Journal of Industrial and Engineering Chemistry 20 (2014) 682–688

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Preparation of copper containing methacrylic polymers and their application for the copper patterns

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ARTICLE INFO

Article history:
Received 2 April 2013
Accepted 23 May 2013
Available online 3 June 2013

Keywords:
Copper
Methacrylic polymer
Lithography
Pattern
Nanomaterial

ABSTRACT

Copper containing methacrylic polymers were prepared by the polymerization of a copper methacrylate complex (Cu[$CH_2{=}C(CH_3)–COO$](COD), where COD = 1,5-cyclooctadiene) with different methylmethacrylate and methacrylic acid compositions. These polymers were found to be soluble in many organic solvents including THF and chloroform. Copper nano-networks or aggregated nanoparticles were obtained when a THF solution of the polymers was reduced using an aqueous sodium borohydride solution. When a thin film of the polymers coated on a silicon wafer was irradiated with an electron beam, nanoparticles were produced on the irradiated area, while the non-irradiated areas could be washed away with a weak base developer, such as a tetramethylammoniumhydroxyde (TMAH) aqueous solution, to produce a copper pattern through an electron beam lithography process.

1. Introduction

There has been increasing interest in the preparation of metallic nanomaterials dispersed in a polymeric matrix because they have the combining properties of the metallic components with those of polymers [1]. For the applications of optical, catalytic, and electronic fields, a variety of synthetic procedures have been developed for the preparation of the metal nanomaterials with various sizes and shapes using metallic salts dispersed in polymeric materials having different functionality. The reduction of metallic salts dispersed in polymers with polar functional groups is one of the most commonly used synthetic procedure for producing these nanomaterials [2–8]. For example, polymeric nanocomposites containing copper nanoparticles were prepared by the reduction of the mixtures of copper salts with poly(carboxylic acid) or poly(vinylpyridine) derivatives [9,10]. One of the disadvantages of this method is the formation of coordination crosslinks through the coordinated bonds of the copper ions with the functional group in the polymer chains [11], then the polymer system can have poor processability due to the very low solubility of the complexes in common solvents. Furthermore, it is difficult to remove the anions or other inorganic moieties originally included in the copper salts from the nanocomposite materials, which might affect the properties of nanocomposites. The nanomaterials in a polymer matrix were also obtained by mixing functionalized nanomaterials with polymeric materials, where a dispersion of nanomaterials can be achieved through electrostatic interactions, hydrogen bonding, and even covalent bonding between the nanomaterials and the polymers. In this case nanomaterials with specific functional groups or polymeric chains should be prepared properly beforehand [11,12].

In this study, copper nanomaterials dispersed in methacrylic polymers were prepared by the reduction of the copper containing methacrylic polymers. The copper containing methacrylic polymers were synthesized by the copolymerization of methyl methacrylate, methacrylic acid, and methacrylate Cu (1,5-cyclooctadiene) complex (MCOD). The polymer was founded to be soluble in organic solvents without forming any crosslinked structures due to protection of the copper carboxylate groups with a non-polar 1,5-cyclooctadiene group. Furthermore, since MCOD is composed of only copper(I) and organic moieties, there are no other inorganic moieties that might affect the properties of copper nanomaterials or patterns in the possible applications. This paper reports the synthesis of MCOD and copper containing methacrylic polymers, the preparations of copper nanomaterials from the methacrylic polymers, and the preliminary electron beam lithography process for the preparation of copper patterns.

2. Experimental

2.1. Materials

Cuprous chloride (CuCl), 1,5-cyclooctadiene, sodium methacrylate, methylmetacrylate (MMA), methacrylic acid (MAA), sodium

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http://dx.doi.org/10.1016/j.jiec.2013.05.033

borohydride and azobis(isobutyronitrile) (AIBN) were purchase from Aldrich Chemical Co. and used without further purification. THF was distilled from sodium and benzophenone in a N_2 atmosphere. The cuprous chloride/1,5-cyclooctadiene complex, CuCl(COD), was prepared by a reaction between CuCl and 1,5-cyclooctadiene (COD) according to the procedure reported in the literature [13].

2.2. Instrumentations

The ^{1}H nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ or deutrated methanol on a 300 MHz Bruker DPX-300 spectrometer. Thermal analysis was carried out on TA DSC2920 and TA TGAQ5000 in a N_2 atmosphere at heating rates of 10 °C/min. The molecular weight of the polymer was measured by gel permeation chromatography using Waters 2414 RI detector, Shodex LF-804 column, and THF as the mobile phase. The Fourier transform infrared spectra (FT-IR) were obtained on a JASCO FT/IT-200 using a KBr pellet mixed with a copper containing polymer or composite generated from chemical reduction. The electron beam reduction experiments for preparation of the copper nanomaterials were performed using a JEM-200CX transmission electron microscope operating at 200 keV. The electron beam lithography experiments were carried out using a JBX-6300FS. The pattern shape was observed by scanning electron microscopy (JSM 6330-F).

2.3. Synthesis of methacrylate CuCl(COD) complex (MCOD)

2.08 g (20 mmol) of CuCl(COD) and 1.08 g (10 mmol) of sodium methacrylate was dispersed in 200 mL of THF. The reaction solution was stirred for 12 h until it turned blue. The solution was then filtered and solvent was removed under a vacuum. The bluish green solid powder was obtained and washed several times to remove NaCl, which is a byproduct of the reaction. The yield was 49%.

Elemental analysis: Calcd. for $C_{12}H_{17}O_2Cu$: C, 56.25; H, 6.64. Found: C, 56.52; H, 6.83. IR: ν 1650 cm^{-1} (C=C stretch of cyclooctadiene), 1636 cm^{-1} (C=C stretch of methacrylate), 1576 cm^{-1} (CO_2^- asym. stretch), 1410 cm^{-1} (CO_2^- sym. stretch), 635 cm^{-1} (CO_2^- deformation).

2.4. Preparation of the copper containing methacrylic polymers (poly(MMA-*co*-MCOD) and poly(MMA-*co*-MAA-*co*-MCOD))

A series of copper containing methacrylic polymers with different copper contents were prepared by the free radical polymerization of MCOD with MMA and/or MAA using AIBN and THF as an initiator and solvent, respectively. Table 1 lists the amounts of monomer, initiator, and solvent used for the copolymerizations. The reaction mixture was refluxed for 17 h under a dry nitrogen atmosphere and poured into *n*-hexane. The precipitate was further purified by several precipitations using methanol and *n*-hexane as the solvent and non-solvent, respectively, and then dried in a vacuum oven. The IR and ^{1}H NMR results clearly indicated that all the monomers had been removed during the purification process. Copper containing methacrylic polymers with different amounts of copper and other monomeric units were obtained (Table 1) in approximately 30% yield due to the lost during the purification process. IR: ν 2996 cm^{-1} (O–CH_3 stretch methacrylate), 2951 cm^{-1} (CH_2 asym. stretch of polymer chain), 2882 cm^{-1} (CH_3 stretch of α-methyl), 2843 cm^{-1} (CH_2 sym. stretch of polymer chain), 1731 cm^{-1} (CO_2^- stretch of methacrylate). 1642 cm^{-1} (C=C stretch of cyclooctadiene), 1615 cm^{-1} (CO_2^- asym. stretch of complex), 1481 cm^{-1} (CH_2 bending of polymer chain), 1445 cm^{-1} (CO_2^- sym. stretch of complex), 1433 cm^{-1} (O–CH_3 deformation of methacrylate), 1385 cm^{-1} (CH_3 bending of α-methyl). ^{1}H NMR ($CDCl_3$) δ: 5.51 (s, cyclooctadiene), 3.60 (s, OCH_3), 2.49 (s, cyclooctadiene), 1.95 (d, CH_2), 1.89 (m, CH_2), 1.81 (s, CH_2), 1.65 (m, CH_2), 1.44 (m, CH_2), 1.21 (m, CH_3), 1.02 (s, CH_3), 0.84 (s, CH_3).

2.5. Chemical reduction

0.10 mL of a 10 wt% aqueous sodium borohydride solution was added to 1.94 g of a THF solution containing 0.06 g of a copper containing polymer. The mixture was then stirred for 10 min. An excess of methanol was then added and the precipitate was washed with methanol several times. For transmission electron microscopy (TEM), the product was dissolved in THF and a drop of the solution applied to a carbon-coated copper grid, which was then dried under a vacuum.

2.6. Electron beam lithography

0.10 g of poly(MMA-*co*-MAA-*co*-MCOD) having MMA/MAA/MCOD = 7/2/1 was dissolved in 1.90 g of THF. A Si wafer was coated with the resulting solution using a spin coater at 2000 rpm for 20 s and then dried in a vacuum oven at room temperature. Electron beam writing was carried out at 500 uC/cm^2 on the copper containing polymer-coated wafer, where the electron beam lithography instrument was set to an acceleration voltage of 100 keV and a beam current 1 nA at room temperature under vacuum. After the electron beam writing process, the copper containing polymer film was developed in a 0.15 wt% tetramethyl ammonium hydroxide (TMAH) aqueous solution for 30 s and rinsed in deionized water.

3. Results and discussion

The methacrylate CuCl(COD) complex monomer (MCOD) was prepared using a two step reaction, as shown in Fig. 1. A cuprous

Table 1
Feed ratio, solubility and molecular weight of copper containing polymers.

Polymer	MMA/MAA/MCOD feed ratio[a]		Solubility (wt%)			M_w (k)	PDI
	wt	mmol	THF	CH_3Cl_3	Methanol		
Poly(MMA-*co*-MCOD)	9/0/1	27.0/0/1.2	>10	3	<1	6.4	1.7
	8/0/2	24.0/0/2.3	7	2	1	4.3	1.7
	7/0/3	21.0/0/3.5	2	<1	2	3.6	1.8
	6/0/4	18.0/0/4.7	1	–[b]	2	3.4	2.0
Poly(MMA-*co*-MAA-*co*-MCOD)	8/1/1	25.2/3.6/1.2	10	<1	11	6.3	1.7
	7/2/1	21.0/7.0/1.2	10	–[b]	19	6.6	1.9
	6/3/1	18.3/10.7/1.2	4	–[b]	24	5.9	1.6

[a] 0.54 mmol of AIBN and 30 mL of THF was used for all the cases.

[b] Not soluble.