4000 Da PEO formed homogeneous mixtures with polysulfone at PEO fractions less than 50%.

Table 3. Comparison of T_g As Determined by DSC and As Calculated for a Mixture of PEO and PSF Using the Fox Equation ($T_{g,PSF}$ = 185 °C, $T_{g,PEO}$ = −66 °C)

% PEO	$T_{g(obsd)}$ (°C)	$T_{g(Fox)}$ (°C)
10		135
15.4	**120**	**113**
20		96
20.1	**75**	**96**
26.1	**51**	**75**
30		63

In summary, monomethylpoly(ethylene glycol) copolymerizes directly with Bisphenol A and 4,4′-dichlorophenyl sulfone to yield PEO-*b*-PSF. The fraction of Me-PEG and/or polymerization stoichiometry control the composition and molecular weight of the block copolymer. When prepared with a 5000 Da Me-PEG, PEO-*b*-PSF's are homogeneous with up to 26% PEO as indicated by a single-T_g intermediate of the two constituent materials.

Experimental Section

Materials. Bisphenol A and K_2CO_3 were purchased from Aldrich and used as received. 4,4′-Chlorophenyl sulfone was purchased from Aldrich and recrystallized from toluene prior to use. Monomethylpoly(ethylene glycol) (5000 Da) was used as received from Polysciences. OnmiSolv *N*-methylpyrrolidinone and toluene were purchased from VWR and used as received.

Example Polymerization Procedure (Run 6). Monomers (Me-PEG, 38.68 g, 0.0077 mol; Bisphenol A, 46.15 g, 0.2022 mol; 4,4′-chlorophenyl sulfone, 59.16 g, 0.2061 mol) and K_2CO_3 (82.60 g, 0.5976 mol) were charged to a 1 L roundbottom flask equipped with a mechanical stirrer and a Dean−Stark trap under a nitrogen purge. Solvents (300 mL of *N*-methylpyrrolidinone, 100 mL of toluene) were charged under a flow of nitrogen. The flask was closed with a rubber septum through which a thermocouple probe was inserted. Reaction was initiated by heating the reagent mixture until toluene refluxed (155−160 °C). Water was removed from the reaction mixture as a toluene/water azeotrope and collected in the Dean−Stark trap. A total of 8.5 mL of water was removed over 3 h. Toluene was distilled from the system as the temperature was raised to 190 °C to effect polymerization. Polymerization was stopped at 6 h and the mixture allowed to cool to room temperature. The viscous polymer solution was precipitated in an excess of water containing sufficient HCl to neutralize residual K_2CO_3. The polymer was washed twice by soaking in a water bath. The polymer was recovered by filtration and dried in a convection oven at 65 °C to a constant weight.

Characterization. ^1H NMR spectra were obtained on a Bruker 300 MHz spectrometer. Samples were dissolved in $CDCl_3$. PEO-*b*-PSF composition was calculated through comparison of the methylene protons (4H, δ 3.6) arising from the PEO fraction and the aryl protons (2H, δ 7.8; 4H, δ 6.9) associated with the polysulfone fraction.

M_n and M_w were determined by GPC using a Hewlett-Packard 1090 system equipped with three Phenomenex columns and eluted at 1.0 mL/min with THF at 40 °C. M_n and M_w are based on PMMA narrow molecular weight standards.

Differential scanning calorimetry was performed on a Perkin-Elmer 7 Series Thermal Analysis System. A temperature range of −50 to +250 °C was scanned at 10 °C/min.

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