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Resorcinol-Formaldehyde Polycondensation in Deep Eutectic Solvents for the Preparation of Carbons and Carbon−Carbon Nanotube Composites

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Deep eutectic solvents (DES, a new class of ionic liquids) have been used as solvents to carry out the polycondensation of resorcinol-formaldehyde (RF). RF gels were characterized by FTIR and solid ^{13}C NMR spectroscopy, and scanning electron microscopy. Solid ^{13}C NMR spectroscopy demonstrated that the use of DES containing small amounts of water (those required to introduce formaldehyde in the solution) favored RF polycondensation as compared to that carried out in regular aqueous conditions (that is, in absence of DES). RF polycondensation also occurred in DES in its pure state (in this case, after lyophilization) albeit the reaction efficiency was difficult to evaluate given to partial elimination of formaldehyde. Carbonization of any of the RF gels obtained in DES (e.g., with or without water) resulted in the formation of monolithic carbons with conversion rates and carbon contents in range to and even slightly above those obtained in aqueous solutions. Finally, we took advantage of the excellent solvent properties of DES to suspend carbon nanotubes (CNTs) within the starting sol. Polycondensation of resorcinol and formaldehyde in DES also containing CNTs in suspension allowed the preparation of carbon−carbon nanotube RF gels and ultimately (i.e., after thermal treatment) carbon composites, having multiwall CNTs (MWCNTs) homogeneously distributed within the whole monolithic structure.

Introduction

The synthesis of carbons via polycondensation of phenols and phenol derivates with aldehydes and subsequent carbonization has attracted great attention because of the possibility to tailor both the structure and the functionality of the resulting materials.[1] Thus, since the first works reported by Pekala and co-workers in the earliest 1990s,[2] numerous articles have appeared in the literature describing not only various synthesis (based on hydrolysis−condensation reactions mostly in aqueous solvents) and processing conditions that can be used to produce organic and carbon aerogels and xerogels, but also how these conditions affect the final structure of these materials.[3]

Besides structural control, recent efforts have also been focused on the design of CA composites with the goal of improving certain properties such as conductivity or catalytic activity, among the most relevant. Thus, both metal and metal oxide nanoparticles have been incorporated within the carbon structure by different synthetic approaches.[4] Less explored has been the incorporation of carbon nanotubes (CNTs)[5] even though the promising features offered by CNT based composites of any type (e.g., small amounts of CNT may contribute to a remarkable enhancement of both the conductivity and the mechanical properties of the composites, and may also be used as supports of metal and metal oxide nanoparticles).[6] The reason behind the limited number of reports on CNT-carbon composites prepared by RF polycondensation resides in the difficulties to disperse the CNTs in the aqueous media where hydrolysis and condensation reactions typically occur which, ultimately, is crucial to achieve a good uniform dispersion of nanotubes throughout the carbon matrix. Apart from different

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approaches where CNTs are not dispersed in the aqueous media (e.g., CNT dispersion in toluene and subsequent impregnation of preformed carbon aerogels or use of carbon matrixes not obtained from polycondensation),[5b,c] the most suitable approach for CNTs dispersion in the aqueous media has been obtained thanks to the aid of surfactants and polymers.[7] On the other hand, the use of a solvent (different than water) suitable for CNTs dispersion where polycondensations are allowed could also offer a plausible alternative for the synthesis of CNT-carbon composites.

Ionic liquids (ILs) have lately gained increased interest as solvents in a number of polymerizations (e.g., free radical,[8] atom transfer radical polymerization,[9] cationic,[10] cationic ring-opening,[11] and metathesis[12]). Polycondensations in ILs have been less explored, and reported studies have mostly focused on the synthesis of polyamide.[13] More recently, polycondensation of phenol with paraformaldehyde using sulfuric acid as catalyst in an IL based on imidazolium salt has also been reported.[14] In this latter case, IL acted not only as a simple solvent but also as a catalyzer promoting the formation of high molecular weight phenol polymers. Besides these features, the use of ILs in polycondensations could offer interesting perspectives for the preparation of CNT-carbon composites given the excellent ability of ILs for CNTs dispersion.[15]

Deep-eutectic solvents (DESs) have been recently reported as another type of ILs.[16] DESs are mixtures for which the freezing point is lower than that of either of its individual components. Examples of DESs include mixtures of quaternary ammonium salts (e.g., choline chloride) with neutral organic hydrogen-bond donors (such as amides, amines, and carboxylic acids).[17] DESs share many characteristics of conventional ILs (e.g., non-reactive with water, non-volatile and biodegradable, among others), but their low cost make them particularly desirable (more than ILs) for applications in the large-scale synthesis of new functional materials. Both ILs and DESs have also gained much attention given their capability to induce textural properties in a number of materials.[18]

In this work, we have explored the suitability of DESs to allow the polycondensation of resorcinol with formaldehyde. The DES of choice was based on a mixture of ethylene glycol (EG) and choline chloride (CCl) in a 2:1 molar ratio (EGCCl-DES). Polycondensation was carried out using basic (sodium carbonate) and acid (chlorhydric acid) catalysis, as well as without catalysts. Catalysts were incorporated in the formaldehyde aqueous solution so that, in these cases, RF gels were synthesized in DES slightly diluted in water. RF gels were also prepared in absence of water (by lyophilization of the starting sol before aging) and in absence of DES (e.g., under regular aqueous solutions), for comparison. Resorcinol-formaldehyde (RF) gels were studied by FTIR and solid ^{13}C NMR spectroscopies, and by scanning electron microscopy. Monolithic carbons were obtained by thermal treatment of RF gels to 800 °C in nitrogen atmosphere. The excellent solvent properties of DESs allowed multiwall carbon nanotubes (MWCNT) incorporation into the RF gel and, after carbonization, the achievement of carbon-carbon nanotube composites where MWCNT were homogeneously distributed within the carbon monolith. The resulting composites were studied by scanning and transmission electron microscopy. Data in regard to the conversion yields, carbon contents, and surface area are also provided.

Experimental Part

1. Preparation of Ethylene Glycol:Choline Chloride Deep Eutectic Solvent (EGCCl-DES). EGCCl-DES was formed by heating ethylene glycol (24.83 g, 0.4 mol) and choline chloride (27.93 g, 0.2 mol) to 80 °C and stirring until a homogeneous liquid was formed.

2. Preparation of RF Gels in Aqueous Solutions (RFW Gels). The preparation of RF gels using basic catalysis (RFW^b gels) was accomplished by dissolution of 358 mg of resorcinol (R) in 0.675 mL of doubled distilled water. Then, an aqueous solution of formaldehyde (F) (0.485 mL, 37 wt %) and sodium carbonate (0.05 mL of a 1.3 M solution) was added to the mixture and stirred for 10 min. The pH of the resulting sol was 8. The resulting mixture was aged for 2 h at room temperature, 6 h at 60 °C, and 5 days at 90 °C.

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The preparation of RF gels using acid catalysis (RFW^{a} gels) and without catalysis (RFW^{nc} gels) was accomplished as described above for RFW^{b} except for the use of chlorhydric acid (0.032 mL of a 5 M solution) or none catalyst, respectively, instead of sodium carbonate solution. The pHs of the resulting sols were 0.7 and 3.0, respectively.

3. Preparation of RF Gels in DES (RFW-DES and RF-DES Gels). *3.1. In Presence of Small Amounts of Water Used for Addition of Formaldehyde (RFW-DES Gels).* The preparation of RFW^{b}-DES gels was accomplished by dissolution of 358 mg of R in 750 mg of EGCCl-DES. Subsequently, an aqueous solution of F (0.485 mL, 37 wt %) and sodium carbonate (0.05 mL of a 1.3 M solution) was added to the mixture and stirred for 10 min. The pH of the resulting sol was 7.5. The resulting mixture was aged as described above for RFW^{b} gels.

The preparation of RFW^{a}-DES and RFW^{nc}-DES gels was accomplished as described above for RFW^{b}-DES except for the use of chlorhydric acid (0.032 mL of a 5 M solution) or none catalyst, respectively. The pHs of the resulting sols were 0.2 and 2.7, respectively.

3.2. In Absence of Water (RF-DES Gels). The preparation of RF^{b}-DES gels was accomplished by dissolution of 358 mg of R in 375 mg of EGCCl-DES. In a different flask, 375 mg of EGCCl-DES was added to an aqueous solution of F (0.485 mL, 37 wt %) and sodium carbonate (0.05 mL of a 1.3 M solution) and stirred for 10 min. The pH of the resulting sol was 7.5. The sol was thereafter freeze-dried for water elimination. The weight loss after lyophilization was 589 mg, 213 mg above that expected from the water originally added in solution (e.g., 376 mg). Given the hygroscopic character of DES, we wondered if part of this water was adsorbed from moisture. Thus, we prepared a solution only containing DES (375 mg), water (500 mg), and sodium carbonate (0.05 mL) and, after lyophilization, the weight lost was 583 mg, 40 mg above that expected from water originally added in solution (e.g., 543 mg). Thus, even taking into consideration the hygroscopic character of DES, the estimated lost of F after lyophilization was about 90%. The freeze-dried mixture of F and sodium carbonate in EGCCl-DES was added to the solution of R in EGCCl-DES and stirred vigorously for another 10 min. The homogeneous mixture was aged as described above for RFW^{b} and RFW^{b}-DES gels.

The preparation of RF^{a}-DES and RF^{nc}-DES gels was accomplished as described above for RF^{b}-DES except for the use of chlorhydric acid (0.032 mL of a 5 M solution) or none catalyst, respectively, instead of sodium carbonate solution. The pHs of the resulting sols (prior to lyophilization) were 0.2 and 2.7, respectively.

4. Preparation of RF Gels from Concentrated Sols (RFW2^{b} and RFW2^{b}-DES Gels). The preparation of RF gels from concentrated sols was accomplished as described above in sections 2 and 3 for the achievement of RFW^{b} and RFW^{b}-DES gels, except for the use of a concentrated solution of R. Such a concentrated sol was obtained by dissolution of 358 mg of R in the selected solvent (e.g., 0.338 mL of doubled distilled water or 375 mg of EGCCl-DES). Then, an aqueous solution of F (0.485 mL, 37 wt %) and sodium carbonate (0.05 mL of a 1.3 M solution) was added to the mixture and stirred for 10 min. The resulting mixture was aged as described above.

5. Preparation of Gels Containing MWCNT (MWCNT-RFW^{b} and MWCNT-RFW^{b}-DES Gels). MWCNT (150 mg) were homogeneously dispersed in either 0.675 mL of double distilled water or 750 mg of EGCCl-DES. After MWCNT dispersion in water or EGCCl-DES, the process was identical to the procedure described above in sections 2 and 3 for the achievement of RFW gels and RFW-DES.

6. Preparation of Carbons from RFW, RFW-DES, RF-DES, MWCNT-RFW, and MWCNT-RFW-DES Gels. Carbons (so-called CW, CW-DES, C-DES, MWCNT-CW and MWCNT-CW-DES) were obtained by carbonization of the above-described RF gels (RFW, RFW-DES, RF-DES, MWCNT-RFW and MWCNT-RFW-DES gels, respectively). Prior to carbonization, RFW-DES, RF-DES, and MWCNT-RFW-DES gels were washed in water for 2 days to recover the DES. The thermal treatment used for carbonization consisted of 4 h at 210 °C followed by 4 h at 800 °C (heating ramp 1 °C/min).

7. Samples Characterization. RFW, RFW2, and MWCNT-RFW gels were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and solid-state ^{13}C cross-polarization magic angle spinning nuclear magnetic resonance (^{13}C−CPMAS-NMR) after water elimination by freeze-drying. RFW-DES, RFW2-DES, RF-DES, and MWCNT-RFW-DES gels were washed in water for 2 days (for DES recovering) and freeze-dried prior to characterization by SEM, FTIR, and solid ^{13}C NMR. FTIR spectra were carried out in a FTIR Bruker IFS60v spectrometer. Solid-state ^{13}C−CPMAS-NMR spectra were obtained in a Bruker AV-400-WB spectrometer, using a standard cross-polarization pulse sequence. Samples were spun at 10 kHz. Spectrometer frequencies were set to 100.32 and 400.13 MHz for ^{13}C and ^{1}H, respectively. A contact time of 3.5 ms and a period between successive accumulations of 4 s were used. The number of scans was 1024. Chemical shifts were referenced to TMS using the CH_2 signal of adamantine observed at 29.5 ppm as a secondary reference. X-ray diffraction (XRD) and Raman spectra of carbons were carried out in a Bruker D8 Advance difractometer using the CuKα radiation (0.02° step size and 1.0 s counting time) and in a Renishaw InVia upon irradiation at 514 nm (100% laser power, 16 mW power, 10 accumulations and 10 s exposure time), respectively. The chemical analysis of carbons was performed by ICP − AES (ICP − Atomic Emission Spectrometry) with a Thermo Jarrel Ash model IRIS Advantage, carbon with a Leco CS − 200, nitrogen and oxygen with a Leco TC − 500. The morphology of freeze-dried gels and carbons was observed by SEM using a Zeiss DSM-950 equipment. Samples were mounted onto the SEM sample holder and gold sputter coated (for 2 min, to obtain a about 5 nm gold film) prior to SEM observation. The accelerating voltage was 15−20 KVolts and the work distance 14−9 mm. The morphology of carbons was also observed by TEM (200 keV JEOL-2000). In this case, carbons were powdered, suspended in water, deposited on carbon-coated grids, and dried in air over 1 day prior to TEM observation. Single point surface area measurements were carried out in a Tri-Star 3000 (Micromeritics Instrument Corp., Norcross, GA).

Results and Discussion

RF gels were produced in EGCCl-DES using a similar procedure to that typically followed in aqueous conditions. Thus, an aqueous solution of formaldehyde (containing either basic, acid or none catalysts) was added to EGCCl-DES where resorcinol (in the appropriate molar ratios) was previously dissolved. The resulting mixture was stirred for homogenization and stored at 90 °C for 5 days in a closed container (to avoid evaporation) until the formation of cross-linked RF gels. Depending on the amount of water in solution, we obtained two different set of gels; those prepared from

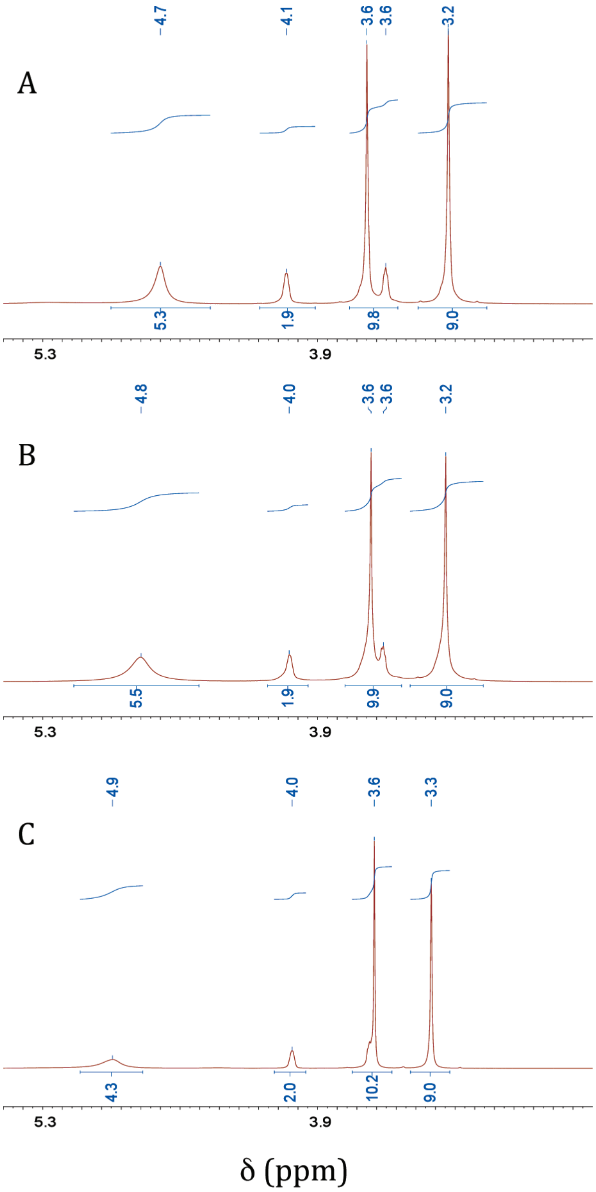

Figure 1. ^1H NMR spectra of D_2O solutions of EGCCl-DES: 53 wt % (a) and 69 wt % (b). The ^1H NMR spectrum of the EGCCl-DES obtained by heating ethylene glycol and choline chloride in a 2:1 molar ratio is also included for comparison (c).

the sol that contains the small amount of water coming from the addition of formaldehyde as an aqueous solution and so-called RFW^b-DES, RFW^a-DES or RFW^{nc}-DES, depending on the use of basic, acid, or none catalysts, respectively (see Experimental Part) and those prepared from a non-aqueous sol obtained by lyophilization of the aqueous one prior to condensation starts and so-called RF^b-DES, RF^a-DES, or RF^{nc}-DES (see Experimental Part). For comparison, RF gels so-called RFW^b, RFW^a, or RFW^{nc} (see Experimental Part) were also prepared following a regular aqueous route (that is, in absence of EGCCl-DES).

Prior to the study of polycondensation reactions in EGCCl-DES, we decided to study if the presence of water in the synthesis of RFW-DES gels could disrupt the supramolecular complexes that characterize DESs. It is worthy to note that, in aqueous solutions, ethylene glycol-choline chloride can be solvated by water molecules rather than forming ion pairs. ^1H NMR spectroscopy is a quite feasible tool to study whether or not ethylene glycol-choline chloride ion pairs are formed given that some chemical shifts are strongly influenced by this event. Thus, we performed ^1H NMR spectroscopy on EGCCl-DES in its pure state (e.g., in absence of water) and on different D_2O dilutions of EGCCl-DES (e.g., 89, 69, 53, 44, and 5 wt %). The spectra of EGCCl-DES in its pure state showed the characteristic signals of choline chloride protons and ethylene glycol (see Figure 1 and Table 1). The presence of halide ion−hydrogen-bond-donor supramolecular complexes that characterize DESs based on choline chloride and ethylene glycol was mostly reflected in the signals at 3.61 and 4.94 ppm. The former integrated 10 H and resulted from the overlapping of underlined methylene groups (e.g., $(HO-CH_2-C\underline{H_2}-N(CH_3)_3$ and $(HO)_2-(C\underline{H_2})_2)$ while the latter integrated 4.3 H and resulted from proton exchange between hydroxyls groups. In some of our previous works on urea-choline chloride and glycerol-choline chloride based DESs,[19] we observed that D_2O dilution was reflected at the ^1H NMR spectra by the appearance of the HDO signal indicative of proton exchange between either amine (for urea based DESs) or hydroxyl groups (for glycerol based DESs), and D_2O. Proton exchange was also reflected in both the partial (or total, for high dilutions) decrease of the signal intensity of such exchangeable protons and the chemical shift of protons bonded to adjacent carbons. In this work, dilution of EGCCl-DES resulted in proton exchange between hydroxyl groups (of ethylene glycol and choline chloride) and D_2O, and in the splitting of the signal at 3.6 ppm as consequence of the upfield shift of methylene groups of ethylene glycol; that is, the higher the dilution, the larger the number of exchanged protons and the upfield shift (see Figure 1 and Table 1, and Supporting Information, Figure S1). Thus, both features were quite noticeable for highly diluted samples (e.g., 5 wt %, EGCCl-DES5 in Supporting Information, Figure S1 and Table 1), revealing the major rupture of the halide ion−hydrogen-bond-donor supramolecular complexes that characterize DES at those dilutions. On the other hand, the ^1H NMR spectra of a highly concentrated sample (e.g., 89 wt %, EGCCl-DES89 in Supporting Information, Figure S1 and Table 1) exhibited signal intensities assigned to exchanged protons close to that of DES in its pure state (5.2 versus 4.3 H, respectively) and nonsplitting of the signal at 3.6 ppm. Intermediate concentrations (e.g., 44 wt %, EGCCl-DES44 in Supporting Information, Figure S1 and Table 1) exhibited an intermediate situation with signal intensities assigned to exchanged protons ranging 6.0 H but with a complete splitting of the signal at 3.6 ppm. In this work, the dilutions used for preparation of RF gels ranged from 69 wt % (for RFW-DES gels) to 53 wt % (for RFW2-DES gels).

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Table 1. ^{1}H-NMR Spectroscopy Data of EGCCl-DES in Its Pure State and of Aqueous Dilutions of EGCCl-DES[a]

	δ (ppm)					
	$(2\times)$[b] ethylene glycol		$(1\times)$[b] choline			
sample	$(\underline{H}O)_2-(C\underline{H}_2)_2$		$\underline{H}O-C\underline{H}_2-C\underline{H}_2-N(C\underline{H}_3)_3$			
EGCCl-DES	4.94[c] (4.3H)	3.61[d] (10H)	4.94[c] (4.3H)	4.03 (2H)	3.61[d] (10H)	3.32 (9H)
EGCCl-DES89	4.84[c] (5.2H)	3.62[d] (10H)	4.84[c] (5.2H)	4.03 (2H)	3.62[d] (10H)	3.28 (9H)
EGCCl-DES69	4.80[c] (5.5H)	3.63[d] (10H)	4.80[c] (5.5H)	4.04 (2H)	3.57[d] (10H)	3.25 (9H)
EGCCl-DES53	4.70[c] (5.3H)	3.65 (8H)	4.70[c] (5.3H)	4.06 (2H)	3.55 (2H)	3.23 (9H)
EGCCl-DES44	4.80[c] (6.0H)	3.66 (8H)	4.80[c] (6.0H)	4.06 (2H)	3.55 (2H)	3.23 (9H)
EGCCl-DES5	4.82[c] (13H)	3.71 (8H)	4.82[c] (13H)	4.11 (2H)	3.57 (2H)	3.25 (9H)

[a] Spectra were recorded using $CDCl_3$ as external reference. [b] The molar ratio of ethylene glycol to choline chloride was 2:1 in every sample. [c] Overlapping between hydroxyl groups of choline chloride and ethylene glycol makes impossible to integrate these signals separately. [d] Overlapping between underlined methylene groups of choline chloride and ethylene glycol (e.g., $(HO-CH_2-C\underline{H}_2-N(CH_3)_3$ and $(HO)_2-(C\underline{H}_2)_2)$ makes impossible to integrate the signals separately in EGCCl-DES and EGCCl-DES89 samples, and difficult in EGCCl-DES69 sample.

The ^{1}H NMR spectra of EGCCl-DES69 and EGCCl-DES53 exhibited also an intermediate behavior but, in overall, they (mainly EGCCl-DES69) were more similar to EGCCl-DES89 than to EGCCl-DES44 (i.e., the intensity of exchanged protons was 5.5−5.3 H and the splitting of the signal at 3.6 ppm was not complete, see Figure 1 and Table 1). On the basis of these results, we could conclude that the presence of the supramolecular complexes that characterize DESs was still major in the reaction medium used for the preparation of RFW-DES and even of RFW2-DES.

Our next concern was to study the chemical make up of RF gels. The major reactions between resorcinol and formaldehyde include an addition reaction to form hydroxymethyl derivatives ($-CH_2OH$), and then a condensation reaction of the hydroxymethyl derivatives to form methylene ($-CH_2-$) and methylene ether ($-CH_2OCH_2-$) bridged compounds.[20] Prior to characterization by FTIR and solid ^{13}C NMR spectroscopy, RFW-DES and RF-DES gels were washed with water and subsequently, freeze-dried. Washing not only allows DES clearance from gels (otherwise, DES signals would overlap those coming from RF) but also DES recovering (see Supporting Information, Figure S2) to be used in subsequent reactions. FTIR and solid ^{13}C NMR spectroscopy of RFW gels were also recorded for comparison. In this case, they were just submitted to freeze-drying prior to characterization (no washing was required). As a general trend, highly cross-linked clusters (7 to 10 nm in diameter)[21] of polymer results from the multistep condensation mechanism described above. Subsequently, the colloidal particles begin to aggregate and assemble into a stiff, interconnected structure that fills the original volume of the aqueous solution. First samples under study were those synthesized using a basic catalyst. Thus, left column Figure 2 shows SEM micrographs of washed and freeze-dried RFW^b-DES and RF^b-DES, and of freeze-dried RFW^b gels resembling such interconnected structure. Interestingly, RF monolithic gels were obtained in every case (inset shows the particular case of RFW^b-DES as a representative example) as consequence of the stiffness of such interconnected structure.

The IR spectrum of a typical RF aerogel synthesized with basic catalyst (RFW^b in Figure 3) shows bands at 2929, 2846, and 1479 cm^{-1} associated with the CH_2 stretching and bending vibrations, whereas the broad band at 3388 cm^{-1} includes the aromatic OH groups of resorcinol. The band at 1610 cm^{-1} comes from aromatic ring stretches, whereas medium to weak absorption bands at 1215 and 1092 cm^{-1} correspond to the C−O stretch and deformation of benzyl ether groups, respectively. Thus, the number of linkages between resorcinol rings (that is, the condensation degree of a particular RF gel) can be estimated from the intensity of bands assigned to methylene (CH_2 groups at 2929, 2846, and 1479 cm^{-1}) and methylene ether groups (C−O benzyl ether groups at 1222 and 1092 cm^{-1}).[22] Interestingly, the IR spectra of gels synthesized in EGCCl-DES (both RFW^b-DES and RF^b-DES in Figure 3) revealed no significant differences as compared to that of RFW^b gels.

Solid ^{13}C NMR spectroscopy has also demonstrated to be a useful tool for the study the RF gels.[23] In terms of condensation, the most interesting signals are those centered at about 59 ppm and 30 ppm (the latter, very broad and with a shoulder at 24 ppm), which are typically assigned to methylene ether and methylene groups (e.g., CH_2-O-CH_2 and CH_2 bridges, respectively). Different types of CH_2 bridges can be distinguished depending on the chemical shift.[23] Thus, the most common 4-4′-methylene bridge has been typically assigned to signals at 30−38 ppm, and the less common 2-4′ and 2-2′-methylene bridges to signals at 22−30 and 18−20 ppm (this latter observed as a shoulder of 2-4′ bridges signal), respectively. The signal at 121 ppm (and its shoulder at 114 ppm) is also interesting in terms of condensation since it corresponds to aromatic carbons of mono- and disubstituted resorcinols bearing CH_2 groups in all *ortho* positions relative to the phenolics OHs. Non-substituted aromatic CH groups in *ortho* positions

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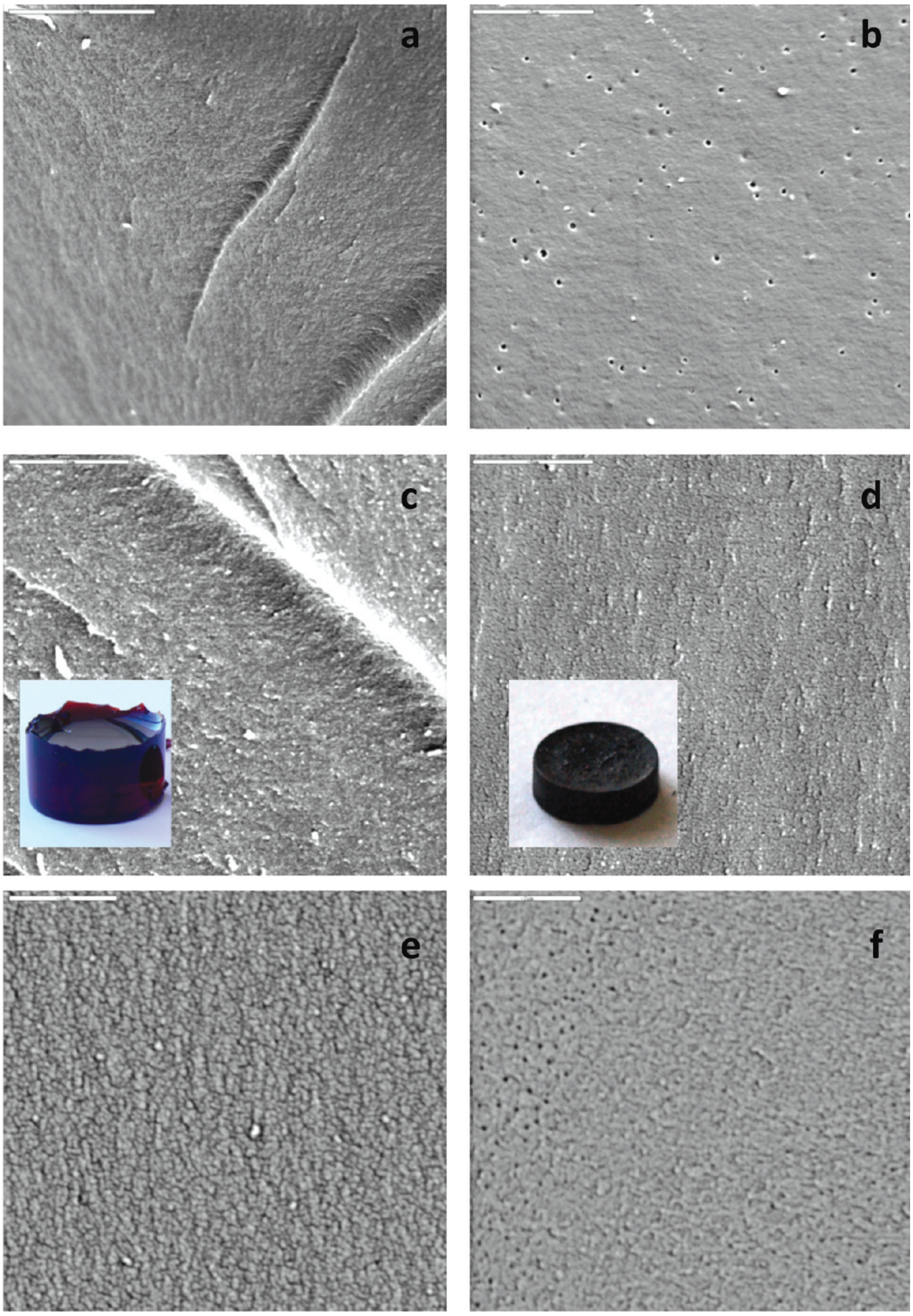

Figure 2. SEM micrographs of (a) RFW^b gel, (b) CW^b obtained by pyrolysis of RFW^b gel, (c) RFW^b-DES gel (inset shows a picture of the gel monolith), (d) CW^b-DES obtained by pyrolysis of RFW^b-DES gel (inset shows a picture of the carbon monolith), (e) RF^b-DES gel and (f) C^b-DES obtained by pyrolysis of RF^b-DES gel. Bars are 10 μm in (a), 5 μm in (b), (c) and (d), and 2 μm in (e) and (f).

appear at 105 ppm while those in *meta* appear at 130 ppm. The ^{13}C NMR spectra of RF gels prepared in DES under basic catalysis (e.g., RFW^b-DES in Figure 4) exhibited intense signals assigned to CH_2-O-CH_2 and CH_2 bridges. Integration of the aromatic phenolic carbon signal at 152 ppm versus the broad signal at 20−40 ppm was basically the same for gels made in water than in DES (just 1.08-fold larger for RFW^b than for RFW^b-DES gels). Interestingly, the ratio of methylene ether groups in RFW^b-DES gels was larger (ca. 2-fold) than in RFW^b gels (Figure 4). These data reveal that the overall incorporation of formaldehyde per aromatic ring (calculated from the integration of the aromatic phenolic carbon signal at 152 ppm versus the broad signal at 20−40 ppm plus that at 59 ppm) was slightly promoted (ca. 1.2-fold) when gels were made in EGCCI-DES rather than in water (Figure 4). Another noticeable feature was the larger intensity of the signals at 130 ppm (assigned to non-substituted aromatic carbons in *meta* positions) in RFW^b than in RFW^b-DES gels in good agreement with the differences in the condensation degree mentioned above. Finally, the ^{13}C NMR spectrum of RF gels prepared in absence of water (e.g., RF^b-DES gels in Figure 4) shows a significant decrease of the ratio of formaldehyde molecules incorporated per aromatic ring (i.e., ca. 1.46-fold as compared to RFW^b gels, see

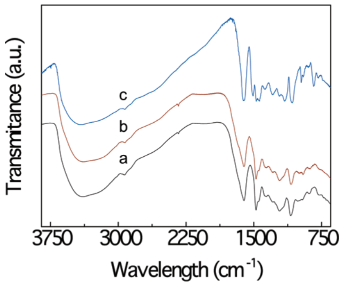

Figure 3. FTIR spectra of RFW^b (a), RFW^b-DES (b), and RF^b-DES (c) gels.

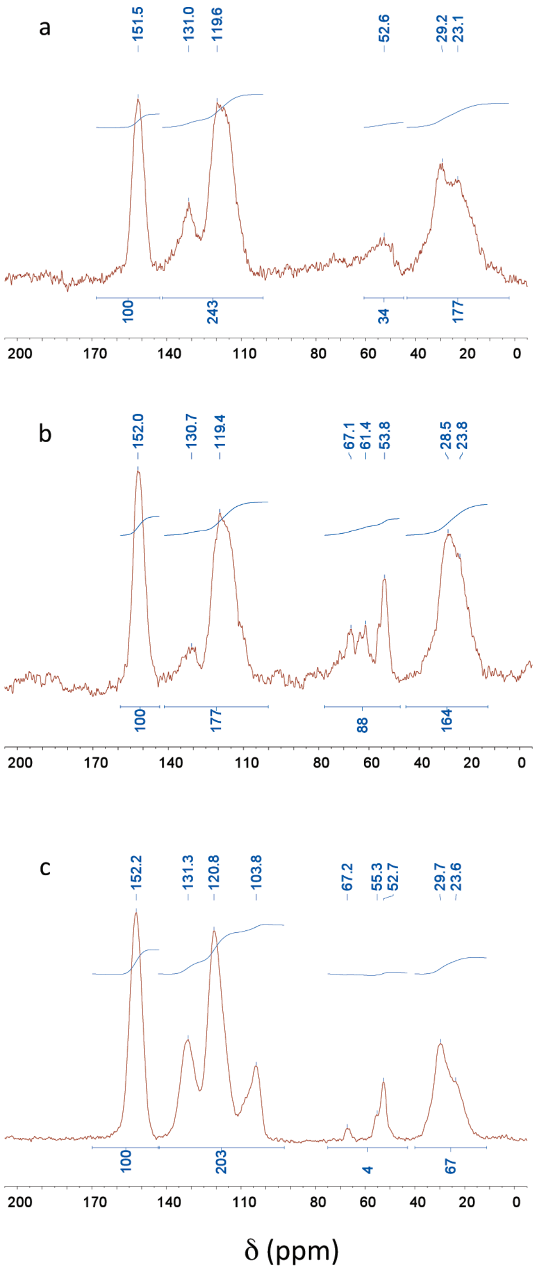

Figure 4. Solid ^{13}C NMR spectra of RFW^b (a), RFW^b-DES (b), and RF^b-DES (c) gels.

Figure 4), but the partial loss of formaldehyde that occurs during freeze-drying (ca. 90%, see Experimental Part for further details) makes difficult any comparison among samples.[23c]

RF gel synthesized using either acid or none catalyst were also studied by SEM, as well as by FTIR and solid ^{13}C NMR spectroscopies. Supporting Information, Figures S3 and S4 show SEM micrographs of RFW^a, RFW^a-DES, and RF^a-DES gels, and of RFW^{nc}, RFW^{nc}-DES, and RF^{nc}-DES gels, respectively. It is worthy to note that RF gels prepared in EGCCI-DES exhibited quite similar textures no matter the use of basic, acid, or none catalyst while those prepared in aqueous solutions with acid or none catalyst exhibited a significant increase of the colloid size that, upon aggregation, form the interconnected structure of RF gels. Such open structure was indeed reflected in the stiffness of the RF gels, so that the monoliths obtained in aqueous solution using acid and none catalysts were fragile and became powder by simple manipulation. FTIR spectroscopy was unable to confirm those textural differences between samples. Actually, the spectra of these gels were similar among them and to those of gels synthesized using basic catalyst (Supporting Information, Figure S5). The ^{13}C NMR spectra of RFW^a-DES and RFW^{nc}-DES gels were also similar among them, but revealed that polycondensation using acid and none catalysts occurred to a lesser extent than when a basic catalyst is used; that is, in both RFW^a-DES and RFW^{nc}-DES gels, the intensity ratio of the aromatic phenolic carbon signal at 152 ppm versus the broad signal at 20−40 ppm was about 0.6-fold below than that obtained for RFW^b-DES (see Supporting Information, Figure S6). Interestingly, the absence of EGCCI-DES resulted in even further decrease of polycondensation in RF gels prepared using either acidic or none catalyst.

Carbonization was only carried out on RFW^b, RFW^b-DES, and RF^b-DES gels, that is, those where according to ^{13}C NMR data polycondensation was optimized. The texture of the resulting carbons (CW^b, CW^b-DES, and C^b-DES, respectively) resembled that of their original RF gels, being quite similar among the different samples (see Figure 2, right column). Carbon conversions ranged 80% for CW^b and CW^b-DES and about 70% for C^b-DES. The elemental analysis performed to obtain the chemical composition of the carbons did not reveal significant compositional variations among different samples; for example, in all cases, carbon and oxygen were the main components (ca. 94 and 3 wt %, respectively). The graphitic character of the resulting carbons was low (in range of that of carbons obtained by thermal treating RFW gels to 800 °C)[1−3] as demonstrates the broad band centered at around 22 degrees in the XRD pattern (see Figure 5). The appearance in the Raman spectra of an intense band at about 1350 cm^{-1} (G band) besides the characteristic one ascribed to graphitic structures (D band) corroborates this issue (see Figure 5). The relative intensities of G band versus D band (e.g., I_D/I_G) were quite similar both for CW^b, CW^b-DES, and C^b-DES (e.g., 0.90, 0.89, and 0.88), in range of data previously reported for carbons obtained at 800 °C.[24] Single point surface

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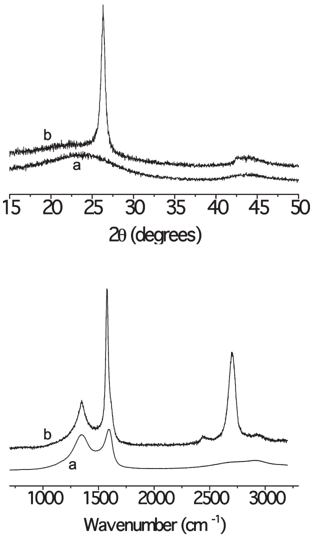

Figure 5. XRD pattern (top) and Raman spectra (bottom) of CW^{b}-DES (a) and MWCNT-CW^{b}-DES (b). The XRD and Raman spectra for CW^{b} and C^{b}-DES are identical to CW^{b}-DES.

area analyses were performed on CW^{b}, CW^{b}-DES, and C^{b}-DES samples to get preliminary insights about textural properties. It is well-known that DESs and ILs have been used to induce texture in materials of different nature.[18] In our case, large surface areas were not obtained in any carbon but there was indeed a significant increase of the surface area of those monolithic carbons coming from RF gels synthesized in presence of EGCCI-DES; that is, while single point analysis provided negligible surface areas for CW^{b} (ca. 7 m^{2}/g), CW^{b}-DES and C^{b}-DES exhibited a significant increase of the surface area up to about 170 and 120 m^{2}/g, respectively.

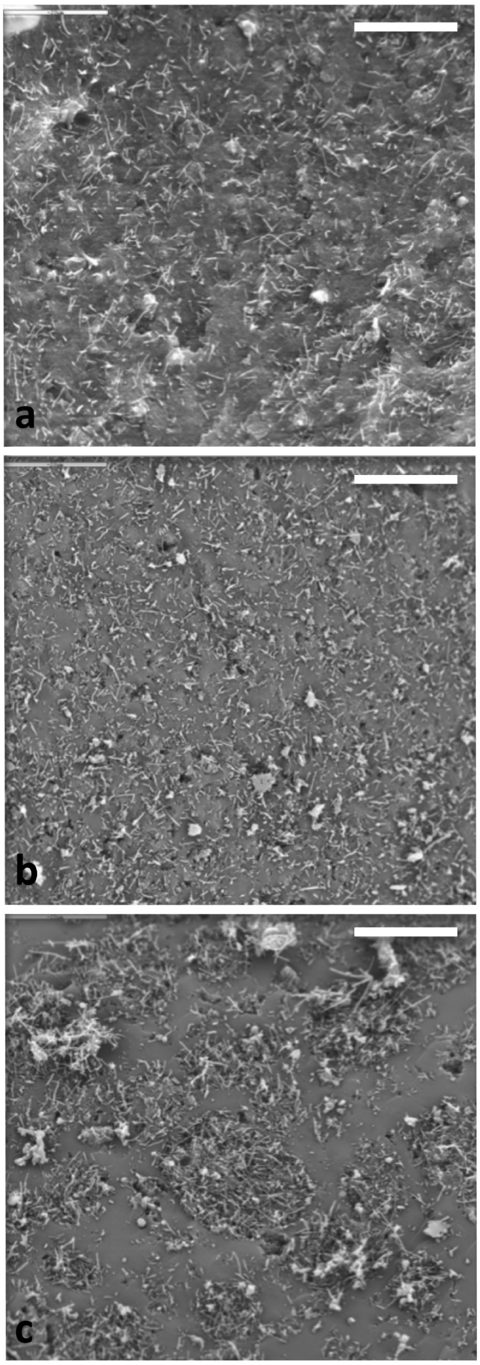

Figure 6. SEM micrographs of (a) RFW^{b}-DES gel containing MWCNT, (b) MWCNT-CW^{b}-DES obtained by pyrolysis of a MWCNT-RFW^{b}-DES gel, and (c) MWCNT-CW^{b} obtained by pyrolysis of a MWCNT-RFW^{b} gel. Bars are 20 μm.

The validity of DESs as solvents for RF polycondensations (versus the use of water) opens interesting perspectives in the synthesis of RF gels. For instance, the excellent solvent properties of DESs allowed increasing the resorcinol concentration at the starting sol. Interestingly, the resulting RF gels (e.g., RFW2^{b}-DES in Experimental Part) exhibited a significant increase of the polycondensation degree (Supporting Information, Figures S7 and S8) as compared to RF gels obtained from both non-concentrated EGCCI-DES based sols and concentrated aqueous sols (RFW^{b}-DES and RFW2^{b} gels, respectively). Moreover, DESs are highly efficient solvents for preparation of homogeneous MWCNT suspensions. Taking advantage of this feature, RFW^{b}-DES gels containing MWCNT can be prepared by simple addition of MWCNT to the RF sols prepared in EGCCI-DES (see Experimental Part for further details). The resulting gels as well as the carbons obtained after carbonization (e.g., MWCNT-RFW^{b}-DES and MWCNT-CW^{b}-DES, respectively) exhibited well dispersed and homogeneously distributed MWCNT within the whole matrixes as demonstrated by SEM micrographs (Figure 6a and 6b, respectively). TEM micrographs also revealed the presence of isolated MWCNT in close contact with the carbon colloids (Figure 7). By contrast, the heterogeneous distribution of MWCNT shown in Figure 6c (e.g., MWCNT-CW^{b}) revealed the difficulties to obtain a homogeneous suspension of MWCNT in aqueous solutions. The homogeneous distribution observed in Figure 6a and 6b must be the consequence of the favorable MWCNT interaction with carbon precursors at the sol state when EGCCI-DES are used as solvent. Actually, such a close interaction was also reflected in the low degree of polycondensation detected by NMR spectroscopy for MWCNT-RFW^{b}-DES gels (Supporting Information, Figure S9) as consequence of the deposition of the RF sol on the walls of the narrow, hydrophilic, solid boundaries

Figure 7. TEM micrograph of MWCNT-CW^b-DES. Bar is 150 nm.

of the MWCNT. This feature is typical for polycondensations carried out in presence of additives. In spite of this event, the degree of polycondensation was good enough, after carbonization, to obtain monolithic carbons with both conversion and carbon content (e.g., 75% and 91 wt %, respectively) in range of those described above for carbons prepared from RF gels without MWCNT. The Raman spectrum of the resulting composites revealed an extraordinary graphitic character (I_D/I_G was 0.34, see Figure 5) as consequence of the presence of MWCNT. Interestingly, the incorporation of MWCNT also resulted in a significant increase of the surface area as compared to similar samples without MWCNT (e.g., 350 m^2/g for MWCNT-CW^b-DES versus 170 m^2/g for CW^b-DES).

Conclusions

In summary, we have demonstrated the suitability of DESs as solvents to carry out the polycondensation of RF gels. Actually, the condensation degree found for RFW-DES gels (those are, RF gels synthesized in partially diluted EGCCl-DES because of formaldehyde incorporation as aqueous solution) was eventually above that obtained for gels prepared in aqueous solutions. The excellent solvent properties of EGCCl-DES allowed increasing the resorcinol-formaldehyde concentration at the starting sol, which resulted in a remarkable enhancement of the polycondensation degree. It is worthy to note that simple washing with water of RF gels synthesized in EGCCl-DES allowed DES recovery and, hence, reusability in subsequent RF synthesis. This recyclability represents an additional advantage of the method reported herein given that may open interesting perspectives in industrial processes where sustainability is an issue. Moreover, the use of EGCCl-DES favored the preparation of homogeneous suspensions of MWCNT that, after resorcinol-formaldehyde polycondensation and subsequent carbonization, allowed the preparation of carbon−carbon nanotube composites with a remarkable homogeneous distribution of MWCNT within the carbon structure (as revealed by SEM) and with an extraordinary graphitic character of the whole composite (as revealed by Raman spectroscopy).

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Supporting Information Available: Additional information in the form of Figures S1−S9. This material is available free of charge via the Internet at http://pubs.acs.org.