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Synthesis and Characterization of “Comb-like” Poly(ionic liquid-co-styrene): Expected Applications in Graphene Dispersion and CO_2 Separation

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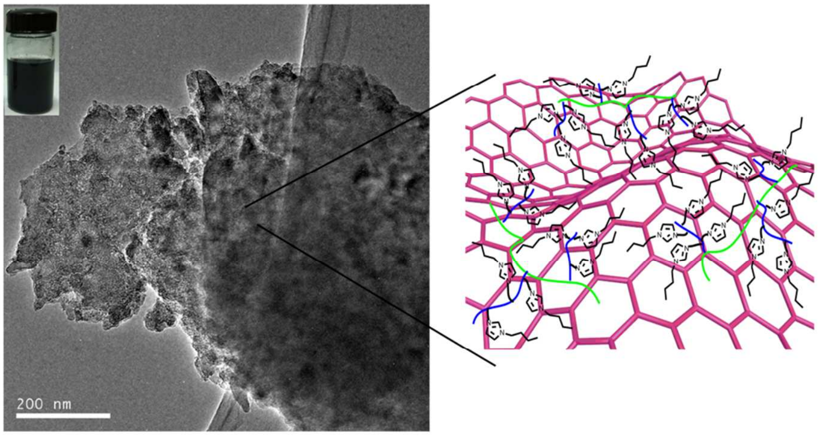
Abstract

Poly(ionic liquid)s (PILs) with well-defined architectures have shown significant potential in various fields, but establishing an easy method for their synthesis remains a challenge. Herein, comb-like copolymers with polystyrene and PIL as backbones and side chains, respectively, were prepared by directly polymerizing ionic liquid monomer by atom transfer radical polymerization using poly(styrene-co-4-vinylbenzyl chloride) as macroinitiators. NMR, GPC, and FTIR were used to characterize the molecular weights and compositions of macroinitiators and resultant copolymers. Results demonstrated successful synthesis, and also indicated that graft density and side chain length of the comb-like copolymers can be readily controlled by tuning macroinitiator composition and polymerization time. DSC and EIS measurements were further performed to investigate the thermal and electrochemical properties of comb-like copolymers with various architectures. Both glass transition temperature and impedance were found to highly depend on structure, particularly on the graft density of side chains. Furthermore, these comb-like copolymers were used both as stabilizer to disperse reduced graphene oxide (RGO) nanoplatelets in organic solvent and as an additive for N_2/CO_2 separation membrane. As compared to neat PIL, a highly stable suspension of RGO in propylene carbonate and composite membrane with enhanced N_2/CO_2 selectivity were obtained in the presence of comb-like copolymers. Given by many advantages of diverse compositions, multiple groups, and tunable structure of PILs, the come-like copolymers show great promising in stabilizing carbon materials and membrane separation.

Keywords Poly(ionic liquid-co-styrene); Comb-like copolymer; Stabilizer for Reduced Graphene Oxide; Additives for N_2/CO_2 Separation Membrane;

Graphic Abstract



A new PIL “comb-like” copolymer was synthesized by directly polymerizing ionic liquid monomer by ATRP using macroinitiator. This polymer is potentially useful in graphene dispersion and CO_2 separation

1. Introduction

Comb-like copolymers are composed of backbones and plurality of side chains. Given their highly tunable structure and properties, these copolymers have shown significant potential in numerous applications. For instance, when the backbone and side chains are hydrophobic and hydrophilic, respectively, these copolymers become so-called amphiphilic copolymers, and show considerable potential as a macro-surfactant.[1] Compared with linear block copolymers, comb-like copolymers are able to form stable emulsions even though the two incompatible monomer units are not distributed into large separated blocks.[2] Based on diverse properties offered by the backbone and side chains, several comb-like copolymers also show excellent absorption ability for stabilizing nanoparticles or on certain substrates to form stable and functionalized thin films.[3-5]

Poly(ionic liquid)s (PILs) are polymers that contain an ionic liquid (IL) in each monomer repeating unit. These materials have gained considerable attention as an interesting class of materials that offer its combination of advantageous ionic liquid properties, such as high boiling point, high ionic conductivity, and good solvation properties, with characteristics typically for polymer, such as facile processing and excellent mechanical properties.[6, 7] These unique characteristics offer PILs with significant potential to be applied for energy storage,[8-10] sensors,[11, 12] electrolytes,[13-15] and conductive composites.[16, 17]

Similar with numerous polymers, PILs can be synthesized by free radical polymerization of IL monomers.[18] High chemical tolerance and thermal stability, excellent electronic and ionic conductivity were identified characteristics of such homopolymers.[7, 19, 20] However, brittleness at room temperature and difficulty in processing homo-PILs limit their application. To overcome these drawbacks, IL monomers are usually copolymerized with other monomers, from which random copolymers with a wide range of IL sequence content can be readily prepared.[21] However, copolymers containing IL and simultaneously possessing well-defined architectures such as block, graft, comb-like, or star shape, are challenging for synthesis. Controlled free radical polymerization has been proven to be able to synthesize such polymers but has to be adapted according to the reactivity of IL monomers. Among PIL copolymers of different architectures, block copolymers have attracted the most substantial attention. Two methods have been reported for the synthesis of these copolymers: 1) sequential polymerization of IL monomers and other monomers;[22] and 2) sequential polymerization of IL monomer precursors, such as vinylpyridine or 4-vinylbenzylchloride (VBC), with other monomers, followed by protonation at low pH or permanent quaternization with alkyl halide or amine. Most examples are based on the latter method and typically use reversible addition fragmentation chain transfer (RAFT) polymerization to prepare the copolymer precursors.[23, 24] For comb-like copolymers composed of PILs, considerably fewer reports are included in comparison with those for block copolymer issues.

Atom transfer radical polymerization (ATRP) is another typical controlled free radical polymerization for synthesis of copolymers with well-defined architectures.[25] The high efficiency of this technique has been proven by synthesizing numerous macromolecules with various topologies from wide range of monomers.[26, 27] However, compared with RAFT, ATRP is rarely used to synthesize PIL copolymers with unique architectures, including block copolymer, which is likely due to its low tolerance to functional group. Using this technique, Texter et al. synthesized an ABA triblock terpolymer by polymerizing the IL monomer of 1-(11-acryloylundecyl)-3-methyl-imidazolium bromide from a bifunctional poly(propylene oxide) macroinitiator with two ATRP initiating termini.[28] Although this study demonstrated the feasibility to prepare block copolymers with IL blocks by directly polymerizing IL monomer, types of monomer and macroinitiators, as well as reaction condition, are strictly limited.

The projected property promotion from combining PILs with comb-like structures and the lack of systemic study on such polymers prompted us to design, synthesize, and characterize this type of copolymers and investigate their applications. To this end, a series of PIL comb-like copolymers with polystyrene as backbone and PILs as side chains were synthesized, and their applications as stabilizer for reduced graphene oxide (RGO) sheets in organic solvent and additives in gas separation membranes were investigated. First, the feasibility of synthesizing such copolymers via ATRP and using copolymer of poly(styrene-co-vinylbenzylchloride) (poly(St-co-VBC)) as macroinitiator was investigated. In addition, polymerization conditions were optimized based on the combined characterizations of nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), and Fourier transform infrared spectroscopy (FTIR). Differential scanning calorimetry (DSC) and electrochemical impedance spectroscopy (EIS) were used to characterize the thermal and electric properties of copolymers with different arm densities and lengths, as well as to further elucidate the structure–performance relationship. Finally, we investigated the use of these comb-like copolymers as stabilizer for RGO dispersion in solvents and additives in gas separation membranes to supply high CO_2/N_2 selectivity, indicating their potential applications in these fields.

2. Experimental

2.1 Materials

Styrene (St) and vinylbenzylchloride (VBC) were purchased from J&K Inc. (Beijing, China). Azobisisobutyronitrile (AIBN), toluene, methanol, propylene carbonate (PC), N-methyl-2-pyrrolidone (NMP), copper(I) chloride (CuCl), and 1,1,4,7,10,10-hexamethyltriethylene-tetramine (HMTETA) were purchased from Aladdin Inc. (Shanghai, China). 1-Vinyl-3-butylimidazolium tetrafluoroborate (IL monomer) was supplied by Beijing HWRK Inc. (Beijing, China). St and VBC were washed with 5% NaOH solution, followed by distilled under reduced pressure to remove the inhibitor. AIBN was recrystallized twice from ethanol before use. CuCl was purified by stirring in acetic acid, filtered, washed with ethanol, and then dried in vacuum at 40 °C for 24 h. GO was synthesized from purified natural flake graphite by modified Hummers method.[29] Other chemical agents were used as received.

2.2 Synthesis of Poly(St-co-VBC)s

The macroinitiator of poly(St-co-VBC) was prepared by random copolymerization of St and VBC. In brief, AIBN (0.1 g), St, and VBC with different feed ratios (total amount of 10 g) and toluene (20 ml) were added into a 50 mL round-bottomed flask equipped with a magnetic stirring bar. The flask was degassed under vacuum and purged with nitrogen for three times to remove oxygen. Then, the flask was placed in an oil bath at 75 °C to conduct polymerization.[30, 31] After polymerization of 20 h, the resultant solution was poured into 100 ml of cold methanol to yield the precipitate as product. The product was then filtered, washed with methanol, and dried in vacuum at 60 °C overnight.

2.3 Synthesis of PIL Comb-like Copolymer

PIL comb-like copolymers were synthesized by ATRP using poly(St-co-VBC) as microinitiators. In a typical process, poly(St-co-VBC) (0.01 g, 0.035 mmol), HMTETA (0.01 g, 0.043 mmol), and IL monomer (0.7 g, 2.94 mmol) were sequentially added into a 25 ml Schlenk flask, followed by air removal using three cycles of vacuum evacuation and dry nitrogen purging. CuCl (0.003 g, 0.03 mmol) was added under N_2 flow protection. The flask was then subjected to two additional evacuation–purging cycles, and then immersed in an oil bath heated to 160 °C. Polymerization was conducted under nitrogen protection because of the sensitivity of Cu(I) to oxygen. After a pre-specified reaction time, the solution was exposed to air to stop reaction, and then poured into 50 ml cold methanol, followed by centrifugation at 4000 r/min to get copolymers. The product was washed with methanol for three times and dried in a vacuum oven at 80 °C for 24 h.

2.4 RGO Dispersed in Solvent with Assistance of the Copolymer

RGO sheets dispersed in solvent were prepared by thermally reducing GO sheets in the presence of comb-like copolymer. GO solution in PC with a GO concentration of 1.0 mg/mL was first prepared by dispersing GO sheets via vigorous stirring and sonication. A similar mass amount of comb-like copolymer (with respect to GO) was then added into the suspension, and reduction was carried out at 150 °C for 3 h.[32] A counterpart RGO suspension without copolymer was prepared in the same manner for comparison. To obtain RGO power for characterization, the resultant suspension was centrifuged at 10000 r/min. The centrifugal sediment was redispersed in PC, and centrifuged again. This process was repeated for three times, and the product was collected and dried in a vacuum oven at 80 °C for 24 h.

2.5 Copolymer as Additives for N_2/CO_2 Separation Membrane

Polysulfone (2.0 g) and 0.1 g of the comb-like copolymer were dissolved in 15 ml N, N-Dimethylformamide (DMF) by stirring the solution in an oil bath at 100 °C. After cooling to room temperature, the solution was doctor-bladed on base membrane using a 300 μm spacer, and the membrane was immediately placed into a vacuum oven at 70 °C for solvent evaporation until no weight loss is observed.

2.6 Characterization

^{1}H NMR spectra were measured on a Bruker AVANCE III 500 NMR spectrometer (Bruker Co., Switzerland) using deuterated dimethyl sulphoxide (DMSO-d_6) as solvent. Chemical shifts were reported in parts per million (ppm). Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet 6700 IR Spectrometer (Thermo Scientific, USA), and the samples, in powder form, along with KBr, were compressed into tablets. The spectra (32 scans) were collected with a spectral resolution of 4 cm^{-1}. The XPS was recorded on a Kratos Axis Ultra-DLD system (Shimadzu Co., Ltd., Hongkong) with Al Kα ray, 1486.6 eV energy, and 200 W power. Molecular weight and molecular weight distribution were determined on a Waters gel permeation chromatograph system (Waters Co., USA) at 80 °C. DMF was used as eluent at a flow rate of 1.0 ml/min, and the calibration of the molecular weight was carried out based on the poly(methyl methacrylate) standard. Differential scanning calorimetry was recorded on a Mettler Toledo DSC analyzer (Mettler-Toledo International Inc., Switzerland) in a nitrogen atmosphere at a heating rate of 10 °C min^{-1} from -20 °C to 300 °C. The ionic conductivities of comb-like copolymers were measured using a CHI660B electrochemical workstation (CH Instruments, Inc. Shanghai, China) over a frequency range of 1 Hz to 10^6 H_Z with an amplitude of 10 mV. In this procedure, a solution containing 5 mM $K_3Fe(CN)_6$, 5 mM $K_4Fe(CN)_6$, and 0.2M KCl was used as electrolyte, and measurements were conducted at room temperature. A mixed gas containing N_2/CO_2 (90/10, vol.%) was used for a permeation measurement of the composite membrane containing copolymers, which was conducted to test the N_2/CO_2 selectivity of the composite membrane. All measurements were conducted on an in-house permeation system at 30 °C and under a feeding pressure of 1.05 bars. The compositions of feeding and permeated gas were measured using gas chromatography of Agilent 6820 (Agilent Technologies Co. Ltd., USA).

3. Results and Discussion

3.1 Preparation and Structural Characterization of Comb-like Copolymers

A series of poly(St-co-VBC) were synthesized as macroinitiators by random copolymerizing styrene and vinylbenzylchloride with different ratios. The average molecular weights, polydispersity index (PDI), and actual St/VBC ratios of these copolymers are shown in Table 1. Poly(St-co-VBC) with a number average molecular weight of ~7.5 kg/mol and St/VBC ratio ranging from ~7/3 to ~1/3 have been successfully synthesized. The relatively low molecular weight is likely due to high initiator concentration and high polymerization temperature. Using these macroinitiators, we synthesized PIL comb-like copolymers by directly polymerizing 1-vinyl-3-butylimidazolium tetrafluoroborate ($ViBuIm^+BF_4^-$) via ATRP method (shown as Scheme 1). NMR was first used to monitor the initiation of macroinitiators and identify the structure of resultantly comb-like copolymers. The representative ^{1}H NMR spectra are shown in Figure 1. The chemical shift corresponding to $–CH_2Cl$ is found as a singlet at 4.5 ppm in the spectrum of poly(St-co-VBC), which indicates the existence of ATRP initiating sites. Upon polymerization, we observed the disappearance of this characteristic signal of macroinitiators, suggesting that initiators were successfully initiated for the growth of side chains from backbone. Apart from the disappearance of the singlet at 4.5 ppm, several chemical shifts arising from PIL moieties were also observed as follows: -N=CHN (9.15 ppm), -NCHCHN- (7.64 ppm), -CHN (5.26 ppm), $NCH_2C_3H_7$ (3.84 ppm), and $-CH_3$ (0.90 ppm). [33]

Figure 2 shows the FT-IR spectra of poly(St-co-VBC) and corresponding PIL comb-like copolymer. For poly(St-co-VBC), the characteristic peaks of 1450–1600 and 700–900 cm^{-1} originating from in-plane C-C vibrations and ring out-of-plane vibrations, respectively, are clearly shown. Several new peaks are observed in the spectrum of PIL comb-like copolymers due to the grafted PIL side chains, among which, the peaks at around 1540 and 1168 cm^{-1} are attributed to imidazolium, and the peak at 1062 cm^{-1} corresponds to BF_4^- anion.[34] XPS was also used to characterize the chemical composition of the comb-like copolymers, toward which both survey scan and high resolution scan were used, as shown in Figure 3. As clearly seen in the survey scan, the characteristic peaks of F_{1s} at 688 eV, B_{1s} at 188 eV, and N_{1s} at 401 eV are detected in the spectra of PIL comb-like copolymer, whereas these peaks are completely absent in macroinitiators. The high resolution scan for N_{1s} further confirms the imidazolium structure, represented by the distinct peak at 401.1 eV which can be assigned to the positively charged nitrogen in imidazolium.[35, 36] The difference in molecular weight between macroinitiator and come-like copolymer was monitored by GPC (Figure 4), which indicates an increase in molecular weight and a decrease in PDI after grafting PIL side chains. The decrease in PDI further confirms the controlled polymerization behavior of ATRP as initiated by the macroinitiator, suggesting that multiple structural parameters such as graft density and side chain length can be readily tailored.

Based on the results from aforementioned measurements, we determined that these comb-like copolymers can be synthesized via ATRP initiated by the poly(St-co-VBC) macroinitiator, and tailoring their architecture is simple. As a proof-of-concept, we synthesized a series of comb-like copolymers with different graft densities and different side chain lengths by simply choosing poly(St-co-VBC) with different St/VBC ratio and controlling reaction time. First, we will discuss the comb-like copolymers with different side chain lengths synthesized by controlling reaction time while the macroinitiator are fixed as poly(St-co-VBC) with St/VBC ratio of 1/1. Table 2 summarizes the molecular weights, PDIs and side chain lengths of the comb-like copolymers obtained upon various polymerization times. On the basis of the change in molecular weight, we find that the polymerization rate is low, and that extending reaction time does not significantly increase the side chain length. When reaction time is controlled at 16 h, the average side chain length is observed to approach the maximum value under our experimental conditions. Further reaction time extension, such as to 24 h, causes backbone chain breakage and, in turn, decreases the molecular weight of comb-like copolymer (results are not shown here). Comb-like copolymers with different graft densities can be prepared from macroinitiators with various St/VBC ratios. Here, the optimum reaction time, i.e., 16 h, was selected to carry out these reactions, which are expected to yield long side chains. Four comb-like copolymers with different graft densities were synthesized from poly(St-co-VBC)s with St/VBC ratios of around 7/3, 1/1, 2/1, and 3/1. Table 3 summarizes the GPC analysis results of these comb-like copolymers. Evidently, all initiators have performed their functions and initiated the growth of side chains, which was indicated by the increased molecular weight from around ~7.5 kg/mol for the macroinitiator to more than 50 kg/mol for the copolymer. More importantly, a decrease in PDI from ~1.5 for the macroinitiator to ~1.3 for comb-like copolymers was observed. Certain studies have shown that initiating site density on the backbone can dramatically affect the length of side chains.[37, 38] Here, we further compared the molecular weights, PDIs, and side chain lengths of comb-like copolymers from macroinitiators with different initiating site densities. The number average molecular weights of comb-like copolymers from macroinitiators with St/VBC ratios of ~7/3, ~1/1, ~1/2, and ~1/3 are 5.32×10^4, 5.49×10^4, 7.18×10^4, and 9.28×10^4 g/mol, respectively. With increasing initiating site density, more IL monomers appear to be grafted on the backbone, because all macroinitiators possess comparable molecular weight. Given the initiating site densities on backbone and average molecular weights of comb-like copolymers, we determined the side chain length, which is represented by the number average molecular weight of the PIL side chain ($M_{\mathrm{n,PIL}}$) for each comb-like copolymer. The results are also summarized in Table 3. Evidently, comb-like copolymers from macroinitiators with low initiating site density possess longer side chains. Low initiating site density appears to benefit the preparation of long side chains. However, PDIs show an opposite trend, as evidenced by the fact that the comb-like copolymer from macroinitiator with St/VBC ratio of ~ 7/3 possessing a PDI of ~1.4, whereas the PDIs of other comb-like copolymers are in the range of 1.2~1.3.

3.2 Properties of PIL Comb-like Copolymers

As a property parameter, glass transition temperature (T_{g}) is of critical importance for polymer process and application. Herein, the $T_{\mathrm{g}}^{'}$s of the PIL comb-like copolymers were determined by DSC measurements. The dependence of T_g on the composite, molecular weight, and side chain density and length can be studied by comparing these results. Figure 5a shows the DSC curves of comb-like copolymers prepared from the macroinitiator with a St/VBC ratio of 1/1 after different reaction times. Only one thermogram step is evidently observed, meaning one T_g, is found for all comb-like copolymers, and all of the comb-like copolymer $T_{\mathrm{g}}^{'}$s fall in the range between the T_g of macroinitiator (~104 °C) and T_g of PIL homopolymer (~114.2 °C). The $T_{\mathrm{g}}^{'}$s of comb-like copolymers did not exhibit dependence on reaction time, although an evident increase in the molecular weight of the side chain is observed. As reaction time increases from 4 h to 16 h, an increase in molecular weight from 3.6×10^4 g/mol to 5.6×10^4 g/mol does not lead to T_g enhancement. To investigate the dependence of T_g on graft density and side chain length. The DSC curves of comb-like copolymers with different graft densities and side chain lengths are shown in Figure 5b. The $T_{\mathrm{g}}^{'}$s of the comb-like copolymers from macroinitiators with St/VBC ratios of around 7/3 and 1/3 are 108.3 °C and 113.8 °C, respectively, indicating that high graft density may contribute to the increase in T_g, given by the short side chain length of the lattercopolymer.

To investigate the electrochemical properties of these PIL comb-like copolymers and elucidate the relationship between molecular structure and charge transfer performance, EIS characterization was used to probe their electrochemical response. Figure 6a represents Nyquist diagrams for the comb-like copolymers from macroinitiator with St/VBC ratio of 1:1 upon different polymerization time, in which diameter of semicircle in middle frequency region reflects the charge transfer resistance. These EIS spectra clearly show a steady reduction in impedance as polymerization time increases from 4 h to 16 h, which can be attributed to the increased length of PIL side chains. The EIS characterization was also conducted for the comb-like copolymers with various graft densities and side chain lengths, as shown in Figure 6b, which indicates the structural dependence of impedance. Much lower charge resistances are found for the comb-like copolymers with high graft densities. These results suggest that the dense side chains even if with short length are beneficial for the charge transfer, and in turn offer the comb-like copolymers with higher electrochemical properties.

3.3 Applications of PIL Comb-like Copolymers

ILs are well-known for their wide applications ranging from green solvents to electrolytes, sorbents, and dispersants, among which incorporation of ILs with nanoparticles shows attractive opportunities for designing functional hybrid nanomaterials.[39] Complexes of ILs with carbon nanotubes and/or graphene are good examples which exhibit significant potentials for preparing supercapacitor and high performance electrode materials. Some researchers have shown that IL can interact with carbon nanotubes (CNTs) or graphene through cation–π and/or π–π interactions.[14, 34] From the view of molecular structure, the comb-like copolymers herein possess plenty of IL groups which can supply strong interaction with carbon materials. At the same time, the backbones composed of -CH, -CH_2, and benzene groups are compatible with organic solvents. This combined affinity with both of carbon materials and organic solvents can supposedly make the comb-like copolymer have the ability to exfoliate and stabilize graphene in suitable solvent. As a proof-of-concept, the comb-like copolymer prepared from macroinitiator with St/VBC ratio of 1/1 and after 16 h polymerization was chosen to stabilize RGO sheets in PC solvent. For comparison, RGO suspension without the comb-like copolymer was also prepared. A thermally reducing process was carried out to obtain these suspensions. The exfoliation state and stability of reduced GO sheets in suspensions were characterized by TEM and gravity settling process. Figures 7a and 7b show the typical TEM images of RGO sheets in PC with and without the assistance of comb-like copolymers. The pictures of the corresponding suspensions after one week of gravity settling are also shown as inserted images. The figures show that exfoliated RGO sheets are formed in the presence of comb-like copolymers. As a result, the suspension is highly stable. However, graphene sheets are stacked into thick multilayers in the absence of comb-like copolymer, and sedimentations are rapidly formed accordingly. As for the morphology of RGO sheets in the presence of comb-like copolymer, thicker layers and rougher surface in comparison with general RGO sheets are observed in both of TEM and AFM images (Figure 7d), indicating polymer coverage on the surface. The polymer coverage is speculated as shown in the schematic of Figure 7f. The existence of imidazolium N atom in the XPS spectra (Figure 7c) of RGO–PIL after repeated centrifugation and rinsing further demonstrates this polymer coverage. Although certain studies reported Raman spectra shifts in G and/or D bands of multi-walled CNTs induced by IL absorption,[14, 17, 40] these shifts are not observed herein, which is consistent with other studies.[41-43] By comparing the Raman spectra of RGO and the RGO–copolymer complex in Figure 7e, particularly the values of I_G/I_D, we can see that the presence of comb-like copolymer did not exert a negative effect on the GO reduction reaction. These results indicate that PIL comb-like copolymers are effective dispersing agents for RGO suspensions in organic solvents, which are of considerable importance in the preparation of polymer/RGO composites with highly dispersed graphene sheets.

More importantly, PILs exhibit superior CO_2 absorption capacity compared with their ionic liquid monomer counterparts [44, 45] and high CO_2 absorption by PILs can be readily achieved by optimizing cation and anion pairs. For polymeric gas separation membrane, gas permeation generally follows a solution-diffusion mechanism, in which gases first dissolve in the membrane materials and then diffuse through the membrane driven by concentration gradient.[46] So the permeability of membrane is positively proportional to both solubility and diffusivity of the gas. PILs have a significant preferential solubility of for CO_2 over other gases such as N_2 and CH_4, which enhances the solubility contribution and in turn enhances the permeability of CO_2. Therefore, permeability of CO_2 through membranes containing PILs is generally higher than that of N_2 and CH_4, meaning that for mixed gases of CO_2/N_2 and CO_2/CH_4, upon the permeation, the downstream gases generally show higher CO_2/N_2 ratio (e.g. lower N_2/CO_2 or CH_4/CO_2 ratio) in comparison with feed gases, leading the separation between CO_2 and N_2 or CH_4.[47, 48] Considering that the comb-like copolymers in this study are composed of polystyrene backbone and PIL side chains, the comb-like copolymers was used as additives to polysulfone membranes to offer new functionality of CO_2/N_2 selectivity. To this end, 5 wt.% comb-like copolymer (Sample prepared from macroinitiator with St/VBC ratio of 1/1 and after 16 h polymerization) with respect to polysulfone was added to the polysulfone solution in DMF, and then coated on the base membrane. In parallel, neat PIL was blended with plolysulfone in the same ratio and coated on the same base membrane for comparison. The N_2/CO_2 gas separation performance of both modified membranes was evaluated and compared by an in-house permeation system.[49] Figure 8 shows the compositions of the downstream gases from different membranes for a feed gas with N_2/CO_2 ratio of 9:1. The downstream gas permeated through the composite membrane with comb-like copolymer shows a considerably lower N_2/CO_2 ratio of 4.5:1, in comparison with that of 7.2:1 for polysulfone membrane, 6.7:1 for the composite membrane with neat PIL, and 9:1 for the base membrane. The higher N_2/CO_2 selectivity induced by the comb-like copolymer is believed to arise from the more homogeneous dispersion of comb-like copolymer in polysulfone. This study provides the demonstration of the N_2/CO_2 selectivity by comb-like PIL, although the selectivity is somehow low, but could be explained as follows: 1) only a small amount of 5wt.% comb-like copolymer was added to composite membrane. Introduction of comb-like structure improve the compatibility of PIL and polysulfone, but we also found that further increase of comb-like copolymer contents, e.g. 10 wt.%, is likely to induce micro-cracks in membrane because of the strong polarity of PIL; 2) from a point view of molecular structure, the ionic liquid units used in this study are composed of imidazolium cations, tetrafluoroborate anions, and alkyl. It has been reported that the CO_2 absorption and N_2/CO_2 selectivity highly depend on their specific cations, anions, and other groups,[18, 45, 48] among ammonium, hexafluorophosphate and benzene are generally beneficial for high CO_2 absorption.[50, 51] Therefore, both low dosage and unoptimized composition of this PIL comb-like copolymer are likely responsible for the low N_2/CO_2 selectivity. Even so, abovementioned gas separation measurements at least provide a new pathway to achieve composite membrane for N_2/CO_2 separation by using PIL comb-like copolymer , simply because PILs are well-known for their diverse compositions of cations, anions and other groups, offering a wide range of polarity and CO_2 affinity for further optimizing such type of materials. Based on the advantages of diverse compositions, multiple groups, and tunable structure of PILs, low dosage and inferior CO_2 absorption could be overcome by optimizing these parameters. So, PIL comb-like copolymers can logically be assumed show great potentials for gas separation membranes.

4. Conclusion

In this work, we designed, synthesized, and characterized a new comb-like copolymer composed of polystyrene as backbone and PIL as side chains by directly polymerizing IL monomers by ATRP and using poly(St-co-VBC) as macroinitiator. Graft density and side chain length can be facilely tailored by tuning macroinitiator composition and reaction conditions. For comb-like copolymers with similar graft density, side chain length in the range of this study did not affect the T_g's of copolymers. In contrast, comb-like copolymers with high graft density showed higher T_g's despite the short side chains. Unlike glass transition temperature, the impedances of the copolymers showed dependence on both side chain length and graft density. Both parameters aided charge transfer, resulting in higher electrochemical properties. These comb-like copolymers show great potentials as effective stabilizers for carbon materials (e.g. CNTs and graphene) and as efficient additives for N_2/CO_2 separation membranes.

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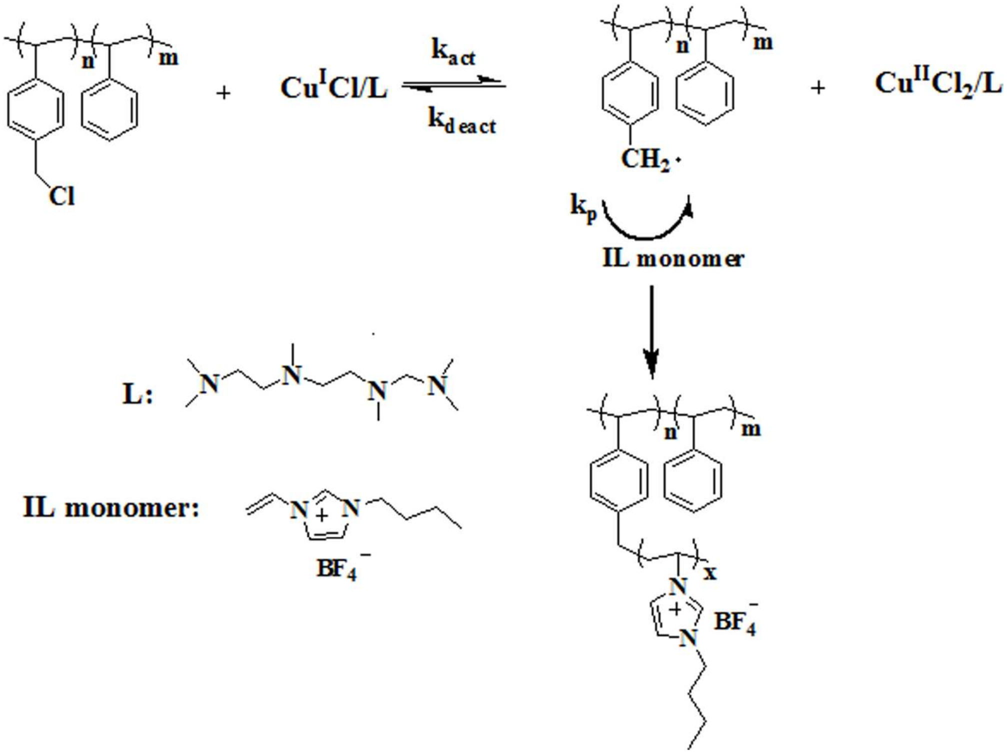
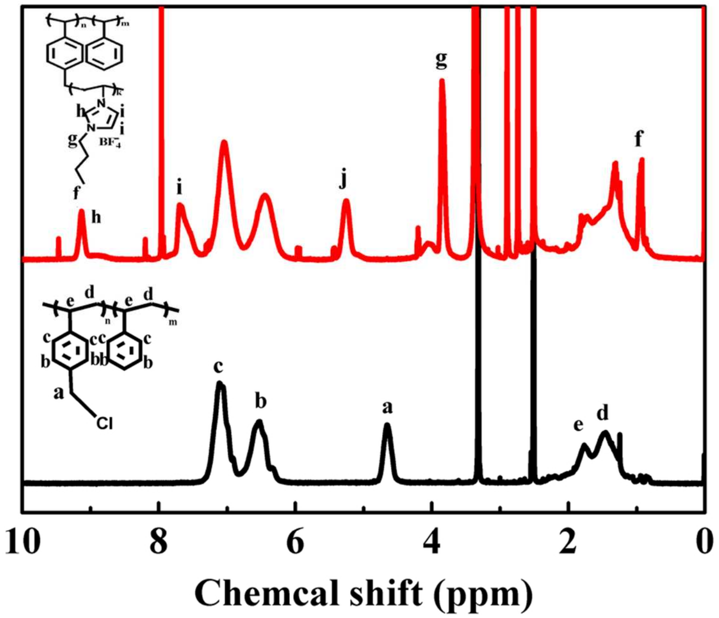


Scheme 1. Preparation of PIL comb-like copolymer via ATRP using poly(St-co-VBC) as macroinitiator.
74x55mm (600 x 600 DPI)



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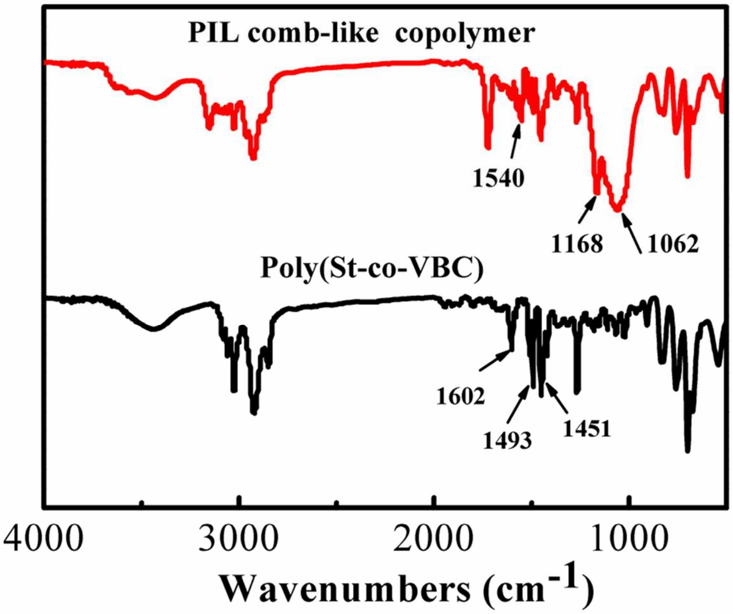

Figure 2. FTIR spectra of poly(St-co-VBC) and PIL comb-like copolymer.
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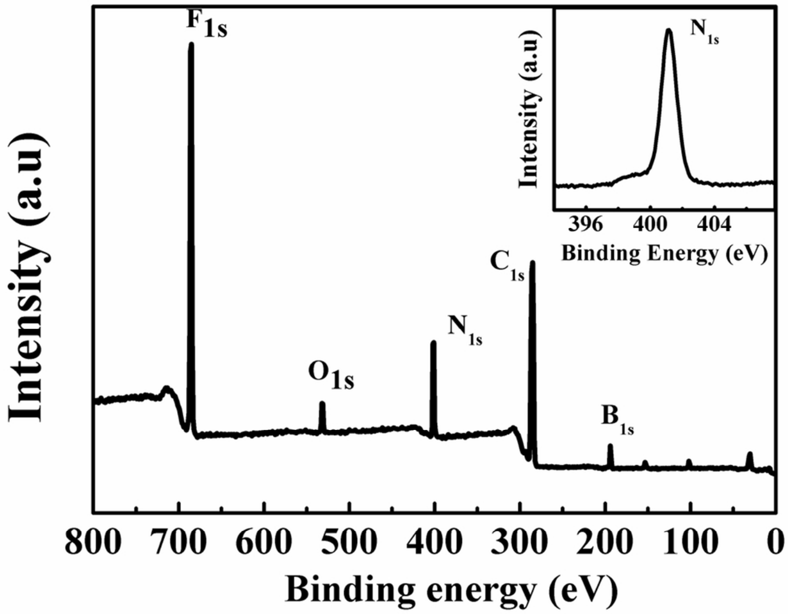

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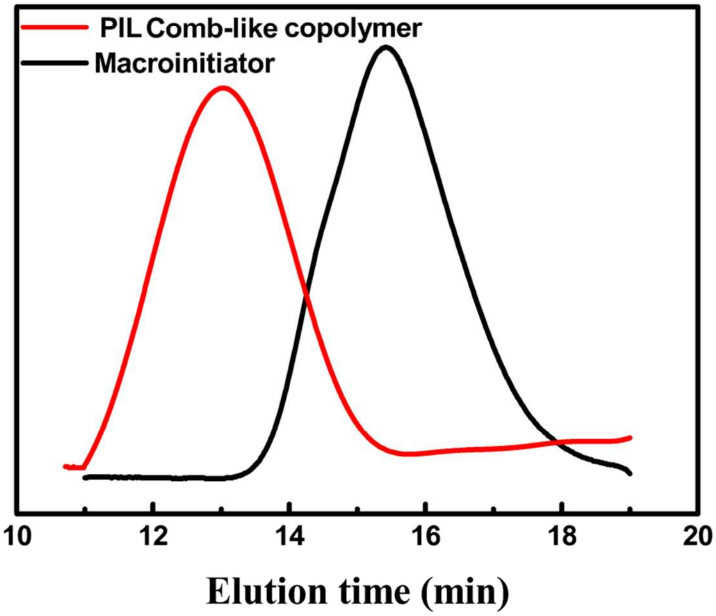
52x37mm (600 x 600 DPI)



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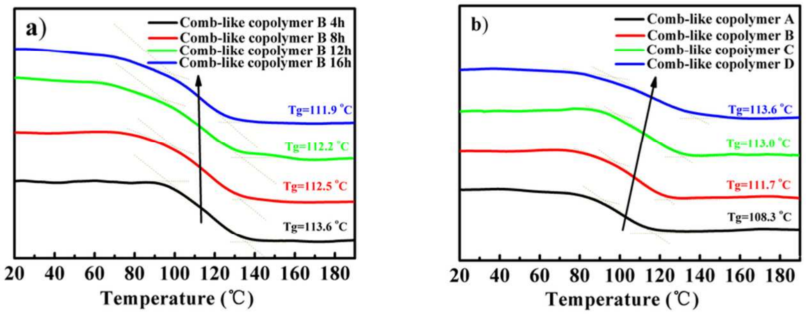

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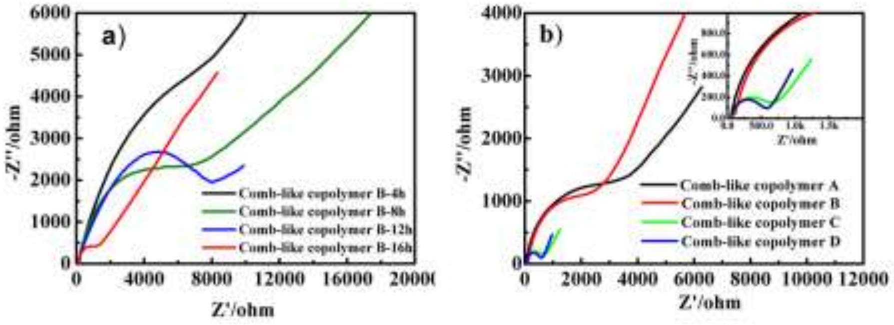

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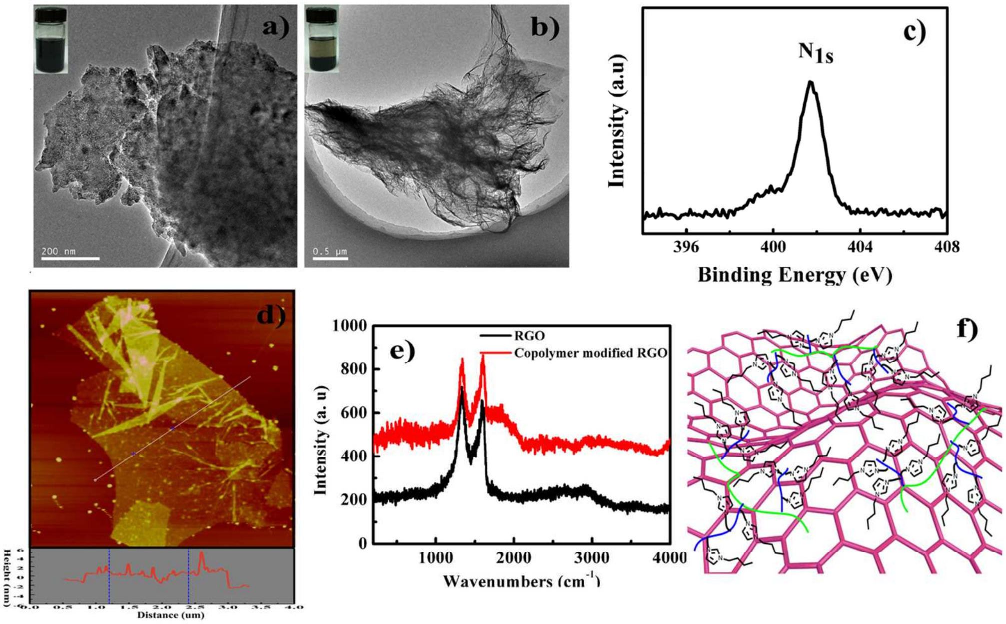

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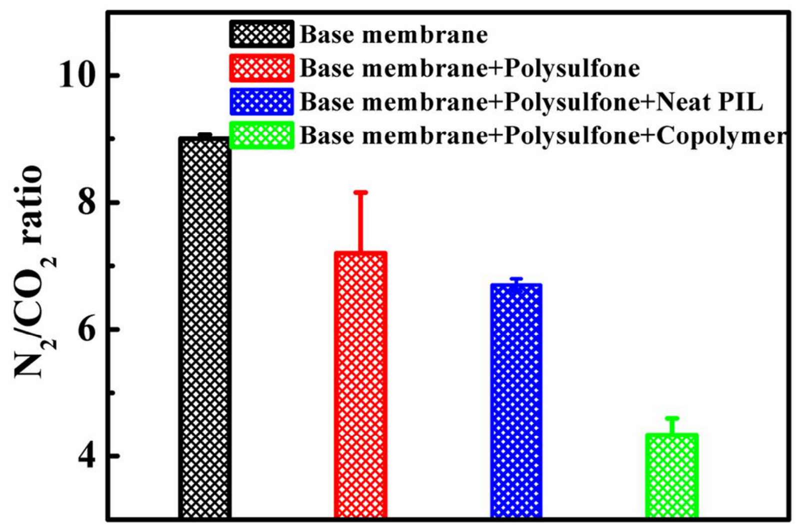

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52x37mm (600 x 600 DPI)

Table1. Average molecular weights and composites of poly(St-co-VBC)s

Macroinitiators	$M_{n\text{-}GPC}\times 10^{-3}$	$M_w\times 10^{-4}$	DPI	x(-CH_2Cl)%[a]	St/VBC
A	7.31	1.56	1.71	29.4	~7/3
B	5.99	1.04	1.51	52.6	~1/1
C	7.41	1.31	1.47	65.7	~1/2
D	8.19	1.46	1.47	74.5	~1/3

a. Determined by NMR

Table 2. Average molecular weights, PDIs, and side chain lengths of PIL comb-like copolymers from macrointiator with St/VBC ratio of 1/1 upon different polymerization times

Exp No	$M_{n\text{-}NMR}\times 10^{-4}$	$M_{n\text{-}GPC}\times 10^{-4}$	$M_w\times 10^{-4}$	PDI	$M_{n,PIL}\times 10^{-3}$
B-4h	3.66	3.69	6.76	1.5	1.4
B-8h	4.03	5.02	8.94	1.72	2.1
B-12h	4.15	5.26	7.78	1.45	2.2
B-16h	4.37	5.65	7.92	1.35	2.4

Table 3. Average molecular weights, PDI, and side chain lengths of PIL comb-like copolymers with different graft densities.

Sample	$M_{n\text{-}NMR}\times 10^{-4}$	$M_{n\text{-}GPC}\times 10^{-4}$	$M_w\times 10^{-4}$	PDI	$M_{n\text{-}PIL}\times 10^{-3}$
A-16h	3.79	5.32	7.70	1.36	3.2
B-16h	4.07	5.49	7.25	1.27	2.3
C-16h	6.73	7.18	9.16	1.29	2.1
D-16h	7.41	9.28	10.68	1.17	2.1