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Polymer 41 (2000) 5063–5071

polymer

Grafting of vinyl polymers to carboxylated poly(arylene ether sulfone) utilizing barton ester intermediates and nitroxide mediation

W.H. Daly*, T.S. Evenson†

Macromolecular Studies Group, Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA

Received 13 November 1998; received in revised form 29 April 1999; accepted 18 May 1999

Abstract

Esters of *N*-hydroxypyridine-2-thione (Barton esters, BE) were appended to a carboxylated poly(arylene ether sulfone), PSF-COOH, backbone. Irradiation of the polymer bound Barton ester in monomer/DMF solution initiated a free radical graft polymerization at 25°C without promoting concomitant homopolymerization. The following monomers were grafted to PSF backbones using this technique: styrene, methyl methacrylate, vinyl pyridine and acrylamide. Since the grafts are attached to the backbone by an ester linkage, the graft segments were cleaved and subjected to independent characterization. Graft length is dependent upon the [BE]/[M], and the degree of BE substitution on the backbone. Treatment of BE modified PSF with styrene in the presence of TEMPO afforded the corresponding TEMPO adducts, which were used to promote the controlled radical graft polymerization of styrene.

Keywords: Carboxylated poly(arylene ether sulfone); Barton ester; Graft copolymer

1. Introduction

Thiohydroxamic esters, including esters of *N*-hydroxypyridine-2-thione, were first used as free-radical precursors by Barton [1], and have come to be known as Barton esters (BE). *N*-hydroxypyridine-2-thione esters are most easily synthesized by reacting the sodium salt of *N*-hydroxypyridine-2-thione and an acid chloride [2]. Carboxylic acids may also be converted to BE using coupling reagents such as chloroformates or dicyclohexylcarbodiimide [3]. Through the use of different carboxylic acid substrates and thiohydroximes, a wide variety of BE can be synthesized [4–6].

The decomposition of BE by heat or visible light initially yields acyloxy radicals and pyridine thiol radicals (Scheme 1, path (a), Homolysis, decarboxylation and induced decomposition of a Barton ester).

Laser flash photolysis studies have shown that the pyridine thiol radical is consumed by attacking the pyridine thione ring of the starting Barton ester producing 2,2′-dipyridyl disulfide and a second acyloxy radical (Scheme 1, path (b)) [7]. Thus, the decomposition of two equivalents of BE yields two active acyloxy radicals and one inert disulfide species. The aliphatic acyloxy radicals lose carbon dioxide rapidly to form carbon centered radicals. If no trapping reagents are present, the radical intermediate can induce the cleavage of another molecule of Barton ester to produce a thioether (Scheme 1, path (c)).

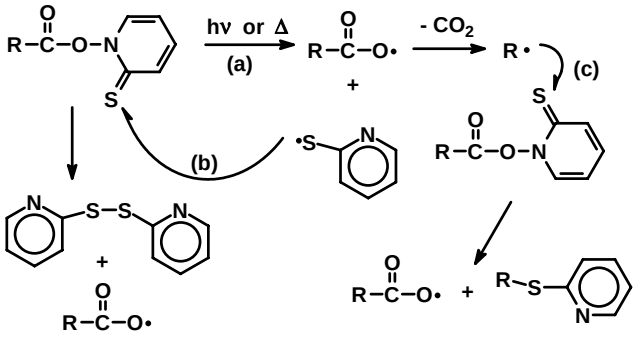
If an appropriate trapping agent (X–Y) captures the alkyl radicals, a more useful organic transformation can be achieved. Barton has used these free radicals in several organic syntheses in the presence of many common functional groups [1–6]. For example, reductive decarboxylation occurs when X–Y is RS–H and decarboxylative chlorination was accomplished in 95% yield [4] when X–Y is CCl_3–Cl. The ease of synthesis and facile decomposition of BE, make them useful in a wide variety of organic reactions including homologation and halogenation. Judicious selection of X–Y allows elaboration of reactive acid derivatives under rather mild conditions.

BE have been used as chain transfer agents to control free-radical polymerizations [8]. Polymerizations of styrene, methyl methacrylate, methyl acrylate and vinyl acetate initiated by either benzoyl peroxide (BPO) or azobisisobutyronitrile (AIBN) were conducted in the presence of BE. The chain transfer constants (C_x) for the various BE (R = $C_{15}H_{31}$, Bz, or Ph) were then calculated by the Mayo method [9] from the molecular weight data obtained by size exclusion chromatography (SEC). The chain transfer mechanism involves induced decomposition of the BE by propagating a radical attack on the thiocarbonyl of the BE as shown below (Scheme 2, Chain transfer via induced decomposition of Barton ester). A key feature on this mechanism is

* Corresponding author.

† Deceased, March 28, 1999.

0032-3861/00/$ - see front matter
PII: S0032-3861(99)00568-6



Scheme 1.

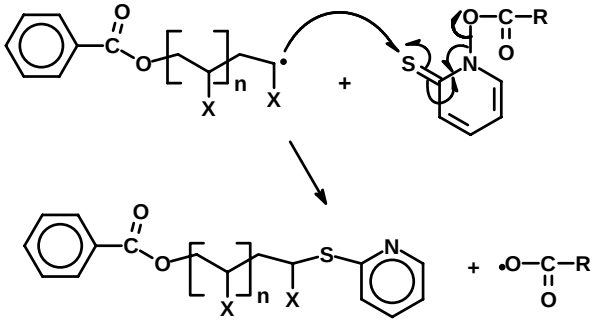
the formation of chains with asymmetric end-groups; the initiating benzoate radical introduces an ester end group and a thiopyridyl group is formed at the other end by the chain transfer process.

There is one prior example of the application of BE to modify polymer film surfaces by grafting [10]. Generation of carboxyl groups on the surface of polyethylene by oxidation followed by esterification with *N*-hydroxypyridine-2-thione introduced Barton ester sites on the film. These esters were then decomposed by visible light in the presence of acrylonitrile to form polyacrylonitrile grafts on the film surface. The average graft length was estimated by infrared (IR) spectroscopy to be 25 monomer units. This is the first reported application of BE as initiators.

Poly(arylene ether sulfone)s are useful membrane materials with applications in ultrafiltration and as support materials for composite membranes because they exhibit excellent mechanical and chemical properties [11]. Extensive efforts have been made to modify their permeability and selectivity by introduction of functional groups directly on the arylene backbone [12,13]. For example a series of aminated poly(arylene ether sulfone) membranes was examined in an effort to enhance the selectivity of the resultant membranes in the separation of carbon dioxide/methane mixtures [14]. Although some positive effects were observed, it was shown that simple substituents tended to reduce the free volume and negatively impact the permeability. Bulky substituents such as phenyl rings did increase the free volume so we anticipated that short chain grafts would be useful in enhancing the membrane properties.

A few examples of poly(arylene ether sulfone) graft copolymers have been synthesized. For example, poly(arylene ether sulfone)-*graft*-polydimethylsiloxane has been prepared by hydrosilylation of vinylsilylated polysulfone by Nagase et al. [15]. Gas permeation of methane and carbon dioxide was indeed enhanced relative to unmodified polysulfone membranes [16]. Photochemical surface grafting of acrylic acid to polysulfones has been achieved by coating commercial ultrafilration (UF) membranes with photoinitiators; the grafting process was accompanied by extensive homopolymerization [17]. Low temperature plasma induced surface modification of polysulfones to introduce peroxide groups facilitated thermally induced grafting with 2-hydroxyethyl methacrylate to enhance the hydrophilicity of the membrane surfaces [18].

The poly(arylene ether sulfone)-*graft*-poly(acrylic acid) copolymers served as supports for covalent binding of enzymes and peptides to the membrane surface [17] and the enzymatic activity was retained as evidenced by specific activity/binding assays. Daly and Lee [19,20] have grafted polypeptides to aminated polysulfones for potential use in reverse osmosis membranes and enantiomer resolutions. It is the goal of this research to show the versatility of BE as initiators in the radical graft copolymerization of vinyl monomers. The unique properties of BE as asymmetric initiators and chain transfer agents present several opportunities for controlling molecular architecture, particularly in preparing graft copolymers without concomitant homopolymerization of the grafting monomer. We have reported on applications and limitations of BE-modified polystyrene and acrylate copolymers as substrates for radical grafting [21]. In particular, we have noted that generation of radicals from BE attached directly to the backbone, i.e. acrylate and methacrylate BE, is accompanied by chain cleavage. In addition in this paper, we explore the conversion of BE substituents to TEMPO adducts to effect controlled radical graft copolymerization.



Scheme 2.

2. Experimental

2.1. Materials

All materials were obtained from Aldrich unless noted otherwise. Styrene was dried over sodium sulfate, passed through a short alumina column, vacuum distilled, and purged with argon before use. All other monomers were distilled and purged with argon before use. Dichloromethane (DCM) and tetrahydrofuran (THF) were obtained from Mallinckrodt. DCM was distilled from CaH_2, and THF was distilled from K unless noted otherwise. Anhydrous dimethylformamide (DMF) was used without further purification. Sodium *N*-oxypyridine-2-thione was obtained from Olin and purified by a previously published procedure [2].

Table 1
Poly(arylene ether sulfone)-*graft*-polystyrene copolymers

Substrate mass (g)	[BE] (mM)[a]	% Weight gain	Molecular weight[b]	Graft length[c]	Exothermic trans.	
					°C	J/deg mg
DS = 0.149						
0.04	1.4	1050	103,000	180	140.2	1.299
0.22	7.4	114	190,000	27	140.9	0.668
0.44	15	32	130,000	20	140.2	0.421
DS = 0.525						
0.05	5.1	860	108,000	86	139.4	1.632
0.27	28	200	102,000	13	145.8	0.047
0.51	52	104	148,000	10	136.6	0.001
DS = 0.957						
0.06	9.8	867	90,000	63	138.6	0.478
0.30	49	200	99,000	15	151.1	0.107
0.60	98	92	198,000	6	141.7	0.004

[a] In 10 ml 75 mol% styrene in DMF.
[b] Number average from SEC based upon polystyrene standards.
[c] Number average calculated from NMR

Acrylamide was obtained from the American Research Company and was 99.9% pure. Carboxylated poly(arylene ether sulfone) (**1**) samples were obtained from the National Research Council, Canada ($M_w = 45,000$, $M_n = 20,000$) [22]. The carboxylated samples tended to absorb up to 7% water so all polymer samples were dried under vacuum at 25°C for 24 h.

2.2. Characterization

Molecular weights were determined with a size exclusion chromatograph (SEC) equipped with a Waters 590 HPLC pump, Dawn DSP multiangle laser light scattering (MALLS) detector, and a Waters 410 differential refractometer (DRI). The dried polymers were dissolved in THF and eluted at a flow rate of 0.9 ml/min through two Phenogel columns from Phenomenex. SEC calibration was performed using polystyrene standards. The samples polymerized in the presence of TEMPO were analyzed by SEC-low angle laser light scattering (LALLS) consisting of a Waters 6000-A HPLC pump, Chromatix KMX-6 LALLS detector, and an Altex Model 156 DRI. The polymers were dissolved in THF and eluted at a flow rate of 1.0 ml/min through a Polymer Laboratories Mixed-B column.

Differential scanning calorimetry (DSC) was performed on a Seiko Instruments DSC Series 6200. Proton nuclear magnetic resonance (NMR) spectra were recorded using a Bruker 250 MHz instrument; samples were dissolved in $CDCl_3$ (with tetramethylsilane) unless noted otherwise. A Perkin–Elmer 1760 FTIR spectrophotometer was utilized to record the infrared spectra of samples either as films or in KBr pellets. Ultraviolet–Visible (UV–Vis) spectra were measured using a Beckman DU-7 spectrophotometer.

2.3. Barton ester chain transfer constant with acylamide

The chain transfer constant for phenyl Barton ester with acrylamide in DMF was found to be 0.08 using the Mayo method [9]. Phenyl Barton ester was prepared by a previously published general procedure [2]. A stock solution of 4 M acrylamide in DMF was prepared, along with a stock solution of phenyl Barton ester in 4 M acrylamide. Polymerizations were conducted at Barton ester concentrations of 0.01, 0.02, 0.04 and 0.08 M. Irradiation of samples proceeded under the following conditions: visible light from a 125 W tungsten lamp placed 30 cm from the sample which was kept at 25°C for 4 h. Polyacrylamide was filtered and washed with DMF then THF. Molecular weights of the dried polymers were then measured by Ubbelohde viscometry in distilled, deionized water at 30°C using Mark–Houwink constants of $K = 6.31 \times 10^{-3}$ml/g and $a = 0.80$ [23]. The viscosity molecular weights for the BE ester concentrations were found to be 75,000, 71,000, 34,000 and 31,000, respectively.

2.4. Poly(arylene ether sulfone)-graft-polystyrene copolymers, *3*

Carboxylated poly(arylene ether sulfone),**1**, (DS = 1.0, 1.50 g) was dissolved in 15 g thionyl chloride and refluxed until evolution of HCl could no longer be detected by litmus paper. The excess thionyl chloride was evaporated, the acid chloride derivative was vacuum dried, and then dissolved in dry DCM purged with nitrogen. The reactor was shielded from light and sodium *N*-oxypyridine-2-thione (1.0 g, 6.7 mmol) was added. The mixture was stirred for 4 h at room temperature. The resultant BE modified poly(arylene ether sulfone), **2**, was purified by precipitation in methanol, filtered and dried. Conversion to Barton ester was confirmed to be DS = 0.96 by UV–Vis spectroscopy (367 nm) of the 0.2 mg/ml polymer in DCM using the extinction coefficient measured for phenyl Barton ester in DCM ($\epsilon = 4200$). Similar treatment of **1** with DS = 0.54 and DS = 0.15 to give Barton esterified polysulfone confirmed by UV–Vis to be

Table 2
Grafting with methyl methacrylate, vinylpyridine and acrylamide

Graft	DS (UV–Vis)	% Mass increase	Graft length (by mass)	Graft length (by NMR)
Methyl methacrylate	0.69	126	10	13
4-Vinyl pyridine	0.73	78	5	10
Acrylamide	0.73	179	16	NA

DS = 0.525 and DS = 0.149, respectively. Grafting was accomplished by adding the poly(arylene ether sulfone–Barton ester) to 10 ml of a stock solution of styrene (75 mol% in DMF) so that the concentration of Barton ester was 1–100 mM. Polymerization was effected by irradiation of samples for 24 h under the conditions described above. The poly(arylene ether sulfone)-*graft*-polystyrene, **3**, samples were isolated by precipitation in methanol, filtered, and dried. The copolymers were weighed then analyzed by SEC, NMR, IR, and DSC. The results are summarized in Table 1. NMR ($CDCl_3$) δ (ppm): 1.30–1.90 (3H, CH_2–CH), 2.25 (6H, CH_3), 6.30–7.10 (5H, PS aromatic-H), 7.10–7.40, 7.80–8.12 (16H, Psf aromatic-H). IR (cm^{-1}) (film): 1491, 1586 (PS), 1234 (S=O), 1119 (Py–S–), 1737 (C=O).

Samples of the copolymers, 0.1 g, were dissolved in 10 ml THF (with inhibitor, undistilled); 0.01 g LiOH monohydrate was then added along with 2 drops of distilled water. When the solutions were heated to 60°C for 24 h, the lithium salt of the carboxylated poly(arylene ether sulfone) precipitated. The supernatant was decanted into 50 ml of methanol acidified with 1 ml 1 M HCl to precipitate the polystyrene grafts. This procedure effected separation of the cleaved polystyrene grafts from the insoluble poly(arylene ether sulfone) backbone. The precipitated polystyrene polymer was filtered, dried, and analyzed by SEC; graft molecular weights were under 5000 Da.

2.5. Grafts of typical vinyl monomers to poly(arylene ether sulfone)

Graft copolymers of poly(methyl methacrylate), poly(4-vinylpyridine), and polyacrylamide on poly(arylene ether sulfone) carboxylated with DS = 0.74 were synthesized. Poly(arylene ether sulfone–Barton ester) was prepared as above except that 1.0 g carboxylated poly(arylene ether sulfone) and 0.255 g (1.71 mmol) sodium pyridinethione-*N*-oxide was used in each case. Conversion to Barton ester was confirmed to be DS = 0.69 for use with methyl methacrylate and DS = 0.73 for 4-vinylpyridine and acrylamide by UV–Vis of a 0.15 mg/ml sample in DCM.

To form methyl methacrylate (MMA) grafts, 1.14 g poly(arylene ether sulfone–Barton ester) was dissolved in 8.0 ml DMF, then 21.70 g (217 mmol) MMA was slowly added while stirring. The slightly cloudy solution was purged with argon and then exposed to visible light for 24 h. The solution was then precipitated in 300 ml methanol, filtered, and vacuum dried at room temperature for 48 h; yield = 2.58 g. NMR ($CDCl_3$) δ (ppm): 0.85–1.03 (2H, CH_2), 1.69–1.82 (1H, CH), 1.90 (6H, $2CH_3$), 3.61 (3H, CH_3), 6.93–7.03, 7.22–7.27, 7.82–8.04 (16H, aromatic). Extraction of the graft copolymer with acetonitrile, a solvent selective for poly(methyl methacrylate), did not yield any homopolymer. An average graft length of 13 was estimated from the relative areas of the PMMA methyl peak (3H, 3.6 ppm) and the polysulfone aromatic peaks (16H, 6.9–8.2 ppm), corrected for the degree of substitution (0.69) of the initiating BE (Table 2). Based upon the weight of the graft copolymer and an average DP of 13, the yield was 85%.

4-Vinylpyridine, 20.75 g (198 mmol), was added to a solution of 1.00 g poly(arylene ether sulfone–Barton ester) in 5.02 g DMF. The solution was purged with nitrogen and exposed to visible light as above for 24 h. The solution was precipitated in 250 ml ethyl acetate, filtered, and vacuum dried as above; 1.78 g of copolymer was isolated. Based upon an average graft DP of 10, this is a 56.5% yield. The copolymer was found to be insoluble in common solvents except for DMF. NMR (DMF-d7) δ (ppm): 0.93–1.24 (2H, CH_2), 1.99–2.13 (6H, $2CH_3$), 2.85–2.89 (1H, CH), 6.00–6.44 (2H, Py Ar–H), 6.58–6.61, 7.19–7.31 (16H, Psf Ar–H), 7.31–7.55 (2H, Py Ar–H). An average graft length of 10 was estimated from the relative areas of the poly(vinylpyridine) aliphatic region (3H, 0.93–1.24, 2.85–2.9) and aromatic region (4H, 6.0–6.5, 7.5–7.8) compared to the poly(arylene ether sulfone) aliphatic (6H, 1.95–2.18) and aromatic region (16H, 6.6–7.3) and corrected for the degree of substitution (0.73).

Acrylamide, 14.01 g (197 mmol), was added to a solution of 1.00 g poly(arylene ether sulfone–Barton ester) in 24.90 g DMF. This caused the polymer to form a fluffy precipitate in the acrylamide solution. The heterogeneous mixture was stirred vigorously and exposed to visible light as above for 24 h. Acrylamide copolymer precipitated from the DMF solution during the course of the reaction. The copolymer was isolated by vacuum filtration, washed with 50 ml THF, and finally vacuum dried as above, wt = 2.79 g. The graft copolymer was insoluble in water and common organic solvents.

2.6. Benzoyloxy-styrene–tetramethyl-1-piperidinyloxy adduct

Phenyl Barton ester, 2.70 g (11.7 mmol), and 5.30 g tetramethyl-1-piperidinyloxy (TEMPO) (34.0 mmol) were dissolved in 135.0 g (1.30 mol) styrene, and the solution was purged with argon. The solution was then exposed to

Table 3
Molecular weight and polydispersity of polystyrene grafts from poly(arylene ether sulfone)–TEMPO adducts

Reaction time (h)	Mass copolymer (g)	Copolymer M_n	Graft M_n	Graft X_n	Graft PD
12	0.47	60,000	42,000	404	1.25
24	0.54	70,000	58,000	558	1.35
36	0.52	80,000	71,000	683	1.25
48	6.08	95,000	89,000	856	1.37

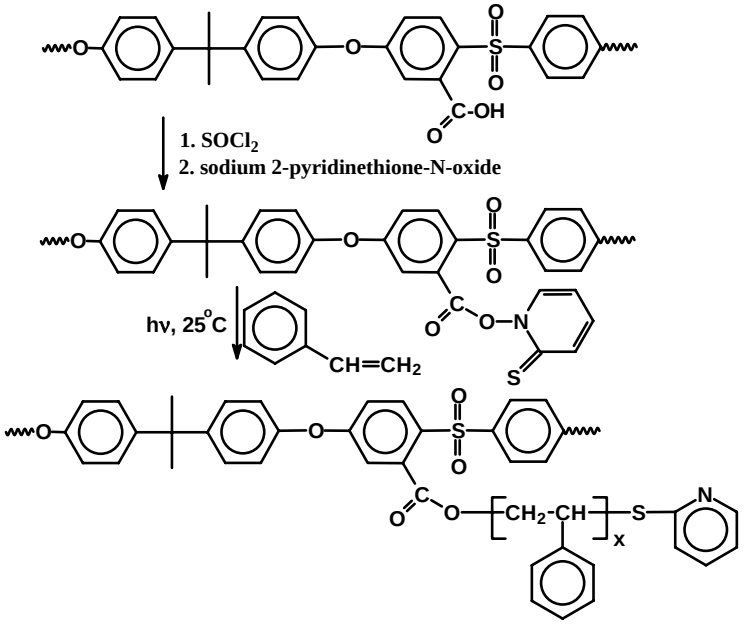
visible light from a 125 W tungsten lamp, 30 cm from the sample, 25°C, for 72 h. The styrene was then removed by rotary evaporation at 50°C. The residue was dissolved in a 1:1 v/v mixture of hexane:DCM and purified by a previously published procedure [24]. The benzoyloxy-styrene–TEMPO adduct was obtained in the 23% yield after chromatography. NMR ($CDCl_3$) δ (ppm): 0.66, 1.03, 1.21, 1.41 (12H, each $-CH_3$), 1.12–1.49 (6H, 3 $-CH_2-$), 3.44 ($J = 8$ Hz, 1H, C*H*H), 4.12 ($J = 8$ Hz, 1H, CH*H*), 4.97 ($J = 4$ Hz, 1H, C*H*), 6.4–8.3 (10H, Ar*H*)} is in agreement with that reported by Hawker [24].

2.7. Controlled radical graft copolymerization from poly(arylene ether sulfones)

Carboxylated poly(arylene ether sulfone) (**1**) (DS = 1.0), was converted to the corresponding Barton ester by the procedure described above. The BE-modified polymer, 0.5 g, was dissolved in 12.76 g (0.123 mol) styrene and 2.98 g DMF along with 0.48 g (3.0 mmol) TEMPO. The solution was purged with argon, then exposed to visible light for 23 h. After diluting the solution with 10 ml of THF, the TEMPO modified polymer, **4**, was precipitated in 250 ml methanol. The precipitate was dissolved in 10 ml DCM and reprecipitated in 100 ml methanol, filtered and dried (recovered 0.49 g). NMR (DMSO-d6) δ (ppm): 0.90, 1.05, 1.16, 1.21–1.35, 1.49 (18H, TEMPO), 1.50–1.80 (6H, Psf CH_3), 3.54, 3.75, 3.85 (3H, CH_2–CH), 6.79–7.19, 7.20–7.35, 7.75–8.16 (aromatic). Integration of the TEMPO region (18H, 0.90–1.49) and styryl aliphatics (3H, 3.45–3.90) and comparison to polysulfone aliphatic region (6H, 1.50–1.85) gives degree of substitution of TEMPO = 31%.

TEMPO-modified poly(arylene ether sulfone), 0.2 g, was dissolved in 13.95 g styrene and 2.64 g DMF along with 4.2 mg TEMPO (10% excess). The solution was purged with argon then heated to 130°C. Samples of the polymerization mixture (1–2 ml) were taken at 12, 24 and 36 h, then the polymerization was stopped at 48 h. The poly(arylene ether sulfone)-*graft*-polystyrene, **5**, samples were precipitated in methanol, filtered, dried and weighed; total weight of the copolymers was 7.61 g (53% conversion). These copolymers were analyzed by SEC–LALLS, and the results are reported in Table 3.

Each sample, 0.2 g, was dissolved in 10 ml THF along with 1 drop of distilled water and 0.1 g (4.2 mmol) lithium hydroxide monohydrate(99.95%). The solutions were heated to 67°C for 24 h. The solutions were precipitated in methanol acidified with 1 M HCl solution. The samples were then dissolved in THF, decanted to remove the



Scheme 3.

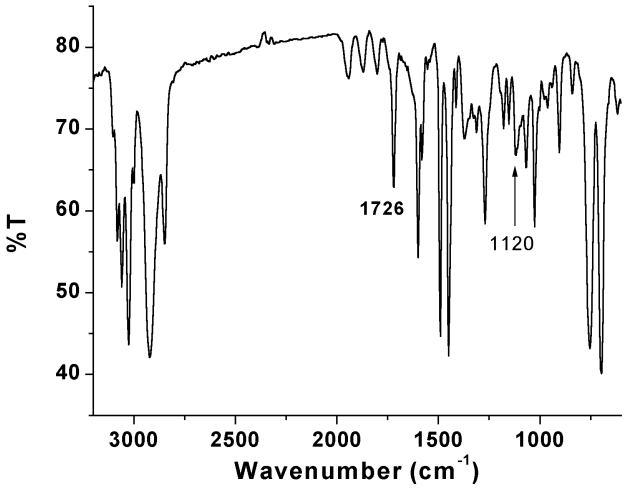


Fig. 1. Infrared spectrum of poly(arylene ether sulfone)-*graft*-polystyrene.

insoluble polysulfone backbone, and reprecipitated in methanol. The polystyrene samples dissolved in THF were analyzed by SEC–LALLS. The data is summarized in Table 3.

3. Results and discussion

3.1. Grafting to poly(arylene ether sulfone) backbone

Carboxylated poly(arylene ether sulfone) (**1**) can be synthesized by sequential lithiation/carbonation of poly(arylene ether sulfone) in THF [22]. The degree of carboxylation can be controlled by the molar ratio of butyl lithium to polysulfone employed in the initial lithiation step. The carboxylated polymers are stable up to 290°C and the glass transitions increase linearly from 190–210°C as the degree of substitution increases. The carboxyl substituent undergoes reactions typical of carboxylic acids, i.e. it can be easily converted to acid chlorides and esters.

Conversion of polysulfone **1** to a Barton ester (Scheme 3, Grafting styrene to carboxylated poly(arylene ether sulfone) via a Barton ester adduct) was effected via an acid chloride intermediate produced by treatment of **1** with neat thionyl chloride. The polymeric acid chloride was dissolved in methylene chloride and allowed to react at room temperature with sodium *N*-oxypyridine-2-thione to form the corresponding Barton ester, **2**. The polymers with BE substituents could be isolated if precautions were taken to avoid heating above 60°C, exposure to light and moisture. The concentration of BE substituents was determined by UV–Vis spectroscopy ($\lambda_{max} = 367$ nm) using the extinction coefficient measured for phenyl Barton ester in DCM ($\epsilon = 4200$). Yields for BE formation exceeded 95% based upon the initial carboxylate content.

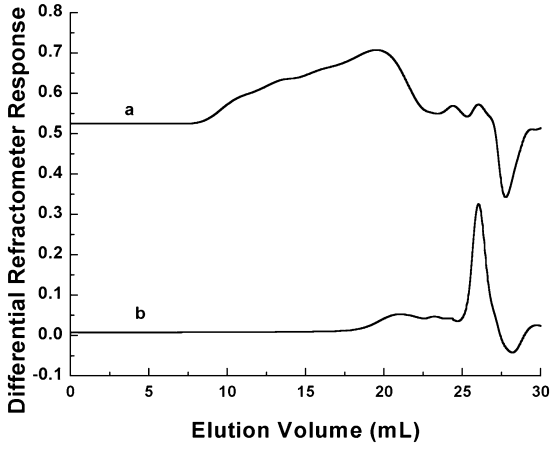


Fig. 2. Size exclusion chromatographs of: (a) poly(arylene ether sulfone)-*graft*-polystyrene; and (b) polystyrene grafts recovered from hydrolysis.

Graft copolymers were produced by adding the poly(arylene ether sulfone–BE) to a mixture of vinyl monomer and DMF (3:1 proportion), and exposing the solution to visible light. Kinetic studies of styrene homopolymerization using phenyl Barton ester as an initiator reveal that the decomposition of the Barton ester via a combination of dissociation and chain transfer has a half-life of 3.2 h [21]. Within 24 h the initiator has been effectively consumed; indeed the yellowish color associated with BE had bleached to colorless. The resultant copolymers can be isolated by precipitation in non-solvents and any homopolymer formed can be extracted with appropriately selected solvents. For example, residual polystyrene can be removed from poly(arylene ether sulfone)-*graft*-polystyrene by extraction with cyclohexane. The homopolymer content does not exceed 5–8%. Since the homopolymerization is very limited, once the initiator has been consumed, the grafting process stops and the yield of graft copolymer will be limited by the initiator concentration and the degree of polymerization achieved before chain transfer to initiator occurs. Thus, if quantitative conversion to all the initiation sites on a carboxylated polysulfone with one BE per repeat unit to grafts with average DPs of 15 were achieved, the maximum weight gain would be 280%. High concentrations of monomers are used to maximize the [M]/[I] ratio and the DP achieved before chain transfer occurs, but the actual amount of monomer consumed in the graft may only be 10–20%. However, the efficiency, i.e. the % monomer converted that appears in the graft, is very high because very little in any homopolymer is formed.

3.2. Characterization of graft copolymers

The structure of poly(arylene ether sulfone)-*graft*-polystyrene, **3**, can be elucidated using both infrared and NMR spectroscopy. A typical infrared spectrum is shown in Fig. 1. The characteristic ester carbonyl absorption at 1726 cm^{-1} indicates that addition of styrene to the aryl carboxylate radical occurs before it undergoes extensive decarboxylation. Attachment of the polystyrene graft via an ester linkage was expected as decarboxylation is reported to be 10^5 times slower for benzoyloxy derivatives than for alkyl carboxylate radical [25]. The ester linkage can be

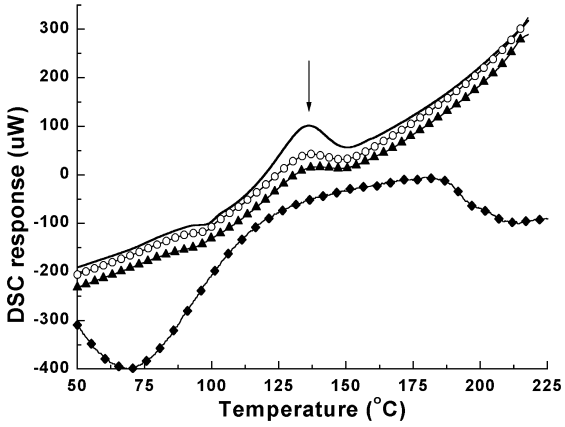


Fig. 3. Differential scanning calorimetry traces for poly(arylene ether sulfone)-*graft*- polystyrene copolymers (DS = 0.15) : (a) — graft DP = 180; (b) –○–, DP = 30, (c) –▲–DP = 20, (d) –◆– unmodified carboxylated poly(aryl ether sulfone).

cleaved by alkaline hydrolysis and the grafts can be isolated and analyzed independently. If the hydrolysis is conducted with lithium hydroxide in THF, the resultant poly(lithium arylene ether sulfone carboxylate) precipitates. This facilitates separation of the graft segments from the backbone polymer. Copolymer molecular weights were estimated by SEC–MALLS in THF, assuming that the d*n*/d*c* for polystyrene homopolymer remains applicable. A typical SEC of a poly(arylene ether sulfone)-*graft*-polystyrene along with the SEC of the corresponding polystyrene grafts is shown in Fig. 2. The molecular weights of the copolymers estimated by SEC appear relatively low due to the compact structure of the graft copolymers.

An IR peak at 1120 cm^{-1} confirms the presence of the pyridine sulfide end group produced by chain transfer to Barton ester. The presence of thiopyridine end groups has also been confirmed by MALDI–TOF mass spectrometry using low molecular weight homopolymers of polystyrene [21]. The polystyrene copolymers are all fully soluble in THF, DCM, chloroform, and toluene. Further, clear films are easily cast from these solutions.

The effects of the degree of carboxylation and backbone polymer concentration on grafting efficiency and graft length was explored using carboxylated poly(arylene ether sulfone)s with degrees of substitution equal to 0.15, 0.54, and 1.0. The results are summarized in Table 1. Graft length determined by NMR was consistent with the graft length estimated from the weight gain. SEC–MALLS of the short grafts proved unreliable due to poor separation and isolation of polymers with molecular weights less than 5000, and the low light scattering intensity of such polymers. The chain transfer constant of phenyl Barton ester in styrene is 0.96 [21]; however, this number does not account for intramolecular chain transfer. Apparently chain transfer along the poly(arylene ether sulfone) chain occurs more readily, resulting in the production of lower molecular weight grafts than estimated from the bulk concentration of BE and monomer in the mixture. If the chain transfer constant is recalculated using the data in Table 1, a "polymer-supported" C_x of 17.2 is obtained.

The graft copolymers appear to be relatively homogenous. As shown in Fig. 3, only a weak glass transition at 95–100°C characteristic of polystyrene is detected and this is most pronounced when the graft segments have high molecular weights. The glass transition of the backbone polymer at 185°C cannot be detected in the graft copolymers. An exotherm around 135–150°C indicative of a first order transition is evident in each of the copolymer DSC traces. (Table 1). The maximum entropy for this transition is observed when the polysulfone contains a low degree of substitution with long polystyrene grafts. The nature of this transition is under investigation.

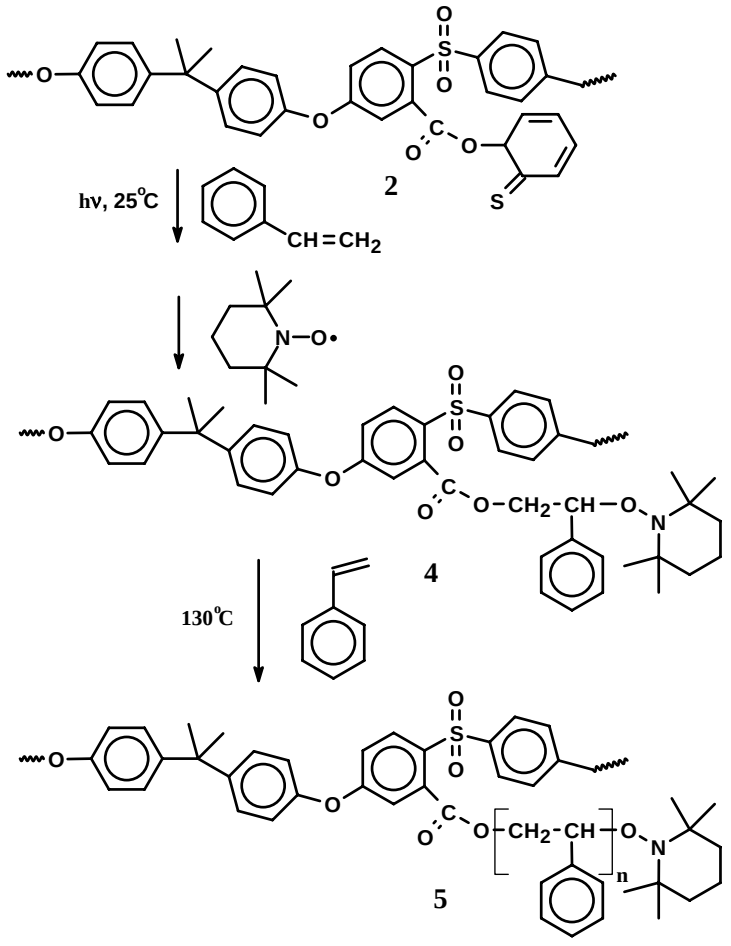
3.3. Other poly(arylene ether sulfone) graft copolymers

The poly(arylene ether sulfone)s elaborated with BE can be employed to produce graft copolymers with methyl methacrylate, 4-vinyl pyridine, and acrylamide. If the chain transfer constant to BE is too high, i.e. for vinyl acetate where C_x to phenyl BE is 80 [8]; attempts to form graft copolymers were unsuccessful. The MMA copolymers are easily dissolved in typical organic solvents, and form clear films. The graft length is comparable to that achieved with styrene monomers as would be expected since the chain transfer constants for the two monomers are comparable.

In an effort to introduce bulky side groups with amine functions to poly(arylene ether sulfone)s, vinylpyridine (VP) copolymers were prepared. Grafting efficiency of VP was much lower then previously observed with styrene and MMA and the resultant copolymer was soluble in DMF only. No apparent swelling was detected when the copolymer was dispersed in dilute HCl. NMR analysis of poly(-methyl methacrylate) ($CDCl_3$) and poly(4-vinylpyridine) (DMF-d7) copolymers provided additional information on graft length. Results for those copolymers and the polyacrylamide copolymer are contained in Table 2.

Efforts to incorporate cyclic pyrrolidine side chains by copolymerization of diallyl dimethyl ammonium chloride (DADMAC) failed, primarily due to the sensitivity of the Barton ester to hydrolysis. When the DADMAC was carefully dried and initiation of homopolymerization was attempted with phenyl BE, only 10% conversion was achieved within the lifetime of the initiator. Clearly BE are not effective initiators for this monomer.

We measured the chain transfer constant C_x for acrylamide to phenyl Barton ester in DMF and found that it was only 0.08. This suggests that acrylamide should be useful in the preparation of long chain grafts, and indeed high yields of grafted polymer were recovered. Unfortunately, the copolymer was insoluble in all solvents; the product precipitates during the polymerization process and this may limit the molecular weights of the grafts. Based upon weight gain, the graft DP was estimated to be only 16.



Scheme 4.

3.4. Synthesis of TEMPO adducts

If BE are decomposed in a mixture of styrene and a three-fold excess of 2,2,6,6-tetramethylpiperidine oxide (TEMPO), the primary adduct of styrene to the benzoate radical is trapped by TEMPO to form a unimer, which has been shown to initiate controlled radical polymerization. Hawker [24] suggests that 80°C is an optimum temperature for trapping a styryl radical with the TEMPO radical, and reported yield for the benzoyloxy-styrene–TEMPO adduct was 42%. We observed that photolysis of phenyl BE at room temperature afforded a unimer, but at a lower yield of 23%. The comparable synthesis of TEMPO adducts on a poly(arylene ether sulfone) substrate was more successful probably due to the ease of isolation of the polymer by precipitation.

3.5. Controlled radical grafting from poly(arylene ether sulfone)

Synthesis of TEMPO adducts to a poly(arylene ether sulfone) backbone was completed utilizing a Barton ester intermediate, **2**, as shown in Scheme 4 (Application of TEMPO adduct to controlled graft copolymerization). Irradiation of a solution of **2** in a mixture of styrene and DMF in the presence of excess TEMPO effects a 31% conversion of the BE substituents to the corresponding TEMPO adducts, **4**. The conversion is calculated from the NMR spectrum by relating the resonances at 0.90–1.49 of the TEMPO fragment to the resonances at 1.50–1.85 for the poly(arylene ether sulfone methyl groups, and confirmed by a similar comparison of resonances at 3.54–3.85 for the styryl aliphatic protons. Adduct **4** can be isolated and stored at room temperature without loss of activity.

Grafting of polystyrene on to the poly(arylene ether sulfone) was then completed by controlled radical polymerization from the TEMPO adduct. A solution of **4** in a styrene/DMF mixture was heated at 130°C for 48 h. Aliquots were removed at 12, 24, and 36 h intervals and the copolymer, **5**, was isolated by precipitation into methanol. The isolated masses of the samples shown in Table 3 reflect the fact that 1–2 ml aliquots were used to obtain the first three samples and the entire polymerization mixture was precipitated to obtain the last sample. The total conversion

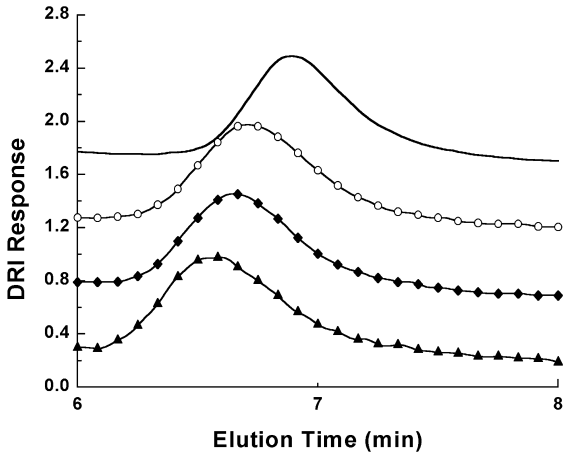


Fig. 4. Size exclusion chromatographs of polystyrene grafts recovered from hydrolysis of poly(arylene ether sulfone)-*graft*-polystyrene mediated by TEMPO at polymerization times: (a) —, 12 h, (b) –○–, 24 h, (c) –◆–, 36 h, (d) –▲–48 h.

of the styrene monomer was 53%. The molecular weights of the copolymers estimated from SEC appear low due to the branched structures. Cleavage of the grafts from the backbone was completed by basic hydrolysis of the ester linkage as described above. SEC of the polystyrene grafts show that M_n for the grafts increased with time and have narrow ($<$1.4) polydispersities as shown in Table 3; these are indicators of controlled radical polymerization. The SEC curves for the grafts are shown in Fig. 4.

4. Conclusions

Converting carboxyl substituents on backbone polymers to BE can produce polymeric initiators. Decomposition of the BE of substituted backbone polymers in the presence of vinyl monomers results in the formation of short chain graft copolymers with minimal concomitant homopolymerization. The average length of the grafts formed depends upon the extent of Barton ester substitution on the backbone as well as the monomer to initiator ratio employed in copolymerization. The technique can be employed to produce copolymers using styrene, methyl methacrylate, vinylpyridine and acrylamide as monomers.

BE can also serve as precursors in the formation of nitroxide unimers, which serve as initiators of controlled radical polymerization. The application of these polymeric nitroxide unimers to the synthesis of controlled radical graft copolymerization of styrene to a poly(arylene ether sulfone) backbone is demonstrated.

Acknowledgements

We wish to thank the Louisiana State University Graduate School for providing a fellowship for T.E. We would also like to thank Michael Guiver of the National Research Council of Canada for the carboxylated poly(arylene ether sulfone) samples and Drew Poche of Southeastern Louisiana University for the use of SEC–LALLS. Tommy Menuet helped with the initial phases of the project as part of the Howard Hughes undergraduate research program. Laura Wolf contributed to the project as part of the Louisiana State University Chemistry Department undergraduate research program.

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