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P. Verge [a] , M. Mallouki [a] , L. Beouch [a] , P. H. Aubert [a] , F. Vidal [a] , F. Tran-Van [a] , D. Teyssié [a] & C. Chevrot [a]

[a] Université de Cergy-Pontoise, Laboratoire de Physico-chimie des Polymères et des Interfaces (LPPI), Institut des Matériaux, Cergy Cedex, France

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Electroactive Polymers with Semi-IPN Architectures for Electrochromic Devices

P. VERGE, M. MALLOUKI, L. BEOUCH,
P. H. AUBERT, F. VIDAL, F. TRAN-VAN, D. TEYSSIÉ,
AND C. CHEVROT

Université de Cergy-Pontoise, Laboratoire de Physico-chimie des
Polymères et des Interfaces (LPPI), Institut des Matériaux,
Cergy Cedex, France

Semi-Interpenetrating Polymer Network architecture containing either PEDOT or PProDOT-Me$_2$ leads to interesting electrochromic devices (ECDs) without need of transparent conducting electrode. Upon applied potential between +1.2 V and −1.2 V these ECDs exhibit 30% contrast variation in the full visible range. Furthermore, the control of the PEDOT content up to 0.3 leads to semi IPN-based materials with interesting change in the reflective properties in the Near Infrared region.

Keywords Electrochromic devices; functional polymer; PEDOT; PProDOT-Me$_2$; radical copolymerization; structural polymer

Introduction

Interpenetrating polymer networks (IPNs) are defined as a combination of two or more polymer networks synthesized in juxtaposition [1]. The aim of these types of polymer associations is generally to obtain materials with better mechanical properties and a possible synergy of the properties compared to those of the components. The semi-IPNs differ from IPNs in that they are composed of a linear polymer entrapped into another polymer network [1]. IPNs lead also to the opportunity to combine at the molecular scale a functional and a structural polymer.

Among functional polymers, Electronic Conducting Polymers (ECPs) have attracted attention notably due to their electronic structure which allows high visible contrasts upon low applied potentials. Nevertheless ECPs are not easily processable and extensive studies have been carried out to improve it. One promising solution is the combination of the ECP with another polymer partner to form IPNs. The second polymer will be a structural partner which notably ensures the mechanical properties of the whole material. Based on an IPN architecture, ECP based electrochromic devices have been developed by combining a poly(ethyleneoxide) (PEO) network

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Address correspondence to C. Chevrot, Université de Cergy-Pontoise, Laboratoire de Physico-chimie des Polymères et des Interfaces (LPPI), Institut des Matériaux, 5 mail Gay-Lussac, Cergy Cedex, F-95031, France. Tel.: +33134257042; Fax: +33134257071; E-mail: claude.chevrot@u-cergy.fr with an ECP to prepare free standing films [2]. In the systems presented here, either poly(3,4-ethylenedioxythiophene) (PEDOT) or poly(3,4(2,2-dimethylpropylenedioxy)thiophene) (PProDOT-Me_2) were chosen as an electrochromic polymer since they are chemically and thermally quite stable. The ECP is then embedded within a PEO network and the resulting thin film (100 μm to 500 μm) is a one-piece flexible device for electrochromic application. Moreover such semi-IPNs can present versatile applications as "active" camouflage or thermal protection depending on the content of ECP incorporated in the PEO matrix [2].

In this paper, we report on the synthesis of branched PEO networks which act as a Solid Polymer Electrolyte (SPE). The semi-IPNs have been synthesized from either poly(3,4-ethylenedioxythiophene) (PEDOT) or poly(3,4-(2,2′-dimethyl)propylene dioxythiophene) (PProDOT-Me_2) and the above mentioned SPE. The synthetic approach leads to the polymerization of the ECP at the edge of the PEO network allowing these materials to be used as electrochromic devices (ECD) or electroemissive devices (EED) in open air.

Experimental

Materials

Anhydrous iron(III) chloride $FeCl_3$ (Acros), Polyethyleneglycol dimethacrylate (PEGDM, 750 g mol^{-1} or 550 g mol^{-1}; Aldrich) and polyethyleneglycol methacrylate (PEGM, 475 g mol^{-1}; Aldrich) were used as received. EDOT was purchased from Bayer and distilled under reduced pressure at 130°C. 2,2′-Azobisisobutyronitrile (AIBN, Aldrich) was recrystallized from methanol and dried under vacuum prior to use. Acetonitrile (ACN, Aldrich, 99.8%), propylene carbonate (PC, Acros, 99.5%), methanol (MeOH, Acros 99.5%), chloroform ($CHCl_3$, VWR, 99–99.6%) and lithium perchlorate ($LiClO_4$, Aldrich, >97%) were used without further purification. Fluorinated tin oxide (SnO_2-F, sheet resistance: $R = 22\ \Omega/sq$), indium tin oxide (ITO, delta Technologies, sheet resistance: $R = 12\,\Omega/sq$,) were used as transparent electrode for optical characterizations.

ProDOT-Me_2 Synthesis

The synthesis of 3,4(2,2-dimethylpropylenedioxy)thiophene monomer was carried out according the procedure described by Caras-Quintero *et al.* [3]

Semi-IPN Synthesis

Synthesis of poly(ethylene oxide)/3,4-poly(ethylenedioxythiophene) based semi-IPN: PEO single networks are prepared as following: 0.5 g PEGM, 0.5 g PEGDM, 10 mg AIBN (1 wt% with respect to the sum of methacrylate oligomers weight) and 20 mg EDOT or ProDOT-Me_2 (2 wt%) are stirred together under argon atmosphere for 30 min at room temperature. The mixture is then poured into a mould made from two glass plates clamped together and sealed with a 500 μm thick Teflon® gaskets. The mould is then kept at 50°C for 4 hours. The sample is then cured for 1 h at 80°C. Finally after room temperature cooling, glass and Teflon® removal, a free-standing monomer-swollen PEO network is obtained. Then, the swollen semi-IPNs are immersed at room temperature for 10 minutes in a $FeCl_3$ saturated chloroform solution in order to promote the oxidative polymerization of EDOT. The film is washed three times with methanol to remove the excess of $FeCl_3$. All PEO/PEDOT or PEO/ProDOT-Me_2 semi-IPNs discussed thereafter have been prepared according to this procedure.

Results and Discussion

Synthesis and Characterization of SPE Materials

A series of branched PEO networks are prepared by radical copolymerization of PEGDM and PEGM using AIBN as initiator. The relative weight proportions of the PEGM are adjusted between 20 and 80%, depending on the wanted SPE properties. The polymerizations are carried out under argon atmosphere at 50°C for 4 h. The samples are then postcured for 1 h at 80°C. The resulting networks exhibited less than 1 wt% extracted material in every cases. As far as the (PEGM/PEGDM 50 wt%/50 wt%) PEO network synthesis is concerned, the radical copolymerization of methacrylate oligomers can be followed by FTIR spectroscopy in the near-infrared region using the $CH_2{=}C(CH_3)$ overtone peak at 6160 cm^{-1} (Fig. 1). The vinyl conversion curve reaches a plateau corresponding to about 60% molar conversion after 4 hours at 50°C. An extra 40% conversion then proceeds during the next two hours when the temperature is raised at 80°C leading to the achievement of the PEO network synthesis (99% conversion). Such peculiar temperature profile was set up to obtain smooth surfaces. Indeed perfect surfaces are needed to obtain valuable optical properties for ECD and EED.

Ionic conductivity measurements are performed from 30°C to 80°C on EMITFSI "saturated" networks. Figure 2 shows the temperature dependence of the ionic conductivity of PEO networks with various PEGDM cross-linker compositions. The conductivity of the PEO networks containing 25 and 50 wt% PEGDM reaches a quite high value, i.e., $10^{-3}\,S\cdot cm^{-1}$ at 30°C to nearby $5\cdot 10^{-3}\,S\cdot cm^{-1}$ at 80°C.

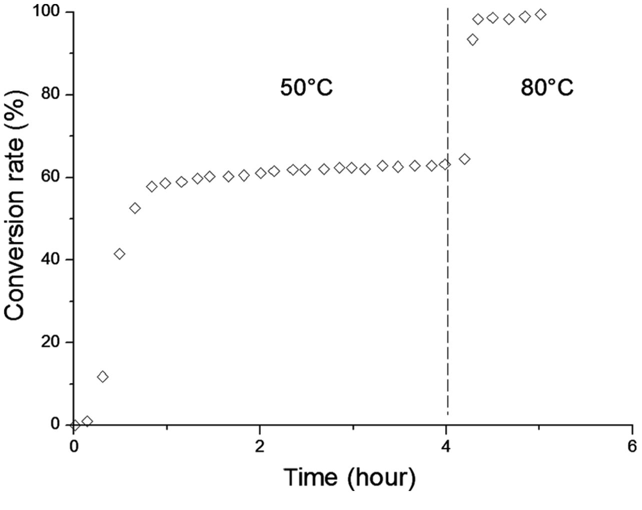


Figure 1. Methacrylate conversion versus time during PEO networks synthesis. AIBN initiator: 1 wt% with respect to PEGDM/PEGM.

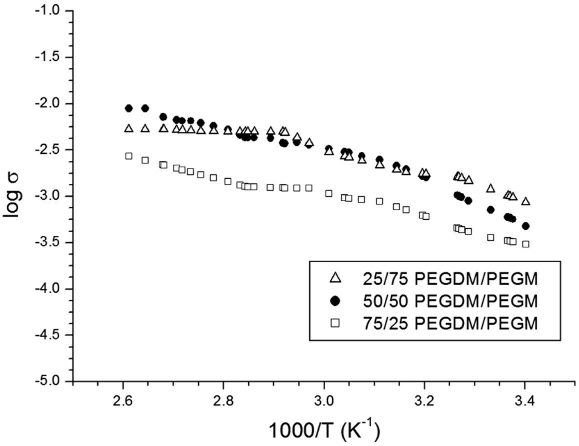


Figure 2. Ionic conductivity for EMITFSI swollen (PEGDM/PEGM) PEO network as a function of the temperature: (▲: (25/75); •: (50/50); □: (75/25).

Those conductivities are only less than one order of magnitude lower than that of neat EMITFSI ($8.10^{-3}\,S\cdot cm^{-1}$ at 25°C). Furthermore, an increase of PEGDM content leads to a decrease of ionic conductivities by a factor 3 in the 30–80°C temperature range. Ionic conductivity can be improved by introducing short poly(ether oxide) side chains into the PEO networks as chain ends in order to build a "branched PEO network" [4]. With more flexible chains, the free volume available for the mobility of counter-ions would be much higher than in unbranched or low branched networks. Therefore PEO networks containing 50 and 75 wt% of PEGM show the highest ionic conductivity and are the best candidates as SPE matrix. However in the forthcoming, a 50 wt% PEGM content is chosen to synthesize the SPEs due to the higher ductility of the resulting materials.

$LiClO_4$/propylene carbonate was also used as electrolyte for electrochromic applications. Then ionic conductivities of EMITFSI and $LiClO_4$/propylene carbonate (23 wt% $LiClO_4$ versus dry sample) swollen PEO networks were compared in Figure 3. One can notice that the ionic conductivities are of the same order of magnitude in both systems. As already mentioned by several authors the ionic liquid has the advantages of being a non volatile solvent with a high ionic conductivity, broadening their field of applications as electrolyte for electrochemical devices [5–8].

Electrochromic Material Synthesis and Characterization

Electrochromic materials are obtained from the above described SPE after addition of either PEDOT or PProDOT-Me_2 as electronic conducting polymer. In both cases the corresponding monomer is mixed in the starting SPE reaction mixture and subsequently, chemically polymerized to PEDOT or PProDOT-Me_2. The oxidative polymerization is carried out by immersing at room temperature the EDOT- (or ProDOT-Me_2) loaded PEO network for various time in a $FeCl_3$ solution. The length of time is set up depending on the required transparency material.

The spectroelectrochemical characterizations of the device were performed by sandwiching the $LiClO_4$ loaded ECP/PEO between two transparent electrodes (ITO glasses) (Fig. 4a,b). When electrically shunting both faces, the ECD exhibits

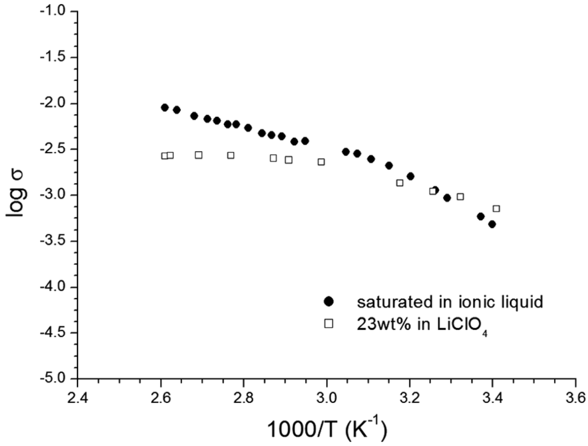


Figure 3. Ionic conductivity for electrolyte saturated (50/50) (PEGDM/PEGM) PEO network as a function of the temperature: ●: EMITFSI; □:$LiClO_4$.

its highest transmittance level i.e., $\%T_0 \sim 15\%$ and $\%T_0 \sim 40\%$ for PEDOT and PProDOT-Me_2 based materials respectively. The quite low values of transmittance are both due to a partial oxidation of the semi-IPN after the synthesis and to the same electrochemical potential between the two sides ($\Delta E = 0\,V$). However, by applying a given voltage, one side is dedoped and behaves very coloured while the other is oxidized and highly transparent. Then the resulting optical behaviour of the system is a low transmission %T1 in the whole visible range wavelength. The optical visible contrast ΔT%, corresponding to $\%T_1 - \%T_0$, is measured between 380 and 800 nm when ΔE varies from 0 to 1.6 V. For both systems, the optical contrast is close to 30% (33% and 30% for PEDOT and PProDOT-Me_2 ECD respectively).

Electroemissive Device Characterization

When increasing the amount of PEDOT within the semi-IPN, its transparency is lost in both IR and visible range and thus cannot be analyzed anymore in transmissive mode. Therefore the reflectivity properties of PEDOT in the infrared range are advantageously used for designing new electroemissive devices. The emissivity ε is the ratio of energy radiated by the material to those of the black body at the same temperature. For an opaque material the reflectivity is complementary to the emissivity. Determination of the emissivity is directly obtained through the reflectivity measurements. Indeed, the reflectivity characterization is highly preferred to emissivity's one due to its easier workings. Usually two electrodes provides the required electronic conductivity to the EED working [9,10]. With its original configuration the semi-IPN EED does not need any additional electrodes since the electronic conductivity, as well as the reflectivity, is afforded by the PEDOT layers. Therefore the reflectivity modulation of PEDOT is obtained by applying a voltage up to ±1.2 V directly to the device. Figure 5 shows the variation of the reflectance (%R) between the oxidized and reduced states, characteristic of the optical changes between 800 and 2500 nm for 0.3 to 11.2 wt% PEDOT loaded semi-IPNs. The %R measurements evidence the optical change upon applied voltage of a thin layer at the surface

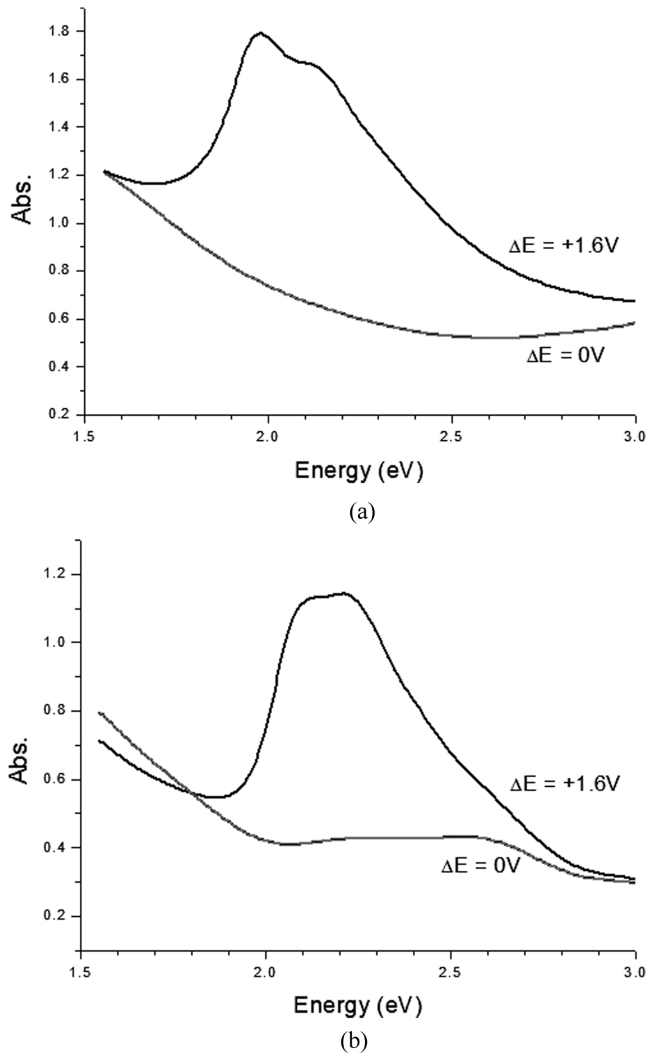
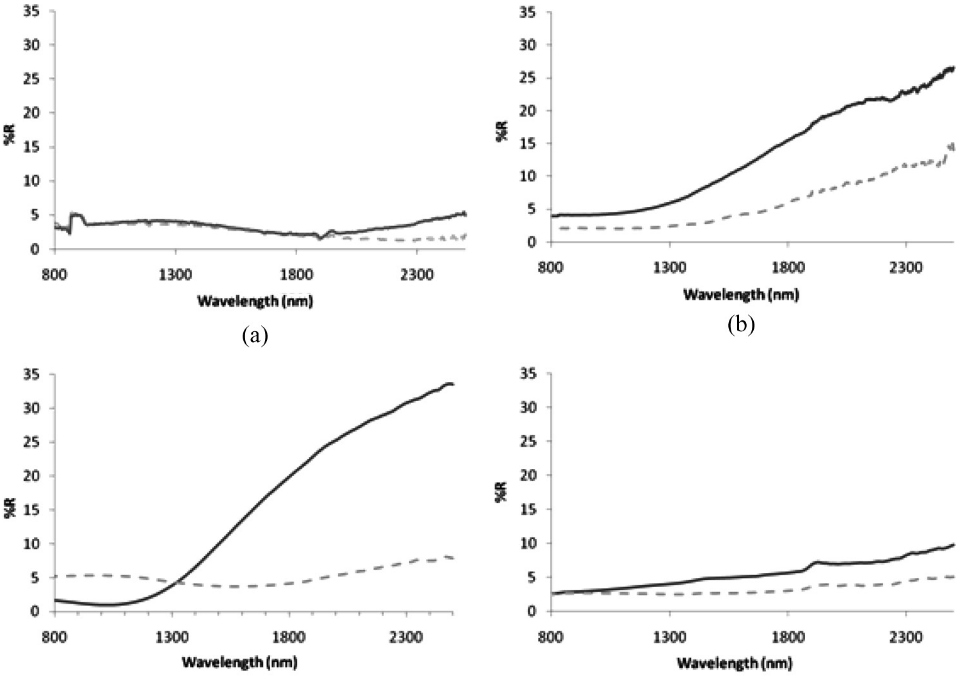


Figure 4. (a) Visible contrast of an ITO|PEDOT/PEO semi-IPN|ITO device in the [350–800nm] range. Applied voltage: ΔE = 0 V (red curve); ΔE = 1.6 V (black curve); (b) Visible contrast of an ITO|PProDOT-Me$_2$/PEO semi-IPN|ITO device in the visible range. Applied voltage: ΔE = 0 V (red curve); ΔE = 1.6 V (black curve).

(around 2 μm depth) facing the incident beam, so-called the active layer. For a 0.3 wt% of PEDOT content the reflectivity is rather low (<5%) as well for oxidized or reduced active layers leading to a negligible optical contrast at 2500 nm c.a. 4% (Fig. 5a). The Figure 5b shows the reflectance for a semi-IPN containing 0.6 wt% PEDOT. The %R at 2500 nm becomes more significant when the active layer is oxidized (%R = 30%) whereas after reduction the device is less reflective (%R = 15%). An optical contrast of Δ%R 15% is then obtained. The highest optical contrast (25%) is achieved for PEDOT content near 1 wt%. For a 1.2 V applied voltage, the PEDOT layer facing the incident beam is getting more reflective at 2500 nm (%R = 33%) and when applying −1.2 V the reduction of the PEDOT layer leads to a low



(a) (b)

(c) (d)

Figure 5. Spectroelectrochemistry in the Near Infrared range of PEO/PEDOT semi-IPN based device. PEDOT content: (a) 0.3 wt%; (b) 0.6 wt%; (c) 1.1 wt%; and (d) 11.2 wt%. Oxidized state: full line; reduced state: dotted line.

value of reflexion (%R = 8%) (Fig. 5c). Surprisingly, further increase of the PEDOT percentage does not improve the optical contrast, on contrary, quite the opposite is observed. When the PEDOT content increases until 11.2 wt%, the PEDOT "layer" thickness on the edges of the film also increases. Then, the quantity of PEDOT in the central part of the film is too high and induces short circuiting, resulting in a hard redox reaction achievement.

Conclusion

An efficient architectural macromolecular concept is proposed combining a functional polymer (an electronic conducting polymer) with a structural polymer (PEO network). Although embedded inside the PEO network, the ECP keeps its electrochromic and electroreflective properties. High optical contrasts in the visible (in absorption) and IR (in reflexion) range are obtained.

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