Synthesis and Nanoimprinting of High Refractive Index and Highly Transparent Polythioethers Based on Thiol-Ene Click Chemistry

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ABSTRACT: This work demonstrates the UV nanoimprinting lithography (UV-NIL) of high refractive index and highly transparent polythioethers based on thiol-ene click chemistry. Herein, 9,9-bis(3-mercaptopropylphenylether)fluorene (BMPF) is designed as a new thiol monomer with a high refractive index, high transparency, and good processability for UV-NIL. Colorless polythioethers are synthesized from BMPF and ene monomers under mild thiol-ene click reaction conditions. Excellent transmittance (96%) of 400 nm light is observed in all the polymer films and high refractive index values of 1.5972–1.6382 are attained. UV-NIL using thiol-ene photopolymerization affords polymer nanoimprinting patterns with various features on the order of 100–500 nm without any fractures. To the best of our knowledge, this is the first report on UV-NIL of high refractive index and highly transparent polymers. Through proper monomer and polymer design, novel polythioethers with suitable glass transition temperature (T_g) values are developed with high refractive index, high transparency, and good UV-NIL processability. Furthermore, UV-NIL based on thiol-ene click chemistry is accomplished at the nanoscale. © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2018**

KEYWORDS: polythioether; thiol-ene click reaction; UV nanoimprinting lithography; photo-radical polymerization; high refractive index; high transparency

INTRODUCTION Polymers with high refractive index and high transparency are attractive for the development of high-performance components in advanced display devices, various lenses, optical waveguides, and diffractive gratings.[1–3] The introduction of substituents with a high molar refraction and a small molar volume, such as aromatic rings, halogen atoms except fluorine, sulfur atoms, and metal atoms, efficiently increases the refractive index of the polymers.[4–6] To date, a variety of high refractive index and highly transparent polymers have been developed by the efficient incorporation of the above components, particularly sulfur atoms and aromatic rings; several examples have accomplished a high refractive index value of over 1.7.[7–10] Recently, the processability of high refractive index polymers has been paid much attentions as well as the performance (e.g., high refractive index, high transparency, and high thermal stability) because nano- and microfabrication of high refractive index polymers is absolutely necessary for the miniaturization of the opto-integrated assembly process and devices. Injection molding is commonly used for the fabrication of high refractive index and highly transparent polymers; however, it is not suitable for nano- and microfabrication. Furthermore, polymers processable by injection molding need a relatively high glass transition temperature (T_g) at around 150 °C.[11,12] However, it is quite difficult to design a polymer with a T_g suitable for injection molding while maintaining a high refractive index and high transparency. Therefore, there is a compelling need to develop a method that enables nano- and microfabrication of high refractive index and highly transparent polymers without sacrificing performance.

UV nanoimprint lithography (UV-NIL) has garnered increasing attention as a next-generation technique for polymer fabrication due to its facile, cost-effective, and high-throughput production process.[13–17] A typical procedure for UV-NIL is as follows: a photopolymerizable monomer mixture is cast onto a substrate, and the mixture is then covered with a patterned mold. The photopolymerization proceeds under UV irradiation to yield polymers fabricated in the nano- and microscale after peeling off the patterned mold. The selection of an efficient photopolymerization system is key for successful UV-NIL.

The thiol-ene click chemistry can be one of promising candidates for UV-NIL. The thiol-ene click reaction is conducted mildly in the presence of organocatalyst or under UV-induced photo-radical polymerization condition.[18–21] UV-NIL using thiol-ene photopolymerization between pentaerythritol

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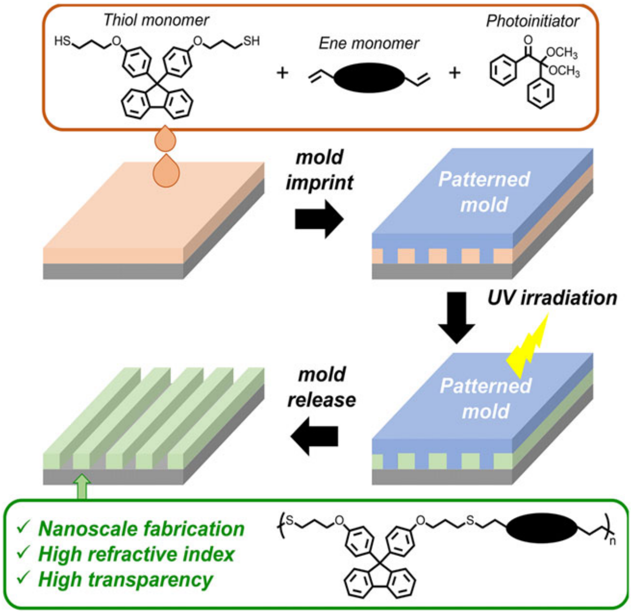


FIGURE 1 Schematic of UV-NIL of P1-P3 by the thio-ene click chemistry. [Color figure can be viewed at wileyonlinelibrary.com]

tetrakis(3-mercaptobutylate) and several commercially available multifunctional enes was first reported by Carter and coworkers, which yielded the corresponding polymer network fabricated with feature size on the order of 100 nm.[22] UV-NIL using silicone-containing monomers, which is primarily used in resist applications, has been also investigated, affording defined features from sub-100 nm to several microns.[23–26] Recently, thiol-ene click chemistry has been investigated for the development of high refractive index materials, because sulfur atoms can be efficiently incorporated into polymer backbones. Zhao and coworkers reported the thiol-ene photopolymerization of commercially available pentaerythritol tetraacrylate and pentaerythritol tetrathioglycolic to give a colorless thiol-ene network material with a refractive index of 1.556.[27] In addition to the incorporation of sulfur atoms, novel materials have been synthesized by using thiol and/or ene monomers with silicon, zinc, tin, zirconium, and germanium atoms, affording materials with refractive index values of 1.563–1.744.[28–30] These results demonstrate that thiol-ene click chemistry is an efficient system for developing high refractive index materials. Thiol-ene click chemistry could also be applicable in the UV-NIL of high refractive index and highly transparent polymers; however, to the best of our knowledge, this has never been explored.

Herein, our aim is to demonstrate UV-NIL of high refractive index and highly transparent polymers based on thiol-ene click chemistry (Fig. 1). A new 9,9-diarylsubstituted fluorene-based thiol monomer, 9,9-bis(3-mercaptopropylphenylether) fluorene (BMPF), was designed and synthesized for this purpose. A 9,9-diarylsubstituted fluorene skeleton can enhance the refractive index of a polymer because of its aromatic content, and the orthogonal structure at the 9-position of fluorene contributes to high transparency by reducing the interchain packing of the polymers.[31–33] Furthermore, the aliphatic segments can provide flexibility in the polymer backbone, affording good UV-NIL processability with a suitable T_g and preventing fractures in the nanoimprinting patterns upon removing the mold. Polymerizations based on the thiol-ene click reaction using BMPF were investigated with several ene monomers: 1,4-bis(acryloyloxy)butane (BAB), divinylsulfone (DVS), and bis[4-(acryloyloxy)thiophenyl]sulfide (BATS). Each polymerization was successfully carried out with both an organocatalytic Michael reaction and a photo-radical polymerization to yield the desired colorless polymers (P1-P3). All three polymers exhibited excellent transparency as high as 96% at 400 nm due to the 9,9-diarylsubstituted fluorene-based structure. Furthermore, P3 with the highest sulfur content achieved the highest refractive index (1.6382). UV-NIL of P1-P3 by utilizing thiol-ene photopolymerization was also investigated. The P1-P3 nanoimprinted patterns with various features on the order of 100–500 nm were successfully fabricated without any fractures.

EXPERIMENTAL

Materials

9,9-Bis(3-bromopropylphenylether)fluorene,[34] 9,9-bis(3-mercaptopropylphenylether)fluorene (BMPF),[34] bis[4-(hydroxy) thiophenyl]sulfide,[35] and bis[4-(acryloyloxy)thiophenyl]sulfide (BATS)[36] were synthesized by reference to previous literatures. All reagents and solvents were used as received unless otherwise stated.

Synthesis of 9,9-bis(3-bromopropylphenylether)fluorene

The 2-butanone solution (45.0 mL) of 9,9-bis(4-hydroxyphenyl)fluorene (4.21 g, 12.0 mmol), K_2CO_3 (4.98 g, 36.0 mmol), and 1,3-dibromopropane (7.3 mL, 72.0 mmol) was stirred at 80 °C for 12 h under the nitrogen atmosphere. After the reaction, the reaction mixture was then diluted with CH_2Cl_2 and washed with brine, and the organic layer was dried over $MgSO_4$. After the removal of solvents, the residue was purified by column chromatography (CH_2Cl_2: hexane = 1: 1) to yield a white solid (4.44 g, 66%). ^1H NMR ($CDCl_3$, δ, ppm): 7.75 (d, 1H), 7.35 (m, 1H), 7.11 (t, 1H), 7.09 (t, 1H), 6.75 (t, 1H), 6.72 (t, 1H), 4.06 (t, 2H), 3.83 (t, 2H), 2.00 (quint, 2H). Note that the purified product contained a small amount of 9,9-bis [4-(2-propenyloxy)phenyl]fluorene as a byproduct. However, this purified product was used for the next reaction without further purification because 9,9-bis[4-(2-propenyloxy)phenyl] fluorene did not have any effect to the next reaction.

Synthesis of 9,9-bis(3-mercaptopropylphenylether) fluorene (BMPF)

The DMF solution (37.5 mL) of 9,9-bis(3-bromopropylphenylether)fluorene (4.44 g, 7.53 mmol) and thiourea (2.28 g, 30.0 mmol) was stirred at 80 °C for 12 h under the nitrogen atmosphere. After cooling to room temperature, a 1 M NaOH aqueous solution (75.0 mL) was added, and the resulting mixture was stirred for 1 h. Then the mixture was acidified with a 1 M HCl aqueous solution to pH = 3. The mixture was

TABLE 1 Synthesis of P1 by Michael reaction condition.

Run	Solvent	Temp. (°C)	Time (h)	M_n[a]	M_w/M_n[a]	Yield (%)[b]	Color
1	DMAc	RT	6	–	–	54	White
2	THF	RT	6	2000	1.08	55	White
3	$CHCl_3$	RT	4	3100	1.38	80	White
4	$CHCl_3$	RT	6	5700	1.28	81	White
5	$CHCl_3$	RT	24	9400	1.56	82	Yellow
6	$CHCl_3$	60	4	3900	2.03	78	White
7	$CHCl_3$	60	6	4600	1.29	70	White
8	$CHCl_3$	60	24	9900	1.44	91	Yellow

[a] Measured by SEC using polystyrene standards in chloroform.

[b] Yields of methanol-insoluble parts.

diluted with CH_2Cl_2 and washed with brine, and the organic layer was dried over $MgSO_4$. After the removal of solvents, the residue was purified by column chromatography (CH_2Cl_2: hexane = 2: 1) to yield a white solid (1.65 g, 44%). ^1H NMR ($CDCl_3$, δ, ppm): 7.75 (d, 1H), 7.35 (m, 1H), 7.11 (t, 1H), 7.09 (t, 1H), 6.75 (t, 1H), 6.72 (t, 1H), 4.00 (t, 2H), 2.70 (q, 2H), 2.03 (quint, 2H), 1.37 (t, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 157.5, 151.7, 139.9, 138.2, 129.2, 127.7, 127.3, 126.0, 120.1, 114.0, 65.4, 64.1, 33.3, 21.3. Anal. calcd for $C_{31}H_{30}O_2S_2$: C 74.66, H 6.06, S 12.86; found: C 74.65, H 6.05, S 13.07.

Synthesis of bis[4-(acryloyloxy)thiophenyl]sulfide (BATS)

To the dry THF solution (8.6 mL) of bis[4-(hydroxy)thiophenyl] sulfide (0.68 g, 2.00 mmol) and dimethylaniline (0.97 g, 8.00 mmol), the dry THF solution (2.4 mL) of acryloyl chloride (0.49 mL, 6 mmol) was added dropwise at 0 °C under the nitrogen atmosphere. The reaction mixture was stirred at room temperature overnight, and the solvent was then removed under reduced pressure. The residue was washed with $NaHCO_3$ aqueous solution and brine, and the organic layer was dried over $MgSO_4$. After the removal of solvents, the residue was purified by column chromatography (ethyl acetate: hexane = 2: 5) to yield a white solid (0.64 g, 68%). ^1H NMR ($CDCl_3$, δ, ppm): 7.33 (m, 4H), 7.25 (m, 4H), 6.39 (dd, 2H), 6.09 (q, 2H), 5.84 (dd, 2H), 4.33 (t, 4H), 3.18 (t, 4H). ^{13}C NMR ($CDCl_3$, δ, ppm): 165.9, 134.5, 133.8, 131.6, 131.4, 130.2, 128.0, 82.9, 32.1. Anal. calcd for $C_{22}H_{22}O_4S_3$: C 59.17, H 4.97, S 21.54; found: C 59.02, H 4.78, S 21.50.

Synthesis of P1 by Michael reaction condition

The typical procedure is as follows (Run 4 in Table 1); To the dry chloroform solution (2.0 mL) of BMPF (0.25 g, 0.50 mmol) and 1,4-bis(acryloyloxy)butane (0.10 g, 0.50 mmol), triethylamine (TEA) (0.1 mL) was added dropwise at room temperature under the nitrogen atmosphere. Then the reaction was continued at room temperature for 6 h. After the reaction, the reaction mixture was poured into methanol to yield a white precipitate. The obtained polymer was collected with filtration, and then dried in vacuo at 80 °C (0.29 g, 81%). ^1H NMR ($CDCl_3$, δ, ppm): 7.73 (br, 1H), 7.35 (br,1H), 7.33 (br, 1H), 7.31 (br, 1H), 7.09 (br,1H), 6.73 (br,1H), 4.08 (br, 2H), 3.98 (br, 2H), 2.76 (t, 2H), 2.68 (t, 2H),2.58 (t, 2H), 2.01 (br, 2H), 1.67 (br, 2H). M_n = 5700 (M_w/M_n = 1.28). T_g = 30 °C.

Synthesis of P1 by photo-radical polymerization in solution condition

The dry chloroform solution (2.0 mL) of BMPF (0.25 g, 0.50 mmol), BAB (0.10 g, 0.50 mmol), and 2,2-dimethoxy-2-phenylacetophenone (DMPhAc) (0.01 g, 3 wt% for total amount of BMPF and BAB) was stirred for 15 min under the exposure of UV light (λ = 365 nm, 10 mW/cm, cumulative radiation = 60 mJ/cm^2). After the reaction, the reaction mixture was poured into methanol to yield a white precipitate. The obtained polymer was collected with filtration, and then dried in vacuo at 80 °C (0.35 g, 96%).

Synthesis of P1 by photo-radical polymerization in bulk condition

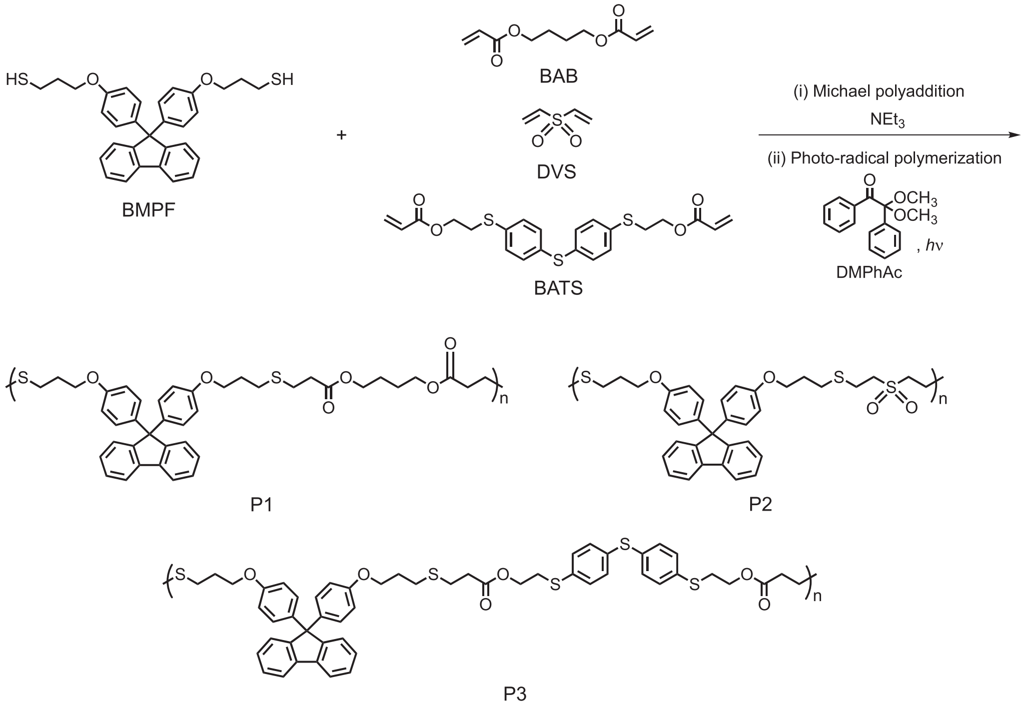
The mixture of BMPF (0.25 g, 0.50 mmol), BAB (0.10 g, 0.50 mmol), and DMPhAc (0.01 g, 3 wt%) was stirred at room temperature until becoming homogeneous. The mixture was then drop-casted onto a glass substrate and UV light was exposed for 1 min to yield transparent P1 film.

UV nanoimprint lithography of P1

Nanoimprinting was carried out using a UV nanoimprint kit (Toyo Gosei Co. Ltd.) including a UV lamp (Eishin Kagaku Co. Ltd. UV mini-light) and a master micro-pattern quartz mold (Toppan Printing Co. Ltd.). A homogeneous mixture of BMPF (0.25 g, 0.50 mmol), BAB (0.10 g, 0.50 mmol), and DMPhAc (0.01 g, 3 wt%) was drop-cast onto the silicon substrate and the quartz mold was set onto the mixture. After exposure to UV light for 1 min, the mold was detached.

Characterization

The ^1H and ^{13}C NMR spectra were recorded with a JEOL JNM-ECX400. The Elemental analysis was carried out on a Perkin-Elmer 2400 II CHNS/O analyzer. The UV–vis spectra were recorded on a JASCO V-630BIO UV–vis spectrophotometer. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated by size exclusion chromatography (SEC) using a HLC-8320 system. The column set was as follows; a guard column (TSK guard column HHR-H)



SCHEME 1 Synthesis of P1-P3.

and three consecutive columns (TSKgel GMH$_{HR}$-M, TSKgel GMH$_{HR}$-M, and TSKgel superH-RC) eluted with chloroform at a flow rate of 1.0 mL/min. Polystyrene standards were employed for calibration. Thermal gravimetric (TG) analysis was performed on a SEIKO TG/DTA6200 at a heating rate of 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was performed on a SEIKO DSC6200 under nitrogen atmosphere. The measurements were conducted the samples heated to 300 °C followed by cooling to −50 °C, and then heating again up to 300 °C at a cooling and heating rate of 10 °C/min. The glass transition temperature (T_g) was determined as the midpoint temperature of the heat capacity change during the second heating step. Scanning electron microscopy (SEM) measurements were performed on a Hitachi SU8000 microscope at accelerating voltages of 2.0 kV. Refractive-indx mesurement was performed on a ATAGO digital Abbe refractometer DR-A1.

RESULTS AND DISCUSSION

Synthesis and characterization of monomers

A new 9,9-diphenylsubstituted fluorene-based thiol monomer BMPF was synthesized by a two-step reaction (Scheme S1). The nucleophilic substitution reaction between 9,9-bis(4-hydroxyphenyl)fluorene and 1,3-dibromopropane to yield 9,9-bis(3-bromopropylphenylether)fluorene. Then the treatment of 9,9-bis(3-bromopropylphenylether)fluorene with thiourea and the following hydrolysis were carried out to yield BMPF. A new ene monomer BATS was synthesized by a two-step reaction from 4,4′-thiobisbenzenethiol. BMPF and BATS were characterized by ^{1}H NMR, ^{13}C NMR, and elemental analysis to confirm that the desired monomers were synthesized (Fig. S1 and S2).

Synthesis and characterization of polymers

The polymerizations of BMPF and ene monomers (BAB, DVS, and BATS) based on the thiol-ene click reaction were investigated by both an organocatalytic Michael reaction and a photo-radical polymerization (Scheme 1). First, the polymerization between BMPF and BAB was carried out by Michael reaction in the presence of triethylamine (Table 1), which enables us to confirm the reactivities of the thiol and ene monomers. As a result of screening reaction conditions (solvent, reaction temperature, and reaction time), colorless P1 that did not dissolve in common organic solvents was obtained using DMAc as a solvent. The reaction did not proceed efficiently in THF, as seen by the M_n and yield of the obtained product. Using chloroform, yellow P1 with M_n ~10,000 was obtained in a relatively high yield (Table 1, Run 5 and 8). The more moderate reaction conditions in chloroform (i.e., a shorter reaction time) afforded colorless P1 with M_n = 3100–5700 in relatively high yields. The obtained colorless P1 showed high solubility in common organic solvents such as chloroform, dichloromethane, toluene, THF, and DMAc (Table S1). The structure of P1 was characterized by ^{1}H and ^{13}C NMR analysis (Fig. 2). The peaks of protons corresponding to methylene groups were clearly observed at 2.76 and 2.68 ppm in the ^{1}H NMR spectrum of P1 (Fig. 2a). The characteristic peaks of carbons corresponding to the carbonyl group (171.9 ppm) and C-9 in the fluorene moiety (64.1 ppm) were also clearly observed (Fig. 2b). These data indicate that the thiol-ene click reaction was successfully carried out under the

TABLE 2 Synthesis of P1-P3 by photo-radical polymerization in solution condition.[a]

Run	Solvent	M_n[b]	M_w/M_n[b]	Yield (%)[c]	Color
P1	$CHCl_3$	–[d]	–[d]	96	White
P2	$CHCl_3$	4300	1.12	69	White
P3	DMAc	3200	1.79	90	White

[a] The polymerization was carried out under the exposure of UV light (λ = 365 nm) for 15 min.

[b] Measured by SEC using polystyrene standards in chloroform.

[c] Yields of methanol-insoluble parts.

[d] The sample did not dissolve in chloroform.

organocatalytic Michael reaction conditions to yield the desired P1.

Prior to the photo-radical polymerization under the solvent-free condition, we conducted the photo-radical polymerization under the typical solution conditions to check the photopolymerizability of the monomers. Photo-radical polymerization of BMPF and BAB was investigated in chloroform for 15 min under exposure to UV light (λ = 365 nm) in the presence of 2,2-dimethoxy-2-phenylacetophenone (DMPhAc) as a photo-radical polymerization initiator. The obtained colorless product did not dissolve even in chloroform and was obtained quantitatively, implying that P1 with a high molecular weight and/or some cross-linking was formed (Table 2). Owing to a recent concern for a sustainable economic manufacturing system, a solvent-free green reaction that could be used in an environmentally friendly and economic manufacturing system was investigated. The bulk mixture obtained from solid BMPF, liquid BAB, and solid DMPhAc was drop-cast onto a glass substrate, and solvent-free photo-radical polymerization was then carried out under UV light in a quite short reaction time (1 min) to yield a colorless and transparent P1 film (Fig. 3). The solvent-free condition may accelerate the polymerization compared to the solution condition, which could lead to the formation of the cross-linked structure and/or large molecular weight in some degree even in short polymerization time (1 min). The fact that the monomers and the formed polymer have no light absorption around 365 nm contribute to the efficient progress of the photo-radical polymerization.

Following the synthesis of P1, polymerizations of BMPF and other ene monomers (DVS and BATS) were investigated under the Michael reaction conditions (Scheme 1 and Table S2). The optimal reaction between BMPF and DVS occurred in chloroform at room temperature for 6 h to yield colorless P2 with M_n = 6900 in 81% yield. P3 was synthesized from BMPF and BATS in DMAc to yield colorless P3 with a high molecular weight (M_n = 10000–48400). The structures of P2 and P3 were also confirmed by ^1H and ^{13}C NMR analysis (Fig. S3 and S4). The synthesis of P2 and P3 by photo-radical polymerization under solution conditions was also carried out to yield colorless P2 and P3 in 69 and 90% yield, respectively (Table 2). The colorless and transparent P2 film (Fig. 3) was successfully prepared by photo-radical polymerization from the bulk mixture of BMPF, DVS, and DMPhAc, which can be considered a solvent-free green process. In contrast, a DMAc solution was used for the direct preparation of P3 films because BATS is a solid, yielding the colorless and transparent P3 film (Fig. 3). Based on these results, BMPF has the ability to polymerize via thiol-ene click chemistry under three different conditions (an organocatalytic Michael reaction, photo-radical polymerization in solution, and solvent-free photo-radical polymerization) to afford the novel colorless polythioethers P1-P3. This good photopolymerizability of BMPF can result in efficient UV-NIL processing (see details below).

The thermal properties of P1-P3 were investigated by TG and DSC analyses. P1-P3 synthesized by the Michael reaction conditions were used for the analyses. As can be seen in the TG profiles (Fig. 4), P1-P3 exhibited a 5% weight loss temperature above 330 °C under a nitrogen atmosphere. This observed thermal stability is sufficient for the optical device fabrication process. In the DSC analysis, the glass transition temperature of P1-P3 was observed at 30, 95, and 23 °C, respectively, which is relatively low due to their flexible aliphatic polymer backbones (Fig. 5).

Optical properties

The optical property is one of the most important characteristics for high refractive index polymers. The transparency of the P1-P3 films was investigated by UV–vis transmission. The P1-P3 films (film thickness 20–30 μm) were prepared by drop-casting each chloroform solution onto glass substrates.

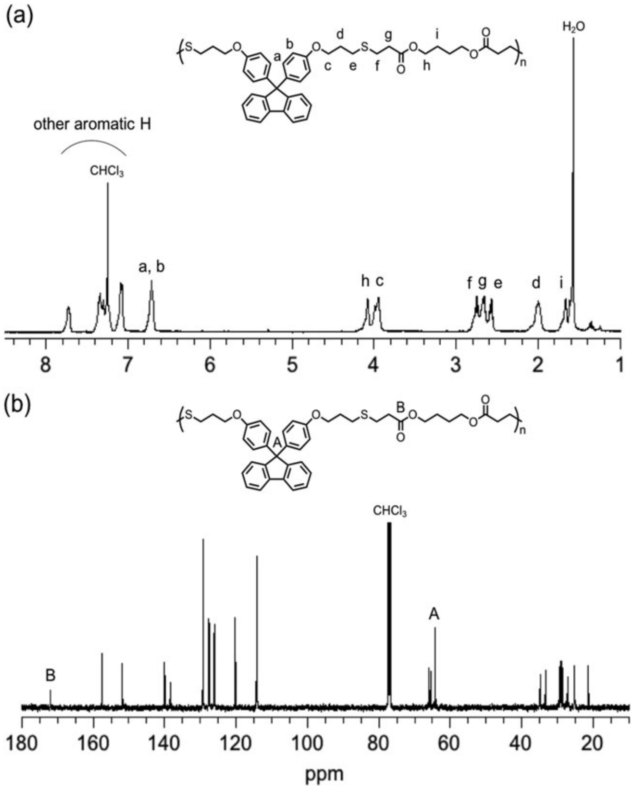


FIGURE 2 ^1H (a) and ^{13}C (b) NMR spectra of P1 in $CDCl_3$.

FIGURE 3 Pictures of P1-P3 films prepared by photo-radical polymerization. [Color figure can be viewed at wileyonlinelibrary.com]

As can be seen in Figure 6, the cut-off wavelengths of the P1-P3 films were ~280 nm, and all films exhibited excellent transparency of 96% at 400 nm. This observed transparency of P1-P3 is one of the highest values among high refractive index polymers. For example, the cut-off wavelength is ~400 nm in most sulfur-containing polyimides that have been commonly studied as high refractive index materials.[37–39] The flexible aliphatic polymer backbone and the orthogonal structure at the 9-position of fluorene may prevent interchain packing, contributing to the excellent transparency of P1-P3. Furthermore, it should be noted that the excellent transparency was maintained even after harsh treatment (thermal treatment at 200 °C for 6 h under ambient atmosphere) due to the high thermal and chemical stability of P1-P3 (Fig. S5).

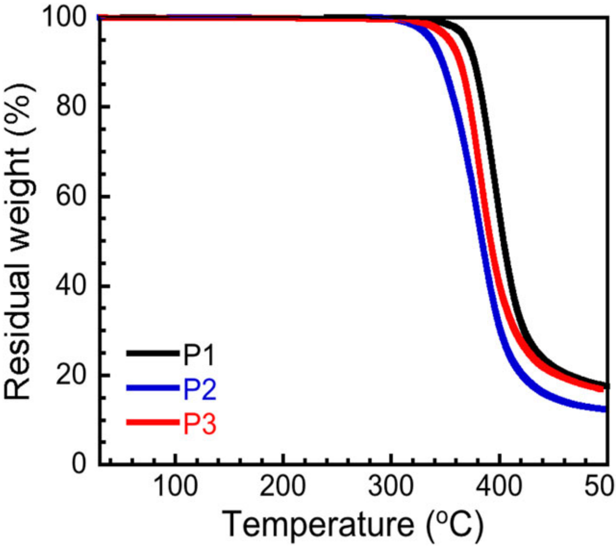


FIGURE 4 TG curves of P1-P3 under a nitrogen atmosphere. [Color figure can be viewed at wileyonlinelibrary.com]

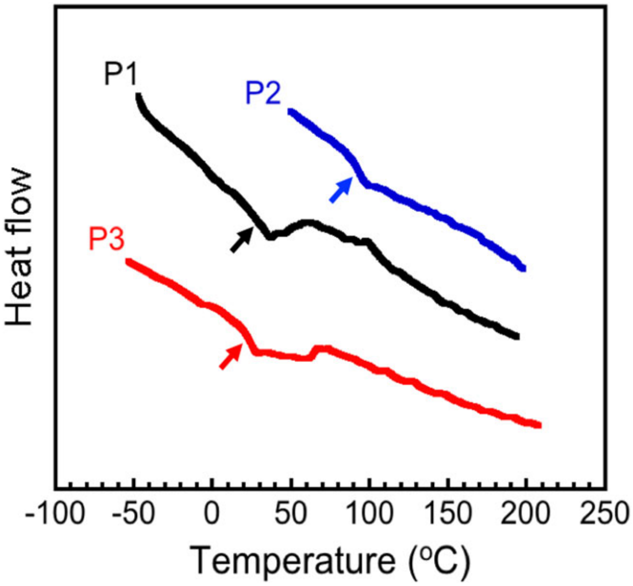


FIGURE 5 DSC profiles of P1-P3 under a nitrogen atmosphere. [Color figure can be viewed at wileyonlinelibrary.com]

The refractive index of P1-P3 was then investigated with an Abbe refractometer (Table 3). P1-P3 exhibited a refractive index of 1.5972, 1.6266, and 1.6382, respectively. The sulfur content in the polymer repeating units in P1-P3 was calculated to be 8.99, 14.87, and 16.44 wt%, respectively. The observed refractive index increases with an increase in the sulfur content; P3 with the highest sulfur content achieved the highest refractive index of over 1.63. The high number of aromatic units might also contribute to the enhanced refractive index of P3.

UV nanoimprint lithography

In order to miniaturize opto-integrated assembly processes and devices, it is quite important to investigate the UV-NIL processability of high refractive index and highly transparent polymers. Additionally, the manipulation of T_g is crucial, because applicable T_g range of the polymers are practically dependent on the process.[40–42] For example, low temperature NIL, including UV-NIL and room temperature NIL, happens under the temperature of below or near to T_g of the polymer.[42] A homogeneous mixture of BMPF, ene monomers, and DMPhAc was drop-cast onto a silicon substrate, and then covered by a patterned quartz mold. The photo-radical

TABLE 3 Optical properties of P1-P3.

Run	Sulfur content (wt%)	Cut-off wavelength (nm)	Transmittance (%)[a]	Refractive index
P1	8.99	317	96	1.5972
P2	14.87	340	96	1.6266
P3	16.44	335	96	1.6382

[a] Transmittance at 400 nm.

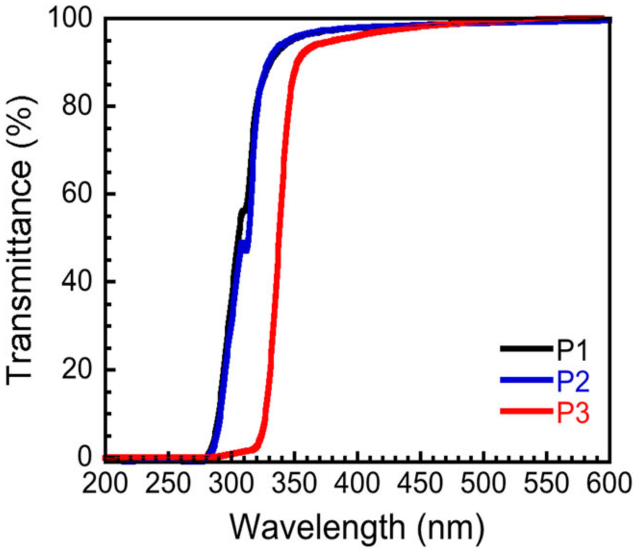


FIGURE 6 UV–vis transmittance spectra of P1-P3 thin films. [Color figure can be viewed at wileyonlinelibrary.com]

polymerization proceeded under exposure to UV light for 1 min, and the mold was then peeled from the substrate. For the preparation of the P1- and P2-based nanoimprinting patterns, the solvent-free green process was employed, whereas a DMAc solution was used for P3-based pattern formation. Figure 7 exhibits the SEM images of the obtained nanoimprinting patterns of P1-P3. The P1-P3 nanoimprinting patterns with various features on the order of 100–500 nm were successfully fabricated in just 1 min, which is due to the good photopolymerizability of BMPF. Fabrication of the defined nanoimprint patterns indicated that P1–P3 provided a clean mold release without fracture or deformation of the embossed structures. Upon releasing the mold, the rigidity of the polymer can be a critical issue for the fabrication of the defined nanoimprinting patterns. If a polymer is rigid, a fracture of the patterns might occur. The flexible polymer backbone, as seen by the relatively low T_g (23–95 °C), contributed to the clean mold release in P1-P3. These results demonstrate that the defined P1-P3 nanoimprinting patterns on a 100–500 nm scale were obtained due to proper monomer and polymer design that enhanced processability for UV-NIL.

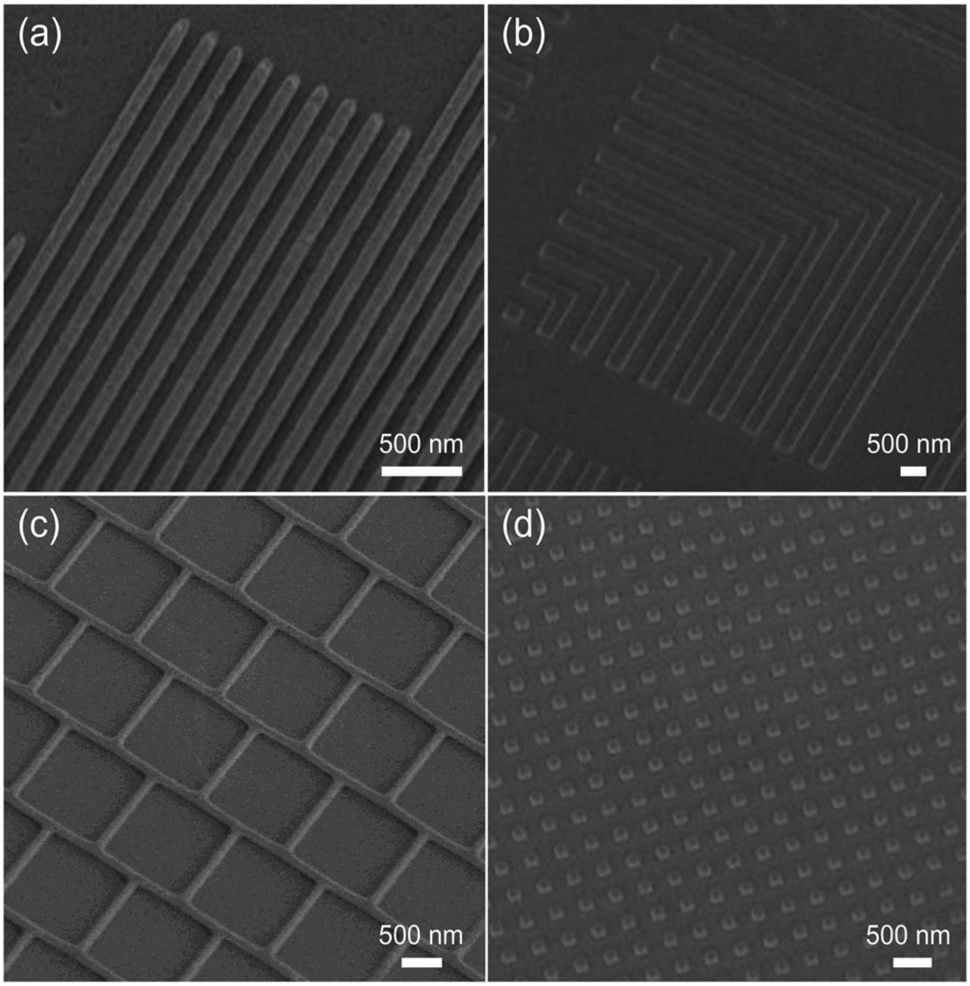


FIGURE 7 SEM images of UV-NIL patterns of P1-P3 (P1: a and b, P2: c, P3: d).

CONCLUSIONS

UV-NIL of high refractive index and highly transparent polymers has been successfully realized based on thiol-ene click chemistry. A novel thiol monomer, BMPF, was designed, that could provide high refractive index, high transparency, and good UV-NIL processability. Colorless polythioethers (P1-P3) were synthesized from BMPF and several ene monomers under mild thiol-ene click reaction conditions. The P1-P3 thin films exhibited excellent transmittance of 96% at 400 nm due to the flexible polymer backbone and the orthogonal structure at the 9-position of fluorene. The refractive indexes of P1-P3 were high values in the range of 1.5972–1.6382 due to the incorporation of sulfur atoms and a fluorene-based aromatic structure. The refractive index increased with an increase in the sulfur content; P3 with the highest sulfur content (16.44 wt%) achieved the highest refractive index of 1.6382. Furthermore, UV-NIL using thiol-ene click chemistry was developed; the defined P1-P3 nanoimprinting patterns with various features on the order of 100–500 nm were readily fabricated without any fractures, which might be a result of the relatively low T_g due to the flexible polymer backbone. Consequently, high refractive index and highly transparent polymers with good UV-NIL processability were developed by proper monomer and polymer design. This result opens a new possibility of thiol-ene click chemistry for the development of optical materials and their nanoscale fabrication.

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