Hyperbranched Poly(ethylene glycol)s: A New Class of Ion-Conducting Materials

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ABSTRACT: A new concept for the synthesis of hyperbranched macromolecules involving the use of AB_x macromonomers containing linear oligomeric units is introduced. This methodology is used for the preparation of a series of novel hyperbranched poly(ethylene glycol) derivatives containing linear poly(ethylene glycol) units of varying lengths and 3,5-dioxybenzoate branching units. An interesting feature of the hyperbranched poly(ethylene glycol) derivatives is their lack of crystallinity, which is used in the design of a new class of polyelectrolyte materials. The dependence of the ionic conductivity on temperature and the concentration of added lithium cations for these novel hyperbranched macromolecules is reported.

Introduction

The deliberate introduction of branches into polymeric materials has become a topic of considerable interest and activity in recent years.[1] This interest is driven by the desire to further manipulate and/or discover novel physical and mechanical properties for both existing and new materials. The most startling examples of these branched polymers are dendritic macromolecules,[2] which are characterized by an extremely large number of branch points that result in a three-dimensional shape in both solution and the solid state.[3] As a class of highly branched macromolecules, dendritic macromolecules can be divided into two distinct families, dendrimers which are prepared in a repetitive stepwise process and have an essentially perfectly branched structure[4] and hyperbranched macromolecules which are prepared in a single step from AB_x monomers and lead to irregular, polydisperse structures.[5]

Traditionally, both dendrimers and hyperbranched macromolecules are prepared from small-molecule AB_x monomers such as 3,5-dihydroxybenzyl alcohol[6] or 1,3-dibromo-5-((trimethylsilyl)ethynyl)benzene.[7] However, the opportunity also exists for functionalized linear polymers to be used as building blocks for dendritic macromolecules.[8] The resulting macromolecules, termed combburst polymers, have received only limited attention, even though they have a number of advantages over traditional dendrimers. The two most promiment examples are Tomalia's[9] synthesis of combburst poly(ethylene imine)s by the repeated grafting of poly(oxazoline) onto poly(ethylene imine) moieties followed by hydrolysis to regenerate the reactive amino groups. This stepwise approach was also employed by Gauthier[10] in his synthesis of combburst polystyrene derivatives by reaction of anionically prepared monofunctional polystyrene with chloromethyl-substituted poly(styrene)s followed by chloromethylation of the grafted material. Recently, Gnanou[11] has also reported the stepwise synthesis of comburst macromolecules containing a central polystyrene layer surrounded by a poly(ethylene oxide) layer. In all the above syntheses, a stepwise approach is used to prepare the combburst structure, and to our knowledge, no attempts have been made to prepare the hyperbranched equivalent of combburst macromolecules by the one-step polymerization of AB_x macromonomers.

In investigating the preparation of hyperbranched combburst macromolecules, the linear polymeric segment was chosen to be poly(ethylene glycol). This choice was governed by its commercial availability, well-defined chain ends, and the crystalline nature of the linear polymer. This last feature allows the effect of hyperbranching on polymer crystallinity to be examined by comparing the hyperbranched derivative with the corresponding linear material and starting macromonomers. Additionally, poly(ethylene glycol) have been extensively studied as a polymeric electrolyte, and to avoid disruption of the ionic comduction by crystallization, the poly(ethylene glycol) is cross-linked. However, this cross-linking leads to difficulties in device fabrication, processing, and evaluation. In an effort to overcome these difficulties, we propose to examine the synthesis of hyperbranched macromolecules based on poly(ethylene glycol) and evaluate the usefullness of such materials as polymeric electrolytes.

Experimental Section

Nuclear magnetic resonance spectroscopy was performed on a Bruker AM 200 FT-NMR spectrometer using deuterated chloroform as solvent and tetramethylsilane as internal reference. Gel permeation chromatography was carried out on a Waters chromatograp connected to a Waters 410 differential refractometer with THF as the carrier solvent. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-7 calorimeter using a scanning rate of 10 °C/min under a nitrogen atmosphere. The glass transition temperature was defined as the halfway point of transition heat flow. Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25-mm thick). Silica gel for flash chromatography was Merck Kieselgel 60 (230−400 mesh). All solvents used for synthesis were dried and distilled in the appropriate manner before use; the commercial reagents were obtained from Aldrich and used without further purification.

8-(*tert*-Butyldiphenylsiloxy)-1-hydroxy-3,6-dioxyoctane, 1. To a solution of triethylene glycol (10.0 g, 66.7 mmol) in dry acetonitrile (100 mL) was added *tert*-butyldiphenylsilyl chloride (9.15 g, 66.7 mmol) at room temperature under nitrogen atmosphere. Triethylamine (4.0 g, 39.6 mmol) in dry acetonitrile (10 mL) was added dropwise, and the stirred reaction mixture was heated at reflux under nitrogen for 3 h. The solvent was evaporated by rotary vacuum evaporation, and the crude product was purified by flash chromatography,

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eluting with CH_2Cl_2 and gradually increasing to 4:1 CH_2Cl_2/ether to give the monoprotected triethylene glycol **1** as a colorless oil: yield 47%. ^{1}H NMR ($CDCl_3$) δ 1.06, 3.57−3.72, 3.81, 7.38, and 7.69. ^{13}C NMR ($CDCl_3$) δ 19.1, 26.8, 61.7, 63.4, 70.4, 70.8, 72.4, 72.5, 127.6, 129.6, 133.6, and 135.6. Mass spectrum *m/z* (FAB) 388.

5-(*tert*-Butyldiphenylsiloxy)-1-hydroxy-3-oxypentane, 2. The hydroxy derivative **2** was prepared from diethylene glycol using the same procedure as for **1**. The crude product was purified by flash chromatography, eluting with CH_2Cl_2 and gradually increasing to 2:1 CH_2Cl_2/ether to give the monoprotected diethylene glycol **2** as a colorless oil: yield 39%. ^{1}H NMR ($CDCl_3$) δ 1.06, 3.60−3.70, 3.80, 7.37, and 7.65. ^{13}C NMR ($CDCl_3$) δ 19.8, 27.1, 62.4, 70.5, 72.3, 127.8, 129.6, 133.4, and 134.8. Mass spectrum *m/z* (FAB) 344.

17-(*tert*-Butyldiphenylsiloxy)-1-hydroxy-3,6,9,12,15-pentaoxyseptadecane, 3. The hydroxy derivative **3** was prepared from hexaethylene glycol using the same procedure as for **1**. The crude product was purified by flash chromatography, eluting with CH_2Cl_2 and gradually increasing to 2:1 CH_2Cl_2/ether to give the monoprotected hexaethylene glycol **3** as a colorless oil: yield 44%. ^{1}H NMR ($CDCl_3$) δ 1.05, 2.49, 3.64, 3.82, 7.40, and 7.69. ^{13}C NMR ($CDCl_3$) δ 19.2, 26.9, 62.0, 63.6, 70.9 72.7, 72.8, 127.6, 129.4, 133.7, and 135.8. Mass spectrum *m/z* (FAB) 520.

1-Bromo-8-(*tert*-butyldiphenylsiloxy)-3,6-dioxyoctane, 4. To a stirred solution of the monoprotected triethylene glycol **1** (10.0 g, 19.2 mmol) in dry tetrahydrofuran (50 mL) was added carbon tetrabromide (9.55 g, 28.8 mmol). Under a nitrogen atmosphere, triphenylphosphine (7.60 g, 29.0 mmol) was added, and stirring continued at room temperature for 15 min. The solvent was then removed under reduced pressure and the crude product purified by flash chromatography eluting with CH_2Cl_2 and gradually increasing to 4:1 CH_2Cl_2/ether to give the bromo derivative **4** as a colorless oil: yield 83%. ^{1}H NMR ($CDCl_3$) δ 1.05, 3.43, 3.64, 3.79, 7.39, and 7.68. ^{13}C NMR ($CDCl_3$) δ 19.2, 26.8, 30.3, 63.4, 70.6, 70.7, 71.2, 72.5, 127.6, 129.6, 133.6, and 135.6. Mass spectrum *m/z* (FAB) 451.

1-Bromo-5-(*tert*-butyldiphenylsiloxy)-3-oxypentane, 5. The monobromo derivative **5** was prepared from **2** using the same method as for **4**. The crude product was obtained as a colorless oil which was purified by flash chromatography, eluting with CH_2Cl_2 and gradually increasing to 3:1 CH_2Cl_2/ether to give the desired **5**: yield 78%. ^{1}H NMR ($CDCl_3$) δ 1.08, 3.29, 3.62−3.72, 7.41, and 7.67. ^{13}C NMR ($CDCl_3$) δ 19.5, 26.9, 30.5, 70.5, 71.9, 127.8, 129.7, 133.4, and 135.5. Mass spectrum *m/z* (FAB) 407.

1-Bromo-17-(*tert*-butyldiphenylsiloxy)-3,6,9,12,15-pentaoxyseptadecane, 6. The monobromo derivative **6** was prepared from **3** using the same method as for **4**. The crude product was obtained as a colorless oil which was purified by flash chromatography, eluting with CH_2Cl_2 and gradually increasing to 3:1 CH_2Cl_2/ether to give **6** as a colorless oil: yield 66%. ^{1}H NMR ($CDCl_3$) δ 1.05, 3.47, 3.65, 3.81, 7.38, and 7.68. ^{13}C NMR ($CDCl_3$) δ 19.4, 27.0, 30.5, 63.7, 71.0, 71.3, 72.5, 127.7, 129.8, 133.8, and 135.6. Mass spectrum *m/z* (FAB) 583.

Methyl 3,5-Dihydroxybenzoate, 7. 3,5-Dihydroxybenzoic acid (10.0 g, 65.0 mmol) was dissolved in methanol (200 mL), and concentrated sulfuric acid (1 mL) was added. The reaction mixture was then heated at reflux for 16 h and the solvent removed under reduced pressure. The crude product was dissolved in ether (250 mL), washed with water (2 × 100 mL) followed by aqueous sodium carbonate (2 × 100 mL), dried, and evaporated to dryness. Final purification by recrystallization from a 1:2 mixture of methanol and water gave **7** as a colorless solid: yield 80%, mp 168−170 °C. ^{1}H NMR (acetone-d_6) δ 3.85, 6.62, 7.03, and 8.63. ^{13}C NMR (acetone-d_6) δ 52.2, 107.9, 108.6, 133.0, 159.3, and 167.1. Anal. Calcd for $C_8H_8O_4$: C, 57.14; H, 4.80. Found: C, 56.92; H, 4.95.

Methyl 3,5-Bis((8′-(*tert*-butyldiphenylsiloxy)-3′,6′-dioxooctyl)oxy)benzoate, 8. A mixture of the monobromo derivative **4** (9.0 g, 23.3 mmol), methyl 3,5-dihydroxybenzoate, **7**, (1.80 g, 10.9 mmol), potassium carbonate (3.0 g, 20 mmol), and 18-crown-6 (100 mg) in acetonitrile (100 mL) was heated at reflux under nitrogen with vigorous stirring for 16 h. The solvent was then removed under reduced pressure and the crude product purified to give the ester **8** as a colorless oil: yield 77%. ^{1}H NMR ($CDCl_3$) δ 1.05, 3.62, 3.68, 3.81, 3.87, 4.11, 6.70, 7.19, 7.39, and 7.68. ^{13}C NMR ($CDCl_3$) δ 19.1, 26.8, 52.2, 61.7, 63.4, 67.6, 67.7, 70.3, 70.75, 70.78, 72.5, 106.9, 108.0, 127.6, 129.6, 131.8, 133.6, 135.6, 159.7, and 166.7. Mass spectrum *m/z* (FAB) 908.

Methyl 3,5-Bis((5′-(*tert*-butyldiphenylsiloxy)-3′-oxopentyl)oxy)benzoate, 9. The ester derivative **9** was prepared from **5**, synthesized using the same procedure as for **8**. The crude product was purified by flash chromatography, eluting with 1:1 hexane/ether and gradually increasing to ether to give **9** as a colorless oil: yield 82%. ^{1}H NMR ($CDCl_3$) δ 1.05, 3.65, 3.74, 3.82, 4.14, 6.71, 7.20, 7.40, and 7.66. ^{13}C NMR ($CDCl_3$) δ 19.0, 26.9, 52.4, 62.2, 67.8, 70.4, 106.9, 108.1, 127.6, 129.8, 131.6, 133.9, 135.7, 159.9, and 166.7. Mass spectrum *m/z* (FAB) 820.

Methyl 3,5-Bis((17′-(*tert*-butyldiphenylsiloxy)-3′,6′,9′,12′,15′-pentaoxoseptadecyl)oxy)benzoate, 10. The ester derivative **10** was prepared from **6** using the same procedure as for **8**. The crude product was purified by flash chromatography, eluting with 1:1 hexane/ether and gradually increasing to ether to give **10** as a colorless oil: yield 70%. ^{1}H NMR ($CDCl_3$) δ 1.05, 3.63, 3.82, 3.88, 4.11, 6.68, 7.19, 7.39, and 7.68. ^{13}C NMR ($CDCl_3$) δ 19.5, 27.2, 52.5, 63.9, 68.0, 69.8, 71.8, 72.6, 107.4, 108.5, 128.0, 130.0, 132.1, 134.0, 135.8, 159.9, and 167.1. Mass spectrum *m/z* (FAB) 1172.

Methyl 3,5-Bis((8′-hydroxy-3′,6′-dioxooctyl)oxy)benzoate, 11. A solution of the silylated derivative **8** (6.50 g, 8.30 mmol) in 3% methanolic hydrogen chloride (20 mL) was stirred at room temperature under nitrogen for 3 h. The solvent was then removed under reduced pressure and the crude product purified by flash chromatography, eluting with ether and gradually increasing to 1:2 ether/acetone to give the monomer **11** as a colorless oil: yield 67%. ^{1}H NMR ($CDCl_3$) δ 3.17, 3.56, 3.67, 3.80, 3.86, 4.13, 6.71, and 7.16. ^{13}C NMR ($CDCl_3$) δ 52.3, 61.6, 67.7, 69.5, 70.3, 70.8, 72.6, 107.4, 108.1, 132.0, 159.7, and 166.9. Mass spectrum *m/z* (FAB) 432.

Methyl 3,5-Bis((5′-hydroxy-3′-oxopentyl)oxy)benzoate, 12. The monomer **12** was prepared from **9** using the same procedure as for **11**. Purification of the crude product by flash chromatography, eluting with ether and gradually increasing to 1:3 ether/acetone, gave **12** as a colorless oil: yield 71%. ^{1}H NMR ($CDCl_3$) δ 3.22, 3.60, 3.78, 3.86, 4.15, 6.72, and 7.20. ^{13}C NMR ($CDCl_3$) δ 52.3, 62.1, 68.5, 70.4, 72.4, 107.5, 108.6, 131.8, 159.9, and 166.7. Mass spectrum *m/z* (FAB) 344.

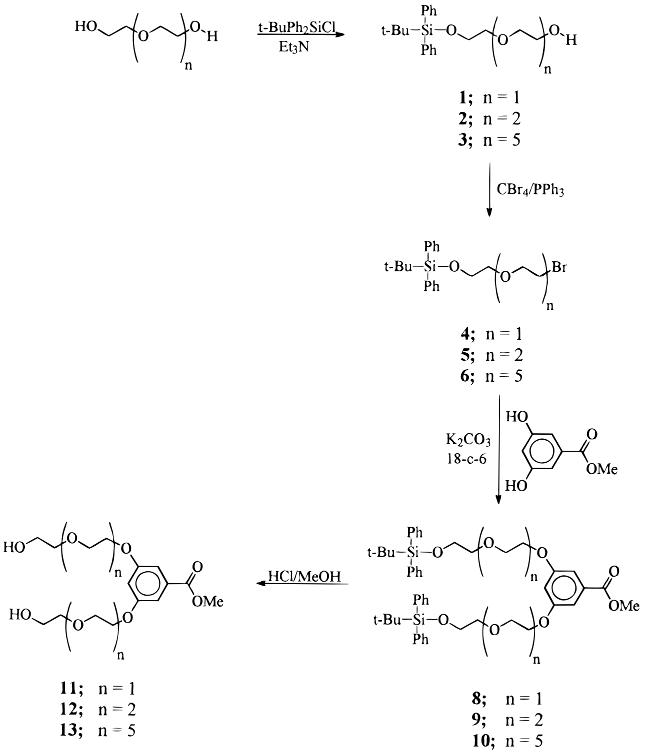
Methyl 3,5-Bis((17′-hydroxy-3′,6′,9′,12′,15′-pentaoxoseptadecyl)oxy)benzoate, 13. The monomer **13** was prepared from **10** using the same procedure as for **11**. Purification of the crude product by flash chromatography, eluting with ether and gradually increasing to 1:3 ether/acetone, gave **13** as a colorless oil: yield 50%. ^{1}H NMR ($CDCl_3$) δ 3.44, 3.65, 3.84, 3.89, 4.16, 6.71, and 7.18. ^{13}C NMR ($CDCl_3$) δ 52.4, 61.7, 67.9, 69.5, 70.5, 72.6, 106.9, 108.0, 131.8, 159.8, and 166.6. Mass spectrum *m/z* (FAB) 696.

Poly[bis(triethylene glycol)benzoate], 14. A mixture of dihydroxy ester **11** (2.00 g, 4.63 mmol) and dibutyltin diacetate (60 mg) was heated at 160 °C under a steam of nitrogen for 20 min followed by continued heating at 200 °C under high vacuum (0.5 mmHg) for an additional 20 min. The crude product was purified by precipitating from tetrahydrofuran into hexane to give the hyperbranched macromolecule **14** as a waxy solid: yield 90%. IR (neat) 3400, 2900, 1720, and 1110 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.53, 3.65, 3.70, 3.83, 4.17, 4.34, 4.41, 6.70, and 7.12. ^{13}C NMR ($CDCl_3$) δ 61.9, 65.1, 68.1, 68.3, 70.0, 71.0, 73.4, 106.9, 108.8, 132.7, 160.7, and 166.4.

Poly[bis(diethylene glycol)benzoate], 15. The hyperbranched macromolecule **15** was prepared from **12** using a similar procedure to **14**. The crude product was purified by precipitating from tetrahydrofuran into hexane to give **15** as a waxy solid in the yield of 81%. IR (neat) 3400, 2920, 1725, and 1120 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.50, 3.65−3.81, 4.25, 6.83, and 7.15. ^{13}C NMR ($CDCl_3$) δ 61.6, 64.8, 69.6, 70.8, 106.5, 108.9, 132.6, 159.8, and 166.2.

Poly[bis(hexaethylene glycol)benzoate], 16. The hyperbranched macromolecule **16** was prepared from **13** using a similar procedure to **14**. The crude product was purified by

Scheme 1



precipitating from tetrahydrofuran into hexane to give **16** as a waxy solid in the yield of 92%. IR (neat) 3400, 2900, 1720, and 1120 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 3.61, 3.83, 4.21, 4.42, 6.83, and 7.17. ^{13}C NMR (CDCl$_3$) δ 61.9, 65.5, 69.0, 69.9, 70.4, 71.3, 73.7, 106.8, 108.8, 133.1, 160.9, and 166.4.

Conductivity Experiments. The electrolyte complexes for the conductivity experiments were prepared by dissolution of the hyperbranched poly(ether ester) **16** and LiClO$_4$ in tetrahydrofuran. Removal of the solvent under reduced pressure gave the electrolyte complexes as waxy solids which were exhaustively dried using standard procedures. Prior to evaluation, the samples were heated at 100 °C under high vacuum (0.5 mmHg) for 30 min. The conductivity of hyperbranched electrolyte complexes were determined by an electrode cell of TPS 3102 accepts ($k = 1$) and TPS 3102 digital conductivity meter over a range of temperatures. The electrode was calibrated using potassium chloride solution.

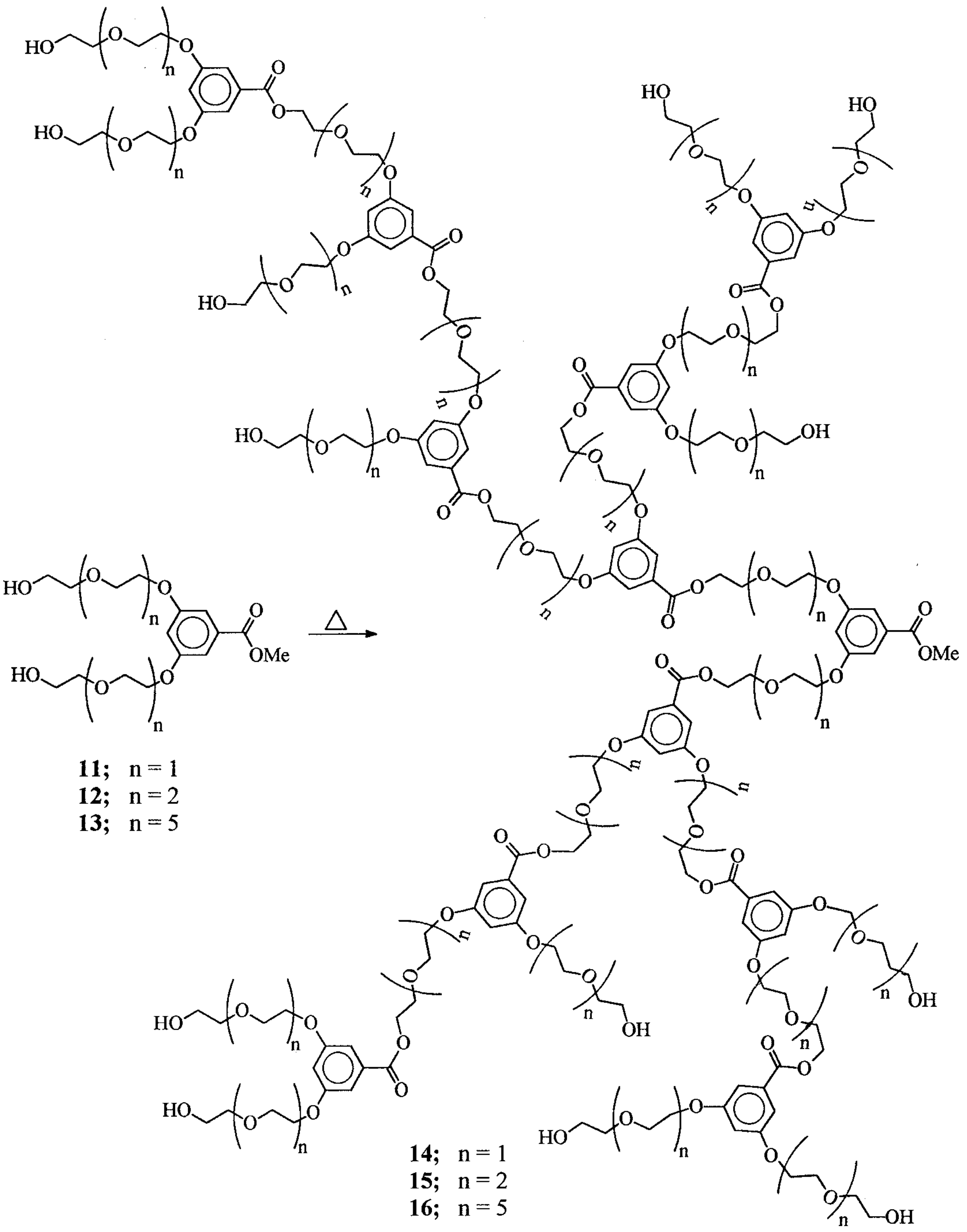
Results and Discussion

Unlike traditional hyperbranched macromolecules which are prepared from AB$_x$ monomers, the synthesis of combburstlike hyperbranched macromolecules relies on the incorporation of short linear polymer chains into the AB$_x$ structure. Our approach to the synthesis of such macromonomers is the coupling of short linear chains, in this case functionalized oligio(ethylene glycol) units, to a branching unit. This gives the AB$_x$ structure, though in a macromonomer form, and polymerization leads to the desired combburst/hyperbranched architecture consisting of linear polymer segments connected by branching units. Our extensive work in the synthesis of hyperbranched polyesters[12] prompted the use of esterification chemistry as the coupling reaction and the 3,5-dioxybenzoate group as the branching units. Therefore, the polymerization reaction involves condensation of the single methyl ester of the branched unit with the two hydroxy chain ends of the dual oligio(ethylene glycol) chains.

The preparation of the required AB$_2$ macromonomers was accomplished by a protection/deprotection approach as shown in Scheme 1. Starting from the commercially available di-, tri-, or hexaethylene glycols, reaction with 1 equiv of *tert*-butyldiphenylchlorosilane in the presence of triethylamine gives the monoprotected oligio(ethylene glycol)s **1**, **2**, and **3** as the major products. Activation of the single hydroxy chain end of **1**, **2**, or **3**, by bromination with carbon tetrabromide and triphenylphosphine, gave the reactive bromo derivatives **4**, **5**, and **6** in excellent yields. Coupling of the linear oligio(ethylene glycol) segments with the branching unit, methyl 3,5-dihydroxybenzoate, **7**, was accomplished by reaction of the bromo derivatives **4**, **5**, and **6** with **7** in the presence of potassium carbonate and 18-crown-6. This results in dialkylation of the branching unit and gives the silylated derivatives **8**, **9**, and **10**, in which two oligio(ethylene glycol) segments have been attached to the same aromatic ring. Deprotection of **8**, **9**, and **10** by reaction with methanolic hydrogen chloride gave the desired AB$_2$ macromonomers **11**, **12**, and **13**, in which there is a single methyl ester group at the "focal point" of the macromonomer and two reactive hydroxy groups at the chain ends of the two linear segments (Scheme 1).

Under similar conditions to that developed previously for the preparation of hyperbranched polyesters, the bulk polymerization of **11**, **12**, and **13** was performed in the presence of catalytic amounts of dibutyltin diacetate at 160 °C under a stream of nitrogen for 20 min followed by the application of high vacuum (0.5 mmHg) at 200 °C for an additional 20 min. During this time, the melt became progressively more viscous and the evolution of volatiles ceased. It was, however, found that prolonged heating at 200 °C, or heating at temperatures in excess of 200 °C, resulted in the production of insoluble materials, presumably due to uncontrolled cross-linking reactions. The hyperbranched poly(ether ester)s **14**, **15,** and **16** were obtained as waxy solids in high yields and proved to be very soluble in a wide range of solvents, such as chloroform, THF, methanol, etc. (Scheme 2). As shown in Scheme 2, the hyperbranched macromolecules consist of linear oligio(ethylene glycol) segments connected by 3,5-dioxybenzoate branch points. Confirmation of the above structures was by a variety of spectroscopic techniques, with ^{1}H and ^{13}C NMR spectroscopies proving to be particularly instructive. Figures 1 and 2 show a comparison of the ^{1}H and ^{13}C NMR spectra of the hyperbranched macromolecules **14** and **16**, obtained from triethylene glycol and hexaethylene glycol, respectively. Examination of the ^{1}H NMR spectra shows resonances for the oligio(ethylene glycol) segments between 3.5 and 4.5 ppm, while the expected aromatic resonances for the 3,5-dioxybenzoate branching units are observed at 6.7 and 7.2 ppm. Integration of these resonances allows the relative amounts of aromatic branching units and linear segments to be determined, and the results obtained were consistent with the values calculated from the starting tri- and hexaethylene glycol macromonomers, respectively. Similar results were obtained from the ^{13}C NMR spectra, which showed characteristic resonances for both the linear and the branching units. Interestingly, the hyperbranched macromolecule **14** obtained from triethylene glycol showed a much greater degree of fine structure than the corresponding derivative **16** from hexaethylene glycol. This behavior can be rationalized by the decreasing influence of the different hydroxy, acyloxy, and phenoxy chain ends on the interior methylene units of the ethylene glycol segments as the chain length is increased.

Scheme 2



The molecular weights of the hyperbranched poly(ether ester) macromolecules **14**, **15**, and **16** were determined by gel permeation chromatography using tetrahydrofuran as the carrier solvent. The hyperbranched triethylene glycol derivative **14** was found to have a polystyrene equivalent molecular weight, M_w, of 50 000 (PD = 2.5), while the hyperbranched diethylene glycol derivative **15** was found to have a polystyrene equivalent molecular weight, M_w, of 95 000 (PD = 2.7) and the hexaethylene glycol derivative **16** was found to have a polystyrene equivalent molecular weight, M_w, of 81 000 (PD = 2.7). While it is difficult to gauge the true molecular weights of these materials due to their three-dimensional shape, the polystyrene equivalent molecular weights do show that the macromolecules have an appreciable molecular size and are certainly not low molecular weight oligiomers of the starting AB_2 macromonomers.

Since this approach to hyperbranched macromolecules deals with the polymerization of what can be classified as macromonomers, a comparison can be made between the glass transition temperatures, T_g, of the macromonomers **11**, **12**, and **13** and the corresponding hyperbranched macromolecules **14**, **15**, and **16**. As expected, due to their lower molecular weights, the macromonomers were found to have lower glass transition temperatures, 227, 224, and 219 K, for the di-, tri-, and hexaethylene glycol macromonomers, respectively, than the corresponding polymers. In comparison, the hyperbranched macromolecule from hexaethylene glycol, **16**, was found to have a glass transition temperature of 234 K compared to 255 K for the hyperbranched macromolecule from triethylene glycol, **14**, and 268 K for the hyperbranched macromolecule from diethylene glycol, **15** (Figure 3). These significant differences in glass transition temperatures for the hyperbranched

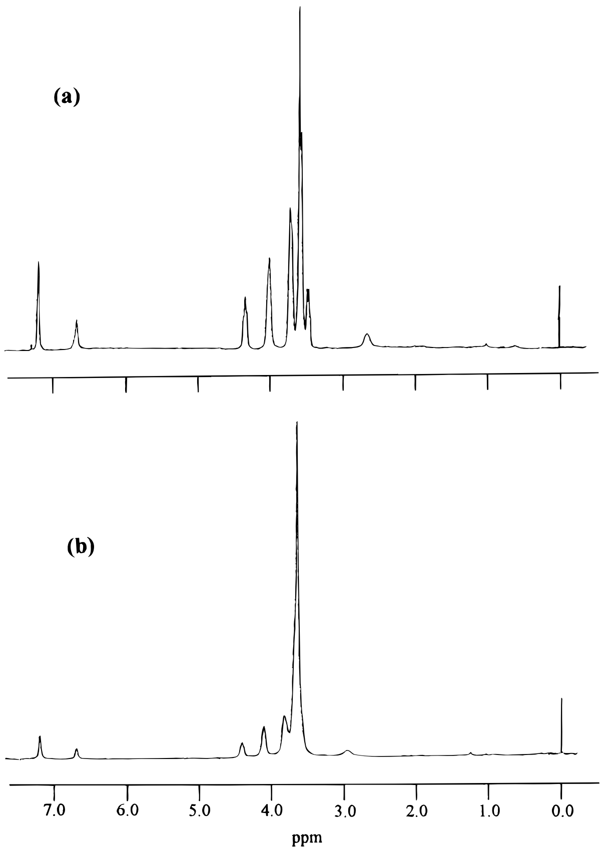


Figure 1. Comparison of 200-MHz ^{1}H NMR spectra of (a) the hyperbranched poly(ether ester) **14** from triethylene glycol and (b) the hyperbranched poly(ether ester) **16** from hexaethylene glycol.

macromolecules **14**, **15**, and **16** are due to the varying proportions of linear poly(ethylene glycol) in the polymer structure.

In an attempt to rationalize this behavior, the hyperbranched macromolecules can be considered to be copolymers of poly(ethylene oxide) ($T_g = 206$ K) and the phenolic-terminated polyester derived from the one-step polymerization of 3,5-dihydroxybenzoic acid ($T_g = 473$ K). Using the standard fox equation and weight fractions of each component as determined from the macromonomer structures, the glass transition temperature of the copolymers can be calculated. For the hexaethylene glycol derivative **16**, a calculated glass transition temperature of 233 K is obtained which compares favorably with the experimental value of 236 K. Similarly, the triethylene glycol derivative **14** was found to have a glass transition temperature of 255 K, which compares favorably with the calculated value of 250 K, while the diethylene glycol derivative **15** was found to have a T_g of 268 K (T_g(calc) = 273 K).

An even more significant observation is that the melting transition of the oligio(ethylene glycol) units is absent in the DSC traces for all of the hyperbranched polymers even after prolonged annealing. This essentially amorphous structure is due to the highly branched nature of the macromolecules and indicates that the inclusion of branching units disrupts packing of the linear segments, which prevents crystallization. Interestingly, this lack of crystallinity has been noted in a number of other hyperbranched and dendritic systems,[13] though it should be noted that for specifically engineered systems, Percec[14] has observed thermotropic nematic, smectic, and crystalline phases in dendritic macromolecules based on liquid-crystalline building blocks.

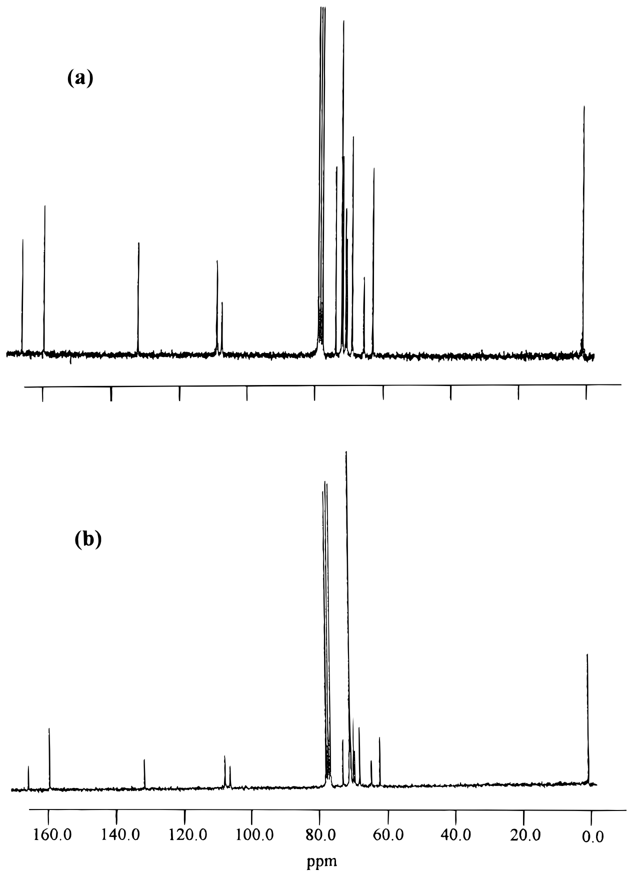


Figure 2. Comparison of 50-MHz ^{13}C NMR spectra of (a) the hyperbranched poly(ether ester) **14** from triethylene glycol and (b) the hyperbranched poly(ether ester) **16** from hexaethylene glycol.

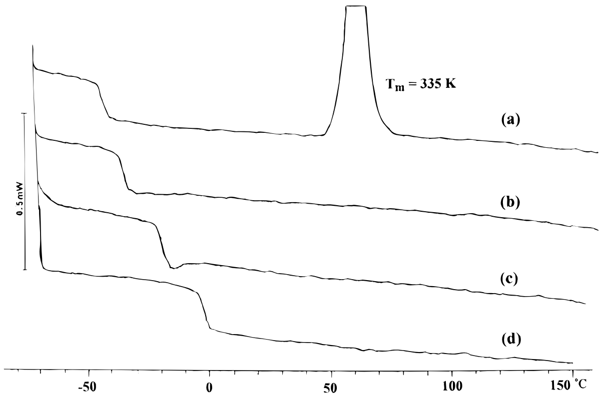


Figure 3. Comparison of the DSC traces for (a) linear poly(ethylene glycol), M_n = 15 000; (b) the hyperbranched poly(ether ester) **16** from hexaethylene glycol; (c) the hyperbranched poly(ether ester) **14** from triethylene glycol; and (d) the hyperbranched poly(ether ester) **15** from diethylene glycol.

This lack of crystallinity in poly(ethylene glycol) based hyperbranched macromolecules is a basic prerequisite for the use of these materials as solid polymeric electrolytes.[15] Additionally, the polymeric electrolyte should have a high solvating power of the appropriate ions which are going to carry the charges between electrodes, good ion transport which requires the solid polymer to display elastomeric behavior, and electrochemical stability of polymer.[16] Since the oligio(ethylene glycol) segments satisfy these last three requirements, the combination of these properties with the amorphous

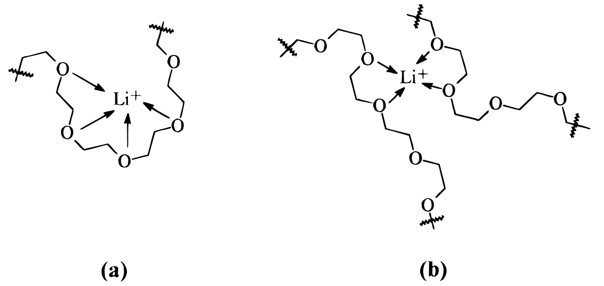


Figure 4. Schematic representations of (a) an intramolecular complex of lithium cations with poly(ethylene glycol) and (b) an intermolecular complex of lithium cations with two poly(ethylene glycol) chains.

nature of the corresponding hyperbranched systems, i.e., **16**, should allow these dendritic materials to function as polymeric electrolytes/ion-containing elastomers. These ion-containing elastomeric materials have been shown to be alternative materials to liquid or solid inorganic counterparts in applications such as high density batteries, electrochemical devices, etc.[17]

To investigate the usefulness of hyperbranched macromolecules as solid polymeric electrolytes, the effect of added ionic species on the glass transition temperature and ionic conductivity of the hyperbranched material was examined. Due to its wide use in a variety of other studies, the ionic species was chosen to be lithium perchlorate, and the hyperbranched macromolecule **16** derived from hexaethylene glycol was examined. As illustrated in Figure 4, the introduction (solvation) between the oxygens of the ethylene glycol units and the lithium cations. For linear polymers, this interaction can be either intramolecular (Figure 4a) or intermolecular (Figure 4b) and gives rise to a progressive increase in the glass transition temperature of the complex as the extent of intermolecular interactions increases.[18] This increase has been shown by a number of workers to follow a linear relationship with salt concentration, which is consistent with physicochemical cross-linking of the linear chains due to the added cations.[19] An investigation into the effect of added cations on the glass transition temperature of **16** provides information as to whether the same intermolecular or intramolecular interactions can occur for hyperbranched macromolecules as for linear polymers.

In this study, the glass transition temperatures of hyperbranched poly(ether ester)–salt complexes were examined for a variety of different lithium perchlorate concentrations ranging from 0.0 mol of lithium per repeat unit to 1.55 mol of lithium per ethylene glycol repeat unit. As can be seen in Figure 5, a linear relationship is observed between T_g^{-1} and $LiClO_4$ concentration, and regression analysis gives

$$T_g^{-1} = T_{g^o}^{-1} - 2.1 \times 10^{-4} c \tag{1}$$

where T_{g^o} is the glass transition temperature of the salt-free hyperbranched poly(ethylene glycol) ester elastomer **16** and c is the concentration of $LiClO_4$ (mol/mol repeat unit of polymer). If one rewrites eq 1 introducing the relative variation of T_g and inserting the value of T_{g^o} = 236 K, one obtains

$$\frac{T_g - T_{g^o}}{T_{g^o}} = \frac{0.049c}{1 - 0.049c} \tag{2}$$

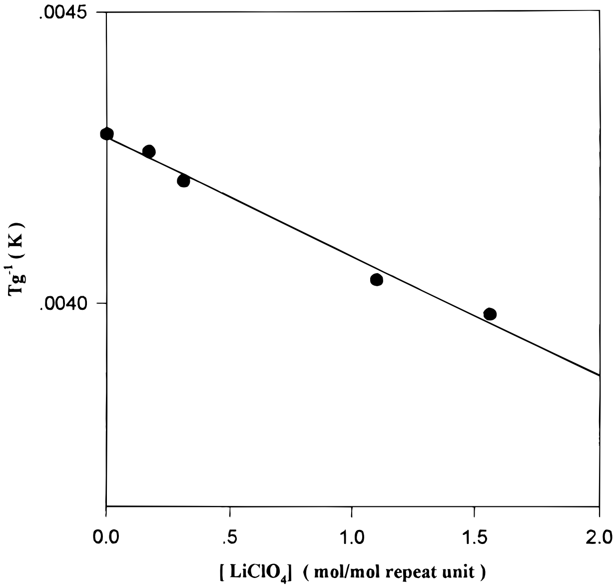


Figure 5. Plot of the inverse of the glass transition temperature for complexes of the hyperbranched poly(ether ester) **16** with varying amounts of lithium perchlorate.

which has the same form of Di Marzio's classical relationship[20]

$$\frac{T_g - T_{g^o}}{T_{g^o}} = \frac{ac}{1 - ac} \tag{3}$$

This result is significant since it demonstrates that the linear hexaethylene glycol segments present in the hyperbranched poly(ether ester) structure **16** are capable of forming intermolecular donor–acceptor interactions and that a progressive increase in cross-link density is observed as the salt concentration is increased. Significantly, the slope of the line in Figure 5 [-2.1×10^{-4} dm^3 mol^{-1} K^{-1}] is similar to the finding of Le Nest et al.,[21] who observed a slope of -2.7×10^{-4} dm^3 mol^{-1} K^{-1} for poly(ethylene glycol) networks cross-linked by multifunctional isocyanates. The small difference between the values for the slopes in this work compared with Le Nest's results can be attributed to the influence of the two different macromolecular architectures. However, the overall similarity does clearly demonstrate that hyperbranched poly(ethylene glycol) derivatives are capable of solvating lithium ions in a manner analogous to cross-linked poly(ethylene glycol) networks.

The ability of the hyperbranched poly(ether ester) **16** to efficiently solvate ionic compounds strongly suggests that such materials could function as solid polymeric electrolytes. To determine the feasibility of this proposal, the ionic conductivity of complexes of **16** and lithium perchlorate was studied as a function of both temperature and the concentration of added $LiClO_4$. The temperature dependence of the conductivity for a range of lithium perchlorate concentrations is shown in Figure 6. Interestingly, the conductivity of the complexes has only a small temperature dependency below 30 °C, while above this temperature the conductivity is observed to increase dramatically with increasing temperature and concentration of lithium cations. The reason for this behavior may be a thermal dissociation of the ionic cross-links which tend to relax from quadrupoles to ion pairs above 30 °C and such a relaxation would lead to increased mobility of the ions and therefore increased conductivity (Figure 7).[15,22] It should also be noted that the conductance at a given temperature increases with

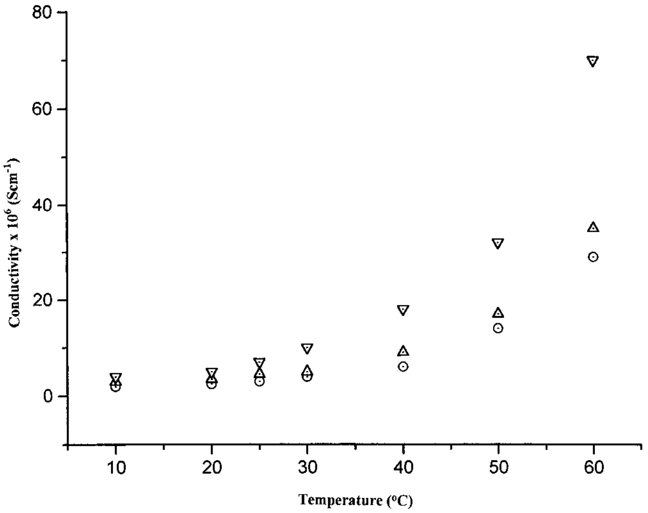


Figure 6. Plot of conductivity vs temperature for complexes of the hyperbranched poly(ether ester) **16** with 0.16 equiv of lithium perchlorate per repeat unit (⊙), with 0.31 equiv of lithium perchlorate per repeat unit (△), and with 0.62 equiv of lithium perchlorate per repeat unit (▽).

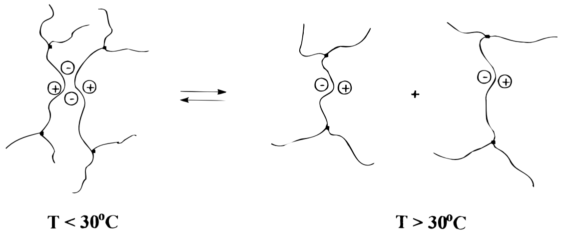


Figure 7. Schematic representation of the relaxation of the quadrupole to ion pairs above 30 °C.

the amount of lithium perchlorate added. Significantly, a conductivity of 10^{-5} S cm^{-1} is obtained at 30 °C for a concentration of lithium perchlorate of 0.62 molecule per repeat unit, and at temperatures of above 60 °C, this value approaches 10^{-4} S cm^{-1}. These values are similar to the conductivity observed for a range of cross-linked poly(ethylene glycol) systems.[23] The high conductivity values obtained for **16** are also indicative of an amorphous structure, which agrees with the DSC studies on these materials and provides further evidence for the disruption of crystallinity due to the dendritic architecture. If the data in Figure 7 are now replotted in a more traditional manner as log(conductivity) vs 1/*T*, a slightly curved plot is obtained, which is a feature common to many polymer–salt systems (Figure 8). Such a relationship is frequently described by the Vogel–Tammann–Fulcher equation, which relates conductivity to conformational and entropic changes in the polymer and is again indicative of an amorphous material.

Conclusion

The concept of using AB_2 macromonomers which contain oligomeric linear segments to produce hyperbranched macromolecules has been successfully demonstrated by the synthesis of hyperbranched poly(ether ester)s is derived from di-, tri-, or hexaethylene glycol. The hyperbranched macromolecules were obtained in good yields with high molecualr weights and proved to be extremely soluble in a wide range of solvents. Unlike normal linear poly(ethylene glycol)s, the hyperbranched derivatives proved to be essentially amorphous, and their experimentally determined glass transition temperatures agreed closely with those predicted by the Fox equation for copolymers of poly(ethylene glycol) and hyperbranched polyesters based on 3,5-dihydroxybenzoic acid. The amorphous nature of the hyperbranched macromolecules allowed these materials to be successfully used as polymeric electrolytes with no detrimental effects due to crystallization. Significantly, the conductivity of the hyperbranched poly(ether ester)–lithium perchlorate complex displayed behavior typically observed for cross-linked oligio(ethylene glycol) networks but are highly soluble and easily processable. Conductance was observed to increase with both increasing temperature and concentration of Li$^+$, with a value of 7×10^{-5} S cm^{-1} being obtained at 333 K with a concentration of [Li$^+$] of 0.62 mol per repeat unit.

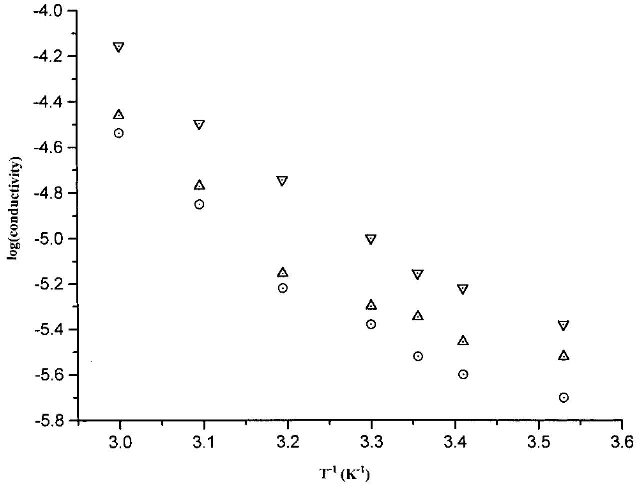


Figure 8. Plot of log(conductivity) vs the inverse of temperature for complexes of the hyperbranched poly(ether ester) **16** with 0.16 equiv of lithium perchlorate per repeat unit (⊙), with 0.31 equiv of lithium perchlorate per repeat unit (△), and with 0.62 equiv of lithium perchlorate per repeat unit (▽).

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