High Refractive Index Copolymers from Aromatic Heterocycle-based Vinyl Sulfides and Phthalimide/maleimide Derivatives

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ABSTRACT:

Herein, we present the rational design and facile synthesis of high-refractive-index copolymers with good optical transparency and tunable thermal stability using aromatic heterocycle-based vinyl sulfides via conventional radical copolymerization. 2-Thiazolylvinylsulfide (2TVS), 1,3,4-thiadiazolylvinylsulfide (1,3,4-TVS), 3-methylimidazolylvinylsulfide (3MIVS), and 5-methlthio-1,3,4-thiadiazolylvinylsulfide (MeSTVS) were selected to enhance the refractive index, and *N*-vinylphthalimide (NVPI) and *N*-phenylmaleimide (NPMI) were chosen as comonomers to achieve improved transparency and thermal stability while maintaining the refractive index. The sulfur, -C=N-, and imide contents in the copolymers were varied by adjusting the monomer structures and their compositions, and their effects on the refractive index, Abbe number, and optical and thermal properties were investigated. The MeTVS monomer in poly(MeSTVS) and poly(MeSTVS-*co*-NVPI) contained three sulfur atoms and two -C=N- units; consequently, these polymers exhibited excellent refractive indices in the 1.7139–1.6567 range at 589 nm, Abbe numbers between 19.1–29.1, good transparency (>90% at 400 nm), and tunable thermal properties (T_g = 49–138 °C, T_{d10} = 244–268 °C). Optically transparent poly(1,3,4-TVS-*co*-NVPI) films (> 95% at 400 nm) with improved thermal stability (T_g = 89–175 °C, T_{d10} = 251–301 °C) were obtained, while maintaining a relatively high refractive index (1.6662–1.6752).

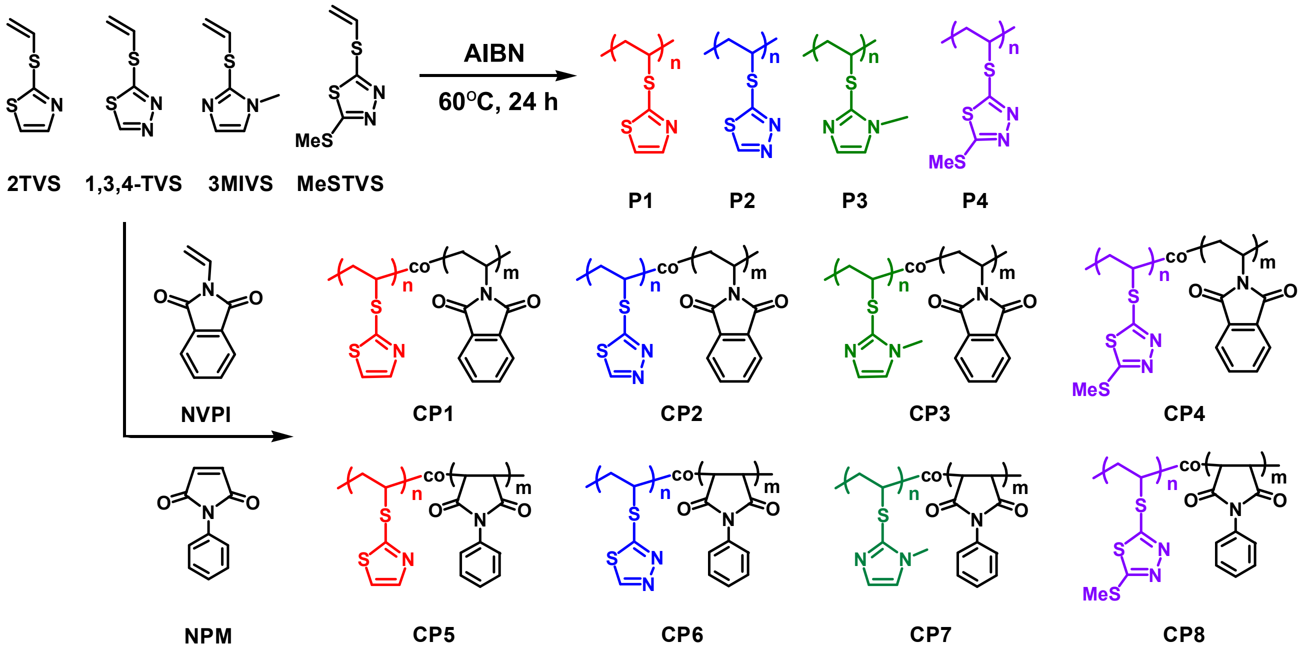
1. Introduction

High-refractive-index polymers have been used in a wide range of applications, and the synthetic ability to crease various functional polymers with high refractive indices of more than 1.7 has advanced considerably.[1-5] Several approaches that enhance the refractive index mainly rely on the incorporation of suitable building blocks with high molar refractions and small molar volumes; such components include sulfur atoms, aromatic and heteroaromatic rings, and heavy atom halogens, and their incorporation into the polymers is based on the Lorentz−Lorenz equation. For instance, new classes of sulfur-containing products have been produced using inverse-vulcanization with elemental sulfur,[5, 6] ring-opening polymerization with carbonyl sulfide,[7] and thiol-ene[8-13] and thiol-yne[14, 15] reactions. Various synthetic methodologies that produce high refractive index polymers and hybrids also rely on the incorporation of phosphorus units,[16] highly polarizable atoms (Si, Ge, Sn)[17], and zinc,[18] zirnonium,[19] and selenium units.[9, 20-22]

In addition, heteroaromatic rings are attractive building blocks for high-refractive-index polymers because -C=N-C- bonds exhibit higher molar refraction (4.10) than -C=C-C- bonds (1.73).[23] Therefore, triazines,[24-26] pyridazines,[27] and pyrimidines,[27-29] which contain -C=N-C- bonds, have been employed as efficient units in main-chain-type polymers to enhance their refractive indices. Moreover, polymethacrylates and polystyrenes with carbazole,[30, 31] thiophene,[32, 33] and thiadiazole[1] side chains have been developed. High-refractive-index polymers have also been prepared from thiadiazole-containing diacrylates for applications in thermal nanoimprint lithography.[34] We also intend to develop an efficient synthetic method for producing high-refractive-index polymers by radical (co)polymerization of (benzo)thiazole-containing *S*-vinyl sulfides.[35] The structural design of side-chain-type high-refractive-index polymers by radical copolymerization allows the manipulation of their refractive index, Abbe number, and thermal properties (T_g and T_{d5}) over a wide range, while maintaining a highly transparent appearance. Such polymers can be synthesized by selecting proper monomer/comonomer structures and their composition, which can be easily tuned by the comonomer feed ratio. However, the understanding and simultaneous achievement of a high refractive index and other essential properties, such as transparency, Abbe number, and thermal properties, are still required for the development of modern advanced materials.

In this study, we developed high-refractive-index copolymers from the following aromatic heterocycle-based vinyl sulfides: 2-thiazolylvinylsulfide (2TVS), 1,3,4-thiadiazolylvinylsulfide (1,3,4-TVS), 3-methylimidazolylvinylsulfide (3MIVS), 5-methylthio-1,3,4-thiadiazolylvinylsulfide (MeSTVS), and phthalimide/maleimide-containing comonomers. This systematic and efficient approach produces high-refractive index polymers using vinyl sulfide-based heteroaromatic rings with one or more -C=N- bonds and one to three sulfur atoms in the monomer units. Both 1,3,4-TVS and the newly developed MeSTVS contain a thiadiazolyl ring with two -C=N- bonds. The additional methylthioether group in MeSTVS may enhance the refractive index and solubility of the resulting polymers. In contrast, 3MIVS has an imidazolyl ring, and 2TVS contains a thiazolyl ring, both of which include -C=N- and -C=C- bonds. The number of sulfur atoms in MeSTVS, 2TVS, 1,3,4-TVS , and 3MIVS is three, two, two, and one, respectively. The presence of a high number of sulfur atoms in the polymer significantly improves its refractive index. *N*-Vinylphthalimide (NVPI) and *N*-phenylmaleimide (NPMI), both of which contain one imide unit and a benzene ring, were chosen as comonomers to achieve improved transparency and thermal stability without lowering refractive index. Matsumoto et al. employed various *N*-substituted maleimides having chemically stable imide ring structures for producing transparent copolymers with rigid poly(substituted methylene) structures; these copolymers exhibited intermediate refractive indices (1.5–1.6) with excellent heat resistance and other properties.[36-39] We also demonstrated the synthesis of high-refractive-index copolymers composed of 2-vinylselenophene and *N*-substituted maleimides with a moderate alternating tendencies (e.g., refractive index = 1.6138 for poly(2-vinylselenophene-*co*-NPMI))[21].

Understanding the structure-property relationships and the molecular aspects (the number of sulfur atoms and -C=N- bonds) of these vinyl sulfide monomers and imide-containing comonomers is crucial for producing high-refractive index polymers; thus, we systematically evaluated the optical and thermal properties and the copolymer structures of two series of NVPI and NPMI-based copolymers. In this study, radical copolymerization was chosen because functional groups (sulfur-rich heteroaromatic rings and imide units with benzene rings) can be introduced in the copolymers using different types of monomers, which considerably increases the possibility of achieving diverse properties via different combinations of the resulting copolymers. Good solubility in conventional organic solvents endowed the copolymers with film-forming ability and good processability under mild conditions. The synthetic approach presented here is the combination of sulfur-containing heteroaromatic rings, which afford a high refractive index, and imide-containing monomers, which provide high thermal stability and transparency. The amount of sulfur and -C=N- bonds in the vinyl sulfide derivatives and their compositions were optimized to obtain transparent copolymers with a high refractive indices, enhanced Abbe numbers, and improved thermal properties.



Scheme 1. Synthesis of (a) high-refractive-index homopolymers by free-radical polymerization of aromatic heterocycle-based vinyl sulfides and (b) high-refractive-index copolymers with *N*-vinylphthalimide (NVPI) or *N*-phenylmaleimide (NPMI).

2. Results and Discussion

A series of vinyl sulfide derivatives with heteroaromatic rings were employed to investigate the effect of the number of sulfur atoms and -C=N- bonds in the monomer units on the refractive index of the resulting homopolymers. In addition to previously reported 2TVS and 1,3,4-TVS,[35] 3MIVS[40, 41] and MeSTVS[42] were designed and synthesized in the current study by the reaction of 1,2-dibromoethane with corresponding commercially available thiol compounds. Two homopolymers, poly(MeSTVS) and poly(3MIVS) (P3 and P4), were newly prepared by bulk polymerization at $[M]_0/[AIBN]_0 = 200/1$ and 60 °C for 24 h, while poly(2TVS) and poly(1,3,4-TVS) (P1 and P2) were shown as comparisons, which were reported in our previous paper.[35] Characteristics of four homopolymers (P1-P4) are summarized in Table 1, and their structures were confirmed by nuclear magnetic resonance (NMR) measurements (Figures S1-S8). Size exclusion chromatography (SEC) analysis of the resulting homopolymers with heteroaromatic rings in the side chains indicated moderate molecular weights with a broad distribution ($M_n = 4700–13000$, $M_w/M_n = 1.58–3.72$). The presence of a flexible sulfide linkage between the aromatic heterocycles and the polymer backbone led to the reasonable solubility of the products, and all homopolymers (P1–P4) were soluble in *N*,*N*-dimethylformamide (DMF), as shown in Table S1. The introduction of the methylthioether group into MeSTVS enhanced the solubility of the resultant homopolymer (P4) in $CHCl_3$ and THF. Similarly, the presence of a methyl group in 3MIVS led to the good solubility of poly(3MIVS) (P3) in $CHCl_3$. Subsequently, the refractive indices of homogenous polymer thin films with thicknesses in the range of 100–140 nm were determined using an ellipsometer. However, poly(1,3,4-TVS) (P2) exhibited poor solubility in $CHCl_3$; therefore, a reliable refractive index value was not obtained for poly(1,3,4-TVS) because of the difficulty in preparing smooth thin films. As shown in Figure 1a, the newly synthesized poly(MeSTVS) (P4) exhibited the highest refractive index of 1.7139 with a low Abbe number (19.1). However, the refractive index of poly(3MIVS) (P3, refractive index = 1.6402, Abbe number = 30.0) was lower than that of poly(2TVS) (P1, refractive index = 1.6925, Abbe number = 26.7). This tendency is consistent with the general assumption that organic polymers with a high refractive indices (1.70 or higher) typically have low Abbe numbers (<20.0).[1] A high sulfur content of more than 50 wt % contributes to a high refractive index of poly(MeSTVS) (P4). However, the sulfur content of poly(3MIVS) (P3, 19.4 wt %) was found to be much lower than those of P1 and P2 (42.0 and 43.1 wt %, respectively), leading to a relatively lower refractive index. Interestingly, both poly(MeSTVS) and poly(3MIVS) (P4 and P3) showed better transparency (> 90% at 400 nm) than poly(2TVS) and poly(1,3,4-TVS) (P1 and P2). These results indicate that the introduction of suitable heterocyclic units in vinyl sulfide derivatives (3MIVS and MeSTVS) could improve the refractive index of polymers while maintaining or even enhancing their transparency. However, a pale yellow color was visible in the poly(MeSTVS) film. Figures 1c and 1d display the thermal properties of the obtained polymers evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The initial decomposition, T_{d10}, which was 10 wt % weight loss measured under nitrogen conditions, of four homopolymers (P1–P4) were in the 242–258 °C range, implying that relatively good thermal stabilities are slightly affected by the structure of the vinyl sulfide derivatives. The glass transition temperature (T_g) values of poly(3MIVS) and poly(MeSTVS) were relatively low (68 °C for P3 and 49 °C for P4, respectively) and intermediate between poly(2TVS) and poly(1,3,4-TVS) (P1 and P2). A higher T_g (> 100 °C) is generally desirable for practical lens applications.[30, 43] Given that MeSTVS-based homopolymer (P4) showed a high refractive index, we then attempted to obtain colorless copolymers with improved thermal properties by radical copolymerization.

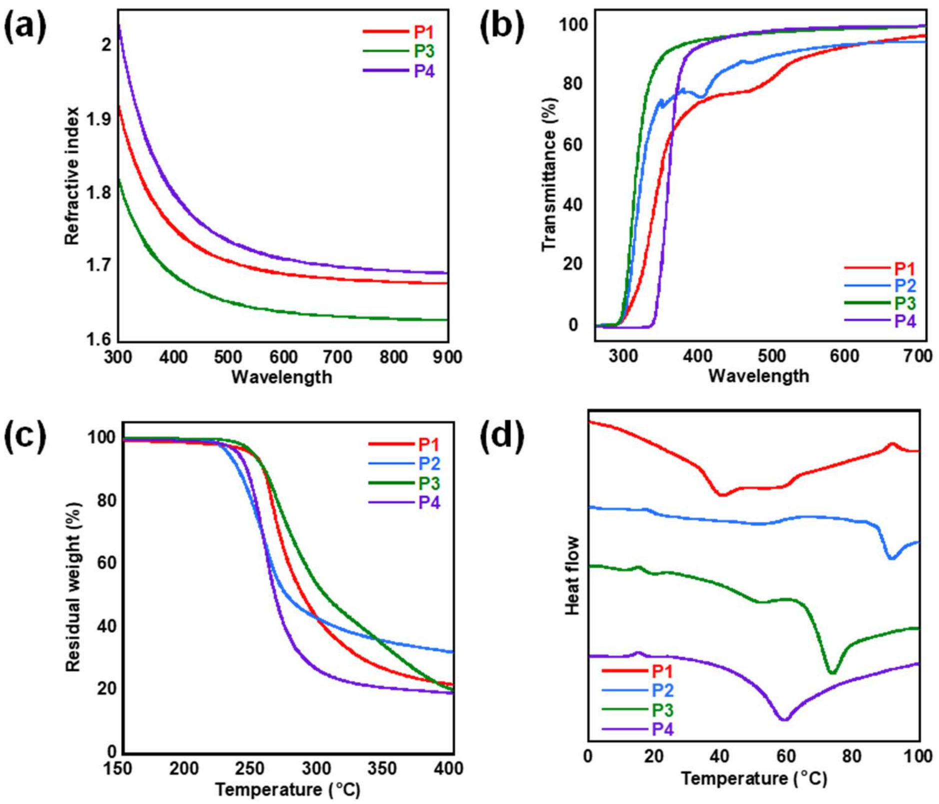


Figure 1. (a) Wavelength-dependent refractive indices determined by ellipsometry and (b) UV-vis transmittance spectra of the homopolymer films. (c) TGA and (d) DSC profiles of the vinyl sulfide-based homopolymers P1–P4 (see Table 1 for detailed polymer samples).

Direct copolymerization of functional monomers, a straightforward and convenient method, affords the required function and properties. However, the aromatic heterocycle-based vinyl sulfides used in this study have characteristic reactivity, implying a limited selection of suitable comonomers. To find a suitable comonomer that would remarkably improve the thermal and optical properties while maintaining high refractive indices, as shown in Scheme 1, NVPI- (CP1-CP4) and NPMI-based (CP5-CP8) copolymers were synthesized using two imide-based monomers and four vinyl sulfide derivatives (2TVS, 1,3,4-TVS, 3MIVS, and MeSTVS). In all cases, radical copolymerization was conducted in DMF at 60 °C for 24 h, and the effects of different monomer combinations and compositions in the feed were examined systematically, as shown in Table 2. The copolymerization afforded the targeted copolymers with M_n ranging from 2300−10000 g/mol and yields of 10−75%. The SEC analysis of NVPI- and NPMI-based copolymers revealed broad dispersities (M_w/M_n = 1.86−3.60, Figures S17 and S18). The structures of the copolymers were confirmed using ^{1}H NMR spectroscopy, displaying broad peaks corresponding to the combined azole moieties and aromatic rings of NVPI and NPMI (Figures S9-S16). Elemental analysis of the NVPI- and NPMI-based copolymers revealed the presence of nitrogen and sulfur atoms (Table S2), and the sulfur content was employed to determine the comonomer compositions. Copolymerization with the NVPI unit afforded its predetermined insertion in a wide range of comonomer compositions, independent of the structure of the vinyl sulfide derivatives, which was predominantly governed by the composition of the feed. In contrast, the NPMI content in the copolymers was 88−90% for CP7 and 69–81% for CP5, which indicates the preferable insertion of NPMI, like 1:2 comonomer sequence,[44, 45] rather than alternative cross-propagation during the copolymerizations of NPMI with 3MIVS/2TVS. In the cases of CP6, CP8, 1,3,4-TVS, and MeSTVS, an approximately 1:1 comonomer composition of NPMI and S-vinyl sulfides was observed, with slightly preferable incorporation of the PPMI unit. A similar tendency was previously observed in alternating copolymerization with electron-accepting NPMI (Q = 2.81, e = 3.24 [46, 47]) and electron-donating phenyl vinyl sulfide (Q = 0.32, e = -1.4[48]) via donor-acceptor interactions in dioxane.[49] In contrast, alternating and random copolymerizations were observed in DMF having high polarity, depending on the concentration.[50] This copolymerization strategy successfully achieved the manipulation of the contents of three key units (sulfur, -C=N-, and imide contents), without unfavorable gel formation and reduced solubility.

These copolymers exhibited good solubility in common solvents, such as $CHCl_3$ and DMF (Tables S3 and S4), as a result of their side chain structures and moderate molar masses; therefore, they exhibited good processability and afforded smooth thin films via a conventional spin-coating process from a $CHCl_3$ solution. The ellipsometry measurements of the uniform thin films prepared by spin-coating (conc. = 1.0 wt. %, 1000 rpm at 60 s) were used for the copolymers. As shown in Figure 2, typical wavelength-dependent refractive indices were detected for all NVPI- (CP1−CP4) and NPMI-based (CP5−CP8) copolymers. Among them (CP1−CP8 in Table 3), poly(MeSTVS-*co*-NVPI)s (CP4) exhibited the highest refractive indices in the 1.6901−1.6567 range and Abbe numbers between 23.5−29.1, depending on the

NVPI content. A similar tendency was observed for poly(2TVS-*co*-NVPI)s (CP1), for which the refractive indices reduced from 1.6881 to 1.6298 with increasing Abbe numbers in the 27.6−35.2 range and increasing NVPI content. In contrast, the effect of the NVPI content was less significant on poly(1,3,4-TVS-*co*-NVPI)s and poly(3MIVS-*co*-NVPI)s (CP2 and CP3). Nevertheless, the refractive index of the NVPI-based copolymers varied with the comonomer composition, and the refractive index increased gradually until it approached that of the homopolymers (e.g., poly(3MIVS) and poly(MeSTVS)). For the NPMI-based copolymers (CP5−CP8), the refractive indices decreased as a result of the higher NPMI content in all cases, while the structure of *S*-vinyl sulfides was less sensitive toward the refractive index. Notably, poly(1,3,4-TVS-*co*-NVPI)s showed relatively high refractive indices (1.6752−1.6662 for CP2), independent of the comonomer content, while poly(1,3,4-TVS-*co*-NPMI)s showed intermediate values (1.6448−1.6191 for CP6), which increased with increasing 1,3,4-TVS content in the copolymers. It is likely that the strong stacking of the 1,3,4-thiadiazolyl unit in the side chain, which is a main reason for the limited solubility of poly(1,3,4-TVS) in organic solvents, can be avoided by the incorporation of imido-containing comonomers more effectively for NPMI than NVPI, affording smooth film-forming properties and solution processability.

Polymers that exhibit high refractive indices and good transparency are often difficult to synthesize. The transparency of the copolymers was evaluated using UV-vis spectrophotometry. For this purpose, copolymer films were produced by drop-casting from a $CHCl_3$ solution (1.0 wt. %), and their thicknesses were adjusted in the 10−20 μm range. As illustrated in Figures 3 and S19, most copolymers showed good transparency in the visible region (> 90% at 400 nm), except for 2TVS-containing copolymers (CP1 and CP5). Excellent transparencies (> 95% at 400 nm) were realized for poly(1,3,4-TVS-*co*-NVPI)s and poly(3MIVS-*co*-NVPI)s (CP2 and CP3). The cut-off wavelengths of MeSTVS-based copolymer films (CP4 and CP8) were around 292−325 nm, whereas 3MIVS-based copolymer films (CP3 and CP7) exhibited lower cut-off wavelengths (277−297 nm). This tendency is probably caused by the molecular design of vinyl sulfide derivatives, which have flexible thioether units and linkages between the C–C main chain and heterocycle-substituted pendant groups, combined with the imide-containing monomer.

Such structural design can efficiently suppress the localization of the π-electrons, owing to the pendant type copolymers, and limited chain transfer interactions between the heterocycle-heterocycle, heterocycle-imide with a benzene ring, and imide-imide pendant groups. Nevertheless, a pale-yellow color was still visible for the drop-cast films prepared from the NPMI-based copolymers (CP5-CP8) and MeSTVS-containing copolymers (CP4), as shown in Figures 3d and S20. The NPMI-based copolymers, which contained an imido group linked directly to the main chain with a flexible linkage between the nitrogen atom and benzene ring, tended to be more yellow in color than NVPI-based copolymers, which exhibited a flexible linkage between the main chain and the nitrogen atom of the phthalimide unit.

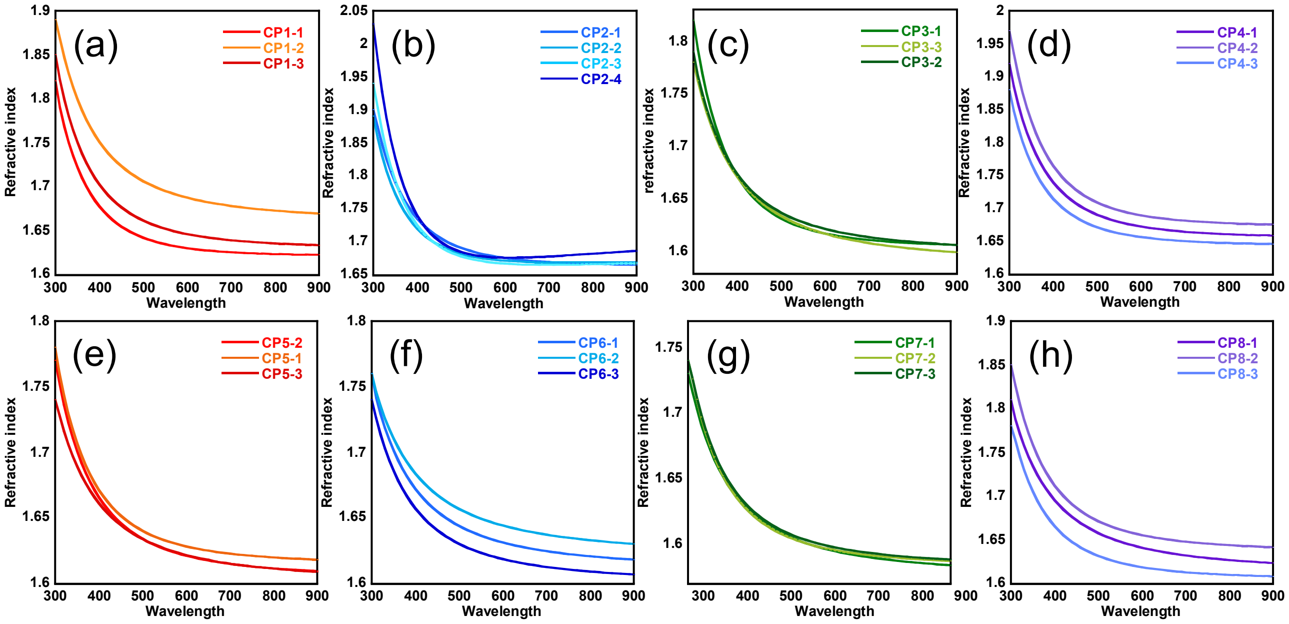


Figure 2. Wavelength-dependent refractive indices of the NVPI-based copolymer films, (a) poly(2TVS-*co*-NVPI)s, (b) poly(1,3,4-TVS-*co*-NVPI)s, (c) poly(3MIVS-*co*-NVPI)s, and (d) poly(MeSTVS-*co*-NVPI)s, and PMI-based copolymer films, (e) poly(2TVS-*co*-NPMI)s, (f) poly(1,3,4-TVS-*co*-NPMI)s, (g) poly(3MIVS-*co*-NPMI)s, and (h) poly(MeSTVS-*co*-NPMI)s, determined by ellipsometry (see Tables 2 and 3 for detailed copolymer samples and results).

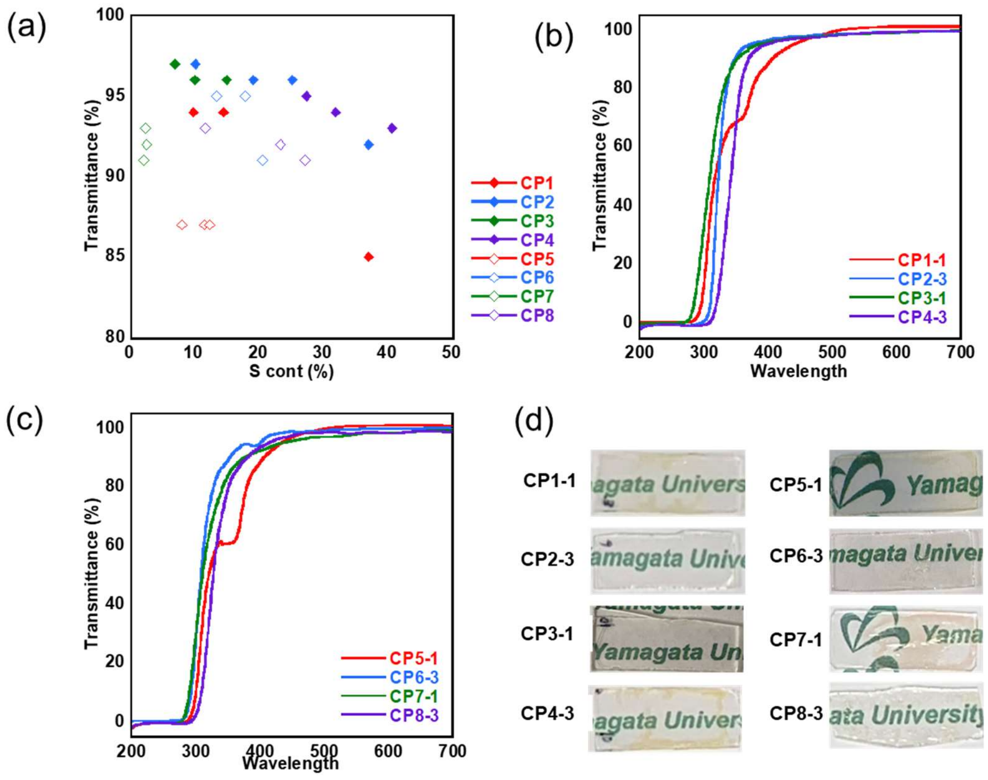


Figure 3. (a) Correlations between transmittance at 400 nm and sulfur content for all copolymers. UV-vis transmittance spectra of representative (b) NVPI-based copolymers (NVPI content = 58-40%, CP1-1, CP2-3, CP3-1, CP4-3 and (c) NPMI-based copolymers (NPMI content = 88-50%, CP5-1, CP6-2, CP7-1, CP8-2). (d) Photographs of representative copolymer films used for the transmittance measurements.

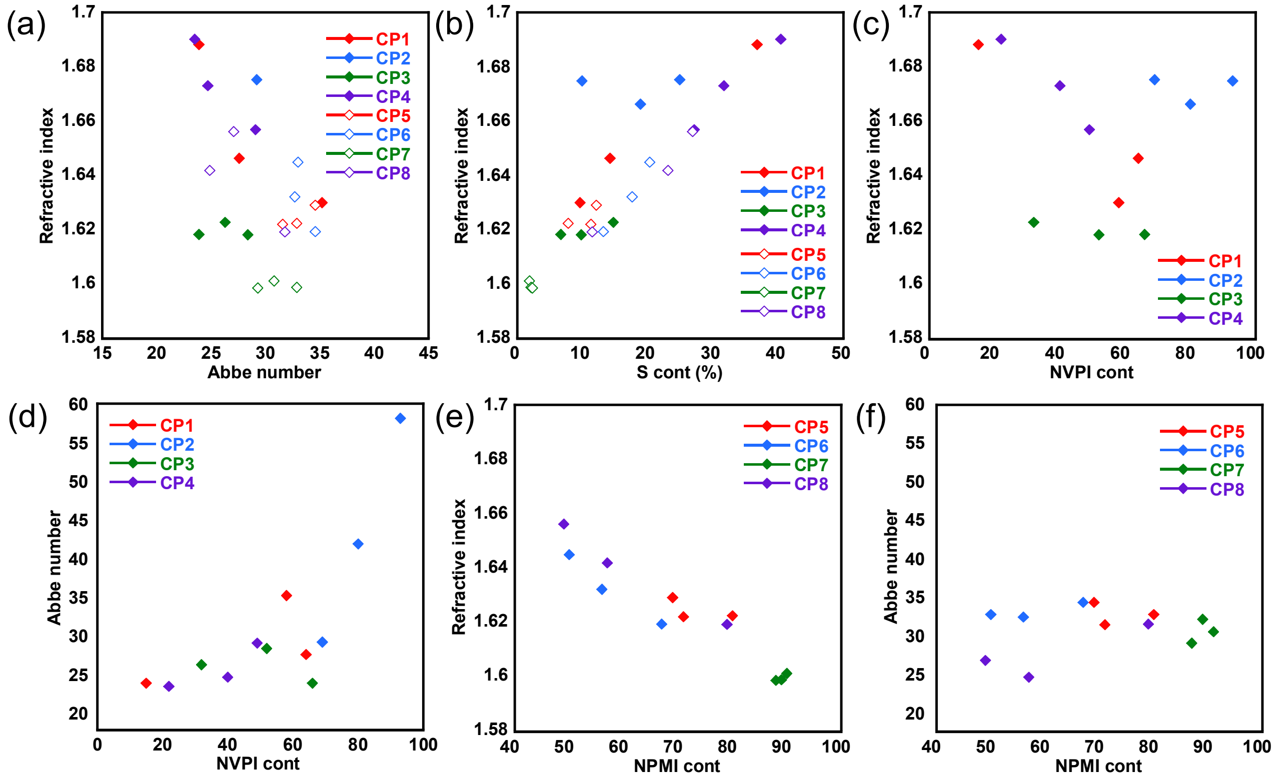


Figure 4. Correlations between the (a) refractive index at 589 nm and Abbe number, (b) refractive index and sulfur content for all copolymers (CP1-CP8), (c) refractive index and NVPI content, (d) Abbe number and NVPI content for NVPI-based copolymers, (e) refractive index at 589 nm and NPMI content, and (f) Abbe number and NPMI content for NPMI-based copolymers.

To investigate the differences between the two series of heterocyclic copolymers composed of NVPI and NPMI, the comonomer composition dependence of the refractive index, Abbe number, transparency, and thermal properties are compared in Figures 3 and 4. As illustrated in Figure 4a, a trade-off relationship between the refractive index and Abbe number was observed. Moreover, the refractive index increased almost linearly with the sulfur content in most cases, regardless of the monomer/comonomer structures and their compositions (Figure 4b). Overall, as shown in Figures 4c and 4e, NVPI-based copolymers (CP1-CP4) showed higher refractive indices than the NPMI-based copolymers (CP5-CP8), which are in the 1.60−1.66 range owing to the limited *S*-vinyl monomer content (< 50%) derived from monomer reactivity. A more detailed analysis suggests that the refractive index decreases more drastically with increasing NVPI content for CP1 and CP4, whereas the refractive indices of CP 2 and CP3 are less sensitive to NVPI content. The Abbe numbers of NVPI-based copolymers (CP1-CP4) vary significantly in the 23−59 range, depending on the NVPI content, whereas the Abbe numbers of the NPMI-based copolymers (CP5-CP8) are less sensitive to NPMI contents (Figures 4d and 4f).

TGA of the copolymers revealed a gradual and/or stepwise thermolysis process (Figure S21), which are apparently distinct from single-step decomposition of the homopolymers (Figure 1d). The T_{d10} of NVPI-based copolymers increased from 239 to 301 °C with increasing NVPI content (Figure 5a). A similar tendency was observed for NPMI-based copolymers, which exhibited increased T_{d10} with increasing NPMI content (Figure 5c). Thermally stable copolymers with higher T_{d10} values more than 280 °C were obtained when the NVPI and NPMI content in the copolymers exceeded 60 and 80 %, respectively. The T_g values of NVPI-based copolymers ranged between 81−175 °C, which increased proportionally with the NVPI content for CP2, CP3, and CP4 (Figures 5b and S22). However, lower T_g values were observed for CP1 were lower (43−94 °C), which are less sensitive to the comonomer content. For NPMI-based copolymers, the T_g values were found to be in the 94−189 °C range, depending on the NPMI content, and the values were higher than those of NVPI-based copolymers (Figures 5d and S22). As the T_g value of a polymer generally depends on various factors, such as π-stacking of the side chains and free volume, the differences in the composition-dependent T_g changes of NVPI- and NPMI-based copolymers may be affected by the different π-stacking of the side chains. Here, it is preferable to compare the thermal and optical properties of NVPI-based and NPMI-based copolymers with similar comonomer compositions. The NPMI content in the copolymers was limited to 49−90%, owing to comonomer reactivity. These results suggest that NVPI-based copolymers are suitable for specific applications, such as ophthalmology, because they exhibit tunable and low T_g values (less than 50 °C, which are close to the body temperature/room temperature).[30] In contrast, NPMI-based copolymers are useful for conventional optical applications, where a high T_g is desirable.

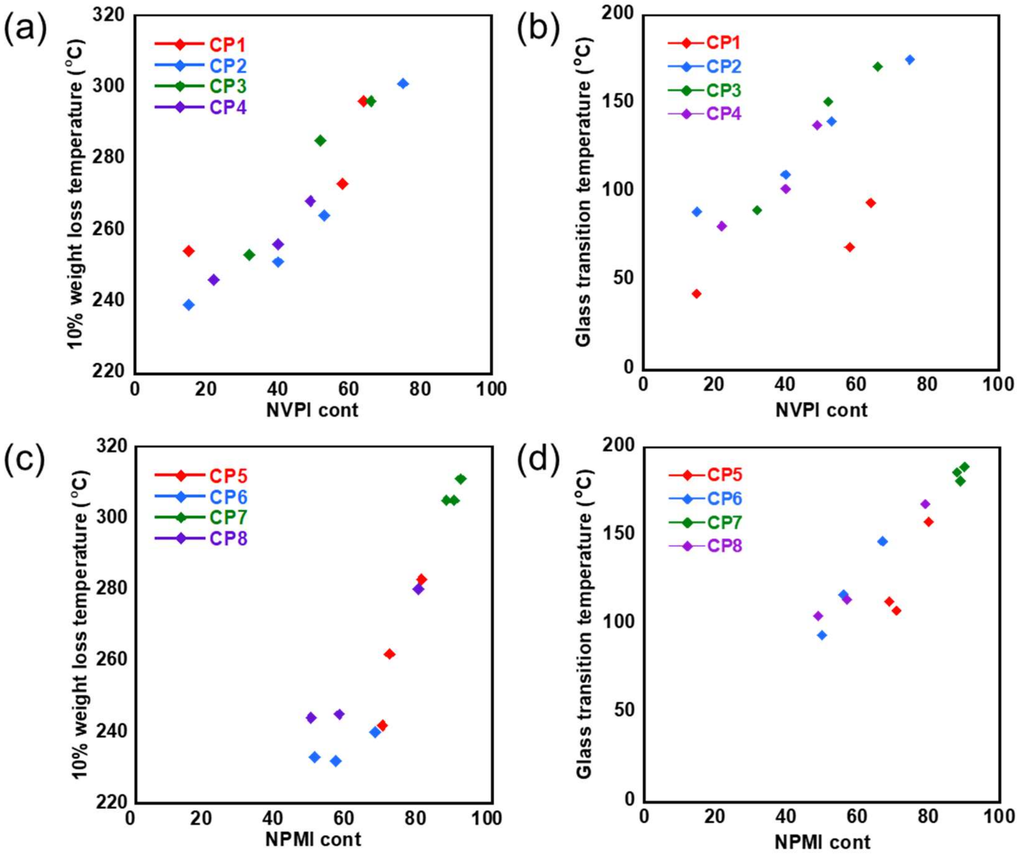


Figure 5. (a) T_{d10} (10% weight loss temperature) and (b) T_g (glass transition temperature) against NVPI content of the NVPI-based copolymers (CP1−CP4). (c) T_{d10} and (d) T_g against NPMI content of the NPMI-based copolymers (CP5−CP8).

3. Conclusion

A series of sulfur-containing copolymers was designed and synthesized from *S*-vinyl monomers bearing five-membered heterocycles with one or two C=N double bonds and different sulfur contents; these monomers were copolymerized with imide-containing monomers attached to a benzene ring. The resultant poly(MeSTVS) exhibited a high refractive index (1.7139), reasonable Abbe number (19.1), good transparency (93%), and relatively low T_g (49 °C). The improved thermal properties of the polymers ($T_{d10} > 245$ °C, $T_g = 78–104$ °C) were achieved by incorporating suitable imide-containing comonomers (NVPI), while maintaining refractive indices greater than 1.65. The radical copolymerization of heterocycle-based vinyl sulfides with high molecular refraction yielded high-refractive-index copolymers. Herein, the refractive index, Abbe number, and optical and thermal properties of the copolymers could be tuned by adjusting the monomer/comonomer structures and their compositions. The transparencies of the copolymers composed of 1,3,4-TVS and 3MIVS were higher those composed of 2TVS and MeSTVS, particularly for NVPI-based copolymers. All copolymers exhibited high thermal properties ($T_{d10} > 245$ °C), regardless of the imide-containing comonomers (NVPI and NPMI). Furthermore, NPMI-based copolymers exhibited high T_g values (94−189 °C), while NVPI-based copolymers showed tunable T_g values (43−175 °C). This diversity-oriented synthetic approach involves the radical copolymerization of aromatic heterocycle-based vinyl sulfides and phthalimide/maleimide derivatives and produces high-refractive-index polymers with tunable Abbe numbers and T_g, while maintaining high transparency and high thermal properties.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request

Table 1. Characteristics of vinyl sulfide-based homopolymers[a)]

Entry	monomer	M_n [b)] (SEC)	M_w/M_n [b)] (SEC)	Sulfur cont.[c)]	Film Thickness (nm) [d)]	RI [d)]	Abbe [d)] number	T_{400} (%)[e)]	T_{d10} (°C) [f)]	T_g (°C) [g)]
P1 [h)]	2TVS	13,000	3.72	42.01	90.8	1.6925	26.7	75	252	30
P2 [h)]	1,3,4-TVS	11,000	3.40	43.10	110.4	n.d.	n.d.	77	242	87
P3	3MIVS	10,000	2.45	19.43	127.7	1.6402	30.0	95	258	68
P4	MeSTVS	4,700	1.58	50.35	112.8	1.7139	19.1	93	244	49

a) Bulk polymerization was conducted at $[M]_0/[AIBN]_0 = 200/1$ and 60 °C for 24 h.

b) Determined by SEC.

c) Sulfur content determined by elemental analysis (Table S4).

d) Film thickness, refractive indices (RI), and Abbe's numbers of the polymers were determined by ellipsometry.

e) Transmittance at 400 nm.

f) The temperature at 10% weight loss (T_{d10}).

g) Glass transition temperature (T_g) determined by DSC.

h) From reference 35.

Table 2. Synthesis, thermal and optical properties of phthalimide/maleimide-containing copolymers [a)]

Entry	Monomers (M_1/M_2)	$[M_1]_0/[M_2]_0/[I]_0$	Yield[b)] (%)	M_n[c)] (SEC)	M_w/M_n[c)] (SEC)	n:m[d)]	T_{d10} (°C)[e)]	T_g (°C)[e)]	T_{400} (%)[f)]	Cutoff wavelength
CP1-1	2TVS /NVPI	25/25/1	52	3,100	1.51	42/58	273	69	94	281
CP1-2		75/25/1	10	3,500	1.46	85/15	254	43	85	298
CP1-3		25/75/1	28	8,200	1.79	36/64	296	94	94	301
CP2-1	1,3,4-TVS /NVPI	25/25/1	40	5,500	1.58	60/40	251	110	96	285
CP2-2		75/25/1	20	4,900	1.61	85/15	239	89	92	279
CP2-3		100/200/1	20	9,200	1.77	47/53	264	140	96	298
CP2-4		25/75/1	75	10,000	2.56	25/75	301	175	97	302
CP3-1	3MIVS /NVPI	100/100/1	16	4,000	1.70	48/52	285	151	96	277
CP3-2		100/200/1	14	7,200	1.84	34/66	296	171	97	297
CP3-3		200/100/1	10	2,600	1.68	68/32	253	90	96	287
CP4-1	MeSTVS /NVPI	25/25/1	53	6,200	1.59	60/40	256	102	94	307
CP4-2		50/25/1	31	5,900	1.51	78/22	246	81	93	325
CP4-3		25/50/1	35	10,000	1.68	51/49	268	138	95	310
CP5-1	2TVS /NPMI	50/50/1	55	3,600	2.91	29/71	262	108	88	288
CP5-2		100/50/1	38	3,700	2.59	31/69	242	113	87	289
CP5-3		50/100/1	68	4,200	3.60	20/80	283	158	87	288
CP6-1	1,3,4-TVS /NPMI	50/50/1	68	6,400	1.86	44/56	231	117	95	282
CP6-2		100/50/1	64	4,500	1.92	50/50	233	94	91	277
CP6-3		50/100/1	75	4,400	1.95	33/67	240	147	95	283
CP7-1	3MIVS /NPMI	50/50/1	42	2,300	2.45	12/88	305	186	92	280
CP7-2		100/50/1	27	2,400	2.41	11/89	305	181	93	282
CP7-3		50/100/1	22	2,500	2.82	10/90	311	189	91	281
CP8-1	MeSTVS /NPMI	50/50/1	47	4,700	2.46	43/57	245	114	92	300
CP8-2		100/50/1	32	4,700	2.26	51/49	244	105	91	292
CP8-3		50/100/1	65	6,900	2.97	21/79	280	168	93	298

a) Free radical copolymerizations were conducted in DMF (conc. = 2.0 mmol/mL) at 60 °C for 24 h.
b) Diethyl ether-insoluble part.
c) Determined by SEC.
d) Estimated from sulfur content determined by elemental analysis.
e) The T_g determined by DSC and T_{d10} determined by TGA.
f) Transmittance at 400 nm.

Table 3. Characteristics and optical properties of phthalimide/maleimide-containing copolymers a)

Entry	Sample b)	S cont. c) (%)	Film Thickness (nm)	n_D (589 nm)	n_F (486 nm)	n_d (587 nm)	n_c (656 nm)	ν_D
CP1-1	Poly(2TVS-*co*-NVPI)	9.60	110.3	1.6298	1.6438	1.6300	1.6259	35.2
CP1-2		36.79	108.4	1.6881	1.7095	1.6884	1.6807	23.9
CP1-3		14.19	121.2	1.6462	1.6640	1.6464	1.6406	27.6
CP2-1	Poly(1,3,4-TVS-*co*-NVPI)	24.92	103.6	1.6752	1.6932	1.6754	1.6700	29.2
CP2-2		36.78	32.4	n.d.	n.d.	n.d.	n.d.	n.d.
CP2-3		18.94	111.7	1.6662	1.6800	1.6663	1.6641	41.9
CP2-4		9.85	119.9	1.6747	1.6868	1.6748	1.6751	58.1
CP3-1	Poly(3IMVS-*co*-NVPI)	9.76	114.7	1.6179	1.6346	1.6180	1.6128	28.4
CP3-2		6.70	133.2	1.6180	1.6369	1.6182	1.6111	23.9
CP3-3		14.72	116.7	1.6225	1.6400	1.6227	1.6163	26.3
CP4-1	Poly(MeSTVS-*co*-NVPI)	31.68	96.5	1.6730	1.6938	1.6732	1.6666	24.7
CP4-2		40.36	90.4	1.6901	1.7128	1.6903	1.6834	23.5
CP4-3		27.10	88.6	1.6567	1.6742	1.6568	1.6516	29.1
CP5-1	Poly(2TVS-*co*-NPMI)	11.28	87.4	1.6218	1.6365	1.6219	1.6168	31.6
CP5-2		12.10	98.3	1.6288	1.6425	1.6289	1.6243	34.6
CP5-3		7.79	74.8	1.6222	1.6361	1.6224	1.6172	32.9
CP6-1	Poly(1.3.4-TVS-*co*-NPMI)	17.61	72.1	1.6319	1.6462	1.6321	1.6268	32.6
CP6-2		20.3	85.6	1.6448	1.6591	1.6450	1.6395	32.9
CP6-3		13.15	66.4	1.6191	1.6324	1.6193	1.6144	34.5
CP7-1	Poly(3MIVS-*co*-NPMI)	2.24	123.6	1.5983	1.6134	1.5985	1.5929	29.2
CP7-2		2.15	113.2	1.5985	1.6124	1.5986	1.5939	32.3
CP7-3		1.88	129.3	1.6008	1.6154	1.6010	1.5958	30.7
CP8-1	Poly(MeSTVS-*co*-NPMI)	23.11	145.8	1.6417	1.6607	1.6419	1.6348	24.8
CP8-2		26.86	83.4	1.6560	1.6743	1.6562	1.6500	27.0
CP8-3		11.52	90.6	1.6190	1.6338	1.6191	1.6143	31.7

a) Film thickness, refractive indices, and Abbe number (ν_D) of copolymers were determined by ellipsometry.

b) See Table 2 for detailed copolymer samples.

c) Sulfur content determined by elemental analysis.

4. Experimental Section

Materials: 2,2′-Azobis(isobutyronitrile) (AIBN, 97 %) was purchased from Kanto Chemical, and purified via recrystallization from methanol. 2-Thiazolylvinylsulfide (2TVS) and 1,3,4-thiadiazolylvinylsulfide (1,3,4-TVS) were synthesized as described previously.[51] *N*-Phenylmaleimide (NPMI, >98%) and *N*-vinylphthalimide (NVPI, >98%) were purchased from Tokyo Kasei Kogyo, and purified by recrystallization from methanol. 2-Mercapto-1-methylimidazole (Tokyo Kasei Kogyo, >98%), 5-methylthio-1,3,4-thiadiazole-2-thiol (Aldrich, >98%), and all the other materials were used as received.

Monomer synthesis: The aromatic heterocycle-based vinyl sulfides were synthesized by the reaction of 1,2-dibromoethane with corresponding thiol compounds, as described previously.[51]

3-Methylimidazolylvinylsulfide (3MIVS): To a two-necked round-bottom flask, 2-mercapto-1-methylimidazole (25.0 g, 0.22 mol), THF (200 mL), and 1,2-dibromoethane (83.0 g, 0.44 mol) were added under a nitrogen atmosphere. Then, 1,8-diazabicyclo[5.4.0]undec-7-ene (67.0 g, 0.44 mol) was added dropwise with stirring at 0 °C. The mixture was refluxed by stirring for 24 h, cooled, and treated with $CHCl_3$ and water. The organic layer was then separated, washed with water, and dried over $MgSO_4$. After the filtration, the solvent was removed under a vacuum. The crude product was purified by distillation under reduced pressure to afford pure 3MIVS as a pale yellow liquid (9.8 g, 34%). bp 90°C/0.08mmHg (lit.[40] 140-142 °C/10 mmHg). ^1H NMR ($CDCl_3$, δ, ppm): 7.1 (dd, 1H, N-CH=CH-), 7.0 (dd, 1H, N-CH=CH-), 6.5-6.4 (dd, 1H, $CH_2=C\textit{H}$-), 5.4-5.0 (dd, 2H, $C\textit{H}_2$=CH-), 3.7-3.6 (m, 3H, $C\textit{H}_3$-N-). ^{13}C NMR ($CDCl_3$, δ, ppm): 137.5 (S-C=N), 128.5 (CH_2=CH-), 123.0 (N-CH=CH-), 116.7 (CH_2=CH-), 33.6 (CH_3-N-). Anal. Calcd for $C_6H_8N_2S$: C, 47.64; H, 5.36; N, 17.05; S, 19.43. Found: C, 47.37; H, 5.33; N, 16.89; S, 18.93.

5-Methylthio-1,3,4-thiadiazolylvinylsulfide (MeSTVS): 5-Methylthio-1,3,4-thiadiazole-2-thiol (10.0 g, 0.061 mol), THF (200 mL), 1,2-dibromoethane (22.8 g, 0.122 mol) were added to a two-necked round-bottom flask under a nitrogen atmosphere. Then, 1,8-diazabicyclo[5.4.0]undec-7-ene (18.6 g, 0.122 mol) was added dropwise with stirring at 0 °C. The reaction and purification were conducted in the same procedure described above. Yield: 2.95 g (25 %), b.p.: 150 °C/0.08 mmHg (lit.[42] 160-168 °C/0.4-0.6 mmHg). ^{1}H NMR ($CDCl_3$, δ, ppm): 6.8-6.7 (dd, 1H, CH_2=CH-), 5.6-5.5 (dd, 2H, $C\mathit{H_2}$=CH-), 2.9-2.7 (s, 3H, CH_3-S-). ^{13}C NMR ($CDCl_3$, δ, ppm): 168.9 (S-C=C-), 162.8 (S-C-S), 127.4 (CH_2=CH-), 120.6 (CH_2=CH-), 17.5 (CH_3-S-). Anal. Calcd for $C_5H_6N_2S_3$: C, 32.98; H, 3,28; N, 14.21; S, 50.26. Found: C, 32.98; H, 3.36; N, 14.22; S, 50.35.

Polymer Synthesis: For the synthesis of a representative NVPI-based copolymer (CP4-1 in Table 2), MeSTVS (0.190 g, 1.0 mmol), NVPI (0.173 g, 1.0 mmol), AIBN (6.6 mg, 0.04 mmol), and DMF (1.0 mL) were placed in a dry glass ampule equipped with a magnetic stir bar. After the solution was degassed by three freeze-evacuate-thaw cycles, the ampule was flame-sealed under vacuum, and then it was stirred at 60 °C for 24 h. The resulting crude product was diluted by adding a small amount of $CHCl_3$, and the mixture was poured into a large excess of diethyl ether to precipitate the product. The resultant polymer was filtrated and then dried under vacuum at 60 °C to afford poly(MeSTVS-*co*-NVPI) as a pale yellow solid (0.192 g, yield = 53%).

For the synthesis of a representative NPMI-based copolymer (CP8-1 in Table 2), MeSTVS (0.190 g, 1.0 mmol), NPMI (0.173 g, 1.0 mmol), AIBN (3.3 mg, 0.01 mmol), and DMF (1.0 mL) were added in the ampule. The copolymerization was conducted at 60 °C for 24 h in the same manner described above to afford poly(MeSTVS-*co*-NPMI) as a yellow solid (0.169 g, yield = 47%).

For the synthesis of a homopolymer (P4 in Table 1), MeSTVS (0.380 g, 2.0 mmol) and AIBN (1.6 mg, 0.01 mmol) were placed in the ampule. The homopolymerization was conducted at 60 °C for 24 h in the same manner described above. After the polymerization, the crude product was dissolved in a small amount of $CHCl_3$, and the mixture was poured into a large excess of methanol to precipitate the product. The resultant polymer was filtrated and then dried under vacuum at 35 °C to afford poly(MeSTVS) as a white solid (33.6 mg, yield = 8.9 %). ^{1}H NMR ($CDCl_3$, δ, ppm): 3.7-2.0 (1H, -CH_2-CH-), 2.8-2.6 (3H, S-SH_3), 1.7-1.2 (2H, -CH_2-CH-).

The same procedure was employed for the production of poly(3MIVS). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.1-6.6 (N-CH=CH-N), 4.0-3.0 (3H, N-CH_3), 2.3-1.7 (-CH_2-CH-).

Instrumentation: The NMR spectra were recorded on a JEOL JNM-ECX400 (400 MHz for ^{1}H ; 100 MHz for ^{13}C). Elemental carbon, hydrogen, nitrogen, and sulfur were analyzed using a Perkin-Elmer 2400 II CHNS/O analyzer. The M_n and M_w/M_n were estimated by SEC relative to polystyrene standards using a Tosoh HPLC HLC-8220 system equipped with refractive index and ultraviolet detectors, four consecutive hydrophilic vinyl polymer-based gel columns (TSK-GELs α-M, α-4000, α-3000, α-2500, with TSK-guard column α), with DMF containing 10 mM LiBr as the eluent at a flow rate of 1.0 mL/min.[35, 51] The T_g values were measured by DSC using a SEIKO DSC6200 under nitrogen atmosphere. TGA was performed at a heating rate of 10 °C/min under a nitrogen atmosphere on a SEIKO TG/DTA6200 instrument. The transparency was evaluated measured by UV-vis measurement using a JASCO V-630BIO UV−vis spectrophotometer. The samples were prepared by drop-casting as follows: 5 mg of the polymer $CHCl_3$ solution (1.0 wt. %) was placed on the glass substrate, and it was allowed to evaporate overnight in an ambient atmosphere. Wavelength-dependent refractive indices $n(\lambda)$ of spin-coated polymer thin films were evaluated by a spectroscopic ellipsometer (J.A. Woollam M-2000U), as described previously.[35, 52] Briefly, Cauchy function for the refractive index $n(\lambda) = A + B/\lambda^2 + C/\lambda^4$ was employed for evaluation of the wavelength-dependence of refractive index. The homogenous polymer thin films were prepared by spin-coating from $CHCl_3$ solutions (conc. = 1.0 wt. %, 1000 rpm at 60 s) on a silicon wafer. The Abbe number (ν_D) was calculated for the polymers as $\nu_D = (n_D-1)/(n_F-n_C)$, where n_D, n_F, and n_C are the refractive indices of materials at wavelength of 589.3, 486.1, and 656.3 nm, that correspond to sodium D, hydrogen F, and hydrogen C line, respectively.

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