

Sodium Thiophenolate Initiated Polymerization of Methacrylate with Sulfur (S₈): High-Refractive-Index and -Transparency Polymers for Lithography

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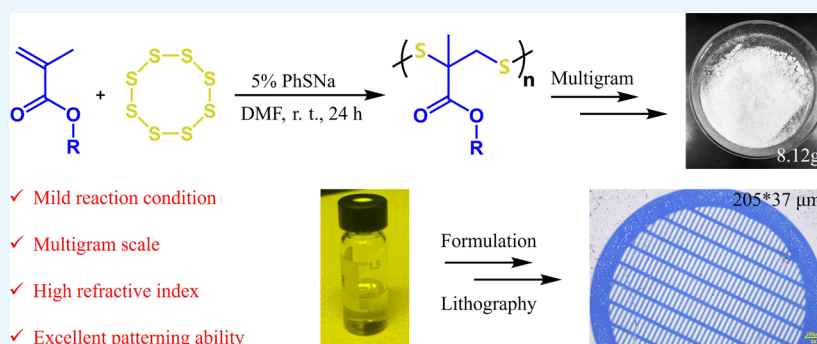
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ABSTRACT: A simple and effective strategy for introducing sulfur into a polymethacrylate matrix at room temperature has been developed, allowing for the polymerization of a variety of methacrylate derivatives with sulfur. The resulting S-containing polymers exhibited a high refractive index of up to 1.72 while retaining over 90% transmittance in the visible region. Additionally, when mixed with 3% photo acid generator (PAG) as photoresist, the formulation demonstrated excellent patterning capabilities. Furthermore, the scalable preparation of high-refractive-index polymers (HRIPs) indicates significant potential for fabrication.

INTRODUCTION

High-refractive-index polymers (HRIPs) are widely used in high-performance optical applications, such as lenses for lithography, waveguide materials for AR/VR holographic technology, and windows for optical devices.^{1,2} The HRIPs are considered to be low cost, have good processability, be lightweight, and have high flexibility. The most commonly used polymer matrices include poly(methyl methacrylate) (PMMA), polycarbonate (PC), polystyrene (PS), etc.³ However, the refractive index (RI) of such polymers is below 1.6, which limits further application. A straightforward approach to increase RI involves blending polymers with inorganic particles; incorporation of inorganic particles into a polymer matrix takes advantage of both components to create original composite materials with new properties.³ However, the intrinsic properties may be degraded because of the aggregation state of the nanoparticles, or due to poor affinity with the matrix, it may cause the problem of optical transparency loss and processing failures.⁴

Consequently, alternative strategies have been employed to synthesize HRIPs, such as introducing highly polarizable atoms (e.g., halogens, sulfur, selenium, and phosphorus) or aromatic groups to the polymer backbone.^{5–7} Among them, sulfur atom-containing polymers typically exhibit high RI due to the high atomic polarizability, good stability, and low dispersion.⁵ The

application of elemental sulfur in polymers could date back to the mid-19th century for the use of mechanical properties enhancement of rubbers, and significant achievements have been made in the synthesis of various S-containing polymers in the past decade,^{8,9} such as S-containing polyacrylate,¹⁰ polyimide,¹¹ polythiocarbonates, etc.¹² Higashihara and Ueda have described a comprehensive review¹³ to summarize the sulfur-containing HRIPs. While the reported synthetic strategies for HRIPs have primarily focused on using at least one sulfur-containing monomer, the direct utilization of elemental sulfur (S₈) in preparing advanced materials is limited due to its highly brittle nature and low solubility in organic solvents.¹⁴

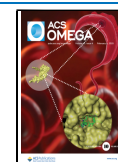
Recently, inverse vulcanization using molten sulfur as both reagent and initiator under 185 °C without any solvent has emerged as an attractive strategy for the synthesis of HRIPs. Pyun and Char¹⁵ reported the utilization of S₈ and 1,3-diisopropenylbenzene to synthesize the over 50% content sulfur polymer via inverse vulcanization. This synthetic methodology

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is simple, scalable, and atom-efficient. Further studies demonstrated that the copolymer exhibits a high refractive index ($n \sim 1.8$) and excellent transparency in the infrared range.^{16–19} Additionally, such polymers and their synthetic procedures have been extensively investigated.^{20–29} However, a major drawback in this procedure is the ring opening of S_8 under harsh conditions with the production of toxic H_2S as byproducts.³⁰ A typical temperature for generating radicals or anionic sulfur is around 160 °C. Wu and colleagues^{31–33} introduced a metal catalyst, Zn diethyldithiocarbamate (DTC), which reduced the required temperature from 160 to 200 to approximately 100–135 °C. A recent study by this group further enabled the reaction at room temperature with photocatalysis;³⁴ various alkenes and alkynes as cross-linkers at ambient conditions afforded sulfur-rich polymers.³⁰

High S-containing materials usually show strong absorption in the visible light range,³⁵ rendering them dark red or brown in color and not suitable for the application that require high transparency. Im and Kim^{2,36,37} reported a process called sulfur chemical vapor deposition (sCVD) to achieve HRIPs with a high content of sulfur, which could apply in the nanoimprint. The RI of poly(sulfur-co-1,4-butanediol divinyl ether) (SBDDVE) prepared by sCVD can reach 1.91 at 632.8 nm, while poly(sulfur-co-divinylbenzene) (sDVB) achieves an impressive refractive index of 1.978 at the same wavelength.²

Very recently, Yang and co-workers³⁸ reported the anionic copolymerization of S_8 and acrylate with monomers in the presence of a phosphazene base (*t*-BuP₂)/benzyl mercaptan (BnSH) as an initiator. This method allowed S_8 to copolymerize with vinyl monomers at room temperature, including methyl methacrylate (MMA). Poly(methacrylate) is a crucial polymer, especially in the microelectronics industry; the resin used in 193 nm photoresist consists of poly(adamantyl methacrylate) and its derivatives.³⁹ In this study, we employed sodium thiophenolate as the initiator to copolymerize with methacrylates at room temperature, compared to the previous report of over 160 °C. The S-content could adjust by the feed ratio of the monomer and sulfur in a certain range. Moreover, this approach provides a simple and scalable method for obtaining high-RI and high-transparency poly(methacrylate), ultimately suitable for lithography applications.

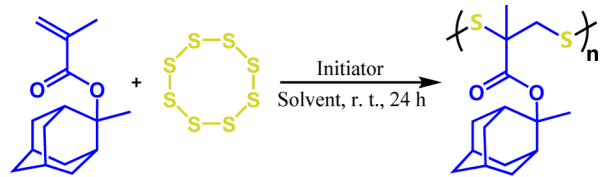
RESULTS AND DISCUSSION

The anionic copolymerization of S_8 with episulfide is well studied in the previous literature.^{40,41} The generation of the S^- initiator is the key factor in the procedure. We started our reaction exploring by using sodium thiophenolate, a common S^- generator⁴² with a tiny unpleasant odor, along with 2-methyl-2-adamantyl methacrylate (MAMA), a monomer often used in photoresist resin. Unfortunately, no reaction occurred in toluene. After several solvents were screened, it was found that the reaction worked well in DMF, and the color of the system turned dark red immediately. The mixture was stirred for 24 h, and the unreacted sulfur particles suspended in the solution. The isolated amounts of the filtrated residue (S_8) suggested that the conversion of sulfur reached 25% at room temperature. Increasing the initiator concentration and adjusting the feed ratio proved to be effective in raising the conversion rate. When the feed ratio of monomer to S came to 5:1 with 5% initiator, the solution turned clearly dark red after 24 h, indicating complete conversion of sulfur into the polymer chain. Further increasing the feed ratio to 10:1 and the initiator to 10% had a negligible effect on the sulfur conversion. To confirm that the reaction

followed an anionic mechanism rather than a radical one, we added 5% TEMPO (2,2,6,6-tetramethylpiperidinoxy) as a radical scavenger, and the polymerization still carried out smoothly, which suggested the anionic mechanism.

As reaction results show in Table 1, a certain amount of unreacted sulfur remained at feed ratios of 1:1 and 2:1,

Table 1. Screening of Reaction Conditions for the Polymerization of 2-Methyl-2-adamantyl Methacrylate with Sulfur^a



entry	feed ratio	initiator %	solvent	conversion ^b
1	1:1	1	toluene	N.D.
2	1:1	1	CH ₂ Cl ₂	N.D.
3	1:1	1	THF	N.D.
4	1:1	1	DMF	25%
5	1:1	5	DMF	38%
6	2:1	5	DMF	62%
7	5:1	5	DMF	>99%
8	10:1	5	DMF	>99%
9	5:1	10	DMF	>99%
10	10:1	10	DMF	>99%
11	5:1 ^c	5	DMF	>99%

^aUnless otherwise specified, reaction conditions: S_8 0.256 g (1 mmol); MAMA and PhSNa feed ratio according to the different condition; 2 mL of solvent; room temperature; 24 h; under argon.

^bSulfur conversion according to the isolated S suspended in the reaction system. ^c5% TEMPO added to the reaction system.

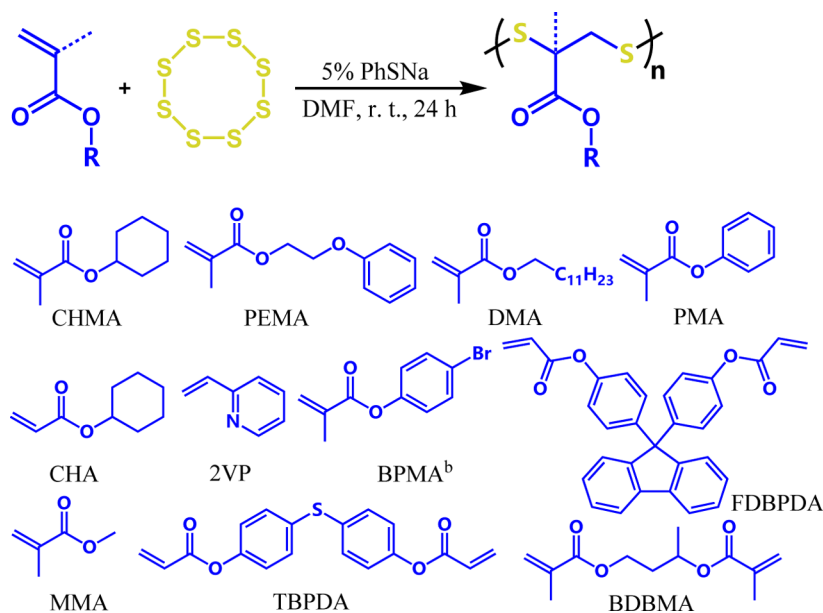
suggesting that the polymer was saturated with a sulfur block of 34% content. As shown in Table 2, when the monomer ratio was

Table 2. M_n and S Content of the Polymers^a

polymer	feed ratio	initiator %	M_n^b kg mol ⁻¹	S content ^c %
P(MAMA ₂₀ -S ₂₀)	1:1	5	4.5	34.7
P(MAMA ₄₀ -S ₂₀)	2:1	5	4.6	34.2
P(MAMA ₁₀₀ -S ₂₀)	5:1	5	9.4	25.7
P(MAMA ₅₀ -S ₁₀)	5:1	10	6.6	25.1
P(MAMA ₂₀₀ -S ₂₀)	10:1	5	9.5	22.9
P(MAMA ₁₀₀ -S ₁₀)	10:1	10	5.5	23.0

^aUnless otherwise specified, reaction conditions: S_8 0.256 g (1 mmol); monomer and initiator feed ratio according to the different condition; 2 mL of DMF; room temperature; 24 h; under argon. ^b M_n was determined by GPC. ^cS content was determined by element analysis.

increased to 5:1, the sulfur content decreased to 25.7%, and further increasing the ratio to 10:1 resulted in a slight change in sulfur content to 22.9%. Gel permeation chromatography (GPC) and elemental analysis were used to confirm the polymer structures. GPC measurements show that when the feed ratio is enlarged from 1:1 to 10:1, the molecular weights of polymers would increase from 4.5 to 9.5 kg mol⁻¹. Compared to the 5% initiator, using a 10% initiator led to a reduction in the molecular weight (M_n) to approximately 6 kg mol⁻¹. The

Table 3. Scope of (Methyl) Acrylates in the Reaction with Sulfur^a

^aUnless otherwise specified, reaction conditions: S₈ 0.256 g (1 mmol); monomer (5 mmol) and PhSNa (6.6 mg); 2 mL of DMF; room temperature; 24 h; under argon. ^bMonomer (2 mmol).

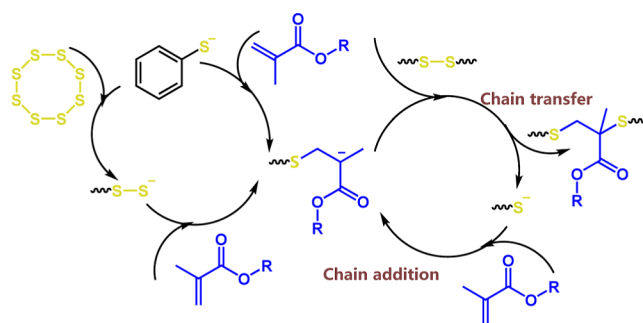
percentage of initiator in the reaction decreased M_n , but it would not affect the S content.

With the optimal reaction conditions established, we subsequently examined various methacrylates as monomers. Generally, sulfur was able to copolymerize with most of the methacrylate, as shown in Table 3, including cyclohexyl methacrylate (CHMA), 2-phenoxyethyl methacrylate (PEMA), dodecyl methacrylate (DMA), phenyl methacrylate (PMA), methyl methacrylate (MMA), and the acrylate, like cyclohexyl acrylate (CHA), also suitable for the reaction. Notably, 2-vinylpyridine (2VP) successfully yielded P(2VP-*c*-S) as a polymer product. Finally, we tried several bifunctional monomers, like (9H-fluorene-9,9-diyl)bis(4,1-phenylene) diacrylate (FDBPDA), thiobis(4,1-phenylene) diacrylate (TBPDA), and butane-1,3-diyl bis(2-methyl acrylate) (BDBMA), and we obtained the cross-linked polymers, respectively.

The polymer of P(MMA₁₀₀-S₂₀) was analyzed by using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). The molecular segment peaks appeared at a spacing of 132.0 (Figure S5), which corresponds to the MMA-S unit in the matrix. The repeating block suggests that sulfur is alternately distributed along the main chain. Furthermore, three distinct fractions were observed in P(MMA₁₀₀-S₂₀) (Figure S5).

The mechanism of anionic copolymerization of monomer and sulfur was proposed in Scheme 1. The sodium thiophenolate reacts with the monomer to generate a carbon anion, which can also open the sulfur ring, forming polysulfide anion species. These anions can then be captured by the monomer to regenerate the carbon anion. The carbon anion species can further cleave the S–S bond, and DMF may facilitate the homolytic cleavage of the S–S bond, as reported in previous literature.⁴³ The chain transfer process terminates the carbon anion and generates an active thiolate anion, which can be captured by the monomer to regenerate the carbon anion, completing the chain addition process.

Scheme 1. Proposed Mechanism of Polymerization



Differential scanning calorimetry (DSC) was used to test the consumption of sulfur. The elemental sulfur exhibits characteristic peaks at 109 and 123 °C; no signal was found in the DSC trace for the polymer produced by different feed ratio procedures at that temperature (Figure 1a), which indicated that there was no unreacted sulfur in the desired polymers. The polymers of P(MAMA₂₀-S₂₀) and P(MAMA₄₀-S₂₀) with over 34% sulfur content had a relatively low T_g at about 58 °C, while the T_g of the polymer containing 23–25% sulfur was about 84–91 °C. With more S content, the T_g of polymers trends down.

Proton nuclear magnetic resonance (¹H NMR) was used to analyze the structures of the polymers. P(MAMA₂₀-S₂₀) was synthesized by a feed ratio of [monomer]/[S₈]/[PhSNa] = 20:20:1. As shown in Figure 1b,c, compared to the ¹H NMR of the MAMA monomer, the monomer peaks of double bonds at 5.5 and 6.0 disappeared in the polymer, and broad peaks at 3.0–4.0 were observed in the polymer ¹H NMR spectrum, which could be attributed to the protons bonded to the polysulfide blocks.

The polymer of P(MAMA₂₀-S₂₀) was also characterized by the FTIR spectrum, as shown in Figure 2a; the appearance of S–S vibration at 474 cm⁻¹ confirmed the presence of sulfur chains, and the C–S vibration at 686 cm⁻¹ indicated the sulfur was successfully introduced into the matrix.³⁸ The Raman spectrum

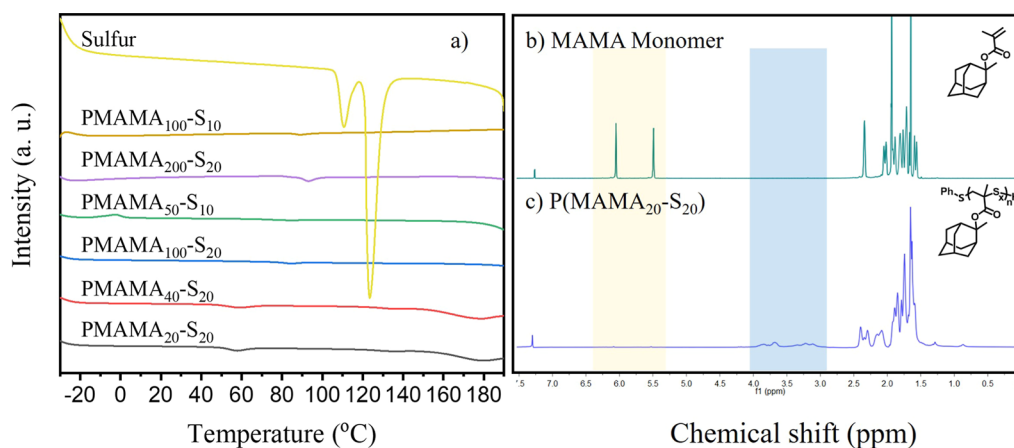


Figure 1. (a) DSC curves. (b,c) ^1H NMR spectra of the MAMA monomer and $\text{P}(\text{MAMA}_{20}\text{-S}_{20})$.

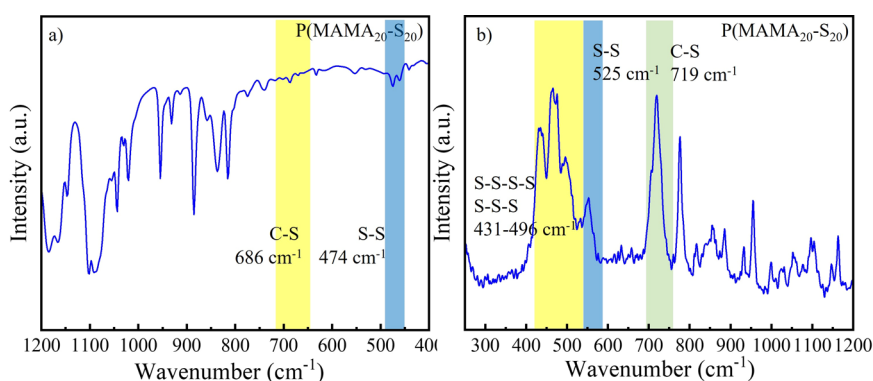


Figure 2. (a) FTIR spectrum of $\text{P}(\text{MAMA}_{20}\text{-S}_{20})$. (b) Raman spectrum of $\text{P}(\text{MAMA}_{20}\text{-S}_{20})$.

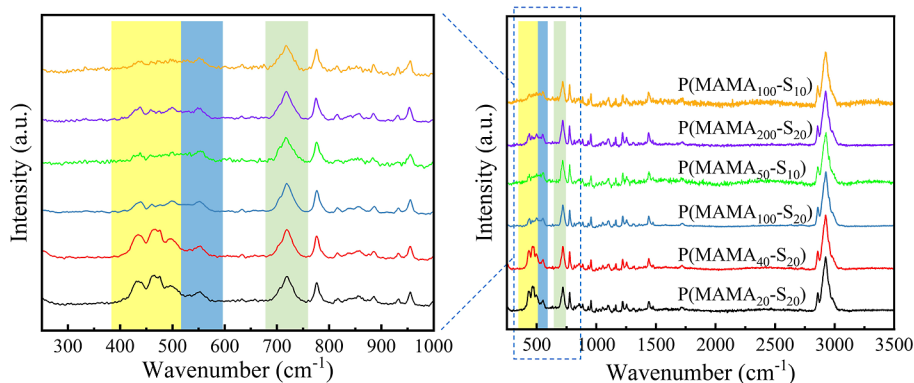


Figure 3. Raman spectra of polymers with different feed ratios.

provided more specific details, as shown in Figure 2b, with the vibration of 431 to 496 cm^{-1} assigned to tetrasulfide (S-S-S-S) and trisulfide (S-S-S), and the peak of 525 cm^{-1} revealed the disulfide (S-S),⁴⁴ and the C-S bonds were visible in spectra between 700 and 750 cm^{-1} as reported⁴⁵ and were observed at 719 cm^{-1} .

Further analysis of Raman spectra in Figure 3 showed that the signals of tetrasulfide (S-S-S-S) and trisulfide (S-S-S) became weak as the feed ratio of the monomer increased, indicating that excessive monomer equivalents would shorten the sulfide chain, while the S-S signal was unchanged. A higher percentage of initiator adding would also affect the length of the sulfide chain as the signal intensity decreased at 431 to 496 cm^{-1} ,

which is shown in the spectra of $\text{P}(\text{MAMA}_{50}\text{-S}_{10})$ and $\text{P}(\text{MAMA}_{100}\text{-S}_{10})$.

The optical properties of the polymers were investigated with different S content. The RI of the polymer films coated on the Si substrate was measured by ellipsometer spectroscopy. The homopolymer of PMAMA showed a typical RI of 1.49 at 632.8 nm ; when the sulfur was introduced into the matrix of 22.9% content, the polymer $\text{P}(\text{MAMA}_{200}\text{-S}_{20})$ RI increased to 1.59 at 632.8 nm . More sulfur content led to higher RI; when the sulfur content reached 25.7% and 34.2%, the RI increased to 1.60 and 1.62, respectively (Figure 4a). The transmittance curves show that the polymers had excellent transparency, and polymer films maintain over 90% transmittance in the visible light-to-near-infrared region compared to the homopolymer (Figure 4b).

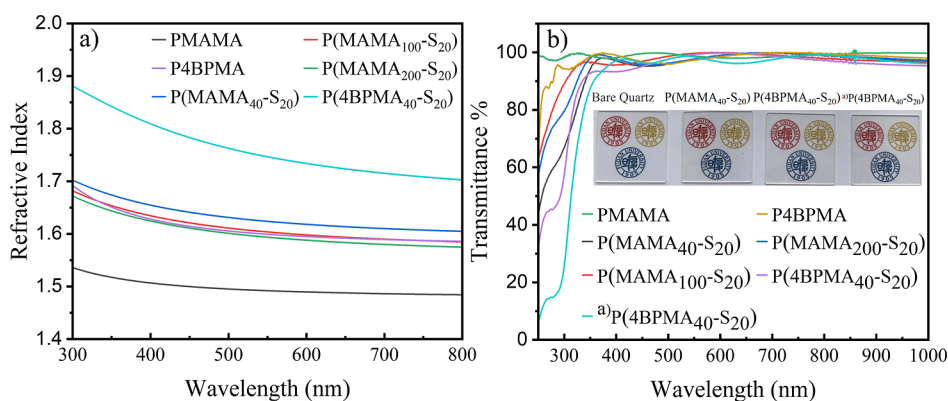


Figure 4. (a) RI curves of polymers (film thickness ~ 300 nm). (b) Transmittance spectrum of polymers (film thickness ~ 150 nm; ^a ~ 500 nm).

With the purpose of enhancing RI, the monomer of 4-bromophenyl methacrylate (4BPMA) was synthesized and polymerized with sulfur. The RI of the homopolymer was recorded at 1.60,⁴⁶ as confirmed by measurement. The S-containing polymer P(4BPMA₄₀-S₂₀) reached 1.72 at 632.8 nm. Meanwhile, the transparency remained above 90% in the visible region; as shown in Figure 4b, the polymer was coated onto a quartz plate and covered with a white sheet displaying a logo. When the thickness of P(4BPMA₄₀-S₂₀) was increased from 150 to 500 nm, the transparency decreased in the 250–350 nm range, but there was no significant impact on the transparency in the region above 400 nm.

To explore the lithography properties, we mixed P-(MAMA₁₀₀-S₂₀) with 3% photo acid generator (PAG) of triphenylsulfonium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (TPS) and then formulated the mixer as a 3% weight solution in solvent of cyclohexanone and CHCl₃ (1:1) as photoresist and then coated on the Si substrate. The exposure procedure (Figure 5a) was taken under 254 nm UV light with a

monomers. The introduction of sulfur into the matrix of polymer increased the RI up to 1.72, and the transmittance remained over 90% in the visible light region. Furthermore, the polymer mixed with PAG as a high-RI photoresist, which showed excellent performance under UV exposure. Finally, a multigram scale reaction obtained 8.12 g of HRIPs, which showed the potential of fabrication.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c09788>.

Experimental details for monomer preparation and polymerization; characterization of polymers including ¹H NMR spectra, IR spectra, and GPC curves; and multiscale preparation and lithography procedure (PDF)

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Notes

The author declares no competing financial interest.

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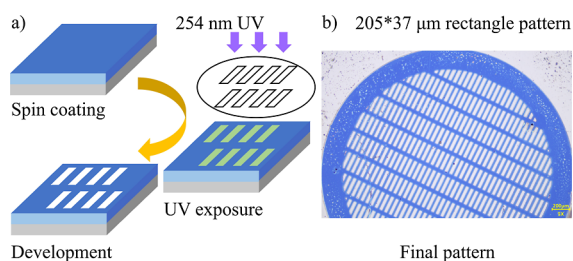


Figure 5. (a) General lithography process by using P(MAMA₁₀₀-S₂₀). (b) ADI image under an optical microscope (205 × 37 μm rectangle pattern).

Cu mask (mask design: 205 μm × 37 μm); after development in 2.38% TMAH (tetramethylammonium hydroxide), the ADI (after development inspect) image under an optical microscope (Figure 5b) showed that the polymer had an excellent patterning ability.

Finally, a simple process was utilized in the scalable preparation. 2-Methyl-2-adamantyl methacrylate and sulfur were enlarged to 11.71 and 2.56 g as a feed ratio of 5:1; after 24 h of reaction, 8.12 g of white solid was obtained.

■ CONCLUSIONS

In summary, we have demonstrated a simple and direct polymerization of sulfur with methacrylate at room temperature. The synthetic method was extended to a variety of functional

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