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Interpenetrating Polymer Networks from Polymeric Imidazolium-type Ionic Liquid and polybutadiene

Frédéric Vidal, Jonathan Juger, Claude Chevrot, Dominique Teyssié (✉)

Laboratoire de Physico-chimie des Polymères et des Interfaces, Université de Cergy-Pontoise,
5 mail Gay-Lussac, 95031 Cergy-Pontoise Cedex – France

E-mail: dominique.teyssie@u-cergy.fr; Fax: +33 134 257 070

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Summary

Interpenetrating polymer networks (IPNs) based on polybutadiene (HTPB) and polymeric ionic liquid (PIL) networks were prepared using an *in situ* strategy. PIL network is obtained from a free radical co-polymerization of an ionic liquid monomer (ILM) and poly(ethylene glycol) dimethacrylate initiated with azobisisobutyronitrile. HTPB network is formed by isocyanate-alcohol addition between the hydroxyl end groups of telechelic HTPB and a pluri-isocyanate cross-linker, catalyzed by dibutyltindilaurate. The IPN containing 72 wt% PIL network exhibits one mechanical relaxation temperature as determined by Dynamic Mechanical Thermal Analysis (DMTA).

Introduction

Ionic Liquids (ILs) have considerable potential as electrolyte materials due to their attractive properties such as high ionic conductivity and high matrix mobility at room temperature [1-4]. For example ILs have been successfully used in the design of electromechanical actuators [5-7].
All solid-state polymer electrolyte (SPE) films are generally chosen as the most convenient materials for applications in electronic devices, but in this case the ionic conductivity is still too low compared with expected standards. In order to increase the ionic conductivity of SPEs, one way consists in designing materials based on ionic liquid monomers. Pioneering work has been performed by Ohno et al. in this field describing SPEs obtained from ILs carrying a polymerizable group which show an ionic conductivity as high as 10^{-4} $S.cm^{-1}$ at room temperature [8-16].

Interpenetrating Polymer Networks (IPNs) have been described as a combination of two (or more) cross-linked polymers [17]. The intimate entanglement of these networks ensures a good miscibility of the two components and a good dimensional stability. Moreover, an improved combination of the properties of its components is sometimes observed. IPN architectures could represent an interesting solution for the application of SPEs in practical electrochemical devices such as actuators based on conducting polymers. For instance in a HTPB/PEO IPN, the poly(ethylene oxide) partner acts as the SPE in the presence of salt whereas the polybutadiene network ensures convenient mechanical properties [18-20]. However, to our knowledge, IPNs based on Polymeric Ionic Liquids (PILs) have not been described yet.

It would appear thus potentially interesting to prepare IPNs based on PILs for actuator applications. The PIL network should ensure the ionic conductivity and the second polymer network would help improving the mechanical properties. In this study, the synthesis of an IPN based on one PIL and polybutadiene (HTPB) is described. The PIL network is obtained by free radical copolymerization of an ionic liquid composed of a polymerizable anion / free imidazolium cation on one hand and poly(ethylene glycol) dimethacrylate as a cross-linker on the other hand. The HTPB network is formed by polyaddition of the OH functions of hydroxytelechelic polybutadiene (HTPB) with a NCO cross-linker (Desmodur® N3300). The viscoelastic behavior of the IPN was studied by DMTA and the interpenetration of the two networks is discussed.

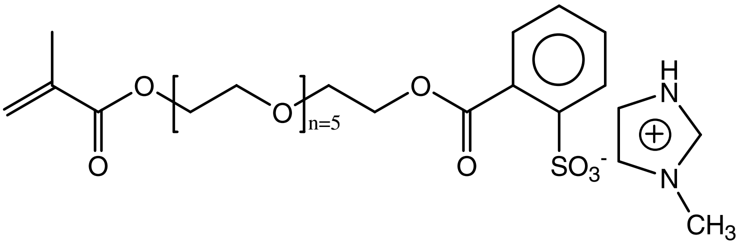
Experimental part

Materials

Poly(ethylene glycol) dimethacrylate (PEGDM, Mw=875 g.mol-1) (Acros), poly(ethylene glycol) methacrylate (PEGM, Mw=360 g.mol-1) (Aldrich), polybutadiene – α,ω dihydroxyl functionalized (HTPB, Mw=2800 g.mol-1) (Aldrich), α,α' azobisisobutyronitrile (AIBN) initiator (Aldrich), Desmodur® N3300 (pluri-NCO cross-linker, 21.8 moles of NCO per gram of Desmodur) (Bayer), dibutyltindilaurate (95%) (DBTDL) (Aldrich), N-methylimidazole (99%) (Aldrich), 2-sulfobenzoic anhydride (Aldrich), hydroquinone (Acros) were used without further purification. Toluene (VWR), methanol (Carlo Erba), dimethylsulfoxyde (Merck) and chloroform (amylene stabilized) were used as received. AIBN was recrystallized in methanol before use.

Synthesis of the ionic liquid monomer

The synthesis of the ionic liquid monomer (ILM) (scheme 1) has been carried out according to the procedure described by Ohno et al. [8], except for the fact that



Scheme 1. Structure of the ionic liquid monomer [8].

poly(ethylene glycol) methacrylate (PEGM) (1,75g), 2-sulfobenzoïc anhydride (0,9g) are mixed in chloroform and stirred for three days at room temperature in the presence of a small amount of hydroquinone (10 mg) to prevent free radical polymerization during the synthesis.

^{1}H NMR characterization ($CDCl_3$): δ (in ppm) = 1.81 (s, 3H), 3.58 (m, ~21H), 3.70 (s, 3H); 5.42 (s, 1H); 5.99 (s, 1H); 7.12 + 7.15 (s + s, 1H + 1H); 7.29 (m, 4H); 8.63 (s, 1 H); 9.09 (s, 1H). « Advance DPX 250 » (250 MHz) (BRUKER).

Synthesis of single networks

Given amounts of Ionic Liquid Monomer (ILM) and PEGDM in various relative proportions are poured into a flask containing 0.7mL methanol such that for all network preparations, the total weight of precursors is 0.5g. AIBN is then added to the mixture (5 wt% with respect to methacrylate precursors). The solution is stirred under argon atmosphere during 30 minutes at room temperature and the mixture is poured into a mould made from two glass plates clamped together and sealed with a 500 µm thick Teflon® gasket. The mould is then kept at 50°C for 5 hours. The sample is then post-cured for 2 hours at 80°C. The sample is finally dried for 8 hours at 50°C under vacuum.

The chosen (ILM/PEGDM) proportions are as following: (1/0) i.e. (ILM homopolymer); (1/0.1); (1/0.33); (1/0.5); (1/1); (1/1.5); (1/2) and (0/1) (PEGDM network).

IPN preparation

The following amounts: 0.30g ILM, 0.20g PEGDM, 0.16g HTPB dissolved in a minimum volume of a solvent mixture (dimethylsulfoxyde - toluene in 1/2.4 volume proportions) are poured into a flask. Desmodur® is then added to the mixture ([NCO]/[OH] = 1.1) as well as AIBN initiator (5wt% with respect to methacrylate precursors). The solution is stirred under argon during 30 minutes and then DBTDL catalyst is finally added ([DBTDL]/[OH] = 0.1). The mixture is poured into a mould made from two glass plates clamped together and sealed with a 500 µm thick Teflon® gasket. The mould is kept at 60°C for 5 hours. The sample is then post-cured for 2 hours at 80°C and dried for 8 hours at 50°C under vacuum.

Under these experimental conditions, a PIL/HTPB (72/28 w/w) IPN is obtained.

Characterizations

Dynamic Mechanical Thermal Analysis (DMTA) measurements are carried out on single network and IPN samples (typically L*w*t = 15*8*0.5 (mm)) with a Q800 model (TA Instruments) operating in tension mode (strain between 0.05 and 0.07%, pretension: 10^{-2} N). Experiments are performed at 1 Hz frequency and with a heating rate of 3°C/min from -80 to 40°C. The set up provides the storage and loss moduli (E' and E'') and the damping parameter or loss factor (tanδ) defined as the ratio tanδ=E''/E'.

Glass transition temperature (Tg) values are measured on a DSC Q100 model (TA Instruments). Tg values are taken as the onset point from the second heating curves recorded in the temperature range of -90 to 40°C at a 20°C.min^{-1} heating rate.

Results and discussion

The ionic liquid monomer (ILM) (Scheme 1) is prepared according to the procedure described by Ohno et al. [8]. The ILM is a benzenesulfonate monomer bearing an (ethylene glycol) methacrylate oligomer side-chain and having a free N-methylimidazolium cation as counter-ion. The glass transition temperature (Tg) of the monomer is low: about -60°C as determined by DSC.

The IL monomer is used in a first step for the synthesis of the corresponding homopolymer (PIL). The free radical polymerization of ILM is performed in methanol solution and initiated with 5% AIBN by weight with respect to ILM at 50°C (5 hours). The PIL glass transition temperature as determined by DSC is equal to -20°C (Table 1).

In a subsequent step the IL monomer has also been used in the preparation of a series of six single networks with different cross-linking densities. In this case the free radical copolymerization of ILM and PEGDM initiated with AIBN (5% of the total precursor weight) is carried out in methanol solution as well. In this series of PIL networks different (ILM/PEGDM) relative weight proportions were screened as follows: (1/0.1); (1/0.33); (1/0.5); (1/1); (1/1.5) and (1/2). Finally the network (0/1) – i.e. a pure PEGDM network was synthesized in the same conditions for comparison. All the networks were then characterized by DSC (Table 1). As expected, the Tg of the PIL homopolymer (-20°C) is much higher than the Tg of the ILM (-60°C). Surprisingly, the whole series of (ILM/PEGDM) networks i.e. from (1/0.1) to (1/2) proportions display Tg values which are lower than that of the PIL homopolymer. This result can be understood taking into account the Tg value of the pure PEGDM network (–45°C): indeed increasing the PEGDM content in the network (from 9% to 66% by weight) results in Tg values which progressively get closer to the Tg value of the pure PEGDM network.

The second partner in the IPN, the α,ω-hydroxytelechelic polybutadiene (HTPB) network is obtained through cross-linking reaction at 50°C between HTPB and Desmodur® in the presence of DBTDL as catalyst ([DBTDL]/[OH] = 0.1) and toluene as solvent [16].

Table 1. Tg values of network as a function of PEGDM proportion. Monomer (ILM), homopolymer (PIL) and PEGDM network are taken as references.

Compound	ILM	PIL Homopolymer	ILM/PEGDM (1/0.1) Network	ILM/PEGDM (1/0.33) Network	ILM/PEGDM (1/0.5) Network
Tg (°C)	-60	-20	-24	-34	-44

Compound	ILM/PEGDM (1/1) Network	ILM/PEGDM (1/1.5) Network	ILM/PEGDM (1/2) Network	PEGDM network
Tg (°C)	-43	-43	-43	-45

(ILM/PEGDM) networks of (1/0.1) and (1/0.33) composition are sticky materials with no satisfactory mechanical properties. Thus, they could not be characterized by DMTA and they were not considered as suitable partners for HTPB as far as the subsequent IPN preparation is concerned. By contrast the (1/0.5), (1/1), (1/1.5) and

(1/2) (ILM/PEGDM) networks behave as self-supported films. However only the network with the composition (1/0.5) has been chosen for the IPN preparation because it bears the highest ILM content, which should thus lead to the highest conductivity value. In this respect, only the (1/0.5) (ILM/PEGDM) network has been characterized by DMTA (Figure 1). Three temperature domains can be observed. First at low temperature, the material is in the glassy state, the storage modulus E' is almost constant. In an intermediate temperature range, a strong decay of E' is observed during the so-called main or α relaxation where tanδ displays a maximum (Tα= -4°C). Then, the elastic part of the modulus E' reaches a rubbery plateau.

The polybutadiene network which will be the second partner in the IPN has also been characterized by DMTA. However, the HTPB modulus does not reach a plateau after the relaxation but undergoes a slow and steady decrease as the temperature increases. It has been reported and it is believed here that the non homogeneity cross-linking density of the HTPB network can explain the decay of the storage modulus on the rubbery plateau [21-24].

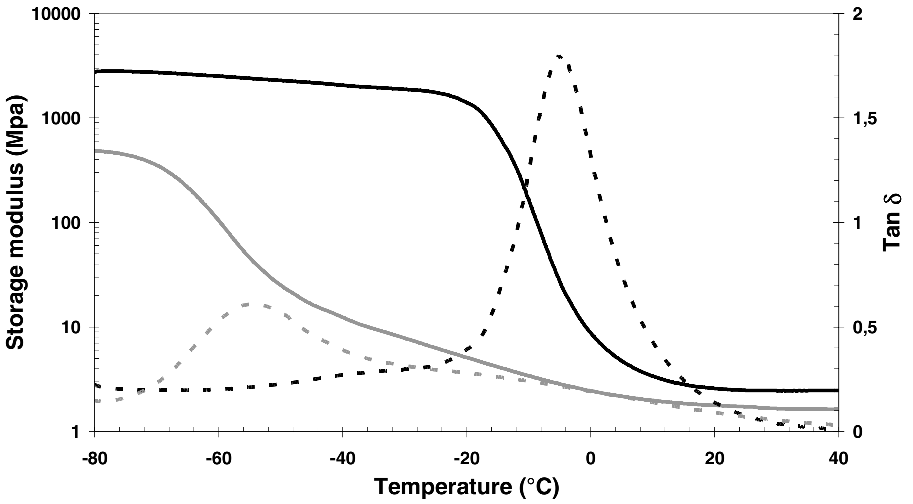


Figure 1. Storage modulus (solid line) and tanδ (dashed line) as function of temperature for single networks. Black line : (1/0.5) (ILM/PEGDM) network; grey line: HTPB network.

When considered as a partner compound or introduced in an IPN architecture, the (ILM/PEGDM) network will be referred to as PIL for simplicity.

The preparation of a PIL/HTPB IPN composed of 72 % (ILM/PEGDM : 1/0.5) and 28 % HTPB by weight was then attempted. However the IPN synthesis cannot be carried out in the absence of solvent since the HTPB and ILM precursors are not miscible. Methanol, which has been used for the PIL network preparation, cannot be used anymore since the alcohol groups of the solvent would react with the Desmodur® NCO functions which must be kept untouched until HTPB cross-linking is achieved. Dimethylsulfoxyde (DMSO) was then chosen as a polar solvent, but neither DMSO and nor toluene can dissolve the mixture of the IPN precursors, i.e. the ionic liquid monomer and the HTPB. Therefore a mixture of DMSO and toluene (in 1/2.4 volume proportion respectively) was used for the IPN synthesis. A minimum volume of toluene/DMSO mixture is then added to insure the homogeneity of the precursor mixture.

A second type of material which cannot truly be referred to as an IPN, a PIL/HTPB (72/28) cross-linked combination was tentatively prepared without any solvent, i.e. simply mixing the precursors and trying to carry out the reaction in the bulk for comparison. Since the starting materials are not miscible, the resulting material, although cross-linked, should not be a true IPN and an important phase separation can be expected.

The materials resulting from those two synthetic pathways, i.e. prepared with or without solvent were characterized by DMTA and some conclusions on the extent of the interpenetration between PIL and HTPB networks in the two kinds of materials can be drawn. First the modulus curves of the two samples are clearly different. Indeed, the storage modulus curve corresponding to the "IPN" synthesized without solvent shows two distinct relaxations whereas the curve corresponding to the IPN synthesized from a homogeneous solution only exhibits one single transition some 20°C higher at mid-height (Figure 2). Moreover, the tanδ curve corresponding to the "IPN" synthesized without solvent also shows two distinct transitions corresponding to the HTPB and PIL phases i.e. at -64°C and at –8°C respectively (Figure 2). This result indicates that the material exhibits dual phase morphology -as expected- and is not at all an interpenetrating network architecture. By contrast, the PIL/HTPB IPN (72/28) prepared in the presence of the solvent mixture exhibits only one main relaxation at +11°C and it is noticeable that the relaxation corresponding to the HTPB phase is totally absent at -64°C. One should consider that the macro-phase separation is prevented in this case or at least that phase segregation is limited. As an unexpected result, the tanδ of the main relaxation observed at +11°C is higher than that of the PIL

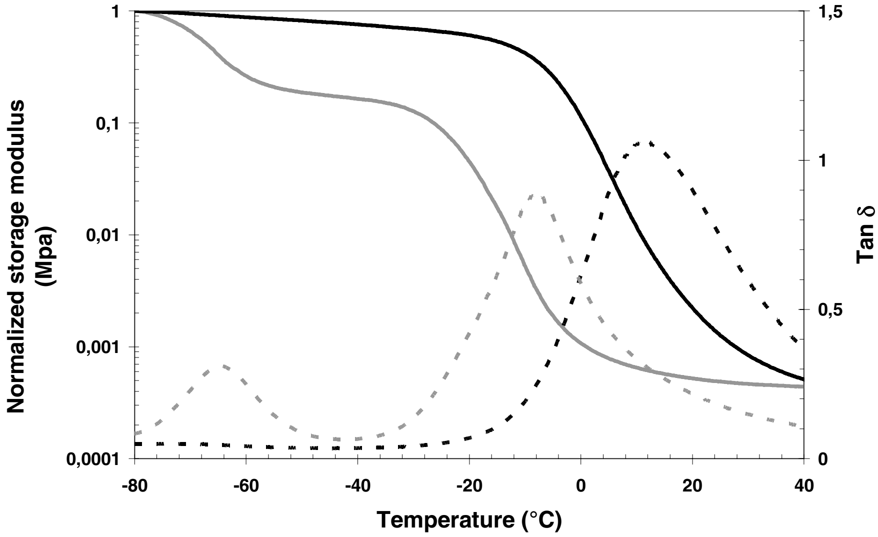


Figure 2. Normalized storage modulus (solid line) and tanδ (dashed line) as function of temperature for (PIL/HTPB) IPN (72/28): black line: IPN prepared in DMSO/toluene mixture; grey line: material prepared without solvent.

single network (-4°C), which corresponds to a 15°C shift. Such phenomenon has been already reported [25-27] and could be assigned either to a local increase of PIL phase cross-linking density or to confined PIL chain environment inside the HTPB network. Further experiments involving synthesis of IPNs with different PIL/HTPB weight proportions should allow understanding this unusual behaviour and will be reported shortly.

Conclusion

The polymerization and cross-linking of an ionic liquid monomer into a polymer network is described. Then, interpenetrating polymer networks combining the ionic liquid based network and a polybutadiene network have been prepared. The synthesis involves a one pot-one shot process in which all precursors are first dissolved together in a DMSO/toluene mixture before the networks are formed in the presence of each other leading to an IPN. When the ionic liquid based network and the polybutadiene network are combined in (72/28) weight proportions in the IPN, the resulting material exhibits a single relaxation as observed by DMTA analysis. This result shows that the two polymers are correctly interpenetrated and that no macro-phase separation can be detected at the DMTA scale. In our knowledge, it the first time that the synthesis of an IPN based on an ionic liquid polymer is reported.

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