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Plasticization of cross-linked polymer electrolytes

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Abstract

The plasticization of cross-linked poly(ethylene oxide)/poly(propylene oxide) copolymer electrolytes was investigated using low mol. wt. poly(ethylene oxide) PEO as plasticizer. These plasticizers were grafted on to the polymer networks (internal plasticization) or free (external plasticization). The conductivities of the plasticized polymer networks were measured at room temperature using LiClO_4 as salt. Plasticization increased the conductivity and the gain depended on the plasticization-type, on the size of the plasticizer connected to the size of the copolymer and on the nature of the plasticizer. The glass-transition temperatures of the polymers were also measured and they varied in an opposite way versus conductivity.

Keywords: Polymer electrolytes; Plasticization; Solid-state batteries

1. Introduction

The last ten years an important work was devoted to the improvement of the performances of polymer electrolytes for their use in lithium solid-state batteries. The plasticization [1] is an interesting mean to modify the conductivity, the interfacial and mechanical properties of polymer electrolytes. This work presents the experimental results obtained from cross-linked networks plasticized by non-volatile macromolecules. Internal and external plasticizations were evaluated and compared. In the first case, the macromolecule was grafted on to the polymer network by means of an amino group, and free in the second case.

2. Experimental

2.1. Sample preparation

The three-dimensional structure of the polymer electrolyte was realized by the reaction of a diamino polyether with a diepoxy compound [2]. This reaction was catalyzed by LiClO_4 , which was also the charge carrier.

LiClO_4 (from Fluka) was dissolved in ethanol and mixed with a poly(ethylene oxide)/poly(propylene oxide) (PEO/PPO) copolymer (2000 or 6000 mol. wt. from Texaco) and with the plasticizer. For internal plasticization, the plasticizers were PEONH_2 (from Fluka

for PEONH_2 mol. wt. 5000 or synthesized from PEOOH 350 and 750 mol. wt.) or aminated Brij and Igepal (commercial names of alkyl-PEO from Aldrich). For external plasticization, they were 350 and 750 mol. wt. PEOOH (from Aldrich). The cross-link agent BDDGE (butanediol diglycidyl ether, (from Aldrich, 95%)) was incorporated into the mixture, after the solvent being evaporated. The cross-linking reaction took place at 80 °C and samples were dried under primary vacuum at 100 °C for 15 h. The ratio between total ether units and lithium was 21 and the epoxy/amine molar ratio was 2.

2.2. Plasticizer synthesis

The synthesis [3] was carried out in two steps. The first step was a phase-transfer catalysis. A mixture of PEOOH 350 (70 g, 0.2 mol), tosyl chloride (from Fluka, 40 g, 0.21 mol), dichloromethane (400 ml), 30% soda solution (400 ml) and aliquat 336 (phase-transfer agent from Aldrich, 4.5 ml) was stirred for 4 h at room temperature. The organic phase was separated, washed several times with saturated brine, dried over MgSO_4 and evaporated under reduced pressure. The tosylate derivative was precipitated with ether and recrystallized from ethanol. The spectroscopic characteristics of the synthesized tosylate were as follows:

(i) IR: ν (NaCl) = 3100, 1600, 1170 and 820 cm^{-1}

(ii) NMR data: ^1H NMR (CDCl_3): δ = 2.4 (s, 3H), 3.3 (s, 3H), 3.9 (m, 28.9H), 7.6 (d, 2H_{arom}), 7.8 (d, 2H_{arom}).

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In the second step, a mixture of the above tosylate (15.15 g, 0.03 mol), sodium diformamide (12 g, 0.12 mol), and anhydrous dimethylformamide (DMF) (100 ml) was heated at 110 °C with stirring, under argon. After 2 h, the solvent was distilled under reduced pressure. The residue was dissolved in dichloromethane (90 ml), filtered and washed with small portions of dichloromethane. The filtrate was evaporated under reduced pressure and the residue was mixed with 5% ethanolic hydrochloride (300 ml). The resulting mixture was refluxed for 2 h. After cooling, the solution (ethanol and HCl) was evaporated under reduced pressure. Toluene and triethylamine were added with stirring and the solution was filtered and evaporated. The amine was precipitated with ether and recrystallized from ethanol. The spectroscopic characteristics of the synthesized amine were follows as:

- (i) IR: ν (NaCl) = 3370 and 1590 cm^{-1}
- (ii) NMR data: ^1H NMR (CDCl_3): δ = 3.3 (s, 3H), 3.9 (m, 28.9H), 7.3 (s, CHCl_3).

2.3. Electrochemical measurements

The conductivity of the polymer was measured at room temperature by impedance spectroscopy (Solartron 1250 frequency response analyzer and SI 1286 electrochemical interface) on symmetrical nickel/nickel cells.

2.4. Glass-transition temperature (T_g) measurements

The glass-transition temperature measurements were realized by a differential scanning calorimetry (DSC) cell connected to a Dupont 990 thermal analyzer.

3. Results and discussion

Figs. 1 and 2 show the conductivity variation of a cross-linked 2000 mol. wt. PEO/PPO copolymer with

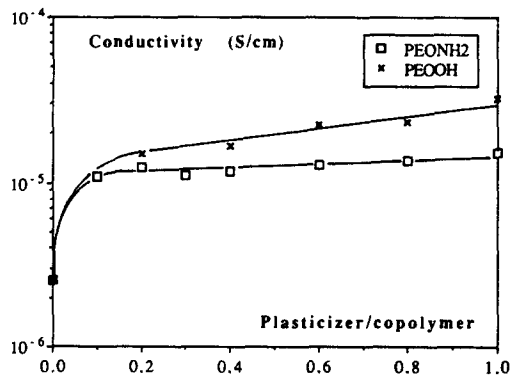


Fig. 1. Internal and external plasticization vs. ionic conductivity; 2000 mol. wt. cross-linked PEO/PPO copolymer; 350 mol. wt. PEO plasticizer; LiClO_4 ($\text{O/Li}=21$); $T=25$ °C.

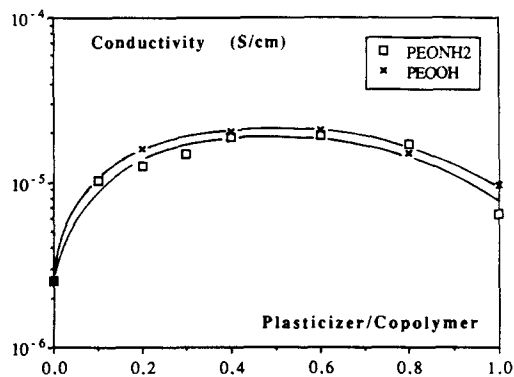


Fig. 2. Internal and external plasticization vs. ionic conductivity; 2000 mol. wt. cross-linked PEO/PPO copolymer; 750 mol. wt. PEO plasticizer; LiClO_4 ($\text{O/Li}=21$); $T=25$ °C.

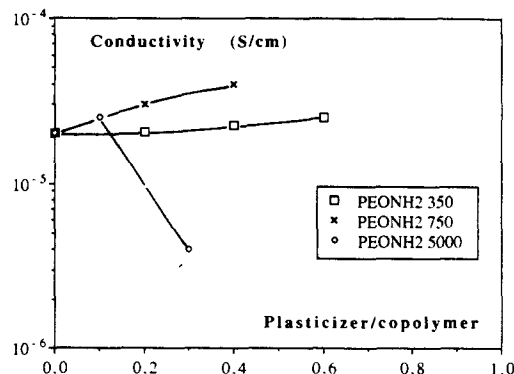


Fig. 3. Internal plasticization vs. ionic conductivity; 6000 mol. wt. cross-linked PEO/PPO copolymer; 350, 750 and 5000 mol. wt. PEONH₂ plasticizer; LiClO_4 ($\text{O/Li}=21$); $T=25$ °C.

the plasticizer/copolymer molar ratio for PEO 350 and 750 as plasticizer. In both cases, the conductivity increased rapidly up to 20% of plasticizer (for the internal and external plasticization). Above this value, two main types of behaviour were observed. When the plasticizer size was small (PEO 350, Fig. 1), the conductivity increased slowly and gradually with an increasing amount of plasticizer. When the plasticizer size was bigger (PEO 750, Fig. 2), the conductivity reached a maximum. These two types of behaviour could be probably connected to the polymer lattice size and to steric effects. External plasticization gave slightly higher conductivities, but the polymer electrolyte exuded with time. Internal plasticization preserved mechanical properties and improved the interfacial properties [4].

Fig. 3 shows the variation in conductivity of a cross-linked 6000 mol. wt. PEO/PPO copolymer with the plasticizer/copolymer molar ratio for PEONH₂ 350, 750 and 5000 as plasticizer (above 40 or 60% of plasticizer, the cross-linking reaction did not occur). The conductivity gain was more important for PEONH₂ 750 than 350. Also in this case, two main types of behaviour were observed. The conductivity increased with the plasticizer amount for PEONH₂ 350 and 750, and

reached a maximum for PEONH₂ 5000. As shown previously, the important parameter seemed to be the plasticizer size connected to the polymer lattice size. A conductivity of 4×10^{-5} S/cm was achieved at room temperature with a 6000 mol. wt. PEO/PPO copolymer which was plasticized with 40% of PEONH₂ 750 and with LiClO₄ as salt. The same non-plasticized network showed a conductivity of 2×10^{-5} S/cm. A plasticized 2000 mol. wt. PEO/PPO copolymer gave nearly the same conductivity but its kinetics of the cross-linking reaction was much faster.

In all cases, the glass-transition temperature (T_g) (Figs. 4 to 6) varied in an opposite way versus conductivity.

Other types of plasticizers were tested. They were constituted by a PEO chain grafted on to an aliphatic chain. The introduction of aliphatic parts into the networks was expected to lower the T_g and thus to increase the conductivity. These plasticizers were obtained from commercial alcohols (Brij or Igepal) and aminated using the procedure described previously. The conductivities (Table 1) were measured for a plasticizer 2000 mol. wt. PEO/PPO copolymer ratio close to 0.2. They were lower than those obtained from pure PEO plasticizers. That was significant for aminated Brij 30

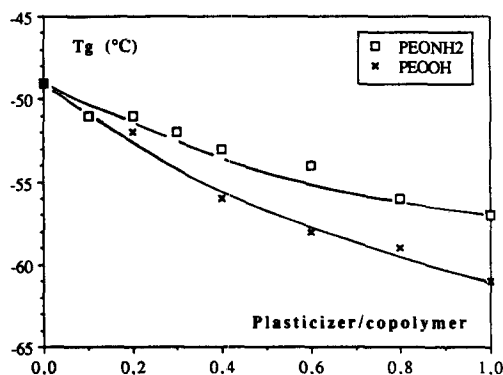


Fig. 4. Internal and external plasticization vs. glass-transition temperature (T_g); 2000 mol. wt. cross-linked PEO/PPO copolymer; 350 mol. wt. PEO plasticizer; LiClO₄ (O/Li=21).

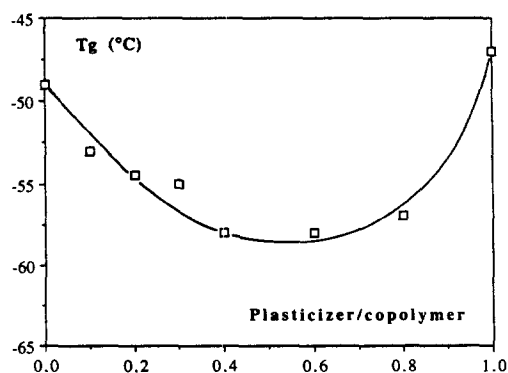


Fig. 5. Internal plasticization vs. glass transition temperature (T_g); 2000 mol. wt. cross-linked PEO/PPO copolymer; 350 mol. wt. PEONH₂ plasticizer; LiClO₄ (O/Li=21).

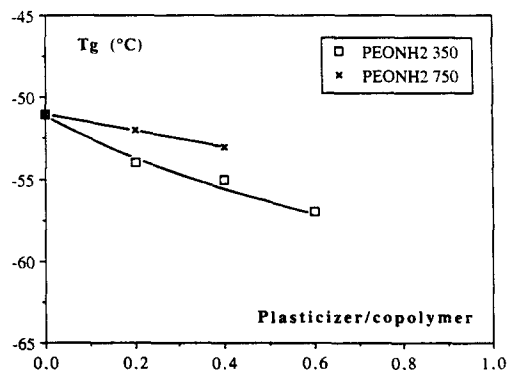


Fig. 6. Internal plasticization vs. glass transition temperature (T_g); 6000 mol. wt. cross-linked PEO/PPO copolymer; 350 and 750 mol. wt. PEONH₂ plasticizer; LiClO₄ (O/Li=21).

Table 1
Influence of the internal plasticization on the ionic conductivity *

Aminated plasticizer	Mol. wt.	<i>m</i>	<i>n</i>	Conductivity (10^{-6} S/cm)
Igepal CO 520	439	9	5	3.2
Brij 30	361	12	4	7.5
Brij 78	1150	18	20	3.8
Brij 58	1122	16	20	3.8

Igepal: $4-C_nH_{(2n+1)}-C_6H_4-(O-CH_2-CH_2)_m-OH$
 Brij: $C_nH_{(2n+1)}-(O-CH_2-CH_2)_m-OH$

* 2000 mol. wt. cross-linked PEO/PPO copolymer; alkyl-PEONH₂ plasticizer; plasticizer/copolymer molar ratio of 0.2; LiClO₄ (O/Li=21); $T=25$ °C.

which had almost the same mol. wt. as 350 mol. wt. PEO. Compared with PEO plasticizers, the presence of aliphatic chains did not increase the conductivity. As a matter of fact, the conductivity decreased with dilution of the complexing PEO/PPO chains by the aliphatic parts of the plasticizer.

4. Conclusions

The plasticization method allowed to increase significantly the conductivity of the polymer networks and improved their interfacial and the electrode-adhesion properties. With the internal plasticization, mechanical properties were better than with the external one, the conductivity being, however, slightly lower. The gain in conductivity depended on the nature of the polymer. It was more important for a pure-PEO plasticizer than for an alkyl-PEO plasticizer.

A conductivity of 4×10^{-5} S/cm was achieved at room temperature with a plasticized PEO/PPO copolymer and LiClO₄ as salt. T_g decreased (10 °C lower) and the mechanical properties were preserved.

The conductivity increased with the size and amount of the plasticizer, up to a maximum. This maximum seemed to be reached as fast as the plasticizer size

was important and proportionally to the polymer lattice size. The denser the plasticized network, the higher was the relative conductivity gain. Actually, whatever the initial network size, all the best compositions seemed to tend to the same values of conductivity.

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References

- [1] G. Calle, J.Y. Sanchez, J.F. Le Nest, D. Foscallo and M. Armand, *3rd Int. Symp. Polymer Electrolytes, Annecy, France, 1991*, pp. 150–151.
- [2] X. Andrieu and J.P. Boeue, Cross-linked polymer solid electrolyte, *Fr. Patent No. 8 914 061* (1989); *Eur. Patent No. 424 827* (1991).
- [3] Y. Han, T. Lu, H. Hu and X. Liu, *Synth. Commun.*, **21** (1991) 79–84.
- [4] C. Arbizzani, M. Mastragostino, L. Maneghello, X. Andrieu and T. Vicédo, *J. Power Sources*, **45** (1993) 161–168.