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Physically crosslinked gel electrolytes based on a self-assembling ABA triblock copolymer

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Abstract

Gel electrolytes were prepared by swelling a self-assembling ABA triblock copolymer with different amounts of a solution of 1 M lithium bis(trifluoromethylsulfonyl)imide salt in γ-butyrolactone. The triblock copolymer had endblocks of polyethylene (PE) and midblocks of poly(ethylene oxide-*co*-propylene oxide) (PEOPO), where the former blocks constituted 10 wt% of the copolymer. Thus, the electrolyte solution was contained in physical networks consisting of PEOPO chains interconnected by crystalline PE phase domains. The gels showed a stepwise increase in the ionic conductivity as a consequence of the melting of the PE domains at approximately 100 °C. Also, the conductivity at room temperature increased significantly after annealing above this temperature. Block copolymer gels containing 70 wt% of electrolyte solution reached conductivities of 1 mS/cm at 20 °C. © 2002 Published by Elsevier Science Ltd.

Keywords: Block copolymer gel electrolyte; Physical triblock copolymer network; Ionic conductivity

1. Introduction

The great efforts made to increase the ionic conductivity of solid polymer electrolytes have so far been insufficient to permit the use of these materials in, for example, rechargeable lithium polymer batteries at room temperature [1]. A successful concept to improve the conductivity has been to add organic solvents to swell the polymers to form gel electrolytes. Feullade and Perche reported on the first gel electrolyte of this kind, based on polyacrylonitrile, already in 1975 [2]. In the ideal case, these gels should combine the fast ionic conductivity characteristic of liquids with the cohesive strength of solids. The selection of the organic solvents is typically aimed at optimising the ionic conductivity, and is to a large extent based on their dielectric constant and viscosity.

In order to improve the mechanical strength of these highly solvent-swollen materials, the polymer component is often chemically crosslinked, by for example UV irradiation, to form a three-dimensional network. An alternative way to prepare gels is to make use of polymers which self-assemble and form physically crosslinked networks [3]. By using these types of polymers, the physical properties and processability of thermoplastics are exploited. Block copolymers, which consist of at least two chemically dissimilar polymer chains, or blocks, covalently joined at the ends, are perhaps the most extensively investigated group of self-assembling polymers [4–6]. For example, different block copolymers have previously been evaluated in solid polymer electrolyte systems [7–14]. Because of the characteristically low mutual miscibility of dissimilar polymers, the different polymeric blocks phase separate to form periodic structures at the nano-level. Especially attractive in the context of gel-forming copolymers is the chain architecture of ABA triblock copolymers, where the polymeric mid(B)block is polar, and constitutes the major part of the block copolymer, and the end(A)blocks are non-polar. These triblock copolymers typically phase separate to form the kind of phase structure shown in Scheme 1, where the A blocks (black chains) form discrete domains which are interconnected by the B blocks (white chains) forming the matrix phase. Because the matrix phase is polar, it may be swelled by an electrolyte solution, that is, a salt dissolved in a solvent (denoted by stars in Scheme 1). Consequently, the insoluble non-polar domains function as physical crosslinks for the B blocks.

In a previous investigation, the properties of solid polymer electrolytes based on a self-assembling ABA triblock copolymer were studied [14]. The triblock copolymer had A

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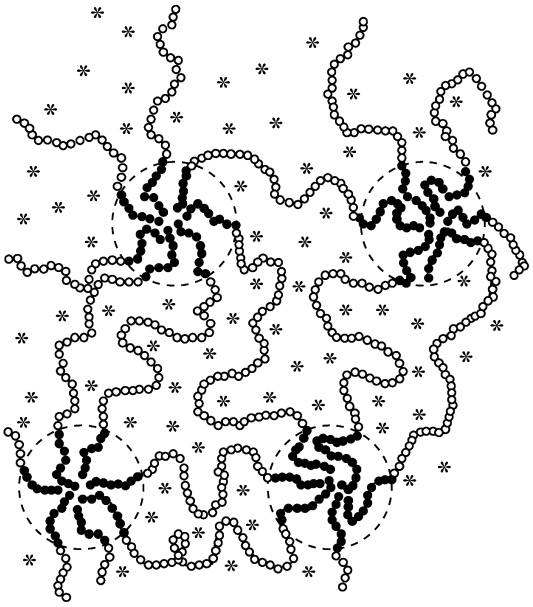

Scheme 1.

blocks of polyethylene, and a B block consisting of a copolymer of ethylene oxide and propylene oxide. The present investigation was focused on studying the properties of gel electrolytes based on the same copolymer. Gels were prepared by swelling the block copolymer with different amounts of an electrolyte solution consisting of lithium bis(trifluoromethylsulfonyl)imide salt dissolved in γ-butyrolactone. The phase behaviour of the electrolytes was subsequently studied by calorimetry and the ionic conductivity at different temperatures was measured by impedance spectroscopy.

2. Experimental

2.1. Sample preparation

The triblock copolymer was prepared by linking monocarboxylic acid functional PE to a dihydroxy functional poly(ethylene oxide-*co*-propylene oxide) (PEOPO) [14]. First, the PEOPO midblock precursor was prepared by anionic copolymerisation of ethylene oxide and propylene oxide initiated from diethylene glycol. The statistical copolymer was found by ^{1}H NMR spectroscopy to contain 77 wt% EO, and by size exclusion chromatography to have $M_n = 13{,}000$ g/mol and $M_w/M_n = 1.2$. The PE endblocks with $M = 700$ g/mol were subsequently attached to the two chain ends of the PEOPO through an esterification reaction. During cooling of the reaction mixture, a physical gel was formed as the PE endblocks crystallised. The triblock copolymer was then purified by first immersing it in dry THF, and then in isooctane. The removal of the PE precursor was confirmed by IR spectroscopy by the absence of any carboxylic acid peak at 1710 cm^{-1}.

Gel electrolytes were prepared by swelling solid electrolytes with an electrolyte solution consisting of 1 M lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, kindly supplied by the 3M company) salt in γ-butyrolactone (γ-BL, Battery Grade, Merck, Selectipur®). Copolymer samples were first transferred to a glove box filled with dry Ar-atmosphere, and then dried at 60 °C under vacuum for 3 days. Precise amounts of a solution of LiTFSI in dimethyl carbonate (Battery Grade, Merck, Selectipur®) were added to glass ampoules containing the copolymer to obtain solid electrolytes with a salt concentration corresponding to 20 coordinating PEOPO oxygens per lithium ion. The dimethyl carbonate was allowed to evaporate under Ar for two days at ambient temperature before the samples were transferred to a glass oven where the residual solvent was removed under vacuum at 60 °C for 3 days. Gel electrolytes were subsequently prepared by adding precise amounts of 1 M LiTFSI in γ-BL to the solid polymer electrolytes. In this way, electrolytes containing 10, 30, 50, and 70 wt% of the electrolyte solution were prepared.

2.2. Impedance spectroscopy

The ionic conductivity (σ) of the electrolytes was evaluated by measuring the dependence of impedance spectra in the temperature region between −40 and 140 C. Samples with a diameter of 18 mm and a thickness of 90 μm were sandwiched between two gold-plated stainless steel blocking electrodes distanced by a PTFE ring. The measurements were carried out using a computer controlled Novocontrol BDC40 high-resolution dielectric analyser equipped with a Novocool® cryostat unit. Samples were analysed in the frequency range 10^{-1}–10^{7} Hz at 100 mV ac amplitude, and the conductivities were subsequently evaluated using the Novocontrol software WinDeta®.

2.3. Calorimetry

The thermal properties of the neat polymer and the electrolytes were analysed with a Mettler TA 3000 DSC system under N_2 purge. Samples were placed in aluminium containers, which were sealed under Ar atmosphere. The samples were first annealed at 150 °C for 5 min before cooling down to −150 °C, and then finally heating up to 150 °C again. The heating and cooling rates were 10 °C/min. Glass transition temperatures (T_g), melt temperatures (T_m), and heats of fusion (ΔH_m) were evaluated from the heating scan.

3. Results and discussion

The ABA triblock copolymer was prepared by linking two monofunctional PE blocks to the chain ends of a linear poly(ethylene oxide-*co*-propylene oxide) through an

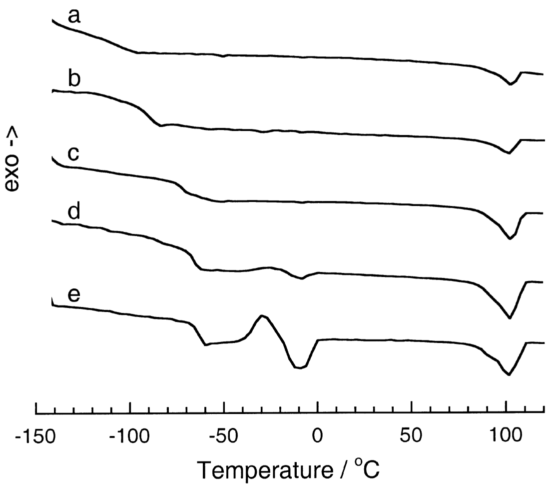

Fig. 1. DSC heating traces of gel electrolytes based on the triblock copolymer containing 70 (a), 50 (b), 30 (c), and 10 wt% (d) of 1 M LiTFSI salt in γ-BL. For comparison, the trace of a solid electrolyte with [Li]/[O] = 0.025 (e) is also shown. The electrolytes were cooled from 25 °C down to -150 °C prior to the heating scan. Scan rate: 10 °C/min.

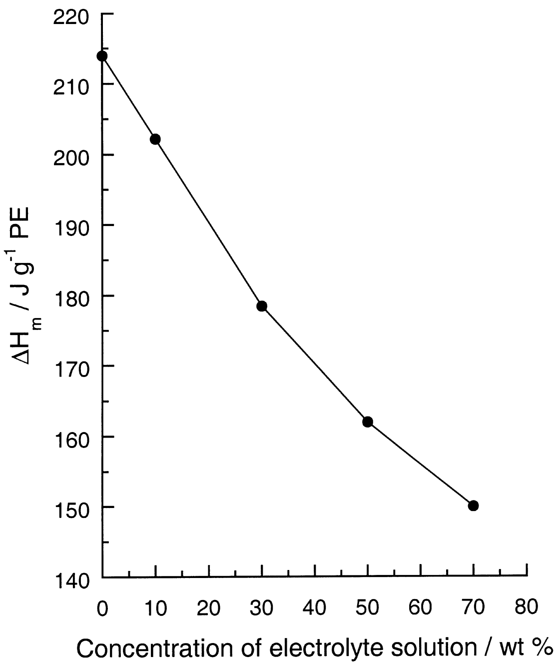

Fig. 2. Variation of ΔH_m of the PE phase, expressed as J/g PE in the gels, with the content of electrolyte solution.

esterification [14]. Thus, the copolymer had a combined molecular weight of 14,400 g/mol, where the PE endblocks constituted 10 wt% of the copolymer. Judging from the physical behaviour of the copolymer, it most probably self-assembled into a physical, micelle-like, network where the PEOPO chains were interconnected by crystalline PE domains (Scheme 1). For example, when cooling a 10 wt% solution of the copolymer in toluene, it was observed to form a self-supporting thermoreversible gel below the crystallisation temperature of the PE blocks at approximately 100 °C [14]. Because of the interconnecting PE domains, the triblock copolymer could only be dissolved in solvents able to dissolve semi-crystalline PE, for example hot toluene and xylene. DSC analysis showed that the neat block copolymer had a PEOPO glass transition at -65 °C, a PEOPO 'cold' crystallisation exotherm at -45 °C, a PEOPO melt endotherm at -10 °C, and a PE melt endotherm at 100 °C. It was noted that the T_g of the PEOPO phase and the T_m of the PE phase were essentially the same as for the PEOPO and PE precursors, respectively. Thus, the PE and PEOPO blocks of the copolymer seemed to be strongly segregated at least up to the T_m of the PE blocks. The DSC heating trace of the block copolymer complexed with LiTFSI salt corresponding to [Li]/[O] = 0.050 is shown in Fig. 1(e). As expected, the T_g increased and degree of 'cold' crystallisation decreased after addition of salt. However, the T_m and ΔH_m of the PE phase remained unchanged, as compared to the neat copolymer. This is a clear indication that the two blocks formed phases which were well segregated in the material.

Gel electrolytes were prepared by swelling samples of the solid block copolymer electrolyte having [Li]/[O] = 0.050 with 10, 30, 50, and 70 wt% of an electrolyte solution consisting of 1 M LiTFSI in γ-BL. Fig. 1 shows the DSC heating traces of the electrolytes. A number of general observations were made as the concentration of electrolyte solution was increased. First, the T_g was lowered. This was expected because of the plasticising effect of γ-BL. Second, the propensity for crystallisation of the PEOPO chains was depressed, and for electrolytes containing more than 10% electrolyte solution, no PEOPO crystallinity was detected. The reason for this observation was, of cause, again the plasticising and dissolving effect of the electrolyte solution on the PEOPO blocks. Third, the level of PE crystallinity decreased. Although this decrease was largely an effect of the dilution of the PE phase, the crystallinity of the PE phase decreased in the electrolytes as increasing amounts of electrolyte solutions were added. This is seen in Fig. 2 where the ΔH_m of the PE phase, expressed as J/g PE in the gels, is plotted as a function of the concentration of electrolyte solution. These values can be compared with value of ΔH_m measured for the neat PE precursor by DSC, 225 J/g, and the literature value for linear PE, 277 J/g [15]. As seen in Fig. 2, the crystallinity of the PE blocks decreased by roughly 30% after addition of 70 wt% electrolyte solution, as compared to the solid electrolyte (0 wt% electrolyte solution). The T_m of the PE phase, however, remained at 100 °C. These observations implied that the PE domains became less rigid after the addition of the electrolyte solution. However, they were not dissolved, and remained to provide coherence to the gels when the physical networks were expanded at the absorption of the electrolyte solution. Finally, no crystallinity of γ-BL was detected. The neat electrolyte solution shows a T_g at -140 °C, and an interval of crystallisation and melt transitions between -110 and -50 °C [16]. Thus, it seemed like the crystallisation of γ-BL was greatly depressed by the

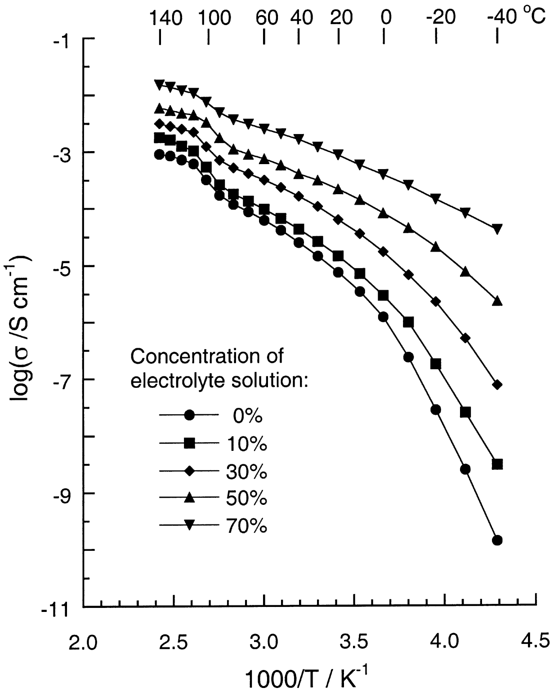

Fig. 3. Arrhenius conductivity plots for gel electrolytes based on the triblock copolymer containing 70, 50, 30, and 10 wt% of 1 M LiTFSI salt in γ-BL. For comparison, the results on the solid electrolyte with [Li]/[O] = 0.025 is also shown (0% electrolyte solution, data from Ref. [14]). The conductivities were evaluated from impedance spectra obtained in the second heating scan from −40 to 140 °C.

presence of the polymer in the gels. It is, however, likely that this was mainly a kinetic effect.

The ionic conductivity of the gel electrolytes and the solid electrolyte with [Li]/[O] = 0.050 measured during the second heating scan are shown as Arrhenius plots in Fig. 3. As expected, σ for the gels increased greatly with increasing concentration of the electrolyte solution and, in the temperature region 0–80 °C, the dependence changed gradually from a VTF relationship for the solid polymer electrolyte to a more Arrhenius-like relationship for the gels. The reason for this was that the transport of ions became less coupled with the segmental motions of PEOPO, as the electrolyte solution was added, and instead became increasingly coupled with the dynamics of the solvent.

It is also seen in Fig. 3 that the electrolytes showed a stepwise increase in σ at the T_m of the PE phase when heated. Correspondingly, during cooling a sharp stepwise decrease in conductivity was noted immediately after 110 °C, the crystallisation temperature of the PE phase (not shown in Fig. 3). The magnitude of the step in σ decreased with increasing concentration of electrolyte solution. The rigid crystalline PE phase domains keep the physical PEOPO networks together by forming the nodes of the network below the T_m. Consequently, it is easy to envisage that when the PE phase domains melt in a quite small temperature range, the segmental mobility of the PEOPO blocks, and thereby also σ, will increase sharply. Thus, the magnitude of the increase in σ decreased with increasing concentration of electrolyte solution, which can be seen in Fig. 3. Thus, the PE phase domains seemed to work as thermoreversible physical crosslinks in the block copolymer gel electrolytes. It was remarkable that although the PE phase of the gel containing 70 wt% electrolyte solution constituted only 3 wt%, σ still increased by a factor of approximately 7 at the PE melting transition between 80 and 110 °C. Thus, the mobility of the copolymer molecules in the gels below T_m seemed to play a significant role for the level of σ also in gels with quite high contents of electrolyte solutions.

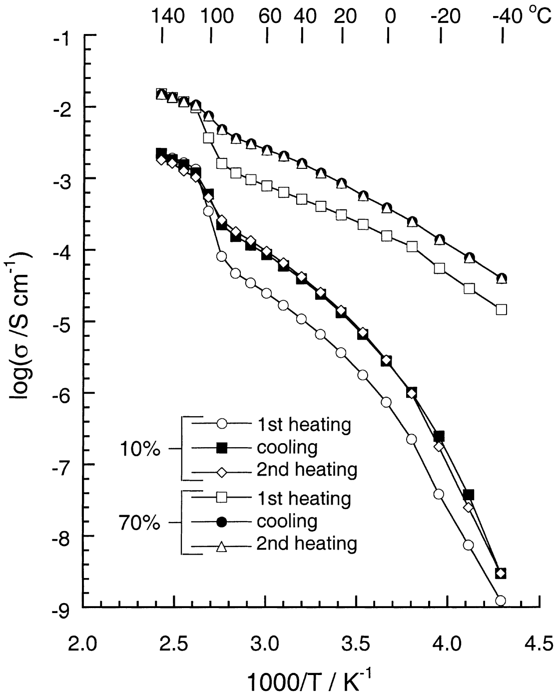

Fig. 4. Arrhenius plots showing thermal hysteresis effects of σ for gel electrolytes based on the triblock copolymer containing 70 and 10 wt% of 1 M LiTFSI salt in γ-BL. The conductivities were evaluated by impedance spectroscopy during the temperature scan: −40 → 140 → −40 → 140 °C.

Fig. 4 shows Arrhenius plots of the ionic conductivity of gels, containing 10 and 70 wt% electrolyte solution, during the first heating, cooling, and the second heating scan. The most interesting feature of the results in Fig. 4 was the hysteresis displayed by the gel electrolytes. Below T_m of the PE phase, the level of σ was significantly higher during the cooling scan, as compared to the first heating scan. In the second heating scan, the level of σ was approximately the same as during the cooling scan. The conductivity above the PE melting point was the same during all the three scans. It was noted that in the approximate temperature region −40 to −10 °C, the conductivity during the cooling of the gel electrolyte containing 10 wt% electrolyte solution was slightly higher than during the second heating scan. This observation may be explained by the crystallisation and melting, respectively, of PEOPO. As seen in Fig. 1, the PEOPO of this electrolyte melted in this temperature region.

The observed hysteresis was obviously a result of differences in the thermal history of the electrolyte samples, and showed that annealing was decisive for reaching high levels of σ with these materials. The unannealed electrolytes, formed essentially through solvent casting, probably contained physical networks in which the triblock copolymer molecules were constrained by the presence of the crystalline PE phase domains. This would lead to a reduced segmental mobility of the ion conducting PEOPO midblocks, and thus to a reduced σ. When the PE end blocks melted at approximately 100 °C, the block copolymer molecules were able to rearrange and form a network in which the PEOPO midblocks were less constrained, which led to an increase in σ.

It is interesting to compare the conductivity results of the physically crosslinked triblock copolymer gel electrolytes with results obtained with chemically crosslinked systems. Aihara and coworkers have studied gel electrolytes based on chemically crosslinked poly(ethylene oxide) networks containing 80% 1 M LiTFSI in γ-BL [17]. They measured σ of the neat electrolyte solution to be $10^{-2.1}$ S/cm at 40 °C, and of the gel to be $10^{-2.6}$ S/cm at the same temperature. This may be compared with $10^{-2.8}$ S/cm measured for the copolymer gel electrolyte containing 70% electrolyte solution in the present study. The main reason for the slightly higher conductivity measured in the investigation by Aihara et al. is most probably the higher content of electrolyte solution in their gel.

4. Conclusions

The present study showed that the polyethylene–polyether–polyethylene triblock copolymer formed physically crosslinked gels swollen by anhydrous electrolyte solutions. Gels containing low amounts of electrolyte solutions were essentially soft self-supporting materials at room temperature, but with increasing amounts of electrolyte solution, the gels behaved more like viscous liquids. The gel electrolytes had ionic conductivities in level with corresponding gel electrolytes based on chemically crosslinked polyethers. It was also shown that annealing of the triblock copolymer gels above the PE melting point was important in order to promote the conductivity below 100 °C.

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References

[1] Tarascon JM, Armand M. Nature 2001;414:359.
[2] Feullade G, Perche P. J Appl Electrochem 1975;5:63.
[3] Alexandridis P, Spontak RJ. Curr Opin Colloid Interf Sci 1999;4:130.
[4] Riess G, Hurtres C, Badahur P. In: Kroschwitz JI,, editors, 2nd ed. Encyclopedia of polymer science and engineering, vol. 2. New York: Wiley; 1985. p. 324.
[5] Pitsikalis M, Pispas S, Mays JW, Hadjichristidis N. Adv Polym Sci 1998;135:1.
[6] Klok HA, Lecommandoux S. Adv Mater 2001;13:1217.
[7] Soo PP, Huang B, Jang YI, Chiang YM, Sadoway DR, Mayes AM. J Electrochem Soc 1999;146:32.
[8] Giles JRM, Gray FM, MacCallum JR, Vincent CA. Polymer 1987;28: 1977.
[9] Gray FM, MacCallum JR, Vincent CA, Giles JRM. Macromolecules 1988;21:392.
[10] Khan IM, Fisch D, Delaviz Y, Smid J. Makromol Chem, Macromol Chem Phys 1989;190:1069.
[11] Hirahara K, Takano A, Yamamoto M, Kazama T, Isono Y, Fujimoto T, Watanabe O. React Funct Polym 1998;37:169.
[12] Li J, Khan I. Macromol Chem 1991;192:3043.
[13] Allcock HR, Prange R, Hartle TJ. Macromolecules 2001;34:5463.
[14] Jannasch P. Chem Mater 2002;14:2718.
[15] Zhu L, Chiu FC, Fu Q, Quirk RP, Cheng SZD. In: Brandrup J, Immergut EH, Grulke EA, editors. Polymer handbook, 4th ed. New York: Wiley; 1999. p. V-17.
[16] Jannasch P. Polymer 2001;42:8629.
[17] Aihara Y, Arai S, Hayamizu K. Electrochim Acta 2000;45:1321.