Synthesis of Novel Aggregating Comb-Shaped Polyethers for Use as Polymer Electrolytes

Patric Jannasch

Department of Polymer Science & Engineering, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden

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ABSTRACT: Polyethers having well-defined comb-shaped architectures were prepared by using poly(4-hydroxystyrene) (PHSt) as a multifunctional initiator for graft polymerization of either ethylene oxide (EO) or a mixture of EO and propylene oxide (PO). The grafting process was performed in 1,4-dioxane using NaH as ionizer for the PHSt hydroxyl groups. The precursor PHSt was prepared by first polymerizing 4-*tert*-butoxystyrene, using butyllithium as initiator in THF at −60 °C, and then deprotecting the butoxy groups. Finally, the terminal hydroxyl groups of the polyether grafts were end-capped with hexadecanoyl units through esterification. The monomer addition sequence in the graft copolymerizations with the same EO/PO feed ratio proved to have a great influence on the crystallization temperature and the crystallinity of the grafts. Also, the end-capping was found to reduce the degree of crystallinity as compared to the corresponding uncapped polymers. Solid polymer electrolytes containing lithium triflate ($LiSO_3CF_3$) salt had ambient temperature ion conductivities of $\sim 10^{-5}$ S/cm at [Li]/[O] = 0.025. Thermal analysis of the electrolytes showed that the polymers aggregated through phase separation of the hexadecanoyl chain ends.

Introduction

There is presently a great demand for solid polymer electrolytes that combine high ion conductivity, electrochemical stability, and good mechanical properties for use in high-energy-density batteries and other electrochemical devices.[1] Most of the promising candidates rely on the use of poly(ethylene oxide) (PEO) as a matrix polymer for lithium salts. In these systems, the ether oxygens act as coordinating sites, promoting the dissociation of the salt. Furthermore, the low rotational barrier of the ether bonds provides a flexible macromolecular chain able to facilitate the transport of ions by segmental movements in the amorphous phase. Although PEO−salt complexes show high conductivities at high temperatures, the propensity for crystallization of PEO at low temperatures ($T_m \sim 65$ °C) severely reduces their conductivity. Moreover, the mechanical properties of PEO are generally very poor.

Several approaches to overcome the above-mentioned problems have been outlined in the literature.[2] Crystallization can for example be largely avoided by the use of polymer architectures where short PEO chains are attached as pendant chains to backbone polymers,[3−6] incorporated in multiblock copolymers,[7] or combined in cross-linked networks.[8−10] Another strategy is to disrupt the stereoregular structure of PEO by including comonomers along the main chain.[10] The most common method to improve the mechanical stability is to form rigid cross-linked networks, for example by UV irradiation of reactive multifunctional PEO oligomers.[9,10] Yet another method is to prepare binary polymer blends in which PEO forms the conducting phase, and the other component acts as a mechanical support.[11,12] These blends often have a co-continuous morphology in which the two phases are interlocked.

One of the most attractive ways to obtain solid polymer electrolytes with high mechanical stability is to incorporate PEO segments in aggregating or self-assembling polymers.[13−17] These polymers usually have the architectures of block and graft copolymers and display ordered microphases. The microphases are formed by local segregation of their dissimilar, covalently linked polymeric segments to form periodic structures. Dimensional stability is achieved by the physical cross-linking resulting from the formation of microphases. The morphology, and consequently the properties, of the copolymers may be controlled by variations in molecular design and sample preparation.

In the current study, aggregating comb-shaped polyethers (hCPE) were prepared and investigated for use as solid polymer electrolytes. Comb-shaped polymers are generally characterized by having a large number of oligomeric grafts attached to a polymeric backbone. In the present case, comb-shaped polyethers (CPE) were prepared by using a poly(4-hydroxystyrene) backbone as a multifunctional initiator for anionic graft copolymerization of ethylene oxide (EO) and propylene oxide (PO). The aggregating character of the polymers was subsequently achieved by incorporating short alkyl segments on the polyether chain ends. It was anticipated that these modified polymers would form continuous networks by interpolymer aggregation through microphase separation of the chain end segments. Solid polymer electrolytes based on lithium triflate were prepared and characterized with respect to thermal properties and ion conductivity. Results of a more detailed study of the ion conductivity and phase behavior of electrolytes based on these aggregating polymers will soon be reported.[18]

Experimental Section

Synthesis of PHSt. PHSt was prepared by anionic polymerization in a sealed glass setup including a 1 L round-bottomed polymerization vessel equipped with a magnetic stirrer, a thermometer, and a rubber septum. The polymerization vessel was degassed by dry N_2 purge. 4-*tert*-Butoxystyrene (99%, Aldrich) was first passed though a column filled with Al_2O_3 to remove the inhibitor. Then, 200 mL of THF (Merck, p.a.) and 20 g of 4-*tert*-butoxystyrene were both degassed and stored separately over CaH_2 (Aldrich, powder, 90−95%) under stirring for 24 h, before vacuum distillation

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Table 1. Preparation and Characterization of the CPE Polymers

	charged amounts[a]								
sample	PHSt (g)	NaH (mmol)	EO (g)	PO (g)	dioxane (mL)	graft[b] content (wt %)	EO[b] content in grafts (wt %)	av[b] graft MW (g/mol)	overall[c] MW (g/mol)
CPE_{eo}	3.00	4.0	50.0		60.0	95	100	2100	730 000
CPE_{st}	3.00	4.0	40.0	10.0	60.0	94	80	1900	670 000
CPE_{dt}	3.00	4.0	40.0	10.0	60.0	94	83	2000	700 000

[a] In the preparation of CPE_{eo} and CPE_{st} the monomers were charged all at once, while in the preparation of CPE_{dt} the monomer mixture was charged in equal amounts in two separate additions. [b] Calculated from ^{1}H NMR results. [c] Calculated by combining GPC results of the PBuOSt precursor and ^{1}H NMR results of the CPE polymers.

into the polymerization vessel. After cooling the polymerization vessel down to −60 °C, the polymerization was initiated by injecting 0.2 mL of 2 M butyllithium in cyclohexane (Aldrich). The polymerization was allowed to proceed for 1 h before quenching with MeOH (Merck, p.a.). Purification of the polymer was performed by successive precipitations in MeOH, followed by drying under vacuum. The gravimetrical yield was found to be >99%. GPC analysis using polystyrene standards from Polysciences, Inc., showed M_n = 32 000 g/mol and M_w/M_n = 1.1. GPC analyses were run with THF on Waters ultra-Styragel columns with pore sizes 10^5, 10^4, 10^3, and 500 Å, using an RI detector. The flow rate was 1.0 mL/min at 25 °C.

Poly(4-*tert*-butoxystyrene) (PBuOSt) was dissolved in acetone (Merck, p.a.) in a concentration of 10% (w/v). The solution was then refluxed for 5 h in the presence of HCl (Merck, 37%, p.a.) to remove the *tert*-butoxy group. Before vacuum-drying, PHSt was repeatedly precipitated in water from acetone solutions to remove the HCl.

Grafting from PHSt. The comb-shaped polyethers (CPE) were prepared by using PHSt as a polymeric initiator for the anionic polymerization of EO and PO. A 200 mL reactor consisting of a glass cylinder fitted between a stainless steel top and bottom and equipped with a high-speed stirrer was used in the grafting. The reactor was also equipped with a gas inlet and outlet, a thermocouple, and a pressure transducer. The amounts of the reactants used in the polymerizations are shown in Table 1. PHSt was first dried 24 h at 80 °C under vacuum to remove residual water and then placed in the reactor. Dioxane (Merck, p.a.) was degassed and stored over CaH_2 under stirring for 24 h, before it was transferred to the reactor by vacuum distillation. A slurry of NaH (Aldrich) in hexane (Merck, p.a.) was injected into the reactor to ionize the hydroxyl groups. After 30 min the reaction mixture was again degassed, and EO (Fluka, >99.8%) or a mixture of EO and PO (Acros, p.a.) was transferred to the reactor by distillation. The graft polymerization took place over a 12 h period at 80 °C under which the pressure was reduced to a constant value.

Chain End Modification of CPE. The hydroxyl chain ends of the CPE polymers were capped with hexadecanoyl chloride. The esterification was carried out in a two-necked glass reactor equipped with an N_2 inlet, a heater, a magnetic stirrer, and a water-cooled column. Approximately 10 g of polyether was dissolved in 50 mL of toluene (Merck, p.a.) at ambient temperature under N_2 purge. A 10 mol % excess of hexadecanoyl chloride (Acros, 98%) was injected, and the temperature was raised to 50 °C. After approximately 20 h, the product was repeatedly precipitated in hexane from toluene solutions to remove unreacted hexadecanoyl chloride. The removal was confirmed by IR spectroscopy by the absence of the acid chloride carbonyl peak at 1800 cm^{-1}. Dried samples were leached with water, before the final drying in a vacuum at 80 °C for 3 days. The polymers, designated hCPE, were then kept in a desiccator until use.

Preparation of Electrolytes. Solid polymer electrolytes with a lithium triflate concentration corresponding to a molar lithium-to-ether oxygen ([Li]/[O]) ratio of 0.025 were prepared in a glovebox under a dry Ar atmosphere. A volume of a 15 wt % solution of lithium triflate salt (Aldrich, 96%) in dimethyl carbonate (Merck, Selectipur) was added to a glass ampule containing 300 mg of hCPE polymer. The dimethyl carbonate was allowed to evaporate under Ar for 2 days at ambient temperature before the sample was transferred to a glass oven where the residual solvent was removed in a vacuum at 50 °C for 3 days.

Measurements. ^{1}H NMR spectra of PBuOSt, CPE, and hCPE dissolved in chloroform-*d* (Glaser AG, >99.80%) were recorded at ambient temperature using a Bruker ARX500 instrument. A spectrum of PHSt was recorded using the same conditions, but using DMSO-d_6 (Glaser AG, >99.80%) as solvent. Chemical shifts are reported as ppm downfield from tetramethylsilane. Typical spectra are shown in Figure 1. The content of the polymers were calculated by integrating and comparing characteristic signals. Consequently, the composition of the polyether grafts was evaluated by comparing shifts from the ether protons arising from the EO and PO units at δ = 3.2−4.1 and the methyl protons from the PO units present at δ = 1.2. Shifts from the phenylene protons in the region δ = 6.1−6.8 and the ether protons were compared to calculate the content of the polyether grafts in the CPE polymers. Finally, the degree of capping with hexadecanoyl chloride was evaluated by comparing the shift from the ether protons and the shift arising from the hexadecanoyl methyl protons at δ = 0.85.

Infrared spectra were recorded with a Bruker IFS 66 FTIR spectrometer, using polymer films cast onto KBr prisms from chloroform (Merck, p.a.) solutions.

The thermal properties of the polymers and the electrolytes were analyzed with a Mettler TA 3000 DSC system under N_2 purge. Samples were placed in aluminum sample containers. The CPE and hCPE polymers and the electrolytes were first annealed at 100 °C for 5 min. After cooling to −150 °C, the samples were heated to 100 °C. PBuOSt and PHSt were cooled to −50 °C after 5 min at 200 °C. Finally, these two samples were reheated to 200 °C. The scan rate was in all cases 10 °C/min. Glass transition temperatures (T_g) were evaluated from the heating scan. Peak values were reported as melting (T_m) and crystallization (T_c) temperatures, and the heats of melting (ΔH_m) and crystallization (ΔH_c) were evaluated by integration of the corresponding peaks.

The ion conductivity (σ) of the electrolytes was evaluated by measuring the temperature dependence of impedance spectra in the temperature range −10 to 100 °C. Samples with a diameter of 18 mm and a thickness of 90 μm were sandwiched between two gold-plated stainless steel blocking electrodes spaced by a PTFE ring. The measurements were carried out using a computer-controlled Novocontrol BDC40 high-resolution dielectric analyzer equipped with a Novocool cryostat unit. Samples were analyzed in the frequency range 10^{-1}−10^7 Hz at 100 mV ac amplitude, and the conductivities were evaluated using the Novocontrol software WinDeta.

Results and Discussion

Well-characterized aggregating comb-shaped polyethers were prepared by the five-step procedure shown in Scheme 1. The first step involved preparation of a PBuOSt backbone polymer by anionic polymerization of 4-*tert*-butoxystyrene. The resulting polymer was found by GPC analysis to have M_n = 32 000 g/mol and a narrow molecular weight distribution with M_w/M_n = 1.1. Decapping to form PHSt was confirmed by NMR

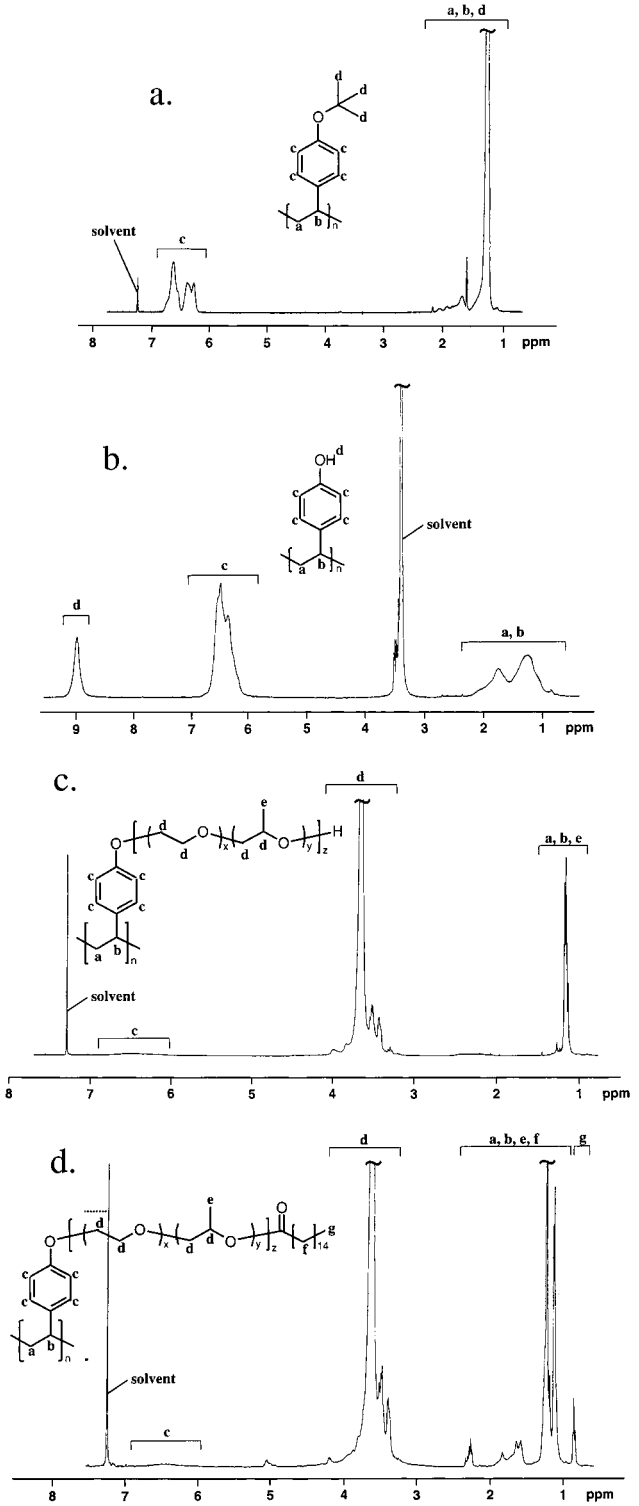
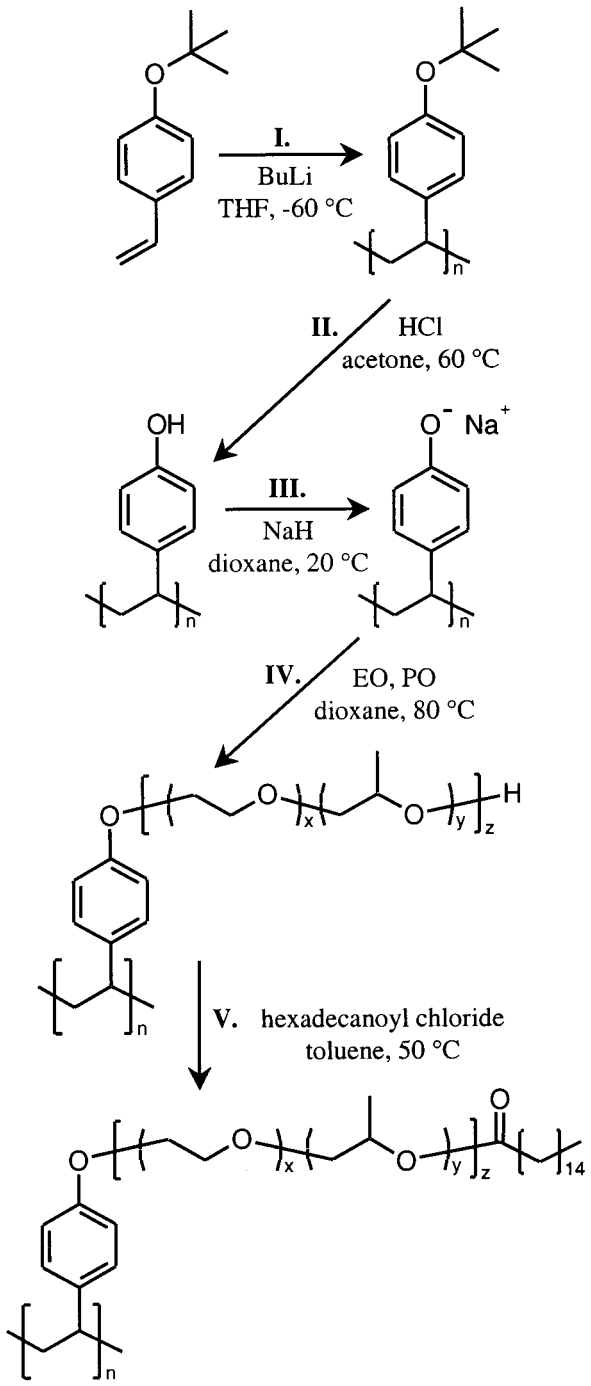


Figure 1. ^{1}H NMR spectra of (a) PBuOSt in chloroform-*d*, (b) PHSt in DMSO-d_6, (c) CPE_{dt} in chloroform-*d*, and (d) $hCPE_{dt}$ in chloroform-*d*.

spectroscopy to be essentially 100% after refluxing PBuOSt in acidic acetone. Grafting from PHSt was performed by first ionizing the hydroxyl groups and then using them for initiation of (i) anionic graft polymerization of EO and (ii) by graft copolymerization of a EO/PO (80/20 wt/wt) mixture. In the final step, the terminal hydroxyl groups of the polyether grafts were end-capped with hexadecanoyl units. The uncapped and the hexadecyl-capped comb-shaped polyethers were designated CPE and hCPE, respectively. Table 1 shows the amounts

Scheme 1. General Scheme for the Preparation of Aggregating Comblike Polyethers by Grafting with EO and PO



charged in the grafting reactions and the molecular data of the CPE polymers.

As mentioned in the Introduction, the use of PEO-based polymers in electrolytes is hampered by their strong propensity to crystallize. In the present study, EO was copolymerized with PO to disrupt the regular structure and decrease the crystallinity of the polyether grafts. A further step undertaken to influence the crystallinity of the CPE polymers was by the mode of monomer addition during the graft copolymerizations. Because EO is more reactive than PO, the former will have a higher rate of consumption.[19] As a result, the composition of the grafts will change gradually along the chains, from EO-rich close to the backbone polymer

to PO-rich close to the chain end. The grafts will thus have a "single" tapered microstructure. If the monomer mixture is charged in two successive additions, the grafts will have a "double" tapered microstructure. This means that the grafts will be EO-rich closest to the backbone polymer, followed by a PO-rich segment, then a second EO-rich chain segment, and finally another segment rich in PO closest to the chain end. The lowest propensity for crystallization can be anticipated for the "double" tapered grafts, where the EO and PO units are more intermixed. Consequently, the microstructure of grafts having the same overall composition can be expected to influence the phase behavior and ion conductivity of the polymers.

Three different CPE polymers were prepared in this study, one using only EO to produce sample CPE_{eo} and two using the EO/PO mixture. In the two copolymerizations, the EO/PO mixture was fed either all at once to produce a sample with "single" tapered grafts (CPE_{st}) or in equal amounts in two separate additions to produce a sample having "double" tapered grafts (CPE_{dt}). The second addition of monomer mixture during the preparation of CPE_{dt} was done after the first one had been completely consumed.

By comparing ^{1}H NMR results of the polymers with the amounts charged during the grafting, it was found that the yield was essentially 100% in all the grafting reactions. In addition, the compositions of CPE_{st} and CPE_{dt} corresponded well with the composition of the monomer feed, which is expected at high yields. Furthermore, no traces of homopolymer were found by GPC analysis of the reaction mixtures. These findings confirmed the absence of significant side reactions during the grafting reactions. In a previous study, where PO was grafted from a poly(ethylene-*co*-vinyl alcohol) backbone polymer with DMSO as solvent, chain transfer to both solvent and monomer was observed.[20] The absence of these side reactions in the present case means that the composition and M_n of the grafts can be conveniently controlled by the monomer feed.

The kinetics of the reaction between phenols and EO, and its influence on the molecular weight and molecular weight distribution of the resulting PEO, has been extensively studied.[21−24] The phenolic hydroxyl groups of PHSt (R−PhOH, pK_a ∼ 10 in water) are much more acidic than those of the growing polyether chains (R′−CH_2CH_2OH, pK_a ∼ 15 in water).[25] Under these conditions essentially all the phenolic hydroxyl groups are converted to the mono-EO adduct prior to further reaction of this monoadduct to form PEO chains.[22] Therefore, chain propagation does not occur even in the presence of excess EO until all the hydroxyl groups have been consumed. This makes it possible to isolate extremely high yields of the monoadduct when equimolar amounts of phenols and EO are reacted using basic catalysts, in some cases exceeding 98%.[23] The acidities of the PEO alcohols are nearly identical when the number of adducts exceeds 3.[26,27] This means that the proton exchange between all the species during the propagation is fast and occurs statistically. Consequently, all the PEO chains start to propagate simultaneously, and the propagating species are equally reactive, resulting in narrow molecular weight distributions of the PEO grafts.[14]

The structural features of the different polymers were studied by IR spectroscopy, as shown for PBuSt, PHSt, CPE_{dt}, and $hCPE_{dt}$ in Figure 2. Characteristics in the

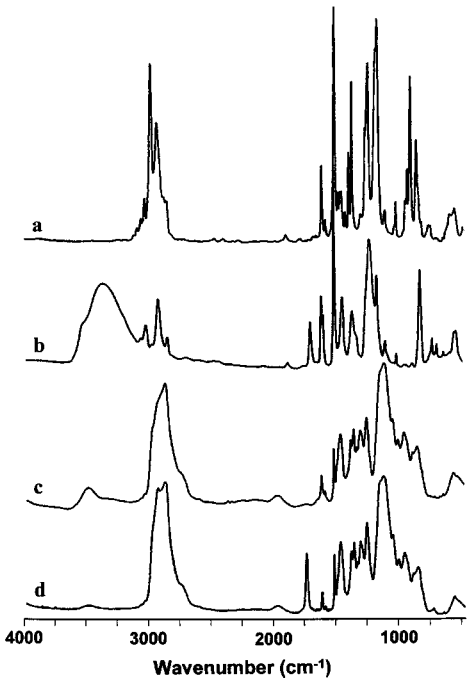


Figure 2. IR spectra for (a) PBuOSt, (b) PHSt, (c) CPE_{dt}, and (d) $hCPE_{dt}$.

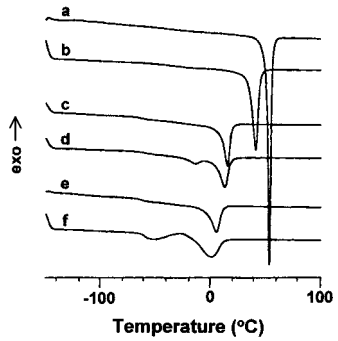


Figure 3. DSC heating traces for the polymers (a) CPE_{eo}, (b) $hCPE_{eo}$, (c) CPE_{st}, (d) $hCPE_{st}$, (e) CPE_{dt}, and (f) $hCPE_{dt}$. The samples were preannealed at 100 °C for 5 min before the cooling−heating cycle.

spectrum of PBuSt (a) are alkyl bands at 2800−3100 cm^{-1} together with ether bands around 1100 cm^{-1}. The spectrum of PHSt (b) showed modified alkyl band, in comparison with PBuSt, and a large broad band at 3100−3600 cm^{-1} arising from the hydroxyl groups. After grafting with EO and PO (c), the alkyl bands at 2800−3100 cm^{-1} were again modified, and a strong ether band appeared at 1100 cm^{-1}. Finally after end-capping the polyether grafts (d), the hydroxyl band at 3100−3600 cm^{-1} disappeared, while the carbonyl peak arising from the ester bond was present at 1735 cm^{-1}.

The phase behavior of the polymers was studied by DSC. Typical thermograms of CPE and hCPE samples preannealed at 100 °C for 5 min are shown in Figure 3, and data from the evaluations are shown in Table 2. The precursor polymers PBuOSt and PHSt were found to have glass transitions at 109 and 169 °C, respectively. The glass transition temperature (T_g) of CPE_{st} and CPE_{dt} were both found at approximately −65 °C, seemingly uninfluenced by the difference in the microstructure of the grafts. No glass transition was detected for CPE_{eo}, probably a result of its high crystallinity. All the CPE polymers showed exotherms (ΔH_c^1) and endotherms (ΔH_m^1) from polyether crystallization and melt-

Table 2. Thermal Properties of the CPE and hCPE Polymers and of the Electrolytes Based on the hCPE Polymers[a]

sample	T_g (°C)	T_c^1 (°C)	ΔH_c^1 (J/g)	T_m^1 (°C)	ΔH_m^1 (J/g)	T_c^2 (°C)	ΔH_c^2 (J/g)	T_m^2 (°C)	ΔH_m^2 (J/g)
CPE_{eo}	n.d.	31	111	52	115				
CPE_{st}	−65	−9	48	14	47				
CPE_{dt}	−64	−25	38	4	38				
$hCPE_{eo}$	−26	22	79	38	80	n.d.	n.d.	n.d.	n.d.
$hCPE_{st}$	−60	−16	o.p.	13	o.p.	o.p.	o.p.	−14	o.p.
$hCPE_{dt}$	−60	−21[b]	o.p.	0	o.p.	o.p.	o.p.	o.p.	o.p.
$hCPE_{eo}$ [Li]/[O] = 0.025	−36	11	56	34	56	−17	<0.1	n.d.	n.d.
$hCPE_{st}$ [Li]/[O] = 0.025	−52	n.d.	n.d.	o.p.	o.p.	−14	12	o.p.	o.p.
$hCPE_{dt}$ [Li]/[O] = 0.025	−54	n.d.	n.d.	n.d.	n.d.	−17	13	−13	12

[a] n.d. = not detected; o.p. = overlapped peaks. [b] The sample also showed a crystallization exotherm during the heating scan.

ing, respectively. The crystallization and melting were, as expected, strongly dependent on copolymerization. The crystallization temperature (T_c^1) was for example 40 °C lower for CPE_{st} than for CPE_{eo}. The results also showed that the preparation of double tapered grafts, by adding the monomers in two steps, had a clear influence on the crystallization properties. T_c^1 for CPE_{dt} was depressed a further 16 °C, as compared to CPE_{st}, down to −25 °C.

DSC analysis of the hCPE samples revealed transitions from three phases, namely the amorphous polyether phase (T_g), the crystalline polyether phase (T_c^1, T_m^1, ΔH_c^1, ΔH_m^1), and the crystalline hexadecanoyl phase (T_c^2, T_m^2, ΔH_c^2, ΔH_m^2). Unfortunately, the transitions of the two crystalline phases occurred in the same temperature region which led to overlapped peaks (Figure 3, Table 2). End-capping was found to decrease the propensity for crystallization of the polyether grafts, as compared to the corresponding uncapped samples (Figure 3). The heating trace of $hCPE_{dt}$ showed a broad crystallization exotherm at ∼−25 °C before the melting endotherm at ∼0 °C. Furthermore, the T_g of samples $hCPE_{st}$ and $hCPE_{dt}$ increased by ∼5 °C after end-capping with hexadecanoyl units (Table 2). This may be a consequence of decreased mobility of the polyether chains due to phase separation of the hexadecanoyl chain ends. A glass transition of sample $hCPE_{eo}$ was observed at −26 °C, presumably because of the decrease in the crystallinity after capping. The only clear indication of the presence of hexadecanoyl chain end units was seen in the heating trace of $hCPE_{st}$, where a small melting endotherm was observed at −14 °C. In the other samples, either the melting and crystallization peaks were not present, or they were overlapped with the corresponding peaks arising from the polyether phases. Methyl hexadecanate, which may be regarded as an analogue of the chain ends, has a melting point of 35 °C.[20]

Solid polymer electrolytes were prepared by adding lithium triflate salt corresponding to [Li]/[O] = 0.025 to the hCPE polymers. Degrees of crystallinity and glass transitions are normally closely linked to the performance of polymer electrolytes. Generally, increasing salt concentrations increase T_g by inducing transient cross-linking through the formation of intra- and interpolymer coordination of ether oxygens with the dissocated ions. This effect decreases segmental motion and thus ion conductivity. On the other hand, the presence of the ion−polymer complexes decrease the propensity for crystallization of PEO-based materials, which promotes ion conductivity. DSC thermograms of the electrolytes are shown in Figure 4. The analysis showed that the crystallinity of $hCPE_{eo}$ decreased by 30% as the result of the added salt, and no crystallization of the polyether grafts in the electrolytes based on $hCPE_{st}$ and $hCPE_{dt}$

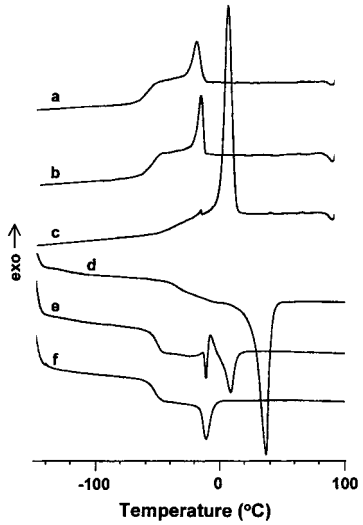


Figure 4. DSC cooling and heating traces for polymer electrolytes containing lithium triflate salt corresponding to [Li]/[O] = 0.025: (a) $hCPE_{dt}$, cooling; (b) $hCPE_{st}$, cooling; (c) $hCPE_{eo}$, cooling; (d) $hCPE_{eo}$, heating; (e) $hCPE_{st}$, heating; and (f) $hCPE_{dt}$, heating. The samples were preannealed at 100 °C for 5 min prior to the cooling−heating cycle.

was detected during the cooling scan. Instead, crystallization of the hexadecanoyl chain ends occurred in the samples at approximately −20 °C. In the case of the $hCPE_{eo}$ electrolyte, the peak was very small. The heating trace of the $hCPE_{st}$ electrolyte showed a complex behavior with a number of overlapped peaks in the temperature range −15 to 15 °C. The peaks are probably a result of melting endotherm from the hexadecanoyl chain ends, followed by a crystallization exotherm from the polyether chains, and finally a melting endotherm from the polyether chains. The corresponding trace of the electrolyte based on $hCPE_{dt}$ showed only melting of the chain ends. The heating traces also showed that the T_g of the samples $hCPE_{st}$ and $hCPE_{dt}$ had increased as a result of the added salt, while the T_g of $hCPE_{eo}$ had decreased by 10 °C. This decrease may be explained by an increased amount of amorphous phase.

The temperature dependence of the ion conductivity (σ) of the electrolytes was evaluated by impedance spectroscopy in the range between −20 and 100 °C. The value of σ at ambient temperature was between 3 and 8 μS/cm for all three samples. However, the Arrhenius plots of the results shown in Figure 5 indicate that the nature of the polyether grafts had a strong influence on σ. The electrolytes based on samples $hCPE_{st}$ and $hCPE_{dt}$ displayed a similar temperature dependence, with σ of the $hCPE_{dt}$-based electrolyte at a slightly higher level. The values of σ measured for the electrolyte based on $hCPE_{eo}$ increased sharply from a low level in the temperature range between −20 and 30 °C, seem-

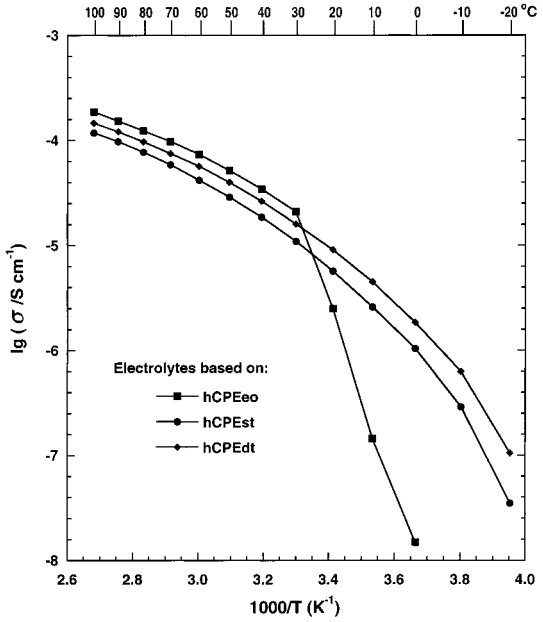


Figure 5. Arrhenius conductivity plots for polymer electrolytes based on (a) $hCPE_{eo}$, (b) $hCPE_{st}$, and (c) $hCPE_{dt}$. The lithium triflate concentration corresponded to [Li]/[O] = 0.025.

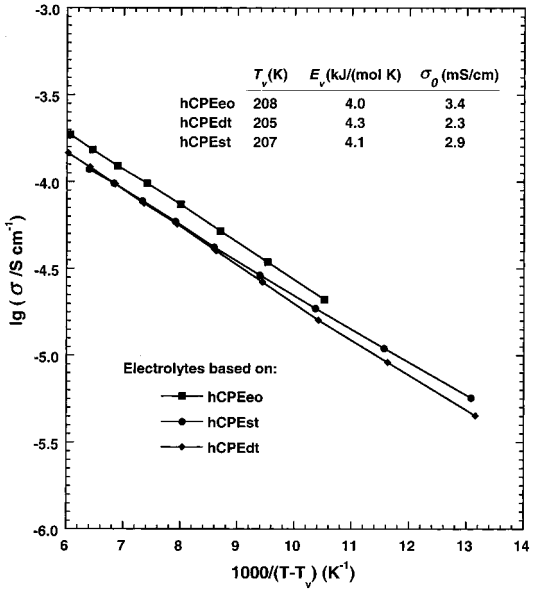


Figure 6. VTF plots of the electrolytes based on hCPE obtained by fitting conductivity data to eq 2. The table shows the obtained VTF parameters.

ingly following an Arrhenius relationship. The reason behind this behavior was most probably the melting of the polyether grafts in this temperature range (Figure 4). It has previously been shown that poly(propylene oxide)−salt complexes do not compare favorably with corresponding PEO complexes above its melting point. This may be due to the added steric hindrance imposed by the methyl group decrease the segmental motion. It may also be that the steric hindrance reduces the polymer−cation interaction.[1,28] These findings may explain why sample $hCPE_{eo}$ had a higher ion conductivity at temperatures above 30 °C, as compared with samples $hCPE_{st}$ and $hCPE_{dt}$ which contained 20 wt % PO.

Previous studies of electrolytes based on branched polyethers have shown similar values of σ at ambient temperature. For example, Bannister et al. have shown that electrolytes based on methacrylates with pendant EO grafts have $\sigma \sim 10^{-5}$ S/cm ($LiSO_3CF_3$, [Li]/[O] = 0.055).[3] Blonsky et al. have measured comparable values of σ using flexible polyphosphazene chains carrying methoxy-capped diethylene glycol chains ($LiSO_3CF_3$, [Li]/[O] = 0.05).[5] Polyether networks have also been found to have σ in the same range. Nishimoto et al. prepared network electrolytes from hyperbranched PEO with chain ends terminated by acrylate groups and measured σ close to 10^{-4} S/cm ($LiN(CF_3SO_2)_2$, [Li]/[O] = 0.04).[9] Network electrolytes prepared from EO−PO copolymers (80 wt % EO) with acrylate functionalized chain ends were found by Kono and co-workers to have σ approaching 10^{-4} S/cm at ambient temperature ($LiClO_4$, [Li]/[O] = 0.05).[10]

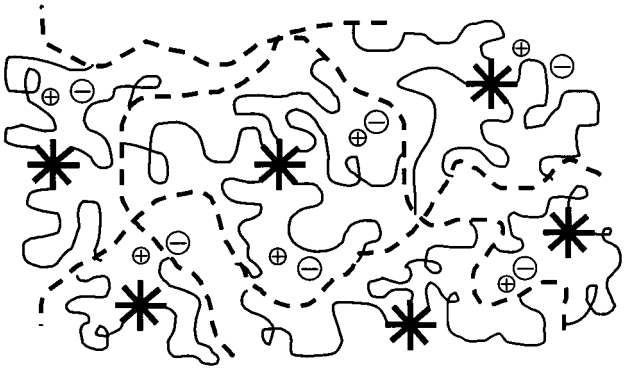
The temperature dependence of σ was similar for the three hCPE electrolytes at temperatures above 30 °C (Figure 5). The shape of the conductivity plots indicates a non-Arrhenius temperature dependence typical of polyether-based solid electrolytes. It should consequently be analyzed using the Vogel−Tamman−Fulcher (VTF) equation:

$$\sigma(T) = \sigma_0 \exp\left(\frac{-E_v}{R(T - T_v)}\right) \qquad (1)$$

where R and T_v are the gas constant (8.314 J/(mol K)) and the Vogel scaling temperature, respectively, and σ_0 and E_v represent the "ultimate" conductivity and the Vogel "activation" energy, respectively.[1,2] The VTF analysis showed that the electrolytes based on $hCPE_{st}$ and $hCPE_{dt}$ followed eq 1 above 0 °C, and the electrolyte based on $hCPE_{eo}$ followed eq 1 above 20 °C. This indicated the close relationship between chain segment mobility and σ in these temperature regions. The reason for the non-VTF behavior at low temperatures was most probably the phase transitions taking place in this region, which can be expected to strongly influence the segmental mobility and thus σ. The VTF plots shown in Figure 6 indicated that the ion conducting process seemed to occur under quite similar conditions for the three electrolytes above 30 °C. VTF parameters were obtained by fitting the conductivity data to eq 1, and the values presented in Figure 6 are also quite similar for the three electrolytes.

It was noted that the viscosity of the hCPE polymers was markedly higher than that of the corresponding CPE polymers. This effect, together with the observed melting endotherms form the hexadecanoyl chains (Figure 4) in the hCPE samples, strongly indicated interpolymer aggregation of the hCPE polymers by phase separation of the chain ends. It is conceivable that the hexadecanoyl chain ends formed descrete "micellar-like" microdomains surrounded by a matrix phase of triflate salt coordinated by the polyether grafts. Scheme 2 shows a graphic representation of the structure of the hCPE polymers in the electrolytes based on this assumption. The PBuOSt backbone polymer had a degree of polymerization of ~300. This number was calculated from the molecular weight found by GPC analysis with polystyrene standards and using the M_n of the styrene repeat unit. This means that a CPE molecule contained an average of 300 grafts. It has previously been shown that hexyl end-capped polymers can aggregate with 20−28 hexyl units per microdomain.[29] Assuming a similar aggregation number in the present case, and a density similar to that of amorphous linear PEO (~1 g/mL), the hCPE polymers may contain $\sim 10^7$ microdomains/$(\mu m)^3$.

Scheme 2. Schematic Picture of the State of Aggregation in the Polymer Electrolytes[a]



[a] Thick, thin, and dashed lines denote hexadecanoyl chain ends, polyether grafts, and PHSt backbones, respectively. Most of the grafts are omitted for clarity.

An investigation of the viscosity in relation to the state of aggregation of the hCPE polymers is currently underway.

Conclusions

Well-defined comb-shaped polymers with predictable compositions and narrow sizes of both grafts and backbone were prepared by grafting PHSt with alkylene oxides. Aggregating polymers were subsequently obtained by attaching hexadecanoyl segments at the chain ends of the grafts. By using an EO/PO (80/20 wt/wt) mixture in the grafting reaction, the crystallinity of the polyether grafts was sharply reduced, as compared to when pure EO was charged. It is conceivable that the most effective depression of the crystallinity would be achieved if the EO/PO mixture is charged continuously during the grafting to obtain a more random distribution of the PO units. The initial measurements of the ion conductivity reported in the present paper showed that electrolytes based on the comb-shaped polyethers complexed with lithium triflate had conductivities in the range of 10^{-5} S/cm at ambient temperature. This is in level with values measured on electrolytes based on other types of comb-shaped polyethers and polyether networks. The present electrolytes were tacky, highly viscous liquids, or gels, at room temperature, with a high adherence to glass and metal. Electrolytes based on aggregating polymers may offer advantages over cross-linked electrolytes in, for example, a coating or laminating process. If desirable, the mechanical stability of the present electrolytes can be further increased by increasing the strength of the interpolymer aggregation. This may be done by introducing chain end segments having higher melting temperatures than that of the hexadecanoyl chains. Furthermore, the ion conductivity is expected to be significantly increased by addition of plasticizers such as mixtures of various carbonates.

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