

Cross-Linked Polymer–Ionic Liquid Composite Materials

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ABSTRACT: A series of composites, some with permanent porosity, comprising polymers and ionic liquids have been prepared by in-situ polymerization. The characteristics of both composites and isolated polymers have been investigated. Slow mass and phase transfer characterize the interaction with a range of polymers (**1–17**) in the *N,N'*-dialkylimidazolium ionic liquids, [emim]BF₄, [bmim]PF₆, or [omim]N(SO₂CF₃)₂. Free-radical homopolymerization of 1-vinyl-2-pyrrolidinone in [bmim]PF₆ or of 4-vinylpyridine in [omim]N(SO₂CF₃)₂ gave viscous solutions from which polymer (*M_w* = 162 500 and 71 500 g mol⁻¹, respectively) could be isolated. Detectable ionic liquid residues were retained in the isolated polymers despite five reprecipitations from methanol. Copolymerization of 4-vinylpyridine (VP) with >5% divinylbenzene (DVB) or trimethylolpropane trimethacrylate (TRIM) in [omim]N(SO₂CF₃)₂, and homopolymerizations of the cross-linking monomers on their own, led with 90–100% monomer conversion to a series of gel-like composite materials, **B–H**, from which cross-linked polymers, **B'–H'**, could be isolated by Soxhlet extraction of the ionic liquid. Copolymers of VP with 5–30% DVB (**E'**, **F'**) showed a low degree of permanent porosity in the dry state. However, poly(DVB) (**G'**) and poly(TRIM) (**H'**) have bulk densities (<0.6 g cm⁻³), intrusion volumes (>0.9 cm³ g⁻¹), BET surface areas (70–320 m² g⁻¹), and morphology (from SEM studies) which demonstrate the porogenic character of the ionic liquids used. Comparisons with the related products **I** and **J** obtained in toluene reveal the sensitivity of these systems both to the properties of the porogen solvent and to the monomer used.

Introduction

Research into the preparation, structure, and properties of new composite and hybrid materials has been driven by a range of possible technological applications as well as by intrinsic interest. We are currently seeking to develop novel materials for use in membrane reactors in which ionic liquids are used as a medium in which to effect a catalyzed chemical change^{1,2} and wish to report on some associated investigations on a series of polymer–ionic liquid composites.

The technical (as opposed to economic) characteristics of composite materials will be determined by the particular application envisaged and, in the case of membranes for use in catalytic reactors, will include coprocessability and compatibility of component materials as well as mechanical and chemical robustness in use.

In our approach we have investigated selected polymer–ionic liquid interactions as a prelude to the design of effective composite materials. These have included studies of the solubility of a range of polymers in selected ionic liquids, polymerizations and copolymerizations in ionic liquids, the characterization of targeted polymer–ionic liquid composites, and the role of cross-linking and gelation.

Polymerizations are among the earliest chemical transformations to have been studied in ionic liquids, with electrochemical polymerization of pyrrole first described^{3a} in *N*-alkylpyridinium chloroaluminate^{3a} and, more recently,^{3b} in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. Related media have been used

to effect the ring-opening polymerization of ethylene carbonate,^{3c} condensation polymerizations leading to polyamides and polyimides,^{3d,e} metal-complex-catalyzed oligomerization,^{4a–c} and polymerization of alkenes^{4d,e} and phenylacetylene.^{4f} Living, atom-transfer or conventional radical homopolymerizations of methyl methacrylate,^{5a–f} 2-hydroxyethyl methacrylate,^{5e–g} methyl, butyl, hexyl, and dodecyl acrylate,^{5h} styrene,^{5c,e,f} and acrylonitrile^{5f} have been carried out in *N,N'*-dialkylimidazolium salts of [PF₆]⁻, [BF₄]⁻, [N(SO₂CF₃)₂]⁻, or [F(HF)]_n⁻. Alternating copolymers of styrene and CO₂^{6a,b} and block copolymers of styrene and methyl methacrylate^{6c} have also been prepared. Very recent papers describe atom-transfer radical copolymerizations of *N*-hexylmaleimide with styrene^{6d} and of butyl acrylate with methyl acrylate^{6e} in similar media as well as the reversible addition–fragmentation chain transfer polymerization of styrene, methyl acrylate, and methyl methacrylate.^{6f}

Interest in polymer electrolytes for possible use in new battery, fuel cell, and other applications has led to the polymerization of monomers or the functionalization of polymers having some of the characteristics of ionic liquids, including materials derived from vinyl and imidazolium groups tethered to oligo(ethylene oxide),^{7a} from *N*-[(4-vinyl)benzyl]-*N'*-ethylimidazolium^{7b} and *N*-vinyl-*N'*-alkylimidazolium^{7c,d} salts or from liquid salts derived from 1-vinylimidazole and vinylsulfonic acid or 3-sulfopropyl acrylate.^{7e}

Carlin et al. have reported a series of studies of gel–polymer electrolytes derived from perfluorinated polymer membranes and ionic liquids.^{2,8a–c} High-temperature proton conducting membranes based on perfluorinated ionomer membrane–ionic liquid composites have also been described.^{8d}

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Table 1. Phase Behavior^a of Selected Polymer Solutions in Ionic Liquids

polymer ^b	IL:	[emim]BF ₄					[bmim]PF ₆					[omim]Tf ₂ N				
	weeks:	0	2	4	6	11	0	2	4	6	15	0	2	4	6	11
1, P(BuVP ⁺ Br ⁻ -VP)		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
2, P(BuVP ⁺ Br ⁻ -VP-styrene)		o	-	-	-	-	o	o	-	-	-	+	+	c	c	c
3, P(BuVP ⁺ Br ⁻ -VP-BMA)		-	-	-	-	-	o	-	-	-	-	c	c	c	c	c
4, P(BuVP ⁺ Tf ₂ N ⁻ -VP)		+	+	+	+	+	c	c	c	c	-	+	+	+	+	+
5, P(MeVIm ⁺ Tf ₂ N ⁻)		-	-	-	-	-	c	c	c	c	c	+	+	+	+	+
6, P(VIm-VPyrr), 50% VPyrr		o	-	-	-	-	+	c	o	o	-	+	+	+	+	+
7, P(MeVIm ⁺ MeOSO ₃ ⁻ -VIm-VPyrr)		+	+	+	+	+	+	+	c	c	c	+	+	+	+	+
8, P(MeVIm ⁺ Cl ⁻ -VIm-VPyrr)		+	+	+	+	+	c	c	c	c	c	+	+	o	o	-
9, P(MeVIm ⁺ MeOSO ₃ ⁻ -VIm-VPyrr-VCap)		o	o	o	o	o	+	c	c	c	c	+	+	+	+	+
10, P(acrylic acid), <i>M</i> _w 2 × 10 ³ g mol ⁻¹		+	+	+	+	+	-	-	-	-	-	-	-	-	-	-
11, P(BMA), <i>M</i> _w 337 × 10 ³ g mol ⁻¹		+	+	+	+	+	-	-	-	-	-	+	+	+	+	+
12, P(ethylene glycol), <i>M</i> _w 10 × 10 ³ g mol ⁻¹		+	-	-	-	-	+	+	+	+	+	+	+	+	+	+
13, P(styrene), <i>M</i> _w 30 × 10 ³ g mol ⁻¹		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
14, P(VP), <i>M</i> _w 160 × 10 ³ g mol ⁻¹		-	-	-	-	-	-	-	-	-	-	+	c	-	-	-
15, P(VP-styrene), 10% styrene		-	-	-	-	-	-	-	-	-	-	+	c	-	-	-
16, P(VP-BMA), 10% BMA		-	-	-	-	-	-	-	-	-	-	+	c	-	-	-
17, P(VPyrr), <i>M</i> _w 10 × 10 ³ g mol ⁻¹		+	+	+	+	-	+	+	c	-	-	+	+	+	+	-

^a Key: + (clear solution), c (cloudy), o (opaque), - (precipitate). ^b 1–5 synthesized, 6–17 commercially available. Abbreviations: BMA (butyl methacrylate), Tf₂N⁻ [(N(SO₂CF₃)₂)₂]⁻, VCap (1-vinylcaprolactam), VIm (1-vinylimidazole), VP (4-vinylpyridine), VPyrr (1-vinyl-2-pyrrolidinone). *M*_w values for 1–9, 15, and 16 were not determined.

Results and Discussion

Polymer Solubilities in Ionic Liquids. The solubilities of a range of polymers were screened in a selection of ionic liquids. The results obtained are shown in Table 1. Polymers chosen for study included homopolymers of acrylic acid (10), butyl methacrylate (11), ethylene oxide (12), styrene (13), 4-vinylpyridine (14), and 1-vinyl-2-pyrrolidinone (17) and copolymers of 1-vinylimidazole (1-vinyl-2-pyrrolidinone, 6) and 4-vinylpyridine (styrene, 15; butyl methacrylate, 16). Polyelectrolytes chosen for study included partially quaternized 4-vinylpyridinium (1–4) and 1-vinylimidazolium (7–9) copolymers and the 1-vinylimidazolium homopolymer 5. Polymers 1–5 were synthesized,¹ and polymers 6–17 were obtained from commercial sources. The three ionic liquids chosen for study were [emim]BF₄, [bmim]PF₆, and [omim]Tf₂N (Tf₂N⁻ = [N(SO₂CF₃)₂)₂⁻) to be representative of typical cations and anions. From the studies of the solvation characteristics of ionic liquids reported so far,^{9a–i} it seems reasonable to conclude that the hydrophobicity of *N,N'*-alkylmethylimidazolium cations [rmim]⁺ (r = e (ethyl), b (butyl); or o (octyl)) and anions increase along the series emim < bmim < omim; BF₄ < PF₆ < Tf₂N. A trial experiment utilizing powdered samples revealed the majority of polymers 1–17 to be insoluble in both [bmim]PF₆ and [omim]Tf₂N (5 wt % concentration). The apparent insolubility of the polymers may have arisen from the relatively high viscosity^{10a,b} of ionic liquids, leading to slow dissolution. To investigate the thermodynamic solubility of the polymers, a second experiment was devised. Polymers 1–17, dissolved in molecular solvents (5 wt %), were added to ionic liquids, and the volatile solvents were removed. The phase behavior of the ionic liquid/polymer solutions was monitored over the course of 11–15 weeks. As can be seen from Table 1, [omim]Tf₂N appeared to be the most effective solvent for a wide range of polymers. The behavior of [emim]BF₄ was similar to that of [bmim]PF₆. Polymers that showed good initial solubility in all three ionic liquids included the *N*-butylpyridinium polyelectrolyte, 1, and the hydrophilic polyether, PEG, 12. Highly hydrophobic poly(styrene), 13, was insoluble in all three ionic liquids. On the other hand, the relatively hydrophobic poly(butyl methacrylate), 11, was freely soluble in two of the ionic

liquids and completely insoluble in the third, for reasons that are not immediately obvious.

Several of the polymer solutions exhibited slow phase separation, suggesting that both polymer dissolution and phase separation may be mass- or phase-transfer-limited. Many initially homogeneous polymer-ionic liquid solutions exhibited phase separation over periods of days to weeks.

The solubility studies, undertaken to guide our program of polymer synthesis and composite assembly, have highlighted a rich range of behavior. It is evident that the factors responsible for polymer solubility in ionic liquids are complex and not readily predicted. The detailed phase behavior of polymer-ionic liquid mixtures requires more in-depth investigation.

Polymer-Ionic Liquid Composites. The key goal of this research program is to develop polymer-ionic liquid composite materials that are suitable for use in catalytic membrane reactors.¹¹ In principle, there are two main methods by which this can be achieved. First, an appropriately porous material may be imbibed with the ionic liquid. This material may be a commercially available porous membrane,^{2,8a–c} a chemically modified membrane, or a polymeric material that is specifically designed and synthesized for the particular application. Second, one may produce a polymer-ionic liquid composite in situ by reaction-induced phase separation (one method among several^{12a–d} of gelling of an ionic liquid solution). Each approach has advantages and disadvantages (not least associated with the point in the process at which catalyst is introduced^{2,8a}). Imbibing ionic liquids into commercially available membranes is simple but does not permit much “tuning” of the interactions between the polymer and the ionic liquid phases (e.g., by modifying factors such as polymer wettability and pore filling). In contrast, the direct formation of composite materials by in situ reaction-induced phase separation should allow fine control over the physical and chemical nature of the composite materials. Moreover, this approach offers a route to “molded” composites in a range of shapes and sizes for various applications (e.g., membranes, monolithic column packings, filled capillaries, etc.). A potential disadvantage of any direct “gelation” route is that residual monomer may remain in the composite after reaction. On the other hand, since

Table 2. Linear Polymers^a

polymer	monomer	solvent	selected characterization data
A'	VPyrr	[bmim]PF ₆	purified product ^b M_w 162 500 g mol ⁻¹ , M_n 61 300 g mol ⁻¹ , PD 2.7 ^c
B'	VPyrr (+1 mol % DVB ^d)	[bmim]PF ₆	composite material (B) transparent tacky syrup; T_{onset} 326 °C, T_{max} 475 °C ^e
C'	VPyrr (+5 mol % DVB ^d)	[bmim]PF ₆	composite material (C) opaque tacky syrup; T_{onset} 309 °C, T_{max} 442 °C ^e
D'	VP	[omim]Tf ₂ N	purified product ^b M_w 71 500 g mol ⁻¹ , M_n 36 200 g mol ⁻¹ , PD 2.0 ^c

^a Polymerization conditions: monomer (1 vol), [omim]Tf₂N (2.5 vol), AIBN, 80 °C, 4 h. ^b After trituration and five reprecipitations. ^c From GPC (calibrated with PMMA standards). ^d DVB (55%; remainder composed of a mixture of 3- and 4-ethylvinylbenzene). ^e From thermogravimetry in flowing air: T_{onset} , onset decomposition temperature; T_{max} , maximal decomposition temperature.

Table 3. Cross-Linked Polymer–Ionic Liquid Composite Materials^a

composite	monomer	X-linker (mol %)	composite appearance	T_{onset} (°C) ^b	T_{max} (°C) ^b	ρ_s (g mL ⁻¹) ^c (T /°C)
E	VP	5 ^d	gel	255	331, 432	1.291 (26.1)
F	VP	30 ^d	waxy solid	286	355, 452, 491	1.301 (24.6)
G	DVB	55	chalky solid	363	469	1.282 (25.8)
H	TRIM	100	waxy solid	262	309, 414, 494	1.327 (25.9)

^a Polymerization conditions: monomer (1 vol), [omim]Tf₂N (2.5 vol), AIBN, 80 °C, 4 h. ^b From thermogravimetry in flowing air: T_{onset} , onset decomposition temperature; T_{max} , maximal decomposition temperature(s). ^c Skeletal density (from helium pycnometry). ^d DVB (55%; remainder composed of a mixture of 3- and 4-ethylvinylbenzene).

the ionic liquids chosen have essentially zero vapor pressure, it should be possible to remove traces of most monomers by evacuation at elevated temperatures.

For our first evaluation, we chose 1-vinyl-2-pyrrolidinone (VPyrr) and 4-vinylpyridine (VP) as monomers for thermal free-radical polymerization studies in ionic liquids. Poly(1-vinyl-2-pyrrolidinone) showed good initial solubility in [bmim]PF₆ and [omim]Tf₂N, whereas contrasting behavior of poly(4-vinylpyridine) was seen. As such, these ionic liquids were chosen to investigate “good” and “poor” solvents/porogens for the formation of linear and cross-linked VP and VPyrr polymers. The results of these polymerizations are summarized in Table 2. In the absence of cross-linker, the free-radical polymerization of VPyrr in [bmim]PF₆ led to a homogeneous viscous solution (**A**) of a linear polymer (**A'**) with a weight-average molecular weight of 162 500 g mol⁻¹. Interestingly, despite repeated reprecipitations, the ¹H NMR spectrum of the free polymer revealed the presence of residues believed to arise from [bmim]PF₆ (~4%). The copolymerization of VPyrr (40% v/v) in [bmim]PF₆ with 1 mol % DVB afforded a transparent, tacky syrup (**B**). Increasing the cross-linker ratio to 5 mol % DVB led to opaque white tacky syrups (**C**). The polymer isolated from **B**, **B'**, dissolved completely in dichloromethane, suggesting that it might be a highly branched copolymer rather than a cross-linked network. The polymer isolated from **C**, **C'**, formed a viscous, milky solution in dichloromethane, suggesting the presence of at least some insoluble microgel particles. None of these reactions yielded a gelled composite that might be suitable for uses as a catalytic membrane.

Polymerization of VP in [omim]Tf₂N led to a homogeneous viscous solution (**D**) of a linear polymer (**D'**) with a weight-average molecular weight of 71 500 g mol⁻¹. Repeated reprecipitation of **D'** afforded poly(4-vinylpyridine) as a white solid. Once again, ¹H NMR spectroscopy revealed the presence of residues from the ionic liquid ([omim]Tf₂N; ~1%), highlighting the difficulty that may exist in removing all traces of these nonvolatile solvents from polymeric materials. The origin and nature of these retained materials are the subject of a separate study,^{13a} particularly to explore

whether the ionic liquid may undergo hydrogen atom abstraction, a possibility raised recently by Muldoon and co-workers.^{13b} We would expect abstraction to occur to a very limited extent, bearing in mind the electrophilic character of [CMe₂CN]⁺, a possible reactant, and the relative unreactivity of imidazolium cations toward hydrogen atom abstraction.^{13c} While free-radical reactions have been successfully investigated in *N,N'*-dialkylimidazolium ionic liquids,^{13d,e} our initial observations suggest that there may be a limit to their usefulness as media in which to carry out free-radical polymerizations.

A series of more promising materials were obtained when higher cross-linker concentrations were employed (Table 3). The copolymerization of VP with 5 mol % DVB in [omim]Tf₂N afforded a transparent poly(4-vinylpyridine)–[omim]Tf₂N composite gel (**E**). An opaque gel was formed when 30 mol % DVB was used (**F**). Both of these gels were completely insoluble in all organic solvents tested. Soxhlet extraction (methanol, 72 h) afforded brittle orange solids with gel fractions of 100%. Materials were also produced by free-radical polymerization of neat 55% DVB (**G**) and 100% trimethylolpropane trimethacrylate (TRIM) (**H**). Both reactions gave rise to opaque white solid polymer–ionic liquid composite materials.

An unusual feature of these composite materials is that the liquid phase has essentially zero vapor pressure: as such, a number of properties can be measured for the composites that usually require “dry” samples. For example, thermogravimetric analysis (Figure 1) was carried out for the polymer–ionic liquid composite materials, **G** and **H**, as well as for the isolated polymers, **G'** and **H'**. The results are interesting since it is possible to check simultaneously for (i) decomposition of the polymer, (ii) decomposition of the ionic liquid, and (iii) loss of any volatiles associated with residual, unreacted monomer. Figure 1a,b suggests that both polymer–IL composites **G** and **H** are somewhat more thermally stable than the respective polymers after extraction of the ionic liquid (**G'** and **H'**). The ionic liquid itself (Figure 1c) is more thermally stable than either the polymers or the composites. The fact that the DVB-

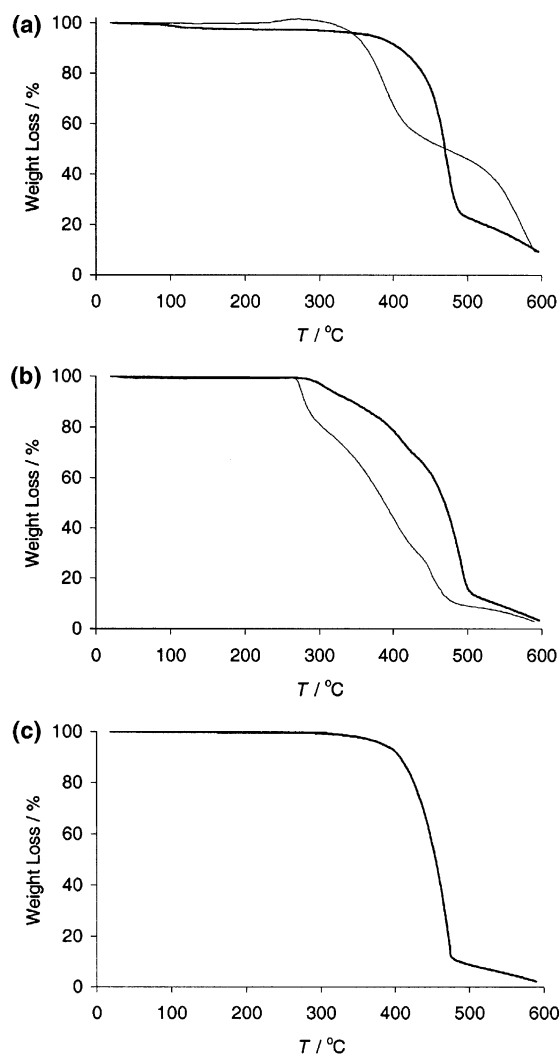


Figure 1. Thermogravimetry traces (in flowing air) for: (a) poly(divinylbenzene)s (55 mol %) before (**G**, bold line) and after (**G'**, faint line) removal of porogen, [omim]Tf₂N; (b) poly(trimethylolpropane trimethacrylate)s (100 mol %) before (**H**, bold line) and after (**H'**, faint line) removal of porogen, [omim]Tf₂N; (c) [omim]Tf₂N.

based composite **G** shows a greater mass loss in the temperature range 20–200 °C is consistent with the fact that the yield in this reaction (90%) was lower than that observed for the methacrylate composite, **H** (yield ~ 100%). The methacrylate composite, **H**, shows good thermal stability and very little mass loss up to at least 250 °C, despite the fact that the material has not been purified or treated in any way after polymerization.

Macroporous Cross-Linked Polymers Using Ionic Liquids as Porogens. Removal of the ionic liquid from the IL–polymer composites by Soxhlet extraction was carried out in order to examine the porous properties of the cross-linked materials. The pore structure was analyzed by N₂ sorption–desorption, by mercury intrusion porosimetry, and by helium pycnometry. The results of this analysis are shown in Table 4. The two materials synthesized using VP (4-vinylpyridine) as the monomer (**E'** and **F'**) exhibited high bulk densities (>0.75 g cm⁻³), low intrusion volumes (<0.3 g cm⁻³), and low BET surface areas (<2 m² g⁻¹). This is indicative of a low degree of permanent porosity in the dry state, although the data suggest that some dry porosity existed in the sample prepared at the higher cross-linker ratio (**F'**). Since both samples **E'** and **F'** show marked weight loss and pronounced shrinkage after extraction of the ionic liquid, it is likely that the degree of cross-linking in these materials^{14a,b} is insufficiently high to support the formation of permanent porosity and that the polymers have some of the properties of gel-type resins.¹⁵ The fact that the resins swell in the presence of [omim]Tf₂N and deswell after Soxhlet extraction is consistent with the fact that the linear, non-cross-linked polymer of VP is somewhat soluble in [omim]Tf₂N (see Table 1).

In contrast, the two polymers synthesized from DVB (**G'**) and from TRIM (**H'**) have relatively low bulk densities (<0.6 g cm⁻³), higher intrusion volumes (>0.9 cm³ g⁻¹), and much higher BET surface areas (70–370 m² g⁻¹). Interestingly, polymers **G'** and **H'**, both of which were prepared using [omim]Tf₂N as the porogen, were quite different in comparison with control polymers (**I** and **J**) synthesized using toluene as the porogen. In the case of the DVB polymer, **G'**, the average pore size of the material was much greater than the equivalent polymer synthesized using toluene (**I**) (see Figure 2a). As a result, the surface area for sample **G'** (73.2 m² g⁻¹) was found to be much lower than for sample **I** (321 m² g⁻¹).¹⁶ In contrast, the poly(TRIM) sample, **H'**, exhibits properties that are very similar to the equivalent material synthesized using toluene as the porogen (**J**). Both samples have high surface areas (~370 m² g⁻¹) and similar average pore sizes (0.040 and 0.029 μm, respectively). Figure 2b shows that the pore size distributions as measured for the two samples by mercury intrusion porosimetry are very similar. Sample **H'**, or similar materials, may be useful for a range of practical applications (e.g., membrane catalysis) because the pore size distribution is relatively broad and incorporates large pores (>100 nm) (to facilitate mass transport) that

Table 4. Cross-Linked Polymers^a

	monomer	cross-linker (mol %)	solvent	yield (%) ^b	ρ_s (g mL ⁻¹) ^c (T/°C)	ρ_b (g mL ⁻¹) ^d	SA _{BET} (m ² g ⁻¹) ^e	V _{tot} (mL g ⁻¹) ^d	A _{tot} (m ² g ⁻¹) ^d	D _{mv} (μm) ^d	P (%) ^d
E'	VP	5 ^f	[omim]Tf ₂ N	~100	1.278 (24.6)	1.050	1.6	0.13 ^g			<10 ^g
F'	VP	30 ^f	[omim]Tf ₂ N	89	1.141 (26.5)	0.768	1.7	0.26 ^g			<10 ^g
G'	DVB	55	[omim]Tf ₂ N	90	1.126 (24.7)	0.242	73.2	2.62	53.6	0.57	63
I	DVB	55	toluene	67	1.080 (25.4)	0.788	321	0.17	19.1 ^h	0.056	14
K	DVB	55	chloroform	59	1.075 (27.9)	0.741	4.5	0.26	66.3	0.033	19
H'	TRIM	100	[omim]Tf ₂ N	~100	1.264 (26.7)	0.559	365	0.89	170 ^h	0.040	50
J	TRIM	100	toluene	97	1.245 (26.7)	0.679	374	0.59	140 ^h	0.029	40
L	TRIM	100	chloroform	97	1.219 (26.5)	0.744	2.5	0.29	62.3	90.2	21

^a Polymerization conditions: monomer (1 vol), [omim]Tf₂N (2.5 vol), AIBN, 80 °C, 4 h. ^b After Soxhlet-extraction (refluxing MeOH, 72 h). ^c Skeletal density (from helium pycnometry). ^d From mercury intrusion porosimetry: ρ_b , bulk density (at 1 psia); V_{tot}, total intrusion volume; A_{tot}, total pore area; D_{mv}, median pore diameter by volume; P, porosity. ^e BET surface area. ^f DVB (55%; remainder composed of a mixture of 3- and 4-ethylvinylbenzene). ^g Most apparent porosity can be ascribed to interparticulate filling at low mercury pressure. ^h BET surface area suggests significant proportion of pores <7 nm that are not detected by mercury intrusion porosimetry.

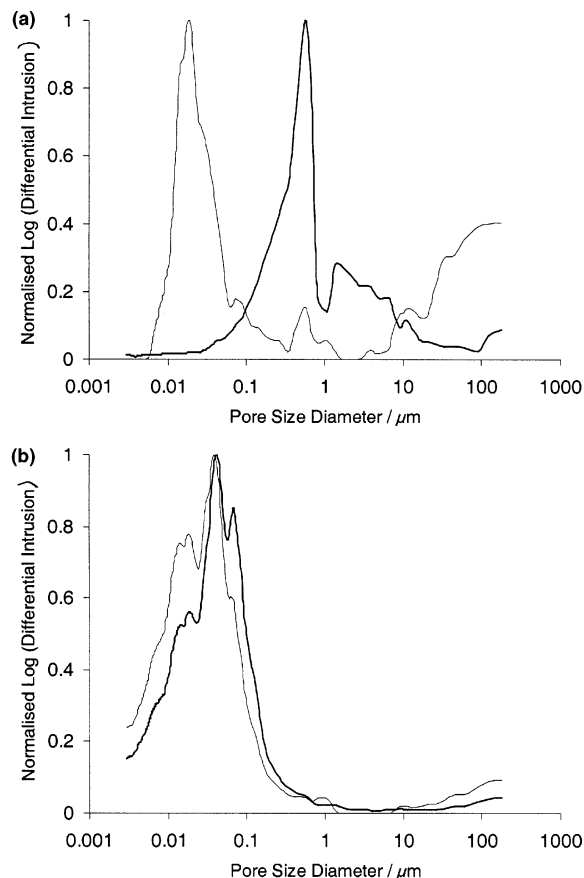


Figure 2. Pore size distributions for: (a) Soxhlet-extracted poly(divinylbenzene)s (55 mol %); polymerizations in [omim] Tf_2N (**G'**, bold line) and toluene (**I**, faint line); (b) Soxhlet-extracted poly(trimethylolpropane trimethacrylate)s; polymerization in [omim] Tf_2N (**H'**, bold line) and toluene (**J**, faint line).

are interconnected with much smaller pores for increased surface area.

The morphology of the porous materials was investigated by electron microscopy (Figures 3 and 4). Sample **G'** exhibited a much coarser structure (Figure 3a) than that observed for the equivalent polymer synthesized using toluene as the porogen (**I**, Figure 3b). In contrast, the two poly(methacrylate) samples, **H'** and **J**, showed very similar morphologies.

The differences between these two pairs of samples may arise from the sensitivity of these systems to the porogen solvent quality, which influences the mechanism of phase separation, nucleation, aggregation, and pore formation.¹⁵ Similar effects have been documented for conventional organic solvent porogens. For example, Peters et al. observed a dramatic porogen effect on the structure of porous copolymer monoliths synthesized from ethylene glycol dimethacrylate (EGDMA), butyl methacrylate, and 2-acrylamido-2-methyl-1-propane-sulfonic acid (AMPS).^{17a} A ternary porogen mixture was used consisting of 10 wt % water and 90 wt % of a mixture of 1-propanol and 1,4-butanediol. The average pore size in the monoliths was tuned by controlling the ratio of the two alcohols. Somewhat surprisingly, the porous structure was found to be *extremely* sensitive to the porogenic solvent composition: for example, when the proportion of propanol was increased from 55 to 63 wt %, the average pore size decreased from ~ 5000 to just 150 nm.^{17a} It was suggested that this could be attributed to the degree of solvation for the AMPS moieties, since the effect was more pronounced at higher AMPS incorporations. In a similar way, the average pore size in EGDMA/glycidyl methacrylate copolymer monoliths was controlled by using a cyclohexanol/dodecanol porogen mixture and varying the ratio of the two alcohols.^{17b} Xie et al. studied a homologous series of alcohols (methanol to dodecanol) mixed with dimethyl sulfoxide as porogens for the preparation of poly-(acrylamide-co-methylenebis(acrylamide)) monoliths and found that the average pore size increased significantly with increasing chain length of the porogenic alcohol.^{17c} Moreover, we have shown that the pore structure in permanently porous cross-linked poly(methacrylate) monoliths using supercritical CO_2 as the porogen is highly sensitive to changes in the CO_2 density.¹⁸ Each of these studies illustrates the sensitivity of the structure of highly cross-linked, permanently porous polyacrylates and polymethacrylates to the precise nature of the porogenic diluent. That the DVB system interacts quite differently with [omim] Tf_2N and toluene, while the TRIM system gives rise to quite similar materials, is further illustrative of this phenomenon.

Conclusions

The solubility of polymers in ionic liquids is characterized most notably by mass- and phase-transfer

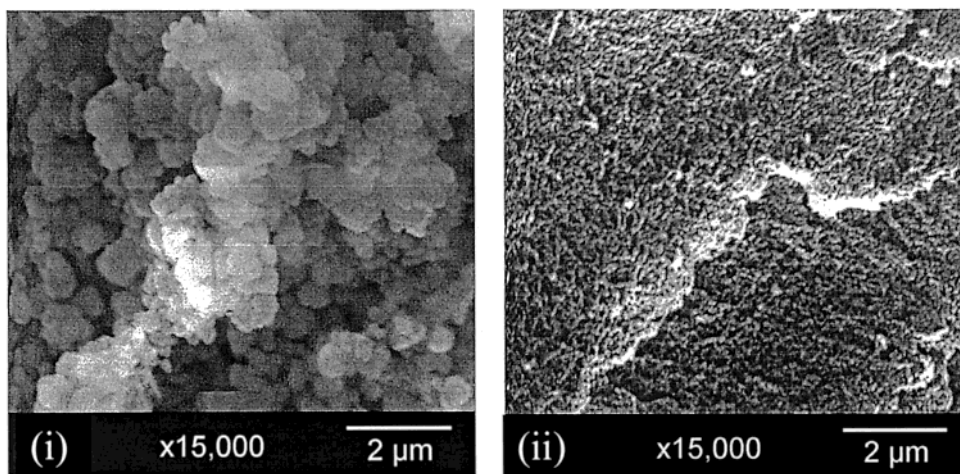


Figure 3. Scanning electron micrographs ($\times 15\,000$) of: (a) Soxhlet-extracted poly(divinylbenzene)s (55 mol %); polymerization in (i) [omim] Tf_2N (**G'**) and (ii) toluene (**I**); (b) Soxhlet-extracted poly(trimethylolpropane trimethacrylate)s; polymerization in (i) [omim] Tf_2N (**H'**) and (ii) toluene (**J**).

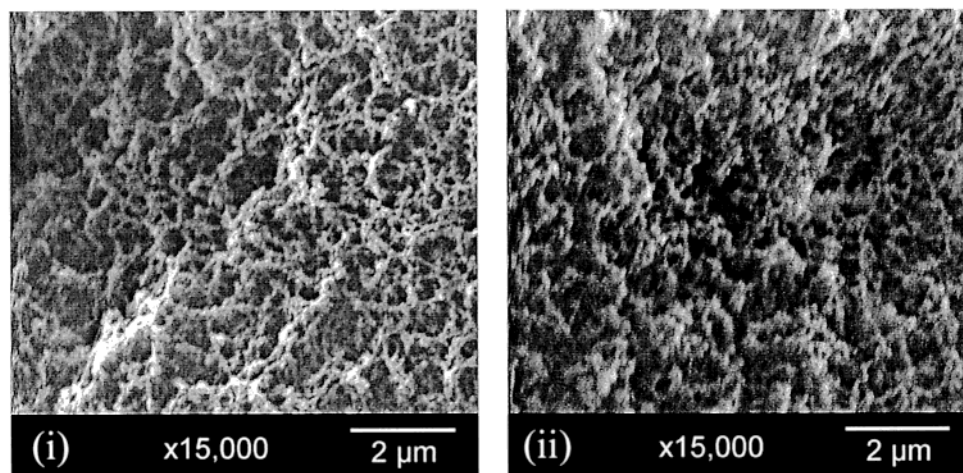


Figure 4. Scanning electron micrograph ($\times 15\,000$) of Soxhlet-extracted poly(trimethylolpropane trimethacrylate)s; polymerization in (a) [omim]Tf₂N (**H'**) and (b) toluene (**K**).

processes. Few general relationships between polymer solubility and polymer functionality or the nature of the ionic liquid are evident. The phase behavior of polymer–ionic liquid mixtures requires more in-depth investigation.

Free-radical-initiated homopolymerizations in *N,N'*-dialkylimidazolium ionic liquids yield polymers which retain 1–4% of the salt residues (determined from ¹H NMR measurements), despite multiple reprecipitations from solvents known to dissolve them. This conclusion, if shown to be general, may limit the usefulness of ionic liquids as media for free-radical polymerizations.

Ionic liquids are porogenic solvents for the efficient polymerization of the cross-linking monomers divinylbenzene and trimethylolpropane trimethacrylate. Little unreacted monomer is detected in the high-gel-fraction ionic liquid–polymer composite by thermogravimetric analysis (made possible because of the involatility of the porogenic solvent). Copolymers of 4-vinylpyridine with 5–30% divinylbenzene have limited permanent porosity.

Pore-size distribution of poly(divinylbenzene) using an ionic liquid as porogen is significantly different from that observed when toluene is used; that for poly(trimethylolpropane trimethacrylate) is similar whether an ionic liquid or toluene is the porogen.

Direct gelation in ionic liquids has led to ionic liquid–polymer composite resin materials suitable for evaluation in catalytic membranes.

Experimental Section

Materials. Poly(1-vinylimidazole-*co*-1-vinyl-2-pyrrolidinone), **6** (Luvitec VPI K72W; comonomer content = 50%), was kindly donated by BASF. Poly(1-methyl-3-vinylimidazolium methyl sulfate-*co*-1-vinylimidazole-*co*-1-vinyl-2-pyrrolidinone), **7** (Luviqat MS370), poly(1-methyl-3-vinylimidazolium chloride-*co*-1-vinylimidazole-*co*-1-vinyl-2-pyrrolidinone), **8** (Luviqat HM552), and poly(1-methyl-3-vinylimidazolium methyl sulfate-*co*-1-vinylimidazole-*co*-1-vinyl-2-pyrrolidinone-*co*-*N*-vinylcaprolactam), **9** (Luviqat HOLD), were obtained from Fluka. Poly(acrylic acid), **10** ($M_w = 2000\text{ g mol}^{-1}$), poly(butyl methacrylate), **11** ($M_w = 337\,000\text{ g mol}^{-1}$), poly(ethylene glycol), **12** ($M_w = 10\,000\text{ g mol}^{-1}$), poly(4-vinylpyridine), **14** ($M_w = 160\,000\text{ g mol}^{-1}$), poly(4-vinylpyridine-*co*-styrene), **15** (styrene content = 10%), poly(4-vinylpyridine-*co*-butyl methacrylate), **16** (butyl methacrylate content = 10%), and poly(1-vinyl-2-pyrrolidinone), **17** ($M_w = 10\,000\text{ g mol}^{-1}$), were obtained from Aldrich. Poly(styrene), **13** ($M_w = 30\,000\text{ g mol}^{-1}$), was obtained from Polysciences. Polymers **1–3** were prepared by the respective

quaternization reaction of polymers **14–16** with butyl bromide in chloroform.¹ Polymer **4** was prepared by the ion-exchange reaction of aqueous solutions of polymer **1** and lithium bis(trifluoromethylsulfonyl)amide.¹ Polymer **5** was prepared by the persulfate-initiated free-radical polymerization of 1-methyl-3-vinylimidazolium bis(trifluoromethylsulfonyl)amide in water.¹ Divinylbenzene (DVB; tech., 55%, mixture of isomers), trimethylolpropane trimethacrylate (TRIM; tech.), 4-vinylpyridine (VP; 95%), and 1-vinyl-2-pyrrolidinone (VPyr; 99%) were obtained from Aldrich and used as supplied. α,α' -Azobisisobutyronitrile (AIBN) was purchased from Fisher and recrystallized (methanol) prior to use. 1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆; $\geq 99\%$) and 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF₄; $\geq 98\%$) were obtained from Solvent Innovation. 1-Methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)amide ([omim]Tf₂N) was prepared by the ion-exchange reaction of aqueous solutions of 1-methyl-3-octylimidazolium chloride and lithium bis(trifluoromethylsulfonyl)amide.¹⁹

Acetone (Prolabo, AnR grade), chloroform (Prolabo, AnR grade), cyclohexane (BDH, GPR grade), dichloromethane (BDH, GPR grade), ethyl acetate (BDH, GPR grade), methanol (BDH, AnR grade), and toluene (BDH, AnR grade) were used as supplied.

Characterization. Gel permeation chromatography (GPC) was used to measure molecular weights and molecular weight distributions with respect to poly(methyl methacrylate) standards. GPC experiments were carried out at 80 °C in DMF (with 0.01 M LiBr to suppress interactions with column packing) using a Waters 150CV instrument fitted with a differential refractometer detector (columns: PLgel 2 $\times$ mixed bed-B, 30 cm, 10 μm ; flow rate = 1.0 mL min⁻¹). ¹H NMR spectra were recorded on a Bruker 400 MHz spectrometer; chemical shifts (ppm) are reported relative to Me₄Si. Onset decomposition temperatures (T_{onset}) and maximal decomposition temperatures (T_{max}) were determined by thermogravimetry in flowing air (heating rate = 20 °C min⁻¹) on a Perkin-Elmer TGA 7 thermogravimetric analyzer. Total intrusion volumes (V_{tot}), bulk densities (ρ_b), total pore areas (A_{tot}), median pore diameters (by volume, D_{mv}), and porosities (P) were measured using a Micromeritics AutoPore IV 9500 mercury intrusion porosimeter. Samples were subjected to a pressure cycle starting at approximately 0.5 psia, increasing to 60 000 psia in predefined steps to give pore size/pore volume information. Skeletal densities (ρ_s) were measured using a Micromeritics AccuPyc 1330 helium pycnometer. BET surface areas (S_{BET}) were evaluated on a Micromeritics ASAP 2010 surface area and pore size analyzer; samples were degassed for 2 h at 110 °C prior to analysis. Scanning electron microscopy was performed on a Hitachi S-2460N scanning electron microscope. The samples were sputter-coated with approximately 10 nm gold before analysis.

General Procedure for Polymer Solubility Screening

Experiments. Polymers **1–17** (25 mg) were individually dissolved in solvent (0.5 mL: acetone **4, 5**; MeOH **1–3, 6–10**; CH₂Cl₂ **11–17**), and the resultant polymer solutions (5 wt %) were injected (glass syringe) into glass vials (2 mL capacity, fitted with silicone–PTFE seals) containing ionic liquid (0.5 mL; [emim]BF₄, [bmim]PF₆, or [omim]Tf₂N); the resultant solutions were briefly agitated. A syringe needle was inserted into each sample vial lid seal (to provide an air bleed), and the volatiles were removed in vacuo (oil pump) at 50 °C for 3 days. Phase changes in the ionic liquid/polymer solutions were monitored over the course of 11 ([emim]BF₄, [omim]Tf₂N) or 15 weeks ([bmim]PF₆).

General Procedures for Polymerizations and Polymer Purification

A degassed (three freeze–pump–thaw cycles) solution of monomer (VP, VPyr, DVB, or TRIM; 29% v/v), DVB (0, 1, 5, or 30 mol %), AIBN (1 mol %), and solvent ([bmim]PF₆, [omim]Tf₂N, CHCl₃, or toluene) in a Schlenk tube was stirred (magnetic follower) under vacuum at 80 °C for 4 h. Linear polymers were purified by repeated reprecipitation. Cross-linked polymers were purified by Soxhlet extraction (refluxing MeOH, 72 h). Purified polymers were dried in vacuo (50 °C) to constant weight.

Polymerization of VPyr and DVB (0, 1, and 5 mol %).

All polymerization reactions were carried out in [bmim]PF₆. Poly(VPyr): **A** (trituted three times with EtOAc and then reprecipitated five times from CH₂Cl₂–EtOAc), white solid, $M_w = 162\,500\text{ g mol}^{-1}$, $M_n = 61\,000\text{ g mol}^{-1}$, $M_w/M_n = 2.7$ (data averaged over two runs). δ_H (CDCl₃, 400 MHz): 1.30–2.50 [m, 6H, CH₂CH₂C(O) + CHCH₂], 3.20 (m, 2H, NCH₂), and 3.50–4.00 (m, 1H, CHCH₂). Attempts to prepare DVB–cross-linked poly(VPyr)–[bmim]PF₆ composite materials afforded tacky syrups (**B, C**); solubility tests suggested the products to have no (**B'**), or very little (**C'**), cross-linking: **B** (1 mol % DVB), transparent yellow tacky syrup (completely soluble in CH₂Cl₂), T_{onset} 326 °C, T_{max} 475 °C; **C** (5 mol % DVB), opaque white tacky syrup (produced milky solution in CH₂Cl₂), T_{onset} 309 °C, T_{max} 442 °C.

Polymerization of VP and DVB (0, 5, and 30 mol %).

All polymerization reactions were carried out in [omim]Tf₂N. Poly(VP): **D'** (trituted three times with EtOAc and then reprecipitated five times from CH₂Cl₂–EtOAc), white solid, $M_w = 71\,000\text{ g mol}^{-1}$, $M_n = 36\,000\text{ g mol}^{-1}$, $M_w/M_n = 2.0$ (data averaged over two runs). δ_H (CDCl₃, 400 MHz): 1.44 (m, backbone; sh at 1.55), 1.84 (m, backbone; sh at 1.90), 6.38 (m, 2H, ArH), and 8.32 (m, 2H, ArH). DVB–cross-linked poly(VP)–[omim]Tf₂N composite materials: **E** (5 mol % DVB), transparent orange gel, T_{onset} 255 °C, T_{max} 331 and 432 °C, skeletal density = $1.291 \pm 0.006\text{ g mL}^{-1}$ (26.1 °C); **F** (30 mol % DVB), pale flesh-colored waxy solid, T_{onset} 286 °C, T_{max} 355, 452, and 491 °C, skeletal density = $1.301 \pm 0.007\text{ g mL}^{-1}$ (24.6 °C). DVB–cross-linked poly(VP)s: **E'** (Soxhlet extraction of **E**), orange solid (~100% conversion), T_{onset} 169 °C, T_{max} 388 °C, skeletal density = $1.278 \pm 0.036\text{ g mL}^{-1}$ (24.6 °C), bulk density = 1.050 g mL^{-1} , $SA_{BET} = 1.6 \pm 0.2\text{ m}^2\text{ g}^{-1}$, total intrusion volume = 0.13 mL g^{-1} , porosity = <10%; **F'** (Soxhlet extraction of **F**), flesh-colored solid (89% conversion), T_{onset} 320 °C, T_{max} 417 °C, skeletal density = $1.141 \pm 0.002\text{ g mL}^{-1}$ (26.5 °C), bulk density = 0.768 g mL^{-1} , $SA_{BET} = 1.7 \pm 0.1\text{ m}^2\text{ g}^{-1}$, total intrusion volume = 0.26 mL g^{-1} , porosity = <10%.

Polymerization of DVB (55 mol %).

Polymerization reactions were carried out in [omim]Tf₂N (**G**), toluene (**I**), or chloroform (**K**). Poly(DVB)–[omim]Tf₂N composite material: **G**, white chalky solid, T_{onset} 363 °C, T_{max} 469 °C, skeletal density = $1.282 \pm 0.001\text{ g mL}^{-1}$ (25.8 °C). Poly(DVB)s: **G'** (Soxhlet extraction of **G**), white solid (90% conversion), T_{onset} 312 °C, T_{max} 386 and 568 °C, skeletal density = $1.126 \pm 0.016\text{ g mL}^{-1}$ (24.7 °C), bulk density = 0.242 g mL^{-1} , $SA_{BET} = 73.2 \pm 0.7\text{ m}^2\text{ g}^{-1}$, total intrusion volume = 2.62 mL g^{-1} , total pore area = $53.6\text{ m}^2\text{ g}^{-1}$, median pore volume = 0.57 mL g^{-1} , porosity = 63%; **I**, white solid (67% conversion), T_{onset} 325 °C, T_{max} 408 and 454 °C, skeletal density = $1.080 \pm 0.009\text{ g mL}^{-1}$ (25.4 °C), bulk density = 0.788 g mL^{-1} , $SA_{BET} = 321 \pm 1\text{ m}^2\text{ g}^{-1}$, total intrusion volume = 0.17 mL g^{-1} , total pore area = $19.1\text{ m}^2\text{ g}^{-1}$, median pore volume = 0.056 mL g^{-1} , porosity = 14%; **K**, white

solid (59% conversion), T_{onset} 331 °C, T_{max} 469 °C, skeletal density = $1.075 \pm 0.014\text{ g mL}^{-1}$ (27.9 °C), bulk density = 0.741 g mL^{-1} , $SA_{BET} = 4.5 \pm 0.1\text{ m}^2\text{ g}^{-1}$, total intrusion volume = 0.26 mL g^{-1} , total pore area = $66.3\text{ m}^2\text{ g}^{-1}$, median pore volume = 0.033 mL g^{-1} , porosity = 19%.

Polymerization of TRIM (100 mol %). Polymerization reactions were carried out in [omim]Tf₂N (**H**), toluene (**J**), or chloroform (**L**). Poly(TRIM)–[omim]Tf₂N composite material: **H**, pale flesh-colored waxy solid, T_{onset} 262 °C, T_{max} 309, 414, and 494 °C, skeletal density = $1.327 \pm 0.004\text{ g mL}^{-1}$ (25.9 °C). Poly(TRIM)s: **H'** (Soxhlet extraction of **H**), white solid (~100% conversion), T_{onset} 263 °C, T_{max} 275, 392, and 448 °C, skeletal density = $1.264 \pm 0.024\text{ g mL}^{-1}$ (26.7 °C), bulk density = 0.559 g mL^{-1} , $SA_{BET} = 365 \pm 2\text{ m}^2\text{ g}^{-1}$, total intrusion volume = 0.89 mL g^{-1} , total pore area = $170\text{ m}^2\text{ g}^{-1}$, median pore volume = 0.040 mL g^{-1} , porosity = 50%; **J**, white solid (97% conversion), T_{onset} 260 °C, T_{max} 272, 397, and 475 °C, skeletal density = $1.245 \pm 0.023\text{ g mL}^{-1}$ (26.7 °C), bulk density = 0.679 g mL^{-1} , $SA_{BET} = 374 \pm 1\text{ m}^2\text{ g}^{-1}$, total intrusion volume = 0.59 mL g^{-1} , total pore area = $140\text{ m}^2\text{ g}^{-1}$, median pore volume = 0.029 mL g^{-1} , porosity = 40%; **L**, white solid (97% conversion), T_{onset} 280 °C, T_{max} 354 and 500 °C, skeletal density = $1.219 \pm 0.016\text{ g mL}^{-1}$ (26.5 °C), bulk density = 0.744 g mL^{-1} , $SA_{BET} = 2.5 \pm 0.2\text{ m}^2\text{ g}^{-1}$, total intrusion volume = 0.29 mL g^{-1} , total pore area = $62.3\text{ m}^2\text{ g}^{-1}$, median pore volume = 90.2 mL g^{-1} , porosity = 21%.

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