A PEO salt complex exhibiting photoresponsive ionic conductivity

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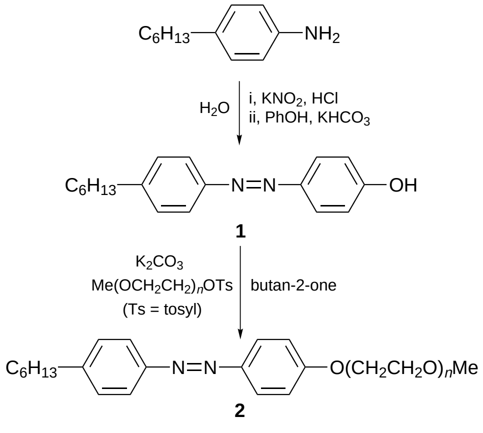
A polymer electrolyte film made of lithium perchlorate dissolved in a mix of high molecular mass poly(ethylene oxide) (PEO) and shorter PEO–azobenzene diblocks, shows a reversible 70% conductivity increase under UV light irradiation at room temperature.

Only few published works have dealt with light-induced reversible ionic conductivity changes in polymer films.[1–3] In most cases the studied effect arises from a single molecular mechanism. For instance, photoactivated reversible cation complexation is obtained for some spiropyrans[1] or crowned malachite greens.[2] Indeed a 5% reversible increase from 5.3×10^{-6} S cm^{-1} at 30 °C, was observed when a polymethacrylate bearing both methoxylated benzospiropyrans and short polyether chains and dissolving zinc chloride, was irradiated by UV light.[1] Fluctuations of very low ionic conductivity, about 10^{-10} S cm^{-1}, were also described for a crowned malachite green dissolved in a PEO matrix containing a sodium salt and submitted to pulsed UV light.[2] A similar effect for conductivities lying around 10^{-8} S cm^{-1} at 80 °C, was also obtained with polyester composite films containing crowned azobenzenes and a lithium salt.[3] In this latter case however the azobenzene based molecules exhibited liquid-crystalline behaviour and the conductivity increase was related to a transition from the nematic phase to the isotropic liquid one.[3] Indeed *cis–trans* photoisomerism of azobenzenes is well known and the birefringent nematic phase of some linear *trans*-azobenzenes can be erased by UV light when the bent *cis* form thus produced disrupts the liquid-crystal order. This effect has been used for image storage in either nematic polymer films[4] or ferroelectric smectic layers.[5] For the present work, we used the azobenzene photoisomerism in a different way allowing efficient light monitoring of ionic conductivity of polymer electrolyte films at levels as high as about 10^{-4} S cm^{-1}.

The chemical method for coupling short monomethylated PEO chains (M_w = 750) with alkylated azobenzene (Scheme 1)† was adapted from literature data.[6] 1-(4-Hydroxyphenyl) 2-(4-hexylphenyl)diazene **1** (AZOH),[6] exhibited several endothermic transitions at 33, 40, 53 and 77 °C on differential scanning calorimetry (DSC) recordings, the intensity of which increased in the same order as the transition temperatures. Several liquid-crystal phases appeared up to the isotropic liquid. For AZOH–PEO **2**, the DSC trace showed a unique melting point at 25 °C near that of the starting methylated PEO (30 °C). When lithium perchlorate was added, the endothermic melting peak became very weak at 36 °C and a glass transition became clearer at −33 °C. Self-supporting polymer electrolyte films were thus prepared by dissolving AZOH–PEO **2** and lithium perchlorate in commercial PEO ($M_w = 5 \times 10^6$) at an O/Li ratio of 12. The glass transition of this polymer electrolyte was at *ca.* −33 °C and the melting point at 36 °C suggesting that both crystalline and amorphous phases were present in the material. This point is of importance since ionic conduction of polymer films is restricted to their amorphous phase.[7]

The effect of UV-light laser irradiation (363 nm) in the conductivity of the films is clearly observable in the impedance spectra showed in Fig. 1. A *ca.* 70% increase of the conductivity arose under UV light. No detectable effect was obtained in identical conditions but for an electrolyte film which did not contain compound **2**. Increasing the light intensity from 0 up to 50 mW cm^{-2} enhanced the conductivity growth according to a logarithmic law. A saturation effect was then observed for light power values above 70 mW cm^{-2}, as expected for an absorption phenomenon. Switching off the UV-light source restored reversibly the initial conducting state within a few minutes (Figs. 1 and 2). As shown in Fig. 3, the magnitude of the light-induced conductivity increase was roughly the same throughout the explored temperature range up to 50 °C. At higher temperatures the light effect tended to disappear.

The photoactivation mechanism of the ionic conductivity in our polymer films appears to be complex. The disorder resulting from the light-induced *trans–cis* structural change of the azobenzene moieties and also possibly from erasing long-range ordering of interacting *trans* azobenzene groups, obviously increased the free volume in the material. However the linear



Scheme 1 Synthesis of compounds **1** and **2**

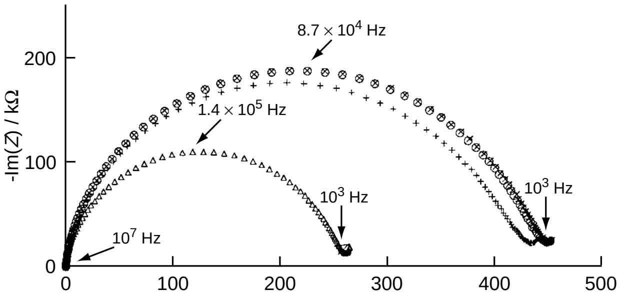


Fig. 1 Nyquist plots of the complex impedances obtained at 20 °C for a polymer film made of PEO (M_w 5×10^6) 50%, AZOH–PEO **2** 50% and LiClO$_4$ (O/Li = 12): (*a*) before UV irradiation (○), (*b*) under UV irradiation (363 nm, 75 mW cm^{-2} (△), (*c*) 5 min after switching off the UV light (+), (*d*) 10 min after switching off the UV light (×). The conductivity cells were made of 410 μm thick polymer films sandwiched between two ITO-covered glass pieces.

part of the Arrhenius plots in Fig. 3 suggests an activated mechanism for the ionic conduction. Therefore an increase of the number of mobile charges in the photoactivated state, arising from a disorder induced ion-pair separation, could be put forward. Closer scrutiny of the 'semi-circles' in Fig. 1, reveals that they in fact include two dielectric relaxations with a different sensitivity to the UV irradiation. The latter could correspond either to a two-phase system or to different conduction mechanisms. One should also take into account that the *cis–trans* thermal back isomerism was probably not a time-limiting step for our system, as suggested by the symmetrical time variation of the conductivity after switching off or on the light irradiation (Fig. 2).

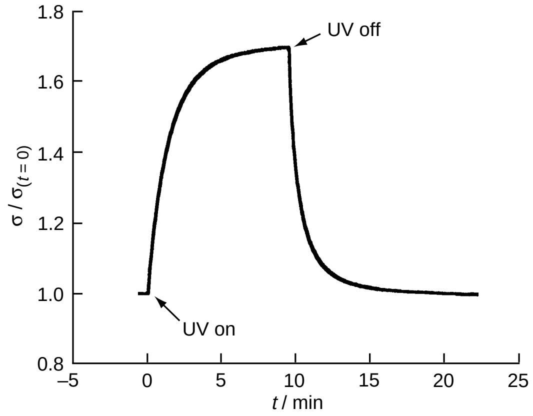


Fig. 2 Time dependence of the conductivity after switching on and off the UV light. Experimental conditions as for Fig. 1 except for the temperature (15 °C) and the laser light power (65 mW cm^{-2}).

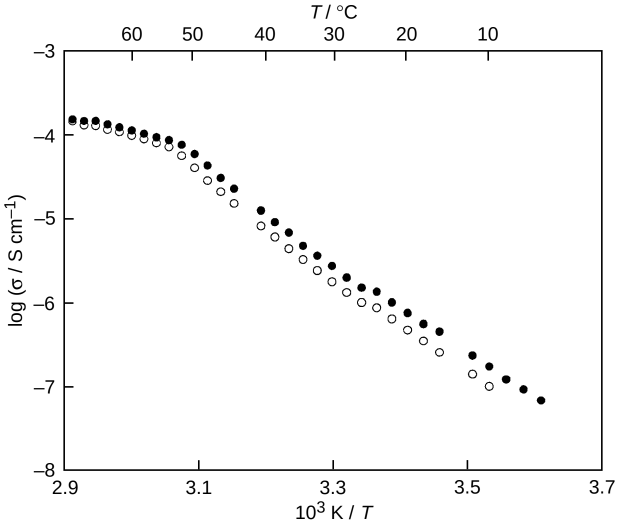


Fig. 3 Conductivity–temperature plots in Arrhenius coordinates. Experimental conditions as for Fig. 1 except for the film thickness (730 μm) (*a*) in the dark (○) and (*b*) under UV light (●).

In conclusion, the possibility of efficient optical control of quite good conductivities for polymer electrolytes is demonstrated. Various technical applications could be envisioned, especially for systems using polymer electrolyte films. Further experiments are presently under way to investigate the mechanism of the optical transition and to obtain even larger effects.

We are indebted to Michel Armand (presently at the University of Montreal, Canada) for having favoured this work.

Footnotes

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† Compounds **1** and **2** were characterized using chromatography and NMR. **2**: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.87 (d, 2 H), 7.78 (d, 2 H), 7.00 (d, 2 H), 4.2 (t, 2 H), 3.85 (t, 2 H), 3.6 (62 H), 3.3 (s, 3 H), 2.6 (t, 2 H), 1.6 (t, 2 H), 1.3 (6 H), 0.9 (t, 3 H).

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Received in Bath, UK, 13th January 1997; Com. 7/00415J