Synthesis of silver halide nanocomposites templated by amphiphilic graft copolymer and their use as olefin carrier for facilitated transport membranes

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ABSTRACT

A novel amphiphilic comb-like copolymer consisting of poly(vinyl chloride) (PVC) main chains and poly(4-vinyl pyridine) (P4VP) side chains, i.e. PVC-*g*-P4VP with 65:35 wt% is synthesized via atom transfer radical polymerization (ATRP). This self-assembled copolymer is used to template the growth of silver bromide (AgBr) nanoparticles with diameters of 10–50 nm, as characterized by UV–vis spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). Upon introduction of ionic liquid, i.e. 1-methyl-3-octylimidazolium nitrate ($MOIM^+NO_3^-$), the surface of AgBr nanoparticles is more partially positively charged due to the interactions between NO_3^- ions and the surfaces of nanoparticles, as revealed by FT-Raman and X-ray photon spectroscopy (XPS). We also demonstrate the ability of AgBr as a new type of olefin carrier by tuning the interactions of positively charged AgBr with the C=C bond of olefin molecules. As a result, the membranes containing AgBr nanocomposites exhibit highly stable separation performances for propylene/propane mixture, i.e. a mixed gas selectivity of 6 and a permeance of 5.7 GPU.

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1. Introduction

There has been a growing interest in the preparation of nanoparticles, nanocomposites, and nanostructured materials, because of their interesting size-related optical, electrical, mechanical and transport properties [1–3]. Due to their small size, nanoparticles exhibit novel properties which are significantly different from the bulk materials. In the past few years, synthesis of nanoparticles via a size-controlled and shaped-controlled procedure has become a new and interesting research topic. These materials are considered to be intriguingly functional materials with potential applications in various fields such as magnetic resonance imaging (MRI) [4], electrochemistry [5], and photoluminescence [6]. In particular, interest in silver has significantly increased due to their interesting optical, electronic, magnetic, mechanical and sensing properties [7,8]. Silver nanoparticles have been used as a material for applications such as antimicrobial activity [9], catalysis [10], surface-enhanced Raman spectroscopy (SERS) [11], and facilitated olefin transport [12]. More recently, the preparation of silver halide nanoparticles has received great attention because of the ability to tune the release of biocidal Ag^+ ions [13] and selective sorption

capacity of cyclohexene from cyclohexane/cyclohexene mixture [14].

The separation of olefin/paraffin mixtures, e.g. ethylene/ethane, propylene/propane or aromatic hydrocarbons from C_4 to C_{10} aliphatic hydrocarbon mixtures is of pivotal importance in the petrochemical industry and currently performed by distillation process. Because this process requires high capital investment and enormous operating costs, an alternative energy-saving separation technology is necessary. Membrane separation technology has been proposed as a possible alternative process to distillation. However, the separation of olefin/paraffin mixtures via conventional polymeric membranes has not been effective because the physico-chemical properties of olefins and paraffins such as their molecular size and solubility are largely indistinguishable [15]. Facilitated transport has been receiving tremendous attention as a potential energy-saving separation technology, because it can simultaneously improve the permeability and selectivity of a membrane [16–19]. During the past several years, polymer–silver salt complex membranes have been intensively studied, where a silver salt with low lattice energy is dissolved in a polymer matrix via coordination bond, and were successfully used as facilitated olefin transport membranes *in solid state* [20–27]. More recently, it was reported that the membranes containing polarized metal nanoparticles activated by the suitable electron acceptors such as *p*-benzoquinone and ionic liquid exhibited highly stable separation performance for olefin/paraffin mixtures [12,28,29].

As far as we know, there has been no report on the separation of olefin/paraffin mixtures through the membranes containing metal halide nanoparticles. First, we synthesized a novel amphiphilic comb-like copolymer, i.e. poly(vinyl chloride)-graft-poly(4-vinyl pyridine) (PVC-*g*-P4VP) via atom transfer radical polymerization (ATRP). Metal halide nanoparticles, i.e. silver bromide (AgBr) were in situ grown within this self-assembled graft copolymer and used as a novel olefin carrier for facilitated olefin transport in solid-state membranes.

2. Experimental

2.1. Materials

PVC ($M_n = 55,000$ g/mol, $M_w = 97,000$ g/mol), 4-vinyl pyridine (4VP), copper(I) chloride (CuCl), 1,1,4,7,10,10-hexamethyl triethylene tetramine (HMTETA), 1-bromohexane, silver *p*-toluenesulfonate (AgPTS), and 1-methy-2-pyrrolidinone (NMP) were purchased from Aldrich. The ionic liquid, 1-methyl-3-octylimidazolium nitrate (MOIM$^+$NO$_3^-$) was purchased from C-TRI. Methanol, dimethyl sulfoxide (DMSO), and diethyl ether were purchased from J.T. Baker. All solvent and chemicals were regent grade, and were used as received without further purification.

2.2. Synthesis of PVC-g-P4VP graft copolymer

3 g of PVC was dissolved in 75 ml NMP in a round flask at 70 °C. After cooling the solution to room temperature, 9 ml of 4VP, 0.24 g of CuCl and 0.66 ml of HMTETA were added to the solution and the reaction flask was sealed with a rubber septum. The mixture was stirred to produce homogeneous solution and purged with nitrogen for 30 min. The mixture was placed in a 90 °C oil bath for 4 h. After polymerization, the resultant polymer solution was diluted with THF. After passing the solution through a column with activated Al$_2$O$_3$ to remove the catalyst, the solution was precipitated into diethyl ether. The polymer was purified to remove unreacted 4VP completely by thrice redissolving in NMP and reprecipitating in diethyl ether. PVC-*g*-P4VP graft copolymer was obtained and dried in a vacuum oven overnight at room temperature.

2.3. Synthesis of N-PVC-g-P4VP

PVC-*g*-poly(4-vinyl-*N*-hexylpyridinium bromide), N-PVC-*g*-P4VP, was synthesized by N-alkylating the pyridine nitrogens of PVC-*g*-P4VP. 1.5 g of PVC-*g*-P4VP was dissolved in 70 ml of NMP with 1.5 ml of 1-bromohexane and then allowed to react at 60 °C for 24 h. The polymer was isolated by precipitation in diethyl ether and dried under vacuum for 24 h.

2.4. Preparation of N-PVC-g-P4VP/AgBr nanocomposites

To prepare the nanocomposites containing AgBr, 1.5 g of N-PVC-*g*-P4VP was dissolved in 60 ml of NMP. Separately, 1.5 g of silver *p*-toluenesulfonate (AgPTS) was dissolved in 18 ml of DMSO. AgPTS solution was then added dropwise to the stirring polymer solution. The mixture was stirred for another 1 h at room temperature. The polymeric composite was precipitated in diethyl ether and was dried under vacuum for 24 h. Finally brown polymeric nanocomposites were obtained.

2.5. Membrane preparation and separation performance

After the AgBr nanocomposites were incorporated into ionic liquid MOIM$^+$NO$_3^-$, the solution was stirred for 5 h under 100 °C until homogeneous phase was observed. Separation membranes were prepared by coating AgBr nanocomposite solution with the different concentrations of ionic liquid onto a polysulfone microporous membrane support using an RK Control Coater (Model 101, Control Coater RK Print-Coat instruments Ltd., UK). The average pore size of the surface of the microporous membrane support was 0.1 μm, and the thickness was approximately 40 μm with asymmetric structure. The thickness of the top nanocomposite layer was found to be approximately 10 μm using scanning electron microscopy (SEM). After annealing at 100 °C for 24 h, the coated membranes were equipped with permeation cell. The gas flow rates were determined using a mass flow meter at 40 psig and 25 °C. Gas permeance is expressed in units of GPU, where 1 GPU = 1×10^{-6} cm^3 (STP)/(cm^2 s cmHg). The effectiveness of AgBr nanocomposite membranes in separating a mixed gas (50:50 vol.% propylene/propane) was evaluated using a gas chromatograph (Hewlett-Packard G1530A, MA) equipped with a TCD detector and a unibead 2S 60/80 packed column.

2.6. Characterization

Nuclear magnetic resonance (^{1}H NMR) measurements were performed with 600 MHz, high resolution NMR spectrometer (AVANCE 600 MHz FT-NMR, Germany, Bruker). FT-IR spectra of the samples were collected using Excalibur Series FTIR (DIGLAB Co.) instrument between the frequency ranges of 4000 and 700 cm^{-1} using ATR facility. UV–vis spectroscopy was measured with spectrophotometer (Hewlett Packard) in the range of 200–800 nm. The WAXS experiment was carried out on a Rigaku 18 kW rotating anode X-ray generator with CuK$_\alpha$ radiation (λ = 1.5406 Å) operated at 40 kV and 300 mA. The 2θ range was from 5° to 70° with a scanning speed of 3°/min, and the distance from the sample to detector was 185 mm. TEM pictures were obtained from a Philips CM30 microscope operating at 300 kV to observe embedded silver bromide nanoparticles. For TEM measurements, the products were dissolved in DMSO, and then a drop of this silver bromide composites dispersion was placed onto a standard copper grid. Raman spectra were collected for the nanocomposite films at room temperature using a Perkin-Elmer System 2000 NIR FT-Raman with a resolution of 1 cm^{-1}. This spectrometer is equipped with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser operating at 1064 nm. X-ray photoelectron spectroscopy (XPS) data were acquired using a Perkin-Elmer Physical Electronics PHI 5400 X-ray photoelectron spectrometer. This system was equipped with a Mg X-ray source operated at 300 W (15 kV, 20 mA). The carbon (C 1s) line at 285.0 eV was used as the reference in our determinations of the binding energies of the silver.

3. Results and discussion

3.1. Synthesis of graft copolymer

Scheme 1 illustrates the reaction scheme for the synthesis of PVC-*g*-P4VP comb-like graft copolymer by ATRP. The "grafting from" method using ATRP technique has been widely used as an efficient polymerization method for the preparation of well-defined graft copolymers due to the controlled chain growth and living nature of polymerization [30]. Here, the P4VP side chains

Poly (vinyl chloride)   4 vinylpyridine   PVC-g-P4VP
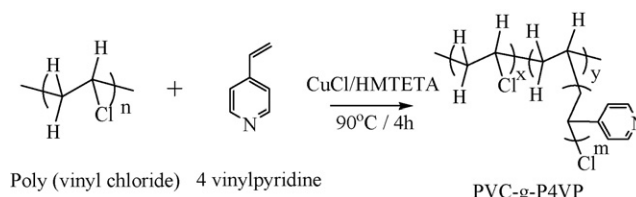
Scheme 1. Synthesis of PVC-*g*-P4VP graft copolymer by ATRP.