Solid State Ionics 257 (2014) 32–37

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Multiwalled carbon nanotube–polyelectrolyte gels: Preparation and swelling behavior for organic solvents

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ARTICLE INFO

Article history:
Received 28 November 2013
Received in revised form 29 December 2013
Accepted 30 December 2013
Available online 4 February 2014

Keywords:
Polyelectrolyte gel
Vinylimidazolium
Carbon nanotube
Organic solvent
Swelling behavior

ABSTRACT

In this article, we report the first multiwalled carbon nanotube–polyelectrolyte gel containing vinylimidazolium-typed ionic liquid monomer as an absorbent of less-polar or nonpolar organic solvents. To prepare such MWCNT–polyelectrolyte gel, the modified MWCNTs with polymerizable vinyl groups on their surfaces were prepared and then underwent copolymerizations with dodecyl methacrylate and vinylimidazolium in the presence of AIBN as initiator, yielding a cross-linked polyelectrolyte. In order to estimate the compatibility between the solvents and the polymers, a series of vinylimidazolium-typed ionic liquid monomers ($[C_n vim][X]$) with different alkyl tail length (C_6, C_{10} and C_{12}) and counter anion (tetrafluoroborate (BF_4^-), dodecylbenzenesulfonate (DBS^-)) were prepared and incorporated into cross-linked polyacrylates. The results showed that the high swelling degree was obtained when the gel matrix had good compatibility with the solvent.

1. Introduction

Carbon nanotubes (CNTs) have attracted great interdisciplinary interest since their discovery because of many unique electrical, optical, and mechanical properties that CNTs possess [1,2]. CNTs have the potential of being transformed into new materials that will employ in a wide range of applications, such as sensors, composites, nanoelectronics, biomedical devices, and high-strength fibers [3–10]. Because of their highly porous and hollow structures, large specific surface areas, surface functional groups and hydrophobic surfaces, CNTs have acted as an effective type of adsorbents for the removal of various inorganic and organic pollutants from wastewater [11–13]. Various methods for CNT chemical modification have been applied to introduce functional moieties which contribute to better nanotube dispersion, and eventually to efficient thermodynamic wetting of nanotubes with polymer matrices [14–16]. Wrapping CNTs with polymer chains through covalent and non-covalent functionalization not only improves their compatibility and stability, but also retains the important physical and chemical features of polymers and creates more opportunity for various applications of CNTs.

Poly (ionic liquid)s (PILs), a special type of polyelectrolytes with IL species in each of the repeating units, have been very recently introduced as a new research focus attracting steadily growing interest in the fields of polymer and material science [17–19]. The properties of PILs commonly prepared via polymerization of monomeric ionic liquids (ILs) are strongly associated with both the polymer and ionic liquid structure, where the structure of the cation and anion (e.g., ion type and substitute groups on the cation) are known to determine the physicochemical properties of ILs [20–22]. Among various types of monomeric ILs, vinylimidazolium salts have received considerable attention because of their favorable properties such as thermal stability, non-flammability, negligible vapor pressure, high charge density and mobility [23,24]. The synergistic effect makes the PIL containing imidazolium salts as a unique class of versatile polyelectrolytes for a variety of applications, such as solid ion conductor, CO_2 sorbents, dispersants, porous materials, and carbon precursors [25–27]. However, application of ILs in polymer science is not limited to traditional polymerization media. ILs are also investigated as the components of the novel polyelectrolyte gels that exhibit a high degree of swelling in less-polar and nonpolar organic solvents [28–31]. Organic solvents are among the most applied chemicals, and they are considered as the typical organic pollutants in environment contamination. Therefore, the synthesis of highly efficient cleanup materials for recovery of organic solvent spilled in the environment and absorbents for waste oils over water has been gathering ever-growing attention [32–39].

In our previous works [40,41], we demonstrated the first example of polymeric absorbent containing modified MWCNTs and showed that prepared polymeric absorbents containing CNTs had much higher swelling in oil and some organic solvents than those without CNTs. Modified MWCNTs in these polymeric absorbents played triple roles simultaneously: as an adsorbent, a comonomer and a cross-linking agent. In the present study, we designed and prepared new polyelectrolyte gel, not only successfully incorporating modified MWCNTs, but also more interestingly keeping the high organic solvent absorbency from the low dielectric media to highly polar solvents. For this end, MWCNTs were functionalized with 3-(methacryloyloxy) propyltrimethoxysilane (MPS) and incorporated into the network of polyelectrolyte gel as a cross-linking agent. The effective parameters on compatibility of the

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http://dx.doi.org/10.1016/j.ssi.2013.12.043

nonpolar polymer chains to the media such as alkyl chain length and counter anion of vinylimidazolium monomer together with another two vital affecting factors on swelling, i.e., initiator and cross-linking agent content were investigated in detail to determine the optimal preparing parameters and further to optimize the properties of the MPGs. Furthermore, the reusability of the MPGs was quantitatively investigated, demonstrating that the absorbents can be used for at least five times.

2. Experimental section

2.1. Materials

Hydroxy multiwalled carbon nanotubes (MWCNT–OH, >95% in purity, >50 nm in diameter, 20 μm in length, –OH content 0.71 wt%, synthesized by catalytic chemical vapor deposition) were purchased from Neutrino Company (Iran). 1-Vinylimidazole was obtained from Fluka and distilled before use. Tetrafluoroboric acid (50% solution in water) and sodium dodecylbenzenesulfonate (SDBS) were purchased from Aldrich. 2,2′-Azobisisobutyronitrile (AIBN, Kanto, 97%) was recrystallized from ethanol. 3-(Trimethoxysilyl) propylmethacrylate (MPS, 98%), 1-bromohexane, 1-bromodecane, 1-bromododecane, dodecyl methacrylate (DDMA), and all other reagents and solvents were purchased from Merck chemicals and used as received.

2.2. Characterization

^{1}H NMR and ^{19} F NMR spectra were recorded on a Bruker Avance-500 MHz FT NMR at room temperature. FT-IR spectra of samples were taken using an ABB Bomem MB-100 FT-IR spectrophotometer. The samples were powdered and mixed with KBr to make pellets. Elemental analyses were carried out by means of a Thermo Finnigan Flash EA 1112 instrument. TGA was acquired under a nitrogen atmosphere with a TGA Q 50 thermogravimetric analyzer. Morphology of gels was observed with a scanning electron microscope (SEM) instrument (Philips, XL30).

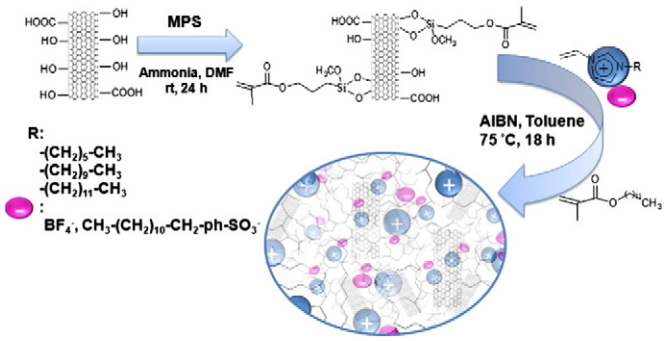
2.3. Preparation of IL monomers ([$C_n$vim][X])

A general route for synthesis of 1-vinyl-3-alkylimidazolium tetrafluoroborate [$C_n$vim][BF_4] was used as follows: 5 mmol of 1-vinylimidazole, 7 mmol of n-alkyl bromide were added to 30 mL of methanol in 100 mL round bottom flask. The mixture was stirred at room temperature overnight, followed at 70 °C for 24 h. The reaction mixture was cooled and added dropwise into 400 mL of diethyl ether. After washing with diethyl ether, the precipitate was filtered off and dried at room temperature until constant weight. For exchange of bromide anion to tetrafluoroborate, 1-vinyl-3-alkylimidazolium bromide was dissolved in 20 mL CH_2Cl_2 in a 50 mL round bottom flask, and aqueous HBF_4 (50%) at a 1.1 + 1 molar ratio was slowly dropped into the flask. After 1 week, [$C_n$vim][BF_4] was separated by extraction with distilled water. The organic layer was collected, dried over Na_2SO_4, filtered and the solvent was removed in vacuum to give the product.

To synthesize 1-vinyl-3-dodecylimidazolium dodecylbenzenesulfonate ([C_{12}vim][DBS]), 1.5 g (6 mmol) of 1-vinyl-3-dodecylimidazolium bromide was dissolved in 15 mL of methanol. Then, a solution of 2 g (6 mmol) of dodecylbenzenesulfonate sodium salt dissolved in water (50 mL) was added to this solution at 65 °C. The mixture was left on stirring for 3 days at room temperature. The product was obtained as a brown waxy solid by extracting four times the milky-white mixture with $CHCl_3$ and by removing the solvent under vacuum at 50 °C.

2.4. Preparation of MWCNT–MPS

MWCNT–OH (0.3 g) was dispersed in 50 mL DMF, and then 1 mL of ammonium hydroxide 25% solution was added. Then, 2 mL 3-(trimethoxysilyl)propylmethacrylate (MPS) was added dropwise over a period of 20 min, and the reaction mixture was stirred at 50 °C for 24 h.



Scheme 1. The schematic preparation of MPGs.

The modified MWCNTs were filtered, intensively washed with DMF, acetone, methanol and deionized water respectively, and then dried under vacuum at 50 °C overnight.

2.5. Preparation of MWCNT–polyelectrolyte gels (MPGs) via radical polymerization

The MWCNT–polyelectrolyte gels (MPGs) were prepared via radical polymerization. Typically, 1.96 mmol of DDMA, 0.10 mmol of [$C_n$vim][X], 0.0020 g of MWCNT–MPS, 0.04 mmol (0.0060 g) of AIBN and 0.1 mL toluene were placed in a 5 mL round bottom flask. The flask was then placed in a constant temperature oil bath at 75 °C for 18 h. The feed ratio of the monomers was adjusted to [$C_n$vim][X]: DDMA = 5:95. The formed gels were washed by swelling in toluene for 5 h, and then air-dried at room temperature. The sample was cut into thin discs, and the discs were dried in an oven at 50 °C for 24 h.

2.6. Measurement of swelling degrees

A quantity of about 0.10 g of dried sliced gel was placed in organic solvents with various polarities from hexane ($\varepsilon = 1.9$) to acetone ($\varepsilon = 21$). After immersion for 2 days, we measured Q of the gels, which is defined as the following equation:

$$Q = \left(W_{wet} - W_{dry}\right)/W_{dry}(w/w)$$

where W_{dry} and W_{wet} are the weights of the dried gel and the wet gel, respectively [42]. For studying the swelling rate of MPGs, at desired

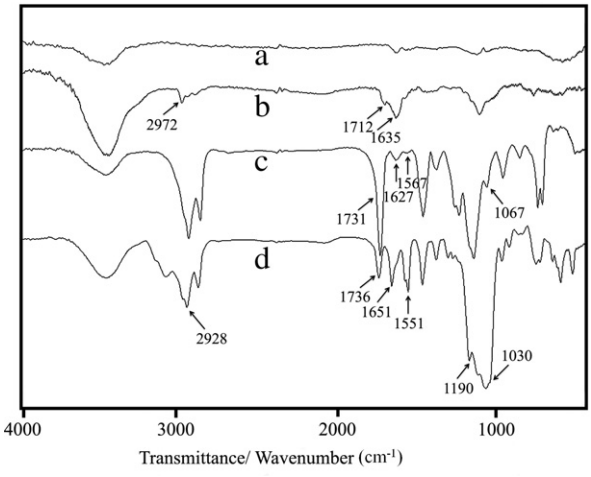


Fig. 1. FT-IR spectra of (a) MWCNT–OH, (b) MWCNT–MPS, (c) $MPG_{12}BF_4$, and (d) $MPG_{12}DBS$.