Feasibility of Conducting Semi-Interpenetrating Networks Based on a Poly(ethylene oxide) Network and Poly(3,4-ethylenedioxythiophene) in Actuator Design

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ABSTRACT: A new type of synthetic pathway—the use of interpenetrating polymer networks (IPNs)—is proposed to design conducting polymer-based actuators. Two types of materials with interesting conducting properties were prepared: (1) a semi-IPN between poly(3,4-ethylenedioxythiophene) (PEDOT) and branched poly(ethylene oxide) (PEO) network; (2) a tricomponent IPN between PEDOT and a PEO/polycarbonate (PC)–based network as the ionic conducting partner. In the first case, the influence of the amount of branching in the PEO network on the EDOT uptake and electrochemical properties was studied. A maximum conductivity (15 S cm^{-1}) was obtained for 60 wt % branched PEO in the material. Moreover, the dispersion profile of PEDOT in the material was shown by elemental analysis and energy dispersion spectroscopy to follow a gradient through the thickness of the film leading to a built-in three-layered device. With respect to PEO/PC materials, the best results were obtained for about 80 wt % PEO in the matrix where the material remains sufficiently elastomeric. In this case, the conductivity reaches about 1 S cm^{-1} for a 10 to 30 wt % polycarbonate content. These materials are capable of reversible 45° angular deflections under a 0.5V potential difference. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3569–3577, 2003

Key words: actuators; networks; conjugated polymers; interpenetrating networks (IPN); polycarbonates

INTRODUCTION

Conducting polymers are now considered a very important class of materials showing interesting electrical and optical properties. However, it is well-known that several among these polymers are insoluble in common solvents and usually decompose before melting.[1] In this case, the conventional methods of polymer processing cannot be used. Extensive studies have been carried out to overcome the poor processability of such compounds. On the other hand, conducting polymers seldom possess good mechanical properties. Two approaches have been widely investigated to obtain conducting materials with both good mechanical properties and good electronic conductivity (i.e., blends of conducting and insulating polymers, the latter being used for its mechanical properties as well as the preparation of conducting composites).[2] One possibly promising solution could be the combination of a conducting and an insulating polymer into interpenetrating polymer networks (IPNs). IPNs are defined as a combination of two or more polymer networks necessarily synthesized in the presence of each other.[3,4] The presence of entangled crosslinks increases the miscibility of the polymers compared to usual blends and leads to a material with good dimensional stability. Semi-IPNs are the combination of at least one crosslinked polymer and one linear polymer. Specific noncovalent interactions between the linear and the crosslinked component can lead to a semi-IPN system where the linear polymer is definitely trapped in the structure although not covalently crosslinked. The aim of these types of polymer associations in general is to obtain materials (1) with better mechanical properties, (2) with dimensional stability, and (3) a possibly improved combination of the properties of its components. The synthesis of several electronic conducting semi-IPNs have been reported.[5–10] In most reported cases, the observed volume percolation threshold for conductivity (generally <5%) is lower than that observed in statistical blends (e.g., 16 vol %).

Conducting polymers have also attracted considerable attention notably because of possible dimensional changes generated by the expulsion/inclusion of ions during oxidation or reduction processes.[11–25] Conducting polymers thus can be used as the active material in actuators or artificial muscles and lead to interesting potential applications (robotics, prosthetics, microvalves, etc.). Among electronic conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has received much attention recently because of its particularly high stability in the doped state and the

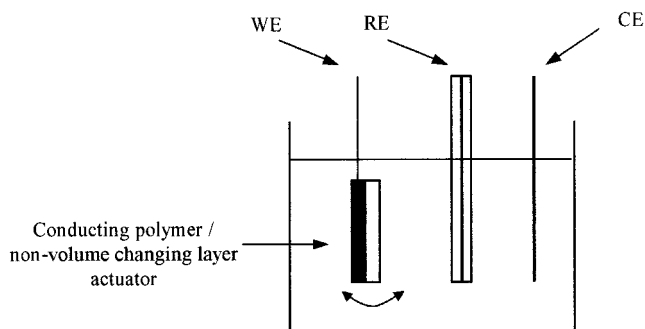*Correspondence to:* D. Teyssié (dominique.teyssie@chim.u-cergy.fr).

Figure 1 A three-electrode electrochemical cell with an actuator as the working electrode (WE). RE and CE are the reference and the counter electrode, respectively.

reversibility of the doping process. This polymer is thus potentially very attractive for applications involving electrochemical actuators.[26]

Most polymer-based electrochemical actuators exhibit dimensional changes when immersed in electrolyte solutions. The polymer actuator is used as a working electrode in the presence of a reference electrode and a counter electrode in a three-electrode device. Thus when the conducting polymer is combined into a bilayered structure with a non-volume-changing layer, the volume change occurring in the conducting polymer can be used to formulate an actuator (Fig. 1).[12,23] However, actuators working in air have also been described. In this case they are necessarily multilayered structures (Fig. 2), in which a relative differential expansion between layers results in bending.[24] To achieve such a "dry system" the electrolyte will be preferentially a solid polymer electrolyte (SPE). The main disadvantage of SPEs is the low diffusion coefficient of the counter-ion species, which leads to a slow responding system.

Solid polymer electrolytes based on poly(ethylene oxide) (PEO) have been investigated extensively as ionic conducting materials.[27,28] The oxygen atoms in PEO can coordinate metal cations (usually Li^+) and improve ion-pair separation, which in turn can favor increased electrical conduction through ion transport. However, one of the main drawbacks of PEO-based SPEs is the often significant degree of crystallization at ambient temperature. Indeed ion migration mainly takes place in the amorphous part of the polymer and the crystalline regions decrease ion mobility both by blocking the paths of ions and by reducing the overall polymer flexibility. To decrease the crystallinity of PEO, a variety of approaches have been used such as the preparation of networks with relatively short PEO segments.[29,30] However, the network nature of the structure decreases the polymer flexibility and, consequently, the ionic conductivity. All these expected improvements nevertheless do not lead to conductivities higher than 10^{-4} S cm^{-1}. Ionic conductivity could also

be improved by introducing short poly(ether oxide) side chains into the PEO networks as chains ends (i.e., building a "branched PEO network").[31] The flexibility of the chains would be less restricted than in an unbranched network and the amount of volume available for the migration of counter-ions would be much higher. Using this approach, branched PEO networks have been reported with a maximum conductivity of 5.1×10^{-4} S cm^{-1} at 30°C.[31,32] In a similar way, SPEs based on polysiloxane networks bearing PEO grafts were synthesized and the optimum conductivity was 7.9×10^{-5} S cm^{-1} at room temperature.[33] Polysiloxanes bearing PEO grafts have also been combined with polysiloxanes into IPN-type SPEs that exhibited ionic conductivities in the range of 10^{-4} S cm^{-1}.[34] Recently the synthesis of IPNs based on PEO and poly(methyl methacrylate) was reported by Siow et al.[35] The ionic conductivity at room temperature is reported as high as 10^{-3} S cm^{-1}.

In this study, we report the synthesis of two kinds of SPEs. The first is a branched solid polymer electrolyte network containing low molecular weight pending PEO chains covalently bound to the network. This SPE, which is a simple network, is obtained by radical copolymerization of poly(ethylene glycol) dimethacrylate and methoxy poly(ethylene glycol) methacrylate. The second SPE is a full IPN synthesized from poly(ethylene glycol) dimethacrylate and diethyleneglycol bis(allyl carbonate). In this latter case, the first network (i.e., PEO-based) will be able to complex lithium salts and act as the solid electrolyte partner and the second network in the IPN will ensure good mechanical properties. Conducting semi-IPNs have been synthesized from poly(3,4-ethylenedioxythiophene) (PEDOT) and the two SPEs just mentioned. Thus the first is a bicomponent conducting system, and the second is a three-component system. The presence of ethylene oxide units both in the PEO and polycarbonate (PC) networks and the ethylenedioxy function of PEDOT, will ensure a compatibilizing effect and should help the formation of the interpenetrating polymer network.[36] The synthetic pathway that will be presented for the two conducting materials ensures a gradual dispersion of the electronic conducting poly-
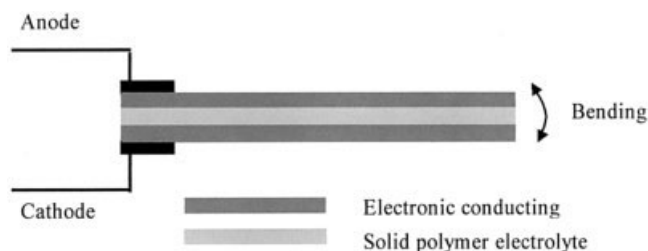

Figure 2 "Dry system" three-layer actuator. The solid polymer electrolyte is sandwiched between the electronic conducting polymer anode and cathode.

mer through the thickness of the network; that is, the quantity of PEDOT decreases from the outside toward the center of the film. The system is thus similar to a layered device with the advantage that the conducting polymer is protected from the environment and the intimate combination of the three polymers needs no adhesive interface. The influence of the morphology and chemical composition of the matrix on the conductivity of the material is a primary focus of this study. The electrical conductivity of these semi-IPN materials is quite high (i.e., 10^1 S cm^{-1}), and thus the actuator capacity was appraised.

EXPERIMENTAL

Materials

Methoxy poly(ethylene glycol) methacrylate (MPEGM, M_w = 300) and poly(ethylene glycol) dimethacrylate (PEGDM, M_w = 875) were obtained from Aldrich Chemical (Milwaukee, WI) and used without further purification. Diethyleneglycol bis(allyl carbonate) (DEGBAC; Aldrich) and 3,4-ethylenedioxythiophene (EDOT; Bayer AG, Leverkusen, Germany) were distilled under reduced pressure before use. Acetonitrile (HPLC grade; Acros Organics, Belgium), dichloromethane (Carlo-Erba, Milan, Italy), methanol (Carlo-Erba), anhydrous iron III chloride (Acros Organics), lithium perchlorate (Aldrich), dicyclohexylperoxydicarbonate (DCPD; Groupe Arnaud, Peroxid-chemie, Germany) were used without further purification. Benzoyl peroxide (BPO; Acros Organics) was dried under vacuum at room temperature. Azobisisobutyronitrile (AIBN; Acros Organics) was recrystallized from methanol and dried under vacuum at room temperature.

Synthesis

Preparation of branched PEO network SPEs

The preparation of branched PEO networks was carried out by free-radical copolymerization in the bulk. PEGDM and MPEGM mixtures containing up to 90 wt % MPEGM were stirred under nitrogen atmosphere with AIBN (0.5 wt % of the total mass). The mixture was poured into a glass mold to yield 250-μm-thick film. The mold was placed in an oven at 80°C for 6 h. The PEO network was postcured for 1 h at 100°C.

Throughout this study, a PEObrX network stands for a PEO network with X wt % of branching MPEGM in the starting copolymerization mixture.

Preparation of PC/PEO IPN SPEs

The DEGBAC, PEGDM, and the initiator mixture (DCPD and BPO, 1 wt % each of the total mass) were stirred together and poured into a glass mold under the same conditions described for branched PEO network preparation. The mixture was heated at 35°C for 2 h to promote the formation of the PEO network. The reaction temperature was then increased to 80°C for 2 h, allowing the PC network and thus the IPN formation. The IPN was postcured for 1 h at 100°C.

Preparation of conducting polymer–based (semi-)IPN

The SPE films were soaked in pure EDOT for given lengths of time from 5 to 60 min after which each surface was wiped off with filter paper. The swollen films were then immersed for 24 h in a FeCl$_3$/water solution (1.5 mol L^{-1}). The film was washed several times with methanol until the solvent remained colorless (i.e., the FeCl$_3$ excess was removed). The film surface was then wiped off with filter paper. The conducting material was dried at 60°C under vacuum for 24 h.

Gel-time study

The macroscopic gel time was determined separately for each network or IPN composition, defined for each system as the time for the magnetic stirrer to come to a complete stop when the experiment was carried out in a flask.

Characterizations

The quality of each network or IPN was determined by measurement of the amount of extractible material after 3 days' dichloromethane Soxhlet extraction. The extractible content (EC) is given as a weight percentage, as follows:

$$EC\ (\%) = \frac{W_0 - W_E}{W_0} \times 100$$

where W_0 and W_E are the weights of SPE samples before and after extraction, respectively.

Glass-transition temperature (T_g) values were taken as the onset point from the second heating curves recorded at a 20°C min^{-1} heating rate on a Mettler TA 4000 (Greifensee, Switzerland).

To examine the swelling behavior, dry films (approximate dimensions 10 × 20 × 0.250 mm) with accurately known weights were immersed in pure EDOT at room temperature. The films were removed from pure EDOT at different times and carefully wiped. The EDOT monomer contents (EMC) in the samples are defined as

$$EMC\ (\%) = \frac{W_s - W_0'}{W_s} \times 100$$

where W_0' and W_s are the weights of SPE samples before and after swelling, respectively.

The two-terminal technique with gold pressure contact was used for the room-temperature conductivity measurements. Measurement of the conductivity was performed along the surface (σ_s) and across the thickness or bulk (σ_b) with a Keithley 197 autoranging microvolt DMM (Keithley Metrabyte, Taunton, MA). For the measurement of σ_s, the interspacing of electrodes (area of 1.8 mm^2) was 1 cm. The bulk conductivity was measured after cutting the film edges to suppress the electrical conductivity contribution through the edges along the surface. The morphology of the samples was observed with a Leica S430i scanning electron microscope (Leica, Milton Keynes, Buckinghamshire, UK). The films were first frozen in liquid nitrogen and fractured mechanically. They were then vacuum-dried at room temperature for 24 h before they were coated with nickel. Sulfur mapping was performed on IPNs using an energy dispersion spectrometer (EDS).

Deformation testing

The setup for the electric stimulation of the films is a simple clamp connected to a generator (see Photo 1 below). After the edges were cut out, the conducting IPNs (approximate dimensions $10 \times 20 \times 0.250$ mm) were immersed in LiCLO$_4$/water solution (10^{-1} mol L^{-1}) for 24 h. The conducting IPNs were maintained vertical with steel clamps to ensure electrical contact with the Thurbly Thandar Instruments PL 320 generator. The displacement response was stimulated by applying a potential between ± 0.5 and ± 1.5 V.

RESULTS AND DISCUSSION

Synthesis and characterization of SPE materials

Moderately to highly branched PEO networks

A series of branched PEO networks were prepared by radical copolymerization of PEGDM and MPEGM with AIBN as initiator (0.5% of the total weight). The relative weight proportions of the MPEGM were varied between 5 and 90% [the 0% sample (i.e., a pure PEGDM network) was taken as a blank]. The polymerizations were carried out under nitrogen atmosphere at 80°C for 6 h. The samples were then postcured for 1 h at 100°C. The resulting networks showed less than 6% extracted material in all cases. Characterization by DSC shows that all networks were amorphous; thus the synthesis of branched PEO networks is effective in giving materials with low T_g values, which are shown in Figure 3 as a function of the amount of MPEGM. The value of T_g decreases from -48°C to -66°C with MPEGM content increasing from 0 wt % (noted as PEObr0) to 90 wt % (noted as PEObr90) (i.e., decreas-
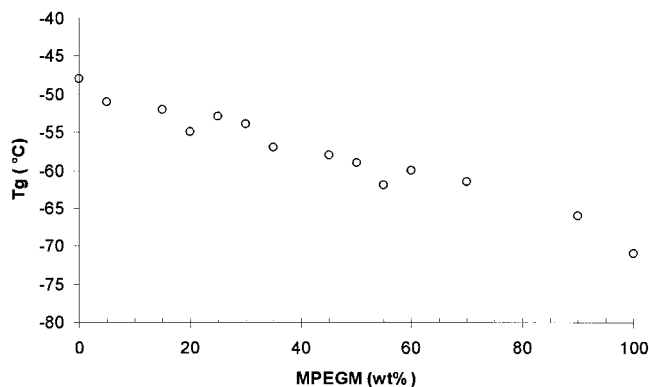

Figure 3 Glass-transition temperatures (T_g) of branched PEO networks as a function of MPEGM wt % (measured at the onset of the second heating at 20°C min^{-1}).

ing the crosslinking density). However, for the EDOT-loaded sample preparation, the MPEGM content was kept below 60 wt % to avoid tearing the sample.

PEO/PC IPNs

IPN SPEs based on a combination of one PEO network and one PC network were prepared exclusively from DEGBAC and PEGDM (i.e., they did not contain branched PEO units). These IPNs were synthesized by a two-step *in situ* method. In this method all reactants are mixed together before initiation, but the reaction mechanisms leading to the two network partners must be different; otherwise a single copolymer network is formed through crossed reactions. However, copolymerization can be prevented even in the case of a single polymerization mechanism, providing the two monomers have quite different reactivities toward free radicals, for instance, as is the case here.[37] Indeed in this work, the *in situ* sequential IPN strategy was chosen because the terminal methacrylate double bonds of PEGDM are more reactive than the allylic double bounds of DEGBAC. Thus two different initiators, each specific to one system and which decompose at two different temperatures, were used. The PEO network was formed first at a moderate temperature (35°C) using DCPD as an initiator, which decomposes at low temperature. Then, by increasing the temperature to 80°C after completion of the first polymerization, the decomposition of BPO occurred, leading to the formation of the polycarbonate network. The general scheme of the *in situ* sequential IPN synthesis is shown in Figure 4.

The time–temperature profiles for the IPN synthesis were determined separately from gel-time experiments (Table I) on PC and PEO systems, respectively. With DCPD as initiator at 35°C, the gel times were 20 min for PEGDM and 30 h for DEGBAC, confirming the widely different reactivity of each type of double
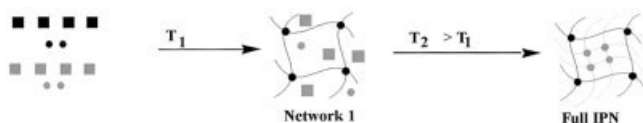
Figure 4 *In situ* sequential IPN synthesis scheme. ■, PEGDM monomer 1; ●, DCPD initiator; ▨, DEGBAC monomer 2; ◉, BPO initiator. Network 1: DEGBAC swollen PEO network.

TABLE II
Amounts of Extractible Compounds (EC) from PEO/PC IPNs as a Function of DEGBAC wt %

	DEGBAC (wt %)			
	0	10	20	30
EC (wt %)	1.2	8.6	11.7	8.4

bonds. Similarly at 35°C with BPO as initiator, the gel time of PEGDM was about 3 h and no gel was observed after 3 days with DEGBAC monomer. At 80°C, BPO leads to PEGDM gel formation within 5 min and to DEGBAC gel within 1 h. Because of the large difference in gel time, it is possible to prepare *in situ* sequential IPNs without noticeable copolymerization between DEGBAC and PEGDM. Thus the monomer and initiator mixture was heated at 35°C for 2 h, leading to the formation of the PEO network through the methacrylate functions; the temperature was then increased and kept at 80°C for 2 h, leading to the formation of the PC network through the allyloxicarbonate functions. Finally, the IPN was postcured for 1 h at 100°C.

To determine more precisely whether copolymerization occurs during the IPN synthesis, a 50/50 wt % PEGDM and DEGBAC mixture was heated with 1 wt % DCPD with respect to PEGDM mass at 35°C for 2 h. The experiment was repeated twice. The resulting materials were then submitted for 3 days to CH_2Cl_2 Soxhlet extraction and the extractible contents were 50 and 58 wt %, respectively, which corresponds approximately to the expected weight percentage of carbonate monomer if it had not polymerized at all. As determined by ^{1}H-NMR, the extracted product was composed of DEGBAC (>95%). Therefore, DCPD was able to initiate the formation of PEGDM networks without initiating allyl monomers (DEGBAC). The formation of the two networks was thus separate and occurred without cross-copolymerization.

A series of POE/PC IPNs was prepared from various relative weight proportions (10, 20, 30 wt %) of DEGBAC. The amounts of extractible material (as measured after Soxhlet extraction in CH_2Cl_2) were below 12% (Table II). Characterization by DSC shows that all investigated IPNs exhibited a single glass-transition temperature (T_g). The T_g values of the IPNs were all about −45°C even though the polycarbonate content varied from 10 to 30 wt %. Because the PC and POE network T_g values were about 96 and −48°C, respectively, the glass-transition temperature of the IPN probably was attributable mainly to the contribution of the PEO network. In the *in situ* two-step IPN synthesis scheme, the morphology of the final IPN generally depends on a number of factors such as the crosslinking density of the first polymer (PEO in this case), the volume fraction of each polymer, the interfacial tension, and the temperature. In the present PEO/PC IPNs, the T_g values close to that of the pure PEGDM network might reflect that the PEO phase is the continuous phase. The PC phase, the T_g of which is not distinct, would thus be dispersed in this continuous phase as suggested by Hou and Siow.[35]

EDOT swelling studies of the PEO networks and the PEO/PC IPNs

According to the procedure described earlier in the experimental section, the mass quantity of EDOT loaded in the SPEs (EMC) can be controlled by the duration of the swelling in pure EDOT. This mass quantity measures the amount of EDOT trapped within the SPE matrix. Figure 5 shows the kinetics of the absorption of EDOT in the different networks. A plateau value around 60 wt % EDOT is obtained after 20 min for a POEbr60 network; for a PEObr0 network, the plateau value is around 40% after 1 h. This high affinity may reflect a specific interaction between the ethylenedioxy function of EDOT and the ethylene oxide units in the PEO chains. Figure 6 shows the EMC of various branched networks for a 20-min immersion in EDOT. It can be observed that the EMC of networks increases from 28 to 55% with decreasing crosslinking density (i.e., with increasing MPEGM content from 0

TABLE I
Gel-Time Values for Different Monomer/Initiator Combinations at 35 and 80°C

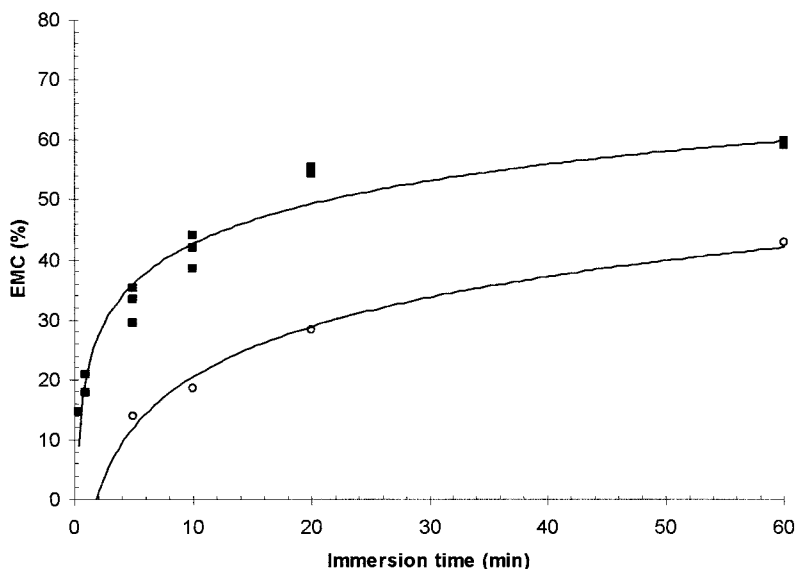| Temperature (°C)	DCPD initiator		BPO initiator	
	PEGDM	DEGBAC	PEGDM	DEGBAC
35	15–20 min	25–30 h	3 h	No gel after 3 days
80	—	—	5 min	1 h

Figure 5 Absorption kinetics of EDOT in PEO-based networks dipped in pure EDOT. ■, PEObr60 network; ○, PEObr0 network.

EDOT polymerization in SPEs

Conducting (semi-) IPNs were prepared by dipping the EDOT-swollen SPE films into an iron III chloride (FeCl$_3$) solution. Several solvents were used for FeCl$_3$ but only the results in acetonitrile and water (which correspond to extreme behaviors) will be described. It was observed that the locus of polymerization, and thus the conductivity of the resulting (semi-) IPN, depends on the nature of solvent. Different processes govern the distribution of the electronic conducting polymer throughout the thickness of the IPNs. Among these processes, the following experiments suggest that the exit rate of EDOT from the film and the entry rate of FeCl$_3$ into the matrix seem to play a major role.

to 60 wt %), which clearly indicates that the volume available in the network for the inclusion of foreign molecules varies in a trend that can be controlled as a function of the chosen synthesis strategy.

Figure 7 shows the EDOT uptake kinetics of PEO and PC single networks as well as various PEO/PC IPNs. Unexpectedly, no specific trends were observed in the swelling behavior of the IPNs as a function of the PC content (i.e., from 10 to 30 wt % EDOT). The EDOT absorption rates of IPNs are close to the absorption rate of the single PEO network. After 1 h, the EMC value for all materials is about 45%. It may also be noticed that the EMC of the single PC network is very low (<1%). With respect to EDOT uptake, the IPN behavior is similar to that of the PEO network.
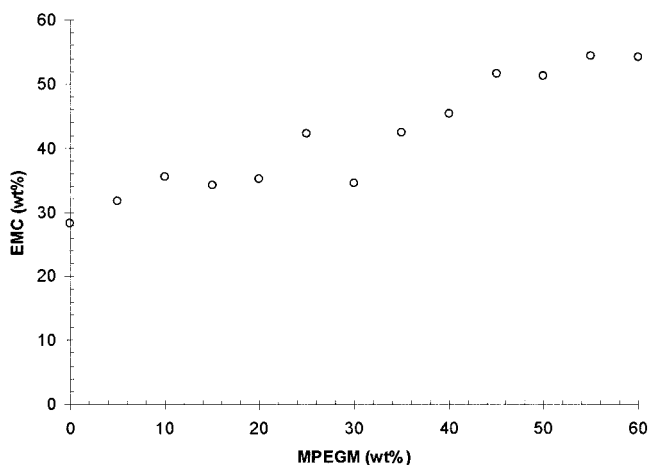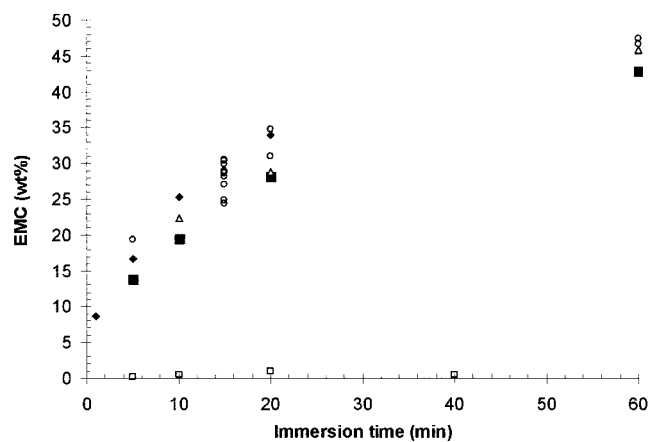

Figure 6 EDOT monomer content (EMC) for 20 min immersion in pure EDOT of various branched PEObrX networks.

Figure 7 EDOT Absorption kinetics of PEO and PC networks and of PEO/PC IPNs dipped in pure EDOT. ■, PEO network; △, PEO/PC (90/10 w/w) IPN; ○, PEO/PC (80/20 w/w) IPN; ◆, PEO/PC (70/30 w/w) IPN; □: PC network.
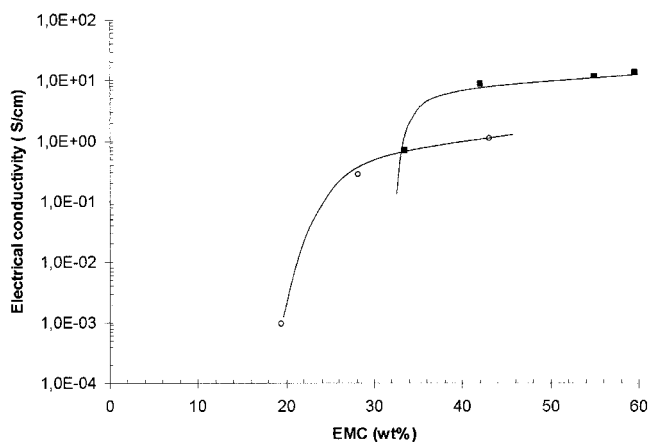
Figure 8 PEO/PEDOT semi-IPN electrical conductivity on the surface as a function of initial EDOT monomer content. ○, PEObr0/PEDOT semi-IPN; ■, PEObr60/PEDOT semi-IPN.

If the EDOT-swollen materials are dipped into an acetonitrile 1.5 mol L^{-1} $FeCl_3$ solution, the EDOT desorption is quasi-instantaneous, as shown by the appearance of a black-colored precipitate corresponding to polymerization in the solution, followed by the PEDOT precipitation on the film surface.[38] In this case, after the film surface was wiped off, the electrical conductivity is as low as 5×10^{-7} S cm^{-1}. Furthermore a fast film degradation was observed within less than 15 min, probably attributable to the release of protons during the oxidative polymerization of EDOT and the subsequent hydrolysis of the methacrylate function in the PEO network.[9] The same experiments in water gave quite different results. Because of the low EDOT solubility in water (about 1.5×10^{-2} mol L^{-1}), the polymerization rate and the diffusion of EDOT from the film into the aqueous $FeCl_3$ solution are much slower, which allows the penetration of $FeCl_3$ into the matrix before a significant amount of EDOT leaves the matrix. Nevertheless some conducting polymer is generated on the film surface and forms a shield that limits the inward diffusion of $FeCl_3$. This behavior can be used to advantage, especially bearing in mind the fact the preparation of IPNs with a gradual dispersion of the conducting polymer throughout the thickness would be an asset. Furthermore, in water, no degradation of the film was observed such that water was chosen as the solvent for $FeCl_3$ in further experiments.

After the general experimental conditions for the preparation of conducting materials were established, the effect of MPEGM content in PEO branched networks (i.e., the influence of the available volume for PEDOT) on the semi-IPN conductivity was investigated and the results are depicted in Figures 8 and 9.

First, two SPE matrix series with extreme crosslinking densities (100 and 40%, which are the maximum

and the lowest useful proportion of PEGDM crosslinker, respectively) were prepared and swollen with increasing initial amounts of EDOT. The conductivities after EDOT polymerization in these samples are compared in Figure 8 as a function of the initial EDOT fraction. As expected, the electrical conductivity increases with the amount of initially absorbed EDOT. It may also be noticed that for an identical initial EDOT content, the conductivity of the lightly crosslinked sample (PEObr60/PEDOT) is higher than the conductivity of the fully crosslinked sample (PEObr0/PEDOT): the electrical conductivity increases, for example, from 1 to 5 S cm^{-1} (for 40% initial EDOT content).

The effect of crosslinking is further confirmed by the results presented in Figure 9, where the electrical conductivity of samples each swollen with their maximal potential EDOT content is plotted against the crosslinking density from 100 to 40%. Thus, each sample containing the maximum possible amount of EDOT should exhibit its maximum conductivity value, which value is on the plateau of its percolation curve, far beyond the percolation threshold. Thus the differences in the conductivities exhibited by this series of samples should reflect mainly the differences in the initial EDOT monomer content, which in turn is controlled by the crosslinking density. Furthermore these conductivity variations should not exceed the limits depicted by the two extreme plateau values appearing in Figure 8 (i.e., 3×10^{-1} and 14 S cm^{-1}). The maximum conductivity value (i.e., 14 S cm^{-1}) appears on this curve as soon as the crosslinking density reaches 50%. This value is close to the conductivity values of pure PEDOT prepared with $FeCl_3$ (between 5 and 15 S cm^{-1}) reported by Jonas et al.[39] This latter value must be considered as a maximum reachable value for that type of PEDOT synthesis, and thus
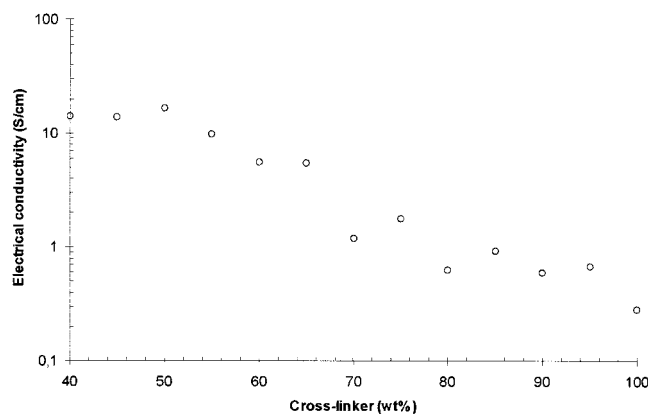

Figure 9 PEO/PEDOT semi-IPN electrical conductivity on the surface as a function of PEGDM (crosslinker) amount in PEO branched networks. Before PEDOT polymerization, PEO branched networks were dipped for 20 min in pure EDOT.

Figure 10 EDS picture of PEObr20/PEDOT semi-IPN cross section. White spots represent the sulfur domains.

no conductivity higher than 15 S cm^{-1} can be expected in our samples even for crosslinking densities lower than 50%. Thus the final conclusion from these two figures is that the increase in the internal volume corresponding to a decrease in the crosslinking density leads to an increase in the absorption of EDOT and a subsequent increase in electrical conductivity within the crosslinking density range available for study. These observations can also be related with the fact that the glass-transition temperatures of the same samples increase by 10°C when the crosslinking density increases.

Finally, in the case of PEO/PC/PEDOT IPN, no specific trend was observed for PC contents varying from 10 to 30 wt %, for which the conductivity value is constant and remains around 1 S cm^{-1}.

For all samples, semi-IPNs and IPNs, the bulk conductivity σ_b was at least 10^2 lower than the electrical conductivity along the surface (σ_s). This result implies that there is an inhomogeneous distribution of PEDOT across the sample thickness; that is, the concentration decreases from the outside toward the center, leading to a very poor connectivity of PEDOT inside the bulk of the matrix. To confirm this point a semiquantitative analysis was performed on one sample: a sulfur element mapping in the PEObr20/PEDOT semi-IPN was carried out with an energy dispersion spectrometer (EDS) across the thickness. The EDS image is reported on Figure 10. The white spots represent the sulfur domains clearly showing that there is a sulfur gradient (i.e., a PEDOT gradient throughout the thickness of the sample). The cross section was also examined by SEM. A homogeneous material was obtained and no phase segregation appears at the SEM level. On the same sample, a sulfur elemental analysis was performed that confirmed a PEDOT content of 5.7 wt %, whereas the initial weight proportion of EDOT loaded in the PEObr20 SPE was 50%. This result means that the main locus of the EDOT polymerization is outside the film, in the water, and only few EDOT molecules could polymerize inside the matrix.

Actuator capacity

All the samples tested for actuator capacity exhibited an electrical conductivity between 10^{-1} and 1 S cm^{-1}.

Conducting semi-IPNs, PEObrX/PEDOT (X = 20, 40, 60) and conducting IPN POE/PC/PEDOT (POE/PC 80/20 weight proportion) were dipped in LiClO$_4$/water solution (10^{-1} mol L^{-1}) for 24 h. The design of the actuators consisted of SPEs with a gradual dispersion of conducting polymers from the surface to the center of the film, with PEDOT playing the role of electrodes. These conducting (semi-) IPNs were used to build actuators that produced bending (Photo 1). The first results demonstrate the feasibility of such actuators, all of which show a bending deformation for an applied potential of ±1.5 V, but it was also possible to move the materials between intermediate positions, for instance, for applied potentials of ±0.5 or ±1 V. The response times ranged from 5 s to 3 min depending on the samples and the applied voltages.

CONCLUSIONS

First of all, because the maximal observed electrical conductivity values of the proposed material were close to values reported for pure PEDOT, these materials could be considered for various applications as electronic conducting elastomers. In this study the feasibility of a new type of IPN-based actuator architecture was demonstrated that would lead to a system with 45° angular deflection under low applied voltages. The device consisted of poly(3,4-ethylenedioxythiophene) and either a branched PEO network or a PEO/polycarbonate IPN. The dispersion of the conducting polymer in this device followed a symmetrical decrease from both outside faces toward the center, where the quantity of electronic conducting polymer was very low, whereas the quantity of ionic conducting polymer was maximum. This gradient dispersion led to electrical conductivity values (reaching 14 S cm^{-1}) that are at least 100 times higher than conductivities across the thickness of the sample. This built-in gradient distribution through the thickness of the material led to an electrochemical and mechanical behavior that was similar to that of a typical three-layer actuator.

This structure, compared against a three-layer actuator, exhibited other advantages, primarily that the conducting polymer is permanently protected from
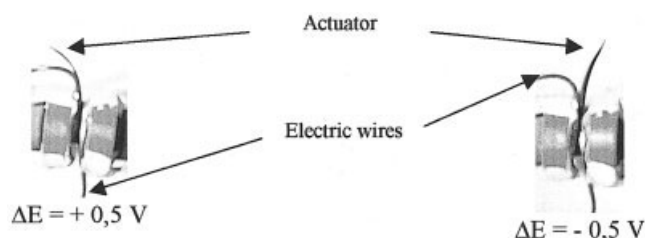

Photo 1 Bending of POE/PC (80/20 w/w)/PEDOT IPN under 0.5 V.

the environment (it is not extractible). Furthermore the problem of adhesive interfaces between the PEDOT and the solid polymer electrolyte was suppressed by construction and replaced by a much larger interaction surface through the architecture of the IPN. The improvement of the time response and other molecular characteristics of the device will be described in a forthcoming study.

References

1. Nalwa, H. S., Ed. Handbook of Organic Conductive Molecules and Polymers, Vol. 2. Conductive Polymers: Synthesis and Electrochemical Properties; Wiley: New York, 1997.

2. De Paoli, M.-A. In: Conductive Polymer Blends and Composites, Nalwa, H. S., Ed.; Handbook of Organic Conductive Molecules and Polymers, Vol. 2. Conductive Polymers: Synthesis and Electrochemical Properties; Wiley: New York, 1997; pp. 773–795.

3. Sperling, L. H.; Klempner, D.; Utracki, L. A., Eds. Interpenetrating Polymer Networks; American Chemical Society: Washington, DC, 1991.

4. Kim, S. C.; Sperling, L. H., Eds. IPNs Around the World: Science and Engineering; Wiley: New York, 1997.

5. Wang, Y. Macromolecules 1992, 25, 3284.

6. Yin, W.; Li, J.; Li, Y.; Wu, J.; Gu, T. J Appl Polym Sci 2001, 80, 1368.

7. Chakraborty, M.; Mukherjee, D. C.; Mandal, B. M. Synth Met 1999, 98, 193.

8. Henry, C.; Armand, F.; Araspin, O.; Bourgoin, J.-P.; Waegner, G. Chem Mater 1999, 11, 1024.

9. Dassonville, P.; Vidal, F.; Randriamahazaka, H.; Chevrot, C.; Teyssié, D. Synth Met 2002, 128, 197.

10. Jeevananda, T.; Begum, M.; Siddaramaiah. Eur Polym J 2001, 37, 1213.

11. Baughman, R. H. Synth Met 1996, 78, 339.

12. Osada, Y.; De Rossi, D. E., Eds. Polymer Sensors and Actuators; Springer-Verlag: Berlin/New York, 2000.

13. Bar Cohen, Y., Ed. Electroactive Polymer Actuator as Artificial Muscle; Bellingham, WA: SPIE, 2001.

14. Lewis, T. W.; Kane-Maguire, L. A. P.; Hutchison, A. S.; Spinks, G. M.; Wallace, G. G. Synth Met 1999, 102, 1317.

15. Hutchison, S.; Lewis, T. W.; Moulton, S. E.; Spinks, G. M.; Wallace, G. G. Synth Met 2000, 113, 121.

16. Madden, J. D.; Cush, R. A.; Kanigan, T. S.; Hunter, I. W. Synth Met 2000, 113, 185.

17. Otero, T. F.; Villanueva, S.; Cortés, M. T.; Cheng, S. A.; Vasquez, A.; Boyano, I.; Alonso, D.; Camargo, R. Synth Met 2001, 119, 419.

18. Mazzoldi, A.; Degl'Innocenti, C.; Michelucci, M.; De Rossi, D. Mater Sci Eng 1998, C6, 65.

19. Marsella, M. J.; Reid, R. J.; McCormick, M. T. Synth Met 2001, 118, 171.

20. Morita, S.; Shakuda, S.; Kawai, T.; Yoshino, K. Synth Met 1995, 71, 2231.

21. Okuzaki, H.; Funasaka, K. Macromolecules 2000, 33, 8307.

22. Pépin-Donnat, B.; Van-Quynh, A. Macromolecules 2000, 33, 5912.

23. Jager, W. H.; Smela, E.; Inganäs, O. Sens Actuators B 1999, 56, 73.

24. Madden, J. D.; Cush, R. A.; Kanigan, T. S.; Brenan, C. J.; Hunter, I. W. Synth Met 1999, 105, 61.

25. Small, C. J.; Too, C. O.; Wallace, G. G. Polym Gels Netw 1997, 5, 251.

26. Chen, X.; Xing, K.-Z.; Inganäs, O. Chem Mater 1996, 8, 2439.

27. Armand, M. B.; Chabagno, J. M;. Duclot, N. J. In: Fast Ion Transport in Solids; Vashista, P.; Vidal, F.; Popp, J.-F.; Plesse, C.; Cheurot, C.; Teyssié, D. Eds.; Elsevier: Amsterdam/New York, 1979; pp. 131–136.

28. MacCallum, J. R.; Vincent, C. A., Eds. Polymer Electrolyte Reviews I; Elsevier: Amsterdam/New York, 1987.

29. Chéradame, H.; LeNest, J. F. In: Ionically Conducting Polyether Networks, MacCallum, J. R.; Vincent, C. A., Eds.; Polymer Electrolyte Reviews I; Elsevier: Amsterdam/New York, 1987; pp. 103–138.

30. Carvalho, L. M.; Guégan, P.; Cheradame, H.; Gomes, A. S. Eur Polym J 2000, 36, 401.

31. Nishimoto, A.; Agehara, K.; Furuya, N.; Watanabe, T.; Watanabe, M. Macromolecules 1999, 32, 1541.

32. Kang, Y.; Kim, H. J.; Oh, B.; Cho, J. H. J Power Sources 2001, 92, 255.

33. Zang, Z.; Fang, S. Electrochim Acta 2000, 45, 2131.

34. Grosz, M.; Boileau, S.; Guégan, P.; Chéradame, H.; Deshayes, A. Polym Prepr (Am Chem Soc Div Polym Chem) 1997, 38, 612.

35. Hou, X.; Siow, K. S. Polymer 2001, 42, 4181.

36. Du Prez, F. E.; Goethals, J. Macromol Chem Phys 1995, 196, 903.

37. Rouf, C.; Derrough, S.; André, J. J.; Widmaier, J. L.; Meyer, G. C. In: Methacrylic-Allylic Interpenetrating Polymer Networks, Sperling, H.; Klempner, D.; Utracki, L. A., Eds.; Interpenetrating Polymer Networks; American Chemical Society: Washington, DC, 1991; pp. 143–156.

38. Malinauskas, A. Polymer 2001, 42, 3957.

39. (a) Heywang, G.; Jonas, F. Adv Mater 1992, 4, 116; (b) Jonas, F.; Morrison, J. T. Synth Met 1997, 85, 1397.