



A new type of sulfonium salt copolymers generating polymeric photoacid: Preparation, properties and application



Qianqian Wang, Chenfeng Yan, Fengjuan You, Liyuan Wang*

Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China

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ABSTRACT

Photoacid generators (PAGs) are critical components in chemically amplified (CA) photoresists system, among which small molecular sulfonium salts are commonly used but possess inherent incompatibility with polymer matrixes and acid migration during the post exposure baking (PEB) processes. PAG-bound polymers would be better choices for CA photoresists to acquire excellent lithographic performance. In this work, a new and convenient way is designed to prepare polymeric PAGs which generate polymeric photoacids and with this method the existing small molecular sulfonium salts can be transformed into polymeric compounds with convenience. Poly (sodium p-styrenesulfonate-co-tertiary-butyl methacrylate) (p(SSNa-co-t-BMA)) was prepared through free radical polymerization and then was further reacted with various sulfonium halides to give sulfonium salt copolymers. Different molecular weights of the copolymers can be obtained from M_n 5.5×10^3 – 2.5×10^4 with distribution coefficient between 1.18–1.88. The ionic copolymers display good solubilities in common resist solvents. The thermal decomposition temperatures (T_d) are around 150–155 °C and the glass transition temperatures (T_g) are above 130 °C. After exposed to light, the copolymers can generate polymeric photoacids. The photoacid generation efficiencies are determined around 0.31–0.34. UV spectra show big difference between the polymeric PAGs and the mixture of the corresponding small molecular sulfonium salts and framework polymers and demonstrate much better transparency of polymeric PAGs. Thick film 248-nm CA photoresist can be formed by one of the polymeric PAGs and partly protected poly(4-hydroxystyrene-co-tertiary-butyl methacrylate) (p(4-HS-co-t-BMA)), and display excellent performance with high height/width (H/W) ratio of 5:1 and resolution of 0.35 μm . These polymeric PAGs also have potentiality to be used in CA photoresists for other photolithography technologies such as 193-nm immersion technology.

1. Introduction

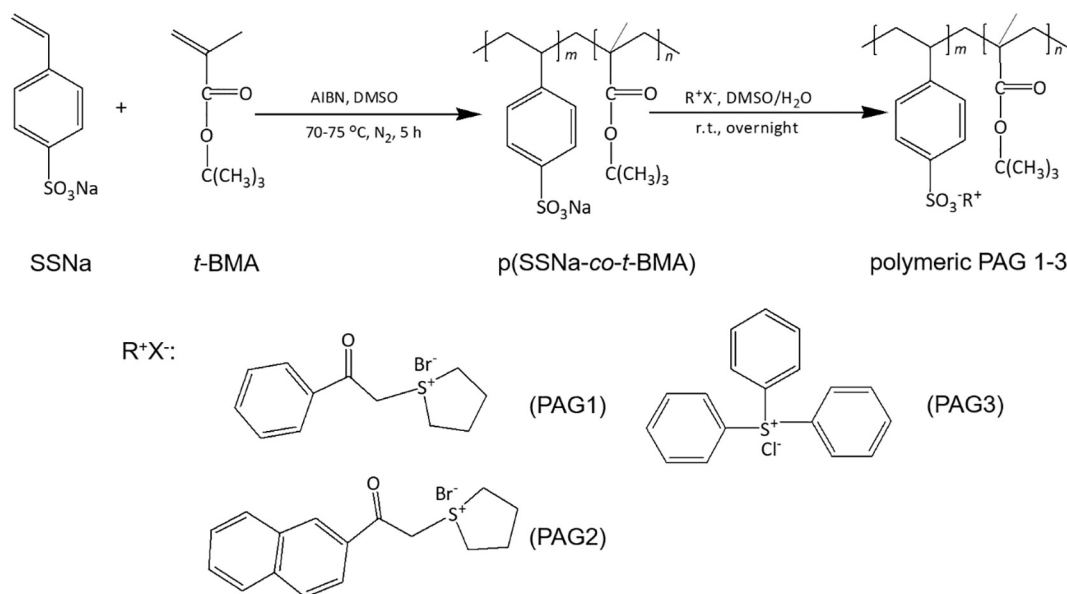
Photoacid generators (PAGs) are key components of chemically amplified (CA) photoresists [1–9]. Sulfonium salts are the most widely used PAGs in CA resists for their high photoacid generating efficiency and thermal stability. The inherent incompatibility between commonly used small molecular sulfonium salt PAGs and polymer matrixes in conventional PAG-blend system leads to problems including phase separation, non-uniformly distribution of PAGs and photogenerated acids, as well as acid migration during post exposure baking (PEB) process [10–12]. These problems do harm to the performance of CA photoresists. A lot of efforts have been done to improve the performance of CA resists. One way is to use molecular glass resist materials [13–19]. These low molar mass materials exhibit better phase compatibility with small molecular PAGs as well as better line-edge roughness (LER). Another effective approach is to prepare polymeric PAGs with PAG units incorporated into the main or side chains [20–25]. In recent years,

polymeric PAGs, including nonionic and ionic, are being actively investigated due to their excellent lithographic features [26–29]. Similar to conventional PAG-blend systems, PAG-bound polymers can generate a certain amount of acids upon light irradiation which act as catalysts for reactions such as cross-linking or deprotection, and result in solubility differentiation between exposed and unexposed areas. Non-ionic polymeric PAGs mainly refer to copolymers introduced with sulfonate ester groups through N-substitution [30, 31]. Ionic polymeric PAGs such as sulfonium salts can be applied with a wide range of light source, especially deep UV and vacuum UV, at the same time applied to E-beam lithography [32–34]. Polymeric PAGs are generally synthesized by copolymerization of PAG monomers containing photosensitive sulfonium or sulfonate units and other functional monomers in the reported literatures [35–38].

Most of the reported polymeric PAGs generate small molecular sulfonic acids after exposed to light, and hence they can't depress photoacid migration effectively, even though the size incompatibility

* Corresponding author.

E-mail address: wly@bnu.edu.cn (L. Wang).



Scheme 1. Preparation of polymeric PAGs.

between the small molecular ionic PAG and polymer matrixes can be avoided. Only when the polymeric PAGs are composed of anionic polymer sulfonates, the generation of polymeric photoacid can prevent acid migration and enhance the imaging performance. [20, 27, 36, 39] Although there are a few reported polymeric PAGs which can generate polymeric photoacids, the preparation processes are generally complicated and which will hinder the practical application of the polymeric PAGs in CA photoresists [3, 20, 22, 23].

Herein we designed a new way to prepare ionic polymeric PAGs which can generate polymeric sulfonic acid after irradiation, and with this method various kinds of sulfonium salts can be transformed into polymeric compounds with convenience. Copolymers are synthesized by free radical polymerization of sodium *p*-styrenesulfonate and tertiary-butyl methacrylate, and then a series of ionic polymeric PAGs with different sulfonium counter ions are obtained by metathesis reactions of the polymeric sodium sulfonates with corresponding sulfonium halides. The typical preparation process is schematically illustrated in Scheme 1.

The preparation method, properties and application as PAGs for DUV photoresists of the ionic polymeric sulfonium salts are studied in detail.

2. Experimental section

2.1. Materials

Sodium *p*-styrenesulfonate (SSNa, 90%), tertiary-butyl methacrylate (*t*-BMA, 99%), 2, 2'-Azobisisobutyronitrile (AIBN, 99%) and 1-Dodecanethiol (98%) were purchased from Aladin Reagents Company (Shanghai, China). Triphenylsulfonium chloride (99%) was purchased from Yingli Company (Changzhou, China). Bromophenol blue (BPB, 99.5%) was received from Yinghai Company (Beijing, China). Dimethyl sulfoxide (DMSO, 99.8%), *p*-toluene sulfonic acid (99.5%), ethanol, ethyl acetate and ethyl lactate were obtained from Beijing Chemical Reagents Company (AR, Beijing, China). 1-(benzoyl-methyl)-tetrahydro-thiophenium bromide and 1-(2-naphthoyl-methyl)-tetrahydro-thiophenium bromide were prepared according to the reported method [40].

2.2. Characterization

The ^1H NMR spectra were performed on a Bruker Avance III

spectrometer (600 MHz) with solvent of DMSO- d_6 . FT-IR spectra were recorded with a Nicolet AVATAR 360 spectrometer. UV-Vis absorption and transparency spectra were obtained on a GBC Cintra 10e spectrophotometer. T_d was determined by thermogravimetric analyses (TGA) performed on a METTLER STAR TA instrument, heating to 600 °C at rate of 15 °C/min with N_2 gas flow of 20 cm^3/min . T_g was determined using differential scanning calorimetry (DSC) performed on a METTLER STAR TA instrument, heating from 25 °C to 150 °C at rate of 15 °C/min with N_2 gas flow of 20 cm^3/min . Molecular weights and the polydispersity of sulfonium salt based copolymers were determined using a Waters 515 HPLC equipped with a Waters 2414 and Agilent mixed columns (MIXED-A, MIXED-B) in DMF with LiBr (0.01 mol/L) at 40 °C at a flow rate of 1.0 mL/min. The molecular weights were estimated relative to polystyrene standards. Polystyrene standards in the M_n range of 1.3×10^3 – 2.7×10^6 was used for calibrations.

2.3. Preparation of p(SSNa-co-t-BMA)

Poly (sodium *p*-styrenesulfonate-co-tertiary-butyl methacrylate) (p(SSNa-co-t-BMA)) were prepared with the process illustrated in Scheme 1. In a three necked round bottom flask equipped with thermometer, a nitrogen inlet and a condenser, 12.4 g sodium *p*-styrenesulfonate (SSNa, 6.00×10^{-2} mol), 25.6 g tertiary-butyl methacrylate (*t*-BMA, 1.80×10^{-1} mol), 1.97 g AIBN (1.20×10^{-2} mol) and 0.759 g 1-dodecanethiol (3.80×10^{-3} mol) were dissolved in DMSO (120 mL). Polymerization reaction was conducted at 70–75 °C for 5 h. After the reaction was completed, the mixture was poured into 800 mL ethyl acetate to give white precipitates. The solid products were collected and dried in vacuum at 50 °C for 24 h. (37.6 g, Yield: 99%) FT-IR (KBr, cm^{-1}): $\nu = 1720$ (C=O of COOR), 2979 and 2924 ($-\text{CH}_2$ and $-\text{CH}_3$). ^1H NMR (600 MHz, DMSO- d_6), δ (ppm) 6.99–7.43 (Ar-H, 4.00H) and 0.7–2.0 (CH_2 and CH_3 , 58.87H). The copolymer composition can be determined by the calculation of ^1H NMR proton peak area.

2.4. Preparation of polymeric PAGs

To the solution of 10 g p(SSNa-co-t-BMA) (1.58×10^{-2} mol SSNa + 4.74×10^{-2} mol *t*-BMA) in DMSO (30 mL), an aqueous solution of 1-(benzoyl-methyl)-tetrahydro-thiophenium bromide (6.78 g, 2.37×10^{-2} mol) was dropped slowly. After the mixture was stirred at room temperature overnight, the solution was poured into 200 mL deionized water to give precipitates. The white precipitates were collected and

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