Polymer supported ionic liquid phases (SILPs) *versus* ionic liquids (ILs): How much do they look alike

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The fluorescence of pyrene has been used for the first time to measure the static dielectric constant of a series of supported ionic liquids phases (SILPs) based on polymeric polystyrene networks.

Ionic liquids (ILs) have been known for some time,[1] but the research on this class of compounds has experienced a tremendous explosion during the last decade.[2] Part of this interest is driven by the lack of knowledge of many fundamental physical parameters and models to explain their unique behaviour.[3] But, most importantly, from the practical viewpoint, the development of the ILs-based chemistry arises from their utility as *environmentally friendly* solvents with multiple applications in synthesis, catalysis and separations.[4] Despite their well recognized advantages, a series of drawbacks have been also highlighted. The difficult procedures for product purification or IL recycling, some toxicity concerns and the problems for application in fixed bed reactors are important issues to be addressed for future industrial scale-up. The use of *supported ionic liquid phases* (SILPs) prepared by the immobilization of molecules with IL-like structures onto solid supports can be an answer to overcome these difficulties.[5,6] This new class of advanced materials shares the properties of true ILs and the advantages of a solid support, in some cases with an enhanced performance for the solid material.[7] Nevertheless a central question to further develop this class of materials is to understand how much the microenvironment provided by the functional surfaces is similar or not to that imparted by ILs. This is not a simple task, since, as mentioned above, the basic knowledge of pure ILs is still in its infancy, and we are just starting to understand the fundamentals of ILs nature. For instance polarity[8–13] and microviscosity[14,15] are just recently started to be unveiled. Hence, the rationalization of the behaviour of the more complex SILPs is an even more difficult challenge. It has been suggested that their advanced properties are, in part, due to the *change of polarity* of SILPs as compared to the standard supports. But this is only a *qualitative* assumption based on the existence of new groups with different polarity on the material. Measurement of a fundamental magnitude related to polarity would help to demonstrate *quantitatively* the above statement.

The polarity of the ILs is one of the basic parameters that seem to determine their final properties and this can also be a determinant for SILPs. Here we report on the semiquantitative assessment of the polarity of a series of SILPs with covalently attached IL-like moieties by means of steady-state fluorescence spectroscopy, using pyrene as a probe. To our knowledge this is the first time that such a probe has been used to evaluate the polarity of a *supported ionic liquid phase* (SILP).

SILPs used for this work were synthesized by covalent binding of IL-like units (alkylimidazolium cations, Chart 1) to either gel type or monolithic PS-DVB resins followed by the corresponding anion exchange. *Monolithic*-SILPs (*M*-SILPs, **1a–d**) are based on highly crosslinked monolithic macroporous resins synthesized by polymerization of chlorovinylbenzene and divinylbenzene.[6] On the other hand, *Gel*-SILPs (*G*-SILPs, **2a,b**) were synthesized by modification of commercially available Merrifield resins with a low degree of crosslinking. Table 1 summarises the composition of each SILP used in the tests with pyrene as a fluorescent probe. Two reference polymers, *M*-PS-DVB (monolithic type, chloromethylated) and *G*-PS-DVB (gel-type Merrifield resin) were also used for those experiments.

The fluorescence spectrum of pyrene (Fig. 1) shows a fine vibronic structure composed of five bands (I–V). The first band (*ca.* 370 nm) corresponds to the transition $S_1^{v=0} \rightarrow S_0^{v=0}$, and its intensity ($I_1$) is dependent on the polarity of the medium, provided the existence of vibronic coupling between S_1 and S_2 states. The third band (*ca.* 382 nm) is associated to the $S_1^{v=0} \rightarrow S_0^{v=2}$ transition and its intensity (I_3) is independent of the polarity.[16,17] Hence, the ratio I_1/I_3 (or *py* value) has been used as an empirical tool (the *py*-scale[18]) to estimate the polarity of several media including micelles,[19] enzymes[20] and biological membranes.[21] Also polystyrene,[22,23] poly(vinylpyridine),[22,24] polyacrylates[23–25] polyelectrolytes,[26] latex,[27] polyethylene,[28] and poly(vinyl acetate)[28] have been tested with pyrene as a polarity probe. Hence *py* values are generally accepted as a reliable polarity scale.

Since the *py* value is affected by numerous experimental artifacts,[29] we have recorded the emission of pyrene in a series of solvents to certify the validity of our experimental setup. The values obtained were found within the range of *py* values described in the literature. For instance: 0.63 for *n*-hexane (0.61 lit.[16]), 1.15 for toluene (1.11 lit.[16]), 1.46 for AcOEt (1.45 lit.[16]) and 1.89 for DMF (1.82 lit.[16]) as shown in Table 2.

The spectra of pyrene adsorbed onto the monolithic highly crosslinked polymers can be seen in Fig. 2.† The spectrum of *M*-PS-DVB polymer shows the five vibronic bands, with a ratio

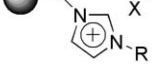

Chart 1 General structure of SILPs studied in this work.

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Table 1 Polymer description

Entry	Polymer	Type	R	X^-	Loading[a]
1	*M*-PS-DVB[b]	*Monolith*	[c]	[c]	3.07[c]
2	**1a**	*M*-SILP[d]	Me	Cl^-	1.64
3	**1b**	*M*-SILP[d]	*n*-Bu	Cl^-	1.65
4	**1c**	*M*-SILP[d]	Me	Tf_2N^-	1.13
5	**1d**	*M*-SILP[d]	*n*-Bu	Tf_2N^-	1.09
6	*G*-PS-DVB[e]	*Gel type*	[c]	[c]	4.3[c]
7	**2a**	*G*-SILP[f]	*n*-Bu	Cl^-	2.72
8	**2b**	*G*-SILP[f]	*n*-Bu	Tf_2N^-	1.87

[a] Expressed as meq. of IL-moiety g^{-1}. [b] *M*-PS-DVB: monolithic poly(styrene-divinylbenzene) 60% (w/w) crosslinking degree, 3.07 mmol Cl g^{-1}. [c] No imidazolium functionalities. [d] *M*-SILP: monolithic macroporous polymer with 60% (w/w) crosslinking degree. [e] *G*-PS-DVB: Merrifield Resin 2% crosslinking, 4.3 mmol Cl g^{-1}. [f] *G*-SILP: modification of commercially available Merrifield resin with a low degree of crosslinking.

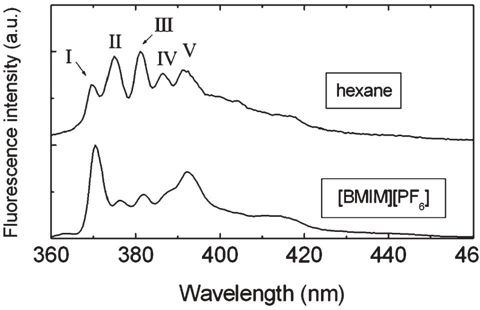

Fig. 1 Fluorescence spectra of pyrene in *n*-hexane and [BMIM][PF_6].

Table 2 Fluorescence data of pyrene in several solvents and polymers. *Py* values (I_1/I_3 ratios) and position of the peaks I and III

Entry	Solvent or polymer	I_1/I_3	λ_1/nm	λ_3/nm
1	*n*-Hexane	0.63	369.5	381.0
2	Toluene	1.15	371.0	382.5
3	Dichloromethane	1.43	371.0	382.5
4	Ethyl acetate	1.46	370.0	381.5
5	Methanol	1.50	370.0	381.0
7	Acetonitrile	1.83	370.0	381.5
8	DMF	1.89	371.0	382.0
10	***M*-PS-DVB**	**1.03**	371.5	383.0
11	**1a**	**1.34**	372.0	383.0
12	**1b**	**1.42**	372.0	383.0
13	**1c**	**1.44**	371.5	383.0
14	**1d**	**1.41**	372.0	383.0
15	***G*-PS-DVB**	**0.93**	372.0	383.5
16	**2a**	**1.61**	371.5	383.0
17	**2b**	**1.57**	372.0	383.5

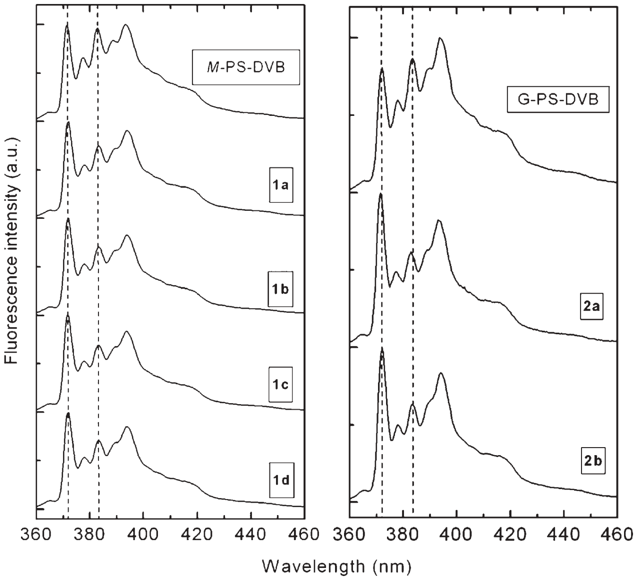

Fig. 2 Fluorescence spectra of pyrene in *M*-PS-DVB and *M*-SILPs **1a–d**, and in the gel type Merrifield resin (*G*-PS-DVB) and *G*-SILPs **2a,b**.

I_1/I_3 of 1.03, in close agreement with the presence of pyrene in a non-polar environment. The introduction of imidazolium groups in the matrix leads to a considerable increase of the *py* value. For instance, polymer **1a** shows a *py* of 1.34, which is clearly reflecting the increased polarity of the matrix upon functionalization. With **1b** (*n*-butyl instead of methyl group) the *py* value is 1.42. Exchanging the chloride in **1a** by bis(trifluoromethanesulfonyl)-imide (Tf_2N^-) (sample **1c**) leads to a *py* of 1.44. And finally, polymer **1d**, with Tf_2N^- anion and *n*-butyl displays a *py* value of 1.41. This difference between *M*-PS-DVB (1.03) and *M*-SILPs **1a–d** (mean *py* = 1.4) clearly reflects, in a quantitative way, the increased micropolarity in the SILPs. No significant differences were found between the position (λ_1 and λ_3) of the fluorescence peaks (those values are ± 0.5 nm). However, if the shape of the curves is examined, it can be seen that band IV in **1a–d** becomes a shoulder integrated with band V, whereas for *M*-PS-DVB this does not occur. This has been reported in an isotropic medium associated with an increase in the polarity of the medium.[16]

For the gel type polymers **2a,b** an even higher change of polarity was recorded. Thus, the *G*-PS-DVB displayed a *py* of 0.93 whereas the IL-containing polymers showed values of 1.61 (**2a**) and 1.57 (**2b**) (Fig. 2). Such differences can be associated with the higher loading of gel-type SILPs. However the higher *py* value found for *M*-PS-DVB compared with *G*-PS-DVB is striking if it is considered that *G*-PS-DVB contains a higher loading of relatively polar C–Cl bonds. This highlights how the intrinsic morphology of the polymeric matrices can be one of the fundamental parameters to be considered in order to understand the behaviour of polymer-supported reagents and catalysts.[30]

In order to obtain a deeper insight regarding the polarity of these SILPs, and provide an easier comparison with known values of ILs, an approximate estimation of the static dielectric constant (ε) of **1a–d** and **2a,b** was achieved using an empirical correlation between *py* values and ε. This correlation (*py vs.* ε) was constructed using our own *py* values and others described in the literature[12,16,17] following the methodology reported by Kirstein *et al.*[26] As can be seen in Fig. 3, the empirical relationship between *py* and ε allows a rough estimation of the ε of the SILPs (marked with vertical lines). Thus, for **1a–d**, $\varepsilon \sim 10$, whereas for **2a,b** $\varepsilon \sim 20$. In this regard, the ε values estimated for the parent non-ionic polymers (*M*-PS-DVB and *G*-PS-DVB) are well below 5. On the other hand the reported value of *py* for [bmim][PF_6] is 1.84 which seems to suggest that the ε estimated values are the lower limits.‡ It has been reported that polarity-sensitive solvatochromic dyes provide polarities for ILs markedly higher than those obtained by microwave dielectric spectroscopy.[8] Nevertheless, it is important to note that, in our case, the estimated ε values for SILPs agree quite

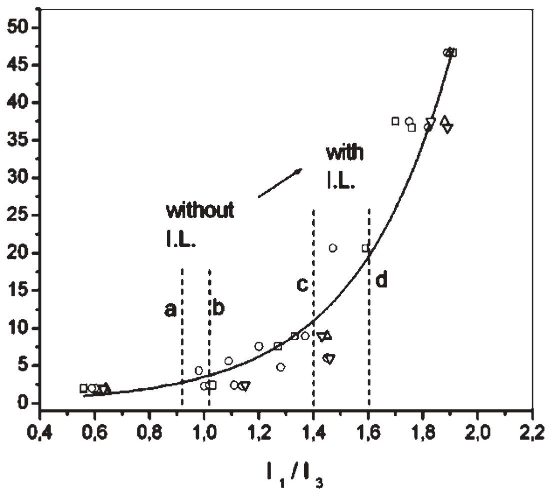

Fig. 3 Static dielectric constant (ε) *vs.* *py* value for homogeneous non-protic solvents (circles: ref. 16; squares: ref. 17; up-triangles: ref. 12; down-triangles: this work). Dashed lines mark the *py* values calculated in this work for: (a) MR; (b) PS-DVB; (c) *M*-SILPs **1a–d**; (d) *G*-SILPs **2a,b**.

well with those reported from microwave dielectric spectroscopy (8.8–15.2 for different ILs), or through vibrational frequencies for single water molecules associated in ILs (15.76 for [C_2MIM][NTf_2]).[8]

In summary, our results quantitatively demonstrate the increased micropolarity of a series SILPs. The ε values deduced from the fluorescence experiments reveal an increase in the polarity of the polymers, from $\varepsilon < 5$ to $\varepsilon \geqslant 10$–20. Moreover, these values reflect that the functional surfaces on the polymers essentially maintain the same polarity of the bulk room temperature ILs. For RTILs, variations in the structure of the cation or the anion are accompanied by changes in polarity following well defined trends. Those trends seem to be absent in SILPs, but the number of cases considered is limited and further studies are needed to analyze if this is a feature typical of SILPs.

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Notes and references

† The polymeric samples were suspended in methanolic solutions of pyrene (0.01 M) and stirred at rt for 2 h. After filtration and washing with MeOH, the polymers were vacuum dried (60 °C) overnight. The samples were introduced into narrow fluorescence cells and excited at 338 nm (Spex Fluorolog 3–11 apparatus, equiped with a 450 W xenon lamp). Emitted light was recorded in front-face mode and the spectra were corrected to account for the different spectral sensitivity of the detector.

‡ The local polarity in SILPs could be even higher, since the emission recorded can have some contribution from pyrene located in hydrophobic sites, hence leading to a reduced overall *py* value. In order to discriminate this effect, we have attempted preliminary lifetime measurements but quenching of the emission by oxygen, made the measurements unreliable. On the other hand, adsorbed water should be also taken into account to explain the properties of the SILPs.

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