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COMMUNICATION

Monomer-Level Strategy for High Refractive Index without Visible-Light Absorption: Vinylthiophene Incorporation into Group 14 scaffolds

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We present a monomer-level design strategy for high-refractive-index polymers that overcomes the trade-off between refractive index and visible-light transparency. Densely incorporating highly polarizable vinylthiophene units around Group 14 element centers results in refractive indices up to 1.69, maintains minimal visible-light absorption, and enables their application as index-enhancing additives for polymers.

High-refractive-index polymers (HRIPs), which generally have a refractive index exceeding 1.6, are indispensable for the development of advanced optical devices, such as organic light-emitting diodes (OLEDs) and charge-coupled devices (CCDs).[1-2] Generally, according to the Lorentz–Lorenz equation, the refractive index (n) of polymers is related to the molar refraction ($[R]$) and molecular volume (V_0) (1):[3,4]

$$n = \sqrt{\frac{V_0 + 2[R]}{V_0 - [R]}} \qquad (1)$$

Thus, the refractive index of polymers can be enhanced by increasing either the molecular polarizability of the repeating units or the packing density of the material.[5,6] A fundamental strategy for achieving a high refractive index involves incorporating sulfur atoms and π-conjugated units with high molar refraction into polymer repeating units.[7-8] Significant improvements in refractive index have been achieved through polymerization approaches, such as thiol-ene polymerization[9] and inverse vulcanization,[10,11] which enable the high-density incorporation of sulfur-rich structures. In addition, increasing the crosslink density in polymer networks enhances refractive index by increasing the packing density.[12,13] However, HRIPs still face challenges, such as coloration caused by the incorporation of excessive sulfur atoms and π-conjugated units resulting in reduced transparency.

In recent years, polymer systems with high refractive indices and high transparencies have been reported. These approaches suppress excessive electronic delocalization while maintaining a high unit density, for example, through non-covalent interactions between thiourea units for backbone densification,[14] or chemical vapor deposition of sulfur.[15,16] In addition, precisely controlled copolymerization enables fine tuning of the density and distribution of high-molecular-refraction units within the repeating structure.[17,18] Nevertheless, many of these strategies rely on sophisticated control of polymer backbones or polymerization modes, which limits the direct transfer of the underlying design principles to other molecular systems or polymerization reactions.

To overcome these limitations, we propose a monomer-level strategy in which designing monomers that inherently exhibit high-refractive-index properties enables the realization of high-refractive-index polymer materials through various polymerization or additive-type methods. In this strategy, we hypothesized that integrating multiple highly polarizable units into a single monomer, while intentionally interrupting electronic conjugation, provides an effective approach to achieving both a high refractive index and high transparency. By densely incorporating these units, the molar refraction ($[R]$) can be increased while limiting the rise in molecular volume (V_0), as guided by the Lorentz–Lorenz equation, while minimizing the unwanted visible-light absorption associated with extended conjugation.

To implement this concept, we focused on vinylthiophene as a building block containing sulfur atoms and aromatic units, and designed a series of monomers by introducing these units onto Group 14 elements (Si, Ge, and Sn), which exhibit high atomic polarizabilities[19] and serve as central molecular scaffolds. This tetrahedral arrangement maximized the molar refraction without extending the conjugation, thereby effectively maintaining refractive enhancement while minimizing visible-light absorption (**Fig. 1**). Furthermore, the tetrafunctional structure of this design enables efficient cross-linking within the polymer network. Given that cross-linking has been shown to enhance the refractive index[20,21], this structural feature is expected to further improve the refractive index by promoting

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network formation and minimizing the free volume of the polymer matrix.

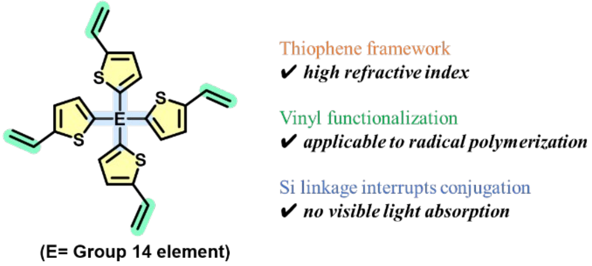

Fig. 1 Design concept of this work.

To validate this design concept, a series of methyl-substituted analogs (**SiVT1–SiVT4**) were synthesized. The monomers were prepared via a consistent synthetic protocol involving the lithiation of 5-bromo-2-vinylthiophene, followed by reaction with tetrachlorosilane or the corresponding methylchlorosilanes. All derivatives were obtained in high yields, and tetrakis(5-vinylthiophen-2-yl)silane (**SiVT4**), featuring four vinylthiophene units, was synthesized in an excellent yield of 92% (**Fig. 2**).

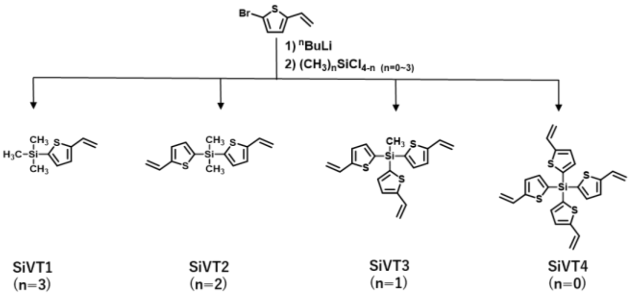

Fig. 2 Synthesis of **SiVT4**, **SiVT3**, **SiVT2**, and **SiVT1**.

The refractive indices of the monomers were measured at 589 nm to evaluate the specific contributions of the vinylthiophene units. While the mono-substituted trimethyl(5-vinylthiophen-2-yl)silane (**SiVT1**) exhibited a refractive index of 1.53, dimethylbis(5-vinylthiophen-2-yl)silane (**SiVT2**) and methyltris(5-vinylthiophen-2-yl)silane (**SiVT3**) exhibited values of 1.61 and 1.65, respectively (**Table 1**). All the monomers except **SiVT1** exhibited high refractive indices (>1.6). Among these, **SiVT4**, which possesses the highest density of vinylthiophene units, exhibited the highest refractive index of 1.68. A clear stepwise increase in the refractive index was observed with increasing vinylthiophene substitution. This trend is further supported by quantum chemical calculations, which predict an increase of approximately 12 Å^3 in molecular polarizability (α) upon substitution of each methyl group with a vinylthiophene unit. According to the Lorentz–Lorenz equation, $\Delta\alpha$ corresponds to a notable increase in molar refraction of ~30.3 cm^3/mol. Notably, this increase surpassed the molar refractive contribution of the standard phenyl group (~ 25 cm^3/mol) (**Table 1**). This substantial contribution from the vinylthiophene units effectively enhances the refractive index.

Furthermore, the effect of the central element on the refractive index was investigated. The germanium and tin analogs, namely, tetrakis(5-vinylthiophene-2-yl)germane (**GeVT4**) and tetrakis(5-vinylthiophen-2-yl)tin (**SnVT4**), were synthesized from the corresponding tetrachlorides using the same procedure as for **SiVT4**. The refractive indices of **GeVT4** and **SnVT4** were determined to be 1.68 and 1.69, respectively (**Table 1**). The slightly higher refractive index observed for SnVT4 may be attributed to the heavy atom effect associated with the Sn center, which increases polarizability. However, this effect is likely partially offset by the larger molecular volume of SnVT4. Therefore, the increase in refractive index due to the heavy atom effect is considered to be limited. This trend contrasts with previously reported tetravinyl-group-14 systems, in which polymers prepared from tetravinylsilane, tetravinylgermane, and tetravinyltin via thiol-ene crosslinking exhibited increasing refractive indices in the order Si<Ge<Sn, owing to the higher polarizability of heavier elements.[22] The differences can be rationalized by considering the molecular volume effects of heavier atoms. Although heavier atoms have higher intrinsic polarizability, their longer E–C bond lengths increase the molecular volume, which can offset the expected enhancement of the refractive index. Quantum chemical calculations revealed that the average Si-C bond length in **SiVT4** is 1.87 Å, whereas the average Ge-C and Sn-C bond length in **GeVT4 and SnVT4** are 1.94 Å and 2.10 Å, respectively. These results support the interpretation that the precise balance between molecular polarizability and molecular volume is critical in determining the refractive index in the present system. The UV-vis absorption properties of the monomers, which directly influence the optical transparency of the resulting polymers, were also evaluated. The maximum absorption wavelengths were λ_{max} = 292.0 nm for **SiVT4**, λ_{max} = 287.5 nm for **SiVT3**, λ_{max} = 287.5 nm for **SiVT2**, λ_{max} = 283.5 nm for **SiVT1**, and λ_{max} = 289.0 nm for **GeVT4**. Notably, none of the compounds exhibited absorption in the visible region (Fig. 3a). In general, incorporation of multiple aromatic rings into a molecular framework often leads to an extension of π-conjugation, resulting in a reduced HOMO–LUMO gap and undesired coloration due to absorption in the visible region. For example, Ochiai et al. reported an arylbismuthine-containing polymer with a refractive index exceeding 1.7, which exhibited coloration resulting from the conjugation between the vinyl units and arylbismuthine moieties.[13]

Table 1. Measured refractive index and calculated polarizability for each monomer (cam-B3LYP/6-311G+(d,p) level)

monomer	SiVT4	GeVT4	SnVT4	SiVT3	SiVT2	SiVT1
Refractive index	1.68	1.68	1.69	1.65	1.61	1.53
Calculated polarizability /Å^3	59.35	59.99	54.07*	47.29	34.73	22.53

* SnVT4 values calculated using the cam-B3Lyp/LANL2DZ level.

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In contrast, the Si and Ge centers employed in this study primarily function as sp^3 hybridized σ-bonded linkages, which do not effectively mediate π-conjugation between the aromatic units. Consequently, even with multiple aromatic and sulfur-containing units, excessive intramolecular electron delocalization was suppressed, preventing undesired extension of the conjugation length and maintaining optical transparency. Furthermore, TD-DFT calculations were performed to analyze the electronic transitions. The longest absorption wavelength for each compound corresponds to the S1 transition resulting from the HOMO–LUMO excitation (**SiVT4**: 282.0 nm, f = 0.2717; **SiVT3**: 278.2 nm, f = 0.7192; **SiVT2**: 277.5 nm, f = 0.7228; **SiVT1**: 272.3 nm, f = 0.4266; **GeVT4**: 276.2 nm, f = 0.3038). These molecular orbitals are mainly localized on the individual vinylthiophene units with minimal electron density at the central Si or Ge atoms, indicating that the Group 14 element center interrupts intramolecular delocalization between multiple vinylthiophene units and effectively limits the π-conjugation length. The controlled electronic structure explains the absence of visible-light absorption (**Fig. 3b**). Finally, thermal radical polymerization of **SiVT4** was performed using 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN) as the initiator (**Fig. 3c**). The thin film was prepared by placing the monomer and initiator between glass plates, followed by thermal polymerization in an oven at 60 °C. The solid-state UV–Vis spectra of the polymer exhibit significant broadening compared to the monomer. The solid-state UV–Vis spectra of the polymer exhibit significant broadening compared to the monomer. However, the overall absorption envelope and spectral region of the primary absorption band are preserved after polymerization. This broadening likely arises from a combination of increased intermolecular interactions, including π–π stacking and excitonic coupling, as well as structural disorder associated with polymer packing. This broadening likely arises from a combination of increased intermolecular interactions, including π–π stacking and excitonic coupling, as well as structural disorder associated with polymer packing. (**Fig. 3d**). ATR-FTIR spectroscopy was performed to monitor the polymerization process. The characteristic C=C stretching band of the vinyl group at 1617 cm^{-1} decreased after polymerization, accompanied by the appearance of aliphatic C–H stretching band at 2919 cm^{-1} (**Fig. 3e**). The spectral changes confirmed the consumption of the vinyl group and the presence of alkyl groups through radical polymerization. The residual vinyl signals were likely due to the suppression of polymerization caused by restricted mobility within the crosslinked, rigid skeleton derived from the monomer.

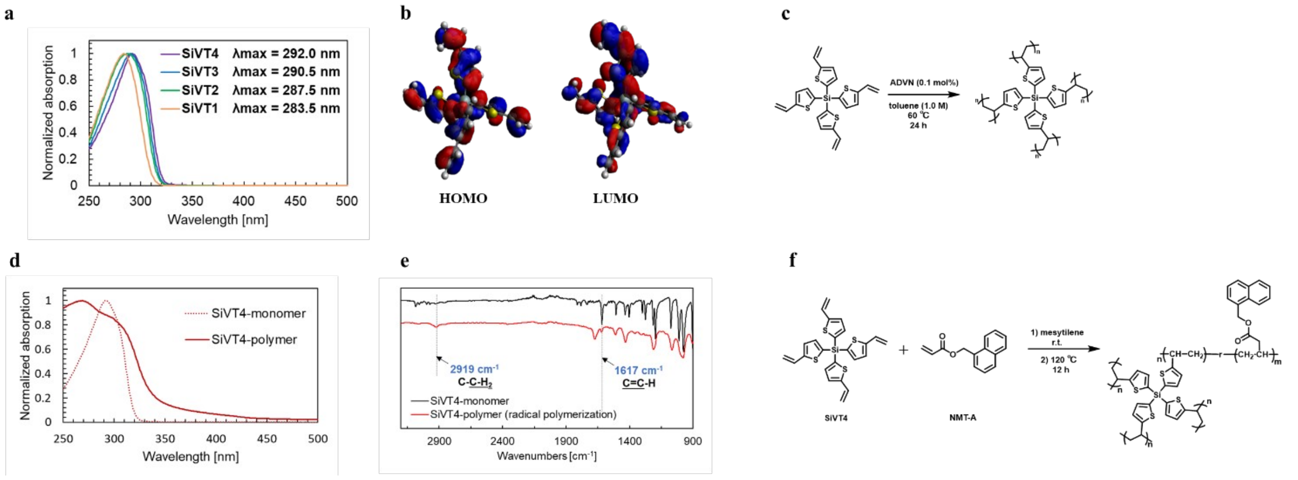

Fig. 3 (a) UV-Vis absorbance spectra of vinylthiophene substituted derivatives in MeCN solution. (b) HOMO and LUMO orbital distributions (c) Polymerization of **SiVT4**. (d) Solid-state UV-Vis absorbance spectra. (e) ATR spectra of **SiVT4** and its corresponding polymer. (f) Copolymerization of SiVT4 and NMT-A.

The practical utility of **SiVT4** as an additive for enhancing the refractive index was demonstrated. A commercially available high-refractive-index liquid monomer, naphthalen-1-ylmethyl acrylate (NMT-A), was copolymerized with **SiVT4**. The refractive index of NMT-A was 1.60 before curing and increased to 1.62 after standing at 100 °C for 1 h to complete polymerization. When 10 wt% **SiVT4** was added, the refractive index remained at 1.60 before curing and increased to 1.67 after curing. With 20 wt% **SiVT4**, the refractive index was 1.61 before curing and increased to 1.68 after curing. The efficiency of this refractive-index enhancement differs from that of previously reported systems. For instance, Sato et al. reported that the incorporation of 25 wt% 2-(4-vinylphenyl)benzothiazole (BTVS) into 2-vinylnaphthalene (VNA) resulted in a refractive index increase of only approximately 0.004 after polymerization.[23] In

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contrast, in this study, a significant increase of 0.06 with only 20 wt% **SiVT4**, representing a 15-fold greater enhancement. The significant increase in refractive index identifies **SiVT4** as a highly effective additive. The enhancement is attributed to cooperative effects of the SiVT4 molecular design: the inherently high molar refraction ($[R]$) of the vinylthiophene units and efficient network formation during curing, which reduces the effective molecular volume (V_0). These results demonstrate that the present molecular design enables both a high refractive index and optical transparency, while retaining compatibility with conventional polymerization. Owing to the inherent reactivity of the vinyl groups[24], this backbone is also expected to be applicable to other polymerizations, including thiol-ene reactions.²⁵²⁴22,25

In this study, we demonstrated a monomer-level design for HRIPs by integrating highly refractive vinylthiophene units with Group 14 element centers. Systematic optical evaluation confirmed that the cumulative contribution of these units provided a molar refraction gain exceeding that of the phenyl group, thereby driving high refractive indices without visible-light absorption. The Group-14-element-centered structure serves as a pivotal scaffold that effectively suppress excessive π-conjugation, a key advantage over conventional highly-conjugated systems that often exhibit undesired coloration. Furthermore, vinyl functionalization allows the direct translation of monomer-level design into a diverse polymer framework via conventional thermal radical polymerization. The tetrafunctional nature of these monomers not only enhances molar refraction but also promotes network densification via crosslinking, resulting in a significant leap in the refractive index that surpasses that of traditional aromatic systems. This study provides a versatile platform for the development of HRIPs, shifting the design focus toward modular optimization at the monomer level. This approach offers a rational framework to overcome the long-standing trade-off between the refractive index and transparency, paving the way for the next generation of advanced optical devices.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article are included in the supplementary information (SI). The supplementary information includes detailed experimental procedures, characterization data, and additional figures supporting this study. See DOI:

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Data availability

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