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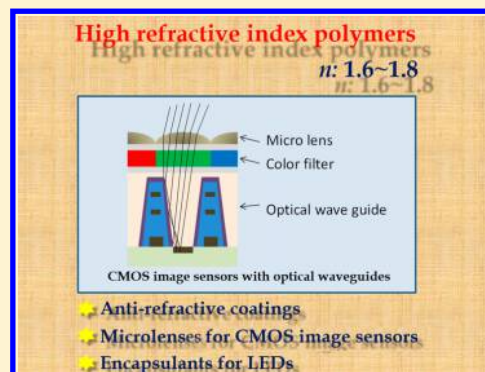**198** PUBLICATIONS **3,183** CITATIONS

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Recent Progress in High Refractive Index Polymers

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ABSTRACT: High refractive index polymers have been widely developed in recent years for their potential applications in advanced optoelectronic fabrications, such as high performance components for advanced display devices, encapsulants for light-emitting diode devices, microlens components for complementary metal oxide semiconductor image sensors, plastic lenses for eyeglasses, and camera, pick-up, and projector lenses. This Perspective describes the recent progress in high refractive index (n) polymers over the past decade and focuses on the design concept to increase n values and Abbe's number (ν) of polymers. After a brief introduction of the basic methodology for developing high-n polymers and important parameters, such as Abbe's number and birefringence, applications of high-n polymers, such as antirefractive coatings, microlenses for CMOS image sensors, encapsulants for LEDs, and high-n thermoplastic lenses, are highlighted.

INTRODUCTION

In the advanced optical devices, the development of highly functional materials has become essential. Polymeric materials possessing a high refractive index (high-n) and a high Abbe's number (high-ν) have received much attention because of their wide variety of applications as optical materials including lenses, prisms, and waveguides, based on the superiority of lightweight, impact resistance, processability, and dying ability compared to inorganic glasses.[1,2] Polymeric materials can be categorized into thermosets and thermoplastics. Thermoset resins derived from episulfides,[3] polythiols,[4] and polyisocyanates[5] have been commercialized in the areas of eyeglasses via a cast molding process. On the other hand, thermoplastics, represented by poly(methyl methacrylate), polycarbonate, and cycloolefin polymers,[6] are employed in an injection molding process for producing camera, pick-up, and projector lenses.

High-n polymers with a high optical transparency are highly required in advanced optoelectronic devices[7−10] such as high-performance substrates for display devices,[9,10] optical adhesives or encapsulants for antireflective coatings,[12] and microlens components for charge coupled device (CCD) or complementary metal oxide semiconductor (CMOS) image sensors.[13] Especially, a very high-n exceeding 1.7 or even 1.8 is frequently desired for the application to polymeric microlenses for CMOS image sensors, although the typical n values of conventional optical polymers are in the range of 1.30−1.70.[14] On the other hand, polymers with both high-n and high-ν values have also been developed for microoptic and optoelectronic applications, such as lenses, prisms, waveguides, and diffractive gratings.[15,16] Not only n and ν values but also birefringence and optical transparency as well as the physical properties should be considered to design high-n polymers for various applications.

This perspective will describe the recent progress in high-n polymers over the past decade and focus on the methods to increase the refractive index values of polymers. After a brief introduction of the basic methodology for developing high-n polymers and important parameters, such as Abbe's number and birefringence, applications of high-n polymers as antirefractive coatings, microlenses for CMOS image sensors, encapsulants for LEDs, and high-n thermoplastic lenses are highlighted.

REFRACTIVE INDEX, ABBE'S NUMBER, AND BIREFRINGENCE

The Lorentz−Lorenz equation,[17] which defines the relationship between the refractive index and individual parameters depending on polymer structure, is quite useful for designing high-n polymers.

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \frac{\rho N_A}{M_W} \alpha = \frac{[R]}{V_0} \tag{1}$$

where n is the refractive index, ρ the density, N_A the Avogadro number, M_w the molecular weight, α the linear molecular polarizability, $[R]$ the molar refraction, and V_0 the molecular volume of the polymer repeat unit.

Equation 2 is then solved for n from eq 1:

$$n = \sqrt{\frac{1 + 2[R]/V_0}{1 - [R]/V_0}} \tag{2}$$

According to eq 2, the n values of a polymer increase by introducing the substituents with high molar refractions and low molar volumes.[18]

The molar refractions and atomic dispersions of common atoms and groups are summarized in Table 1.[19] Obviously, the

Table 1. Atomic Refraction [R] and Atomic Dispersion [ΔR][19]

atom, bond	[R]	[ΔR]	atom, bond	[R]	[ΔR]
−H	1.100	0.023	(C)−N=(C)	4.10	0.16
−Cl	5.967	0.107	N−N=(C)	3.46	0.19
(−C=O)−Cl	6.336	0.131	)C(	2.418	0.025
−Br	8.865	0.211	−CH₂−	4.711	0.072
−I	13.900	0.482	−CN	5.415	0.083
−O− (H)	1.525	0.006	−NC	6.136	0.129
−O−	1.643	0.012	C=C	1.733	0.138
=O	2.211	0.057	C≡C	2.336	0.114
−O−O−	4.035	0.052	5-member ring	0.04	
(C)−S(II)−(C)	7.80	0.22	7-member ring	−0.10	
(C)−S(IV)−(C)	6.98	0.14	8-member ring	−0.47	
(C)−S(VI)−(C)	5.34	−0.02	15-member ring	−0.62	
(O)−N=(C)	3.901	0.167			

introduction of aromatic rings, halogen atoms except for fluorine, and sulfur atoms possessing a high atomic refraction is effective for producing high-n polymers.

Some specified polymers, such as aromatic heterocyclic polymers (1.7−2.0),[20] polythiophene (2.12),[21] and conjugated polymers (2.7),[22] have n values higher than 1.7. However, most of them containing a π-conjugated structure show a low solubility, high optical dispersion, and low optical transmittance in the visible region, restricting their potential for optical applications. Thus, the development of high-n polymers with excellent optical properties is still a challenging topic.

Abbe's number (ν_D), a key parameter of the refractive index dispersion, is also quite important for optical materials used in the visible region. ν_D is given by

$$\nu_D = \frac{n_D - 1}{n_F - n_C} \quad (3)$$

where n_D, n_F, and n_C are the refractive indices of the material at the wavelengths of the sodium D (589.3 nm), hydrogen F (486.1 nm), and hydrogen C (656.3 nm) lines, respectively. ν_D is also defined by eq 4.

$$\nu_D = \frac{6n_D}{(n_D{}^2 + 2)(n_D + 1)} \cdot \frac{[R]}{[\Delta R]} \quad (4)$$

In this equation, ν_D is related to the refractive index (n_D), molar refraction (R), and molar dispersion (ΔR). The higher ν_D means a lower dispersion in the refractive index.[23] There is a general trade-off tendency between the n_D and ν_D values of conventional optical polymers; that is, high-n materials generally lead low-ν values.[22] Thus, the redesign the polymer structures is necessary to meet the requirements for high-n and high-ν values.

The birefringence of a polymer is also an essential parameter and defined as the difference between the in-plane (parallel to the molecular axis, n_{TE}) and out-of-plane (perpendicular to the molecular axis, n_{TM}) refractive index of the polymer. Optical

materials usually require an optically isotropic property; that is, the index of refraction needs to be equal in all directions throughout the polymeric materials. The birefringence is affected by the inherent polymer structures and their processing history and often increased by the combination of components with a high inherent polarizability, rigid-rod morphology, and high orientation.[24] The orientations of the polymer chains during the melt flow in injection-molding, extrusion, or drawing processes also increase the birefringence of the polymer. It is obvious that birefringence cannot be reduced unless polymer molecular chain orientations are perfectly isotropic.

■ SULFUR-CONTAINING POLYIMIDES (PIs)

The n values of a sulfur-containing polymers depend on many factors, such as the sulfur content in the polymer repeating unit, aromatic content, and molecular volume, according to the Lorentz−Lorenz equation.[17] Indeed, high-n polyimides (PIs) containing thioether, sulfone, thianthrene, or thiophene groups in the main chain and high-n poly(arylene sulfide)s for optical application were reported. The PIs are promising materials for optical device applications among the high-n polymers due to their good thermal and physical properties, low dielectric constant, high inherent refractive index, and excellent mechanical properties.[25]

Table 2 summarizes the sulfur-containing PIs with high-n values. Most of them exhibit high-n values in the range of 1.680—1.769 and low birefringence in the range of 0.0048—0.0203. The high-n values are originated from high sulfur content in the monomer repeating unit, high aromatic content, and low molecular volume. Among them, **P12** shows the highest refractive index due to its highest sulfur content and high packing density. Although the sulfur content in the repeating unit is an important factor, the refractive index is also affected by other factors. For example, **P5**, **P13**, and **P14** exhibit relatively low refractive indices due to a lower molar refraction of the sulfonyl and aliphatic groups than the thioether and aromatic groups. **P7** has a higher refractive index than **P4** despite the fact that their sulfur contents are the same. This indicates that the packing density is also an important factor for the n values of polymers. In addition, the flexible thioether or sulfonyl linkages in the PIs endow them with a birefringence (Δn) lower than 0.01. **P6** achieved the lowest Δn value (0.0059) among wholly aromatic PIs, which is attributed to the fluorenyl group that is oriented perpendicular to the polymer main chain. This orientation compensates for the polarizability between the main and side chains.

Optical transparency in PI films is another important properties in optical applications. The significant coloration and low transmittance of aromatic PI films are derived from the intermolecular or intramolecular charge-transfer complexes (CTCs) between the electron-donating diamine moiety and the electron-accepting dianhydride moiety.[36] A cycloaliphatic unit incorporated into the PI backbone would lower polymer−polymer interaction and weaken the intra- and/or intermolecular charge-transfer interactions. In practice, transparent PIs based on dianhydrides with polyalicyclic (cycloaliphatic) units and aromatic diamines have been reported.[37] While the wholly aromatic PIs **P2−P12** show a deep absorbance in the wavelength region of less than 450 nm (transmittances at 400 nm <10%), the semi-alicyclic polyimides **P13−P15** are totally transparent in the visible region (transmittances at 400 nm >90%). However, these alicyclic moieties tend to decrease the refractive indices of the PIs as already described. The

Table 2. High-*n* PIs

Polyimides	S(%)[a]	n_{av}	Δn	ref.
P1	0	1.695	0.078	26
P2	11	1.728	0.0119	26
P3	19.2	1.746	0.0081	27
P4	20.5	1.748	0.0068	27
P5	19.8	1.733	0.0077	7
P6	15.0	1.726	0.0059	28
P7	20.5	1.758	0.0084	29
P8	23.2	1.760	0.0084	30
P9	23.0	1.752	0.0074	31
P10	30.1	1.768	0.0072	31
P11	18.1	1.759	0.0081	32
P12	28.5	1.769	0.0093	33
P13	15.5	1.680	0.0048	34
P14	16.2	1.695	0.0203	34
P15	22.8	1.711	0.0036	35

[a]Sulfur content. [b]Average refractive index at 633 nm. [c]Birefringence.
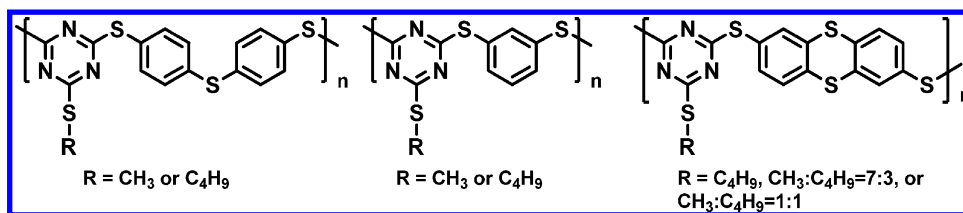
Figure 1. Structures of triazine-containing poly(phenylene sulfide).

breakthrough of a trade-off between the refractive index and transparency is therefore a challenging topic.

POLY(ARYLENE SULFIDE)S

Poly(arylene sulfide)s represented by poly(p-phenylene sulfide) (PPS), poly(arylene sulfide sulfone)s, and poly(arylene ether sulfide)s are good candidates for optical applications. They mainly consist of phenylene and sulfide linkages, providing high-n materials with good mechanical properties and high thermal stabilities.

Takata and co-workers recently reported the fluorene-based polymers containing thioether and heteroaromatic groups.[38,39] They exhibited high-n values in the range of 1.66−1.72, low birefringence, and high thermal stability, while maintaining a high optical transmittance in the visible region. Knauss et al. also reported the synthesis of high-n poly(thianthrene phenylene sulfide) by nucleophilic aromatic substitution polymerization.[40] Although the polymer exhibited a high optical transparency and excellent thermal stability, the n value was not high enough for optical applications. Moreover, the low solubility of the polymer in organic solvents would potentially limit the facile process for optical device applications. Heteroaromatic rings containing −C=N−C− bonds are other candidates to enhance the n values of polymers. As shown in Table 1, the −C=N−C− bond possesses a relatively high molar refraction (4.10) as compared to the −C=C− bond (1.733). Ueda et al. reported that the triazine-containing PPSs improve the solubility by the aid of alkyl side chains.[41,42] The solubility of the polymer was successfully controlled by changing the structure of side chain or main chain while they exhibited high-n values up to 1.772. The introduction of both the triazine moiety and a sulfur atom is an effective way to produce PPSs with high-n values and high transparency in the visible region (Figure 1).

HALOGEN-CONTAINING HIGH REFRACTIVE INDEX POLYMERS

The n values of polymers are increased by introducing highly polarizable atoms or groups according to the Lorentz−Lorenz equation. The heavier atoms than the common atoms (C, H, O, or N) generally show a higher polarizability, leading a great potential to enhance the refractive index of polymers. Actually, many kinds of high-n polymers containing various elements have been reported. Halogen elements, especially bromine and iodine, were the earliest utilized components for designing high-n materials. An array of polymethacrylates containing lateral brominated and iodinated carbazole rings have been reported (Figure 2).[43]

The n values of the polymers vary from 1.67 to 1.77 depending on the number of halogen substituents, components, and the length of the methylene spacers. However, halogenated compounds are usually unstable toward light or other conditions. The WEEE Directive and RoHS legislation

Figure 2. Chemical structure and refractive index values of halogen-substituted polymethacrylates.[43]

regulated by the European Union limits the application of halogen elements in microelectronic devices due to their potential pollution of the environment.[44]

PHOSPHORUS-CONTAINING HIGH REFRACTIVE INDEX POLYMERS

Polyphosphazene and polyphosphonate comprised of phosphorus atoms have been employed for high-n and transparent polymers derived from the high atomic polarizabiliy of the phosphorus atom. First, polyphosphazenes possess an inorganic −P=N− main chain and lead high-n materials due to their increased electron density compared to saturated carbon backbone polymers.

Early studies for high-n polyphosphazenes include the ones with different side groups as reported by Allcock et al.[45−47] Most of the polymers exhibited high-n values in the range of 1.664−1.755 with a good optical transparency. Moreover, the n value is controllable by varying the side groups as shown in Table 3.
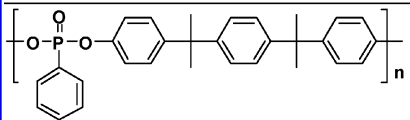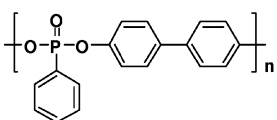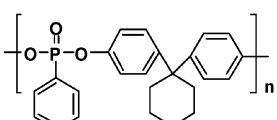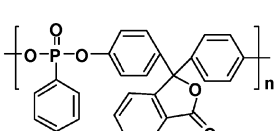
Table 3. Average Refractive Index and T_g Values of Polyhosphazenes[45−47]

polymer	n_{av}[a]	T_g (°C)[b]
	1.750-1.755	90.3
	1.682-1.684	64.8
	1.664-1.666	111.4

[a]Average refractive index at 550 nm. [b]Glass transition temperature.

Polyphosphonates, which have chemical structures similar to polycarbonates, have high-n values and melt processability. These polymers are useful for optical and particularly ophthalmic applications. A series of polyphosphonates with high-n values and optical transparency were reported by McGrath et al.[48] They also reported melt-processable polyphosphonates which have high-n and suitable T_g values as shown in Table 4.[49]

Table 4. Average Refractive Index and T_g Values of Polyphosphonates[48,49]

Polymers	$n_{av}{}^{a}$	T_g (°C)^b
	1.60	124
	1.639	145
	1.606	130
	1.623	186

^{a}Average refractive index at 550 nm. ^{b}Glass transition temperature.

POLYPHENYLQUINOXALINES

Yang et al. reported high-n polyphenylquinoxalines (PPQs) (Figure 3).[50,51] PPQs are represented as a class of high
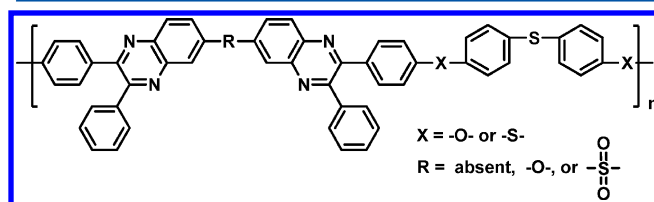

Figure 3. Chemical structure of PPQs.

performance heteroaromatic polymers, characterized by their low moisture absorption, high hydrolytic and thermal stabilities, and good mechanical properties. From the viewpoint of the chemical structure characteristics, PPQs possess a high content of aromatic components with high molar refractions. Actually, the PPQs exhibited high-n values in range of 1.728–1.795 at 633 nm and high thermal stabilities.[50,51] However, the transparency of the films was not very high in the visible region, i.e., transmittances of 56–86% at 450 nm and 0% at 400 nm, and it might also induce an unexpected increase in n values due to anomalous dispersion.
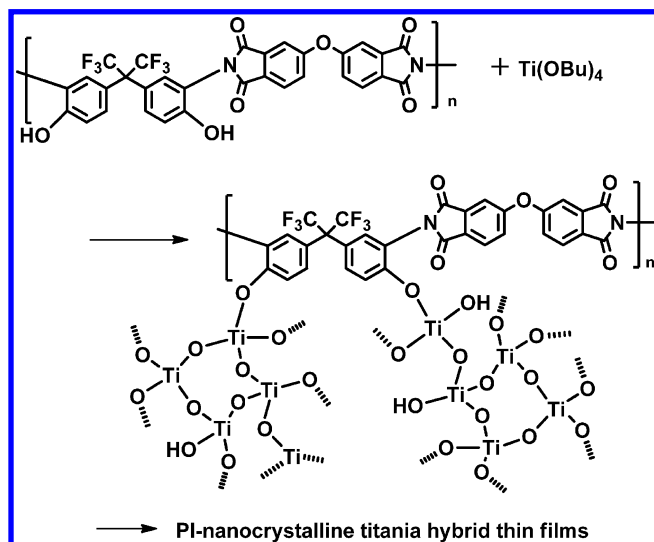
POLYMER–INORGANIC HYBRID MATERIALS

Recently, much attention has been paid to polymer–inorganic hybrid materials because they have enhanced mechanical, thermal, magnetic, optical, electronic, and optoelectronic properties when compared to the corresponding individual polymer or inorganic component.[52–59] The relatively narrow range of available n values of polymers often limits the range of optical applications. A hybrid combining an organic polymer matrix and high-n inorganic nanoparticles could achieve much higher n values. The n values of nanocomposites can be approximately estimated by the equation $n_{comp} = \phi_p n_p + \phi_{org} n_{org}$,[60,61] where n_{comp}, n_p, and n_{org} are the refractive indices of the nanocomposite, nanoparticle, and organic matrix, respectively. ϕ_p and ϕ_{org} are the volume fractions of the nanoparticles and organic matrix, respectively. From the equation, when targeting a definite n_{comp} value with a definite type of nanoparticle, the higher the value of n_{org}, the lower the value of ϕ_p. This is important for the design of high-n nanocomposites for optical applications because overloading nanoparticles often lowers transparency and decreases the processability of the organic matrix.[62]

The most commonly used nanoparticles for high-n polymers include TiO$_2$ (anatase, $n = 2.45$, rutile, $n = 2.70$),[63] ZrO$_2$ ($n = 2.10$),[64] amorphous silicon ($n = 4.23$), PbS ($n = 4.20$),[65] and ZnS ($n = 2.36$).[66] The intensity loss of transmitted light due to Rayleigh scattering should be avoided to develop transparent high-n composites. Thus, the size of the inorganic particles with high-n values should be reduced to less than 40 nm (one-tenth of the wavelength of visible light).[63] The processing in the preparation of nanocomposites is also important. For example, the direct mixing of nanoparticles with the polymer matrix induces the aggregation of nanoparticles. To prevent such aggregation, the surface of nanoparticles is generally modified. Recently, Ueda et al. reported an optically transparent sulfur-containing PI–TiO$_2$ nanocomposite films containing 45 wt % silica-modified anatase-type TiO$_2$ nanoparticles with a refractive index of 1.81 at 632.8 nm.[34]
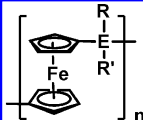
To control the size of titania domains, the combination of *in situ* sol–gel processing with a polymer matrix has been employed. Chen et al. reported a series of high-n PI–nanocrystalline titania hybrid optical materials by the sol–gel process. A soluble PI with carboxylic acid end groups (6FDA-6FpDA-COOH) was prepared from 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 4,4′-(hexafluoroisopropylidene)dianiline (6FpDA), and 4-amino-benzoic acid (4ABA), as shown in Scheme 1.

An esterification reaction undergoes between the carboxylic acid end groups and titanium butoxide [Ti(OBu)$_4$], generating organic–inorganic bonds. The spin-coated hybrid films had a relatively good surface planarity, high thermal stability, tunable n values ($1.571 < n < 1.993$), and optical transparency in the visible range.[67] PI–nanocrystalline titania hybrid optical films have been prepared with a relatively high titania content (up to 50 wt %) and thickness (20–30 μm) from soluble polyimides containing hydroxyl groups and titanium butoxide (Ti-(OBu)$_4$).[68,69] The sol–gel method is very useful for preparing high-n nanocomposites with a well-controlled morphology in the phase separation. Therefore, particle sizes less than a few nanometers can easily be controlled in the derived gels. In addition, the dimensions can also be maintained when subsequently crystallized at elevated temperatures (Scheme 2).

Scheme 1. Preparation of High-*n* PI−Nanocrystalline Titania Hybrid Thin Films by Using COOH-End-Functionalized PI
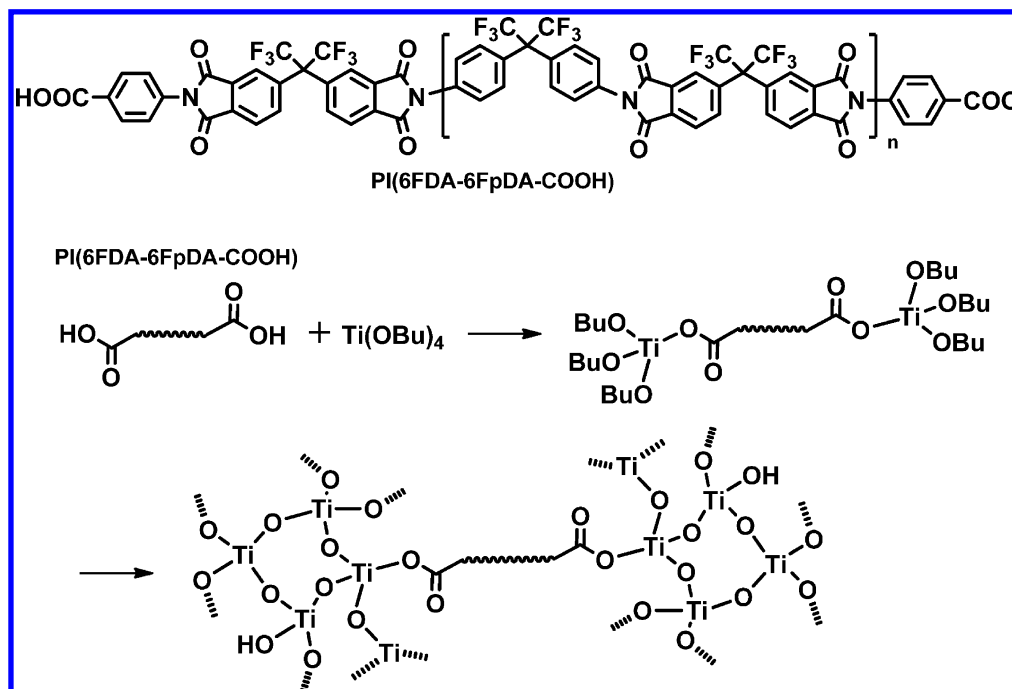
Scheme 2. Preparation of High-*n* PI−Nanocrystalline Titania Hybrid Thin Films by Using OH-Functionalized PI

E	R	R'	n_{589}
Si	CH$_3$	CH$_2$CH$_2$CF$_3$	1.60
Si	CH$_3$	CH$_2$CH$_3$	1.66
Si	CH$_3$	CH$_3$	1.68
Si	CH$_3$	C$_6$H$_5$	1.68
Ge	CH$_3$	CH$_3$	1.69
Sn	^{t}butyl	^{t}butyl	1.64
Sn	mesityl	mesityl	1.69
Sn	naphthyl	naphthyl	1.82
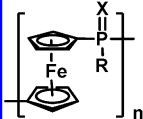
R	X	n_{589}
C$_6$H$_5$	absent	1.74
C$_6$H$_5$	S	1.72

Figure 4. Refractive index determined at λ = 589 nm for polyferrocenes.[62]

ORGANOMETALLIC HIGH-*n* POLYMERS

As described above, the incorporation of inorganic clusters into a polymer matrix is useful to produce high-*n* polymers. However, the issue still remains in the tendency of heterogeneous structures which induces a high optical loss and poor processability. To address this issue, the incorporation of metals into polymers is an effective way for developing high-*n* polymers without significantly increasing the optical dispersion. Manners et al. reported the preparation of an exceptionally high-*n* polyferrocenes with a relatively low optical dispersion (ν_D = 25−30) and showed that the *n* values are tunable by changing substituent groups and the spacer elements (Figure 4).[62]

Indeed, polyferrocenylphosphines and polyferrocenylphosphine sulfides exhibited high-*n* values (*n* = 1.74 and *n* = 1.72, respectively). Tang et al. developed the preparation of a cobalt-metallized, triphenylamine-cored hyperbranched polydiyne by metallization of poly[tris(4-ethynylphenyl)amine], which showed the *n* values as high as 1.713−1.813 in the long wavelength region (600−1700 nm) (Scheme 3).[70] This conjugated polymer absorbed light in the visible region, showing higher *n* values in the shorter wavelength regions. Interestingly, the *n* values could largely be tuned up to 0.048 by UV irradiation. The UV-cured polymer films exhibited a high ν_D (ν_D = 35.5) in the near-IR region.

Quite recently, Stiegman et al. reported a series of bulk inorganic/organic hybrid polymers prepared by the thiol−ene coupling reaction between tri- or tetravinyl monomers containing metals and alkyl or aryl dithiols (Figure 5).[71] These polymers exhibited high-*n* values in the range of 1.590−

Scheme 3. Synthesis of Cobalt-Containing Polymer via Metallization of Hyperbranched Polymer

Figure 6. Schematic of a display (e.g., LCD) with protective and RI-control polymer overlayer films.

1.703 and Abbe's numbers in the range of 24.3−45. All of the polymers were highly transparent over the UV−vis region of the spectrum.

APPLICATIONS OF HIGH-*n* POLYMERS

Antirefractive (AR) Coating. AR coatings have a key technology to reduce the reflection loss at the surface of an optical component and obtain a clear view through the glazing by increasing the light transmittance and avoiding negative effects on the visual observation such as a double image and reflection of the light sources.[72] Polymeric-based optical materials have the potential to be excellent alternatives to traditional inorganic optical films due to their lightweight, high mechanical strength, environmental stability, insensitivity to vibrational stress, low cost, and facile processing. Thus, polymers with high-*n* values and high optical clarity are widely used as AR coatings for photovoltaics, buildings, displays, and opthalmics.[73]

AR coatings for liquid crystal display (LCD) are a typical application that uses polymeric refractive index-control technology as shown in Figure 6. Indeed, the films showing a wide range of *n* values (*n* = 1.3−2.2) and with a thickness of few hundred nanometers are usually required. PET (polyethylene terephthalate) or TAC (triacetyl cellulose) films are usually employed for the protection of the outer layers in modern multilayer LCD stacks. PET and TAC are low-cost and tough polymers with *n* ∼ 1.7 much higher than for air (*n* = 1). Thus, most of the light beam incident on an interface with the large difference of *n* ∼ 0.7 would reflect the interface, which means that a significant fraction of ambient light reflects from
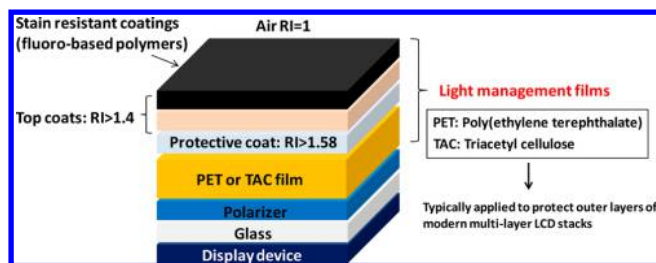
the display surface, causing glare and disappearance of the displayed images for a LCD. To remedy this problem, a multilayer film stack with a gradually varying refractive index can be used to the LCD surface. The stack consists of multiple layers with gradually diminishing refractive index from high adjacent to the PET/TAC surface to low facing air. By this method, the surface reflection is dramatically reduced, leading to a clear image contrast and decreasing the washout by ambient reflections. Recently, Chen and co-workers developed polyimide−titania nanocrystalline nanocomposites for high-*n* layers to fabricate multilayer AR coatings on BK7 optical glass with an *n* value of 1.58.[67] The AR coating was prepared using nanocomposites of poly(methylsilsesquioxane) (PMSSQ, *n* = 1.379) and titania (titania contents: 90 wt % (*n* = 1.943) and 30
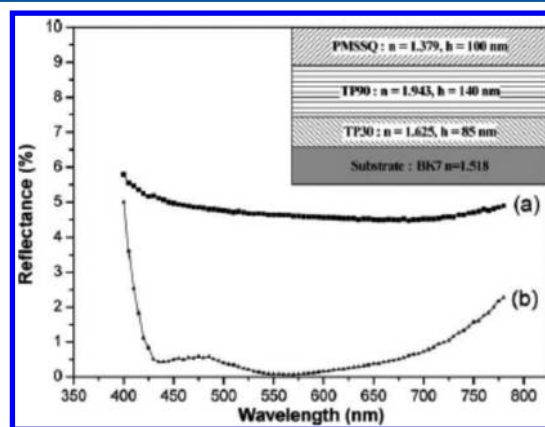

Figure 7. Variation of the reflectance with wavelength: (a) BK7 optical glass and (b) the three-layer antireflection coating. The inset figure shows the structure of the three-layer antireflection coating. Reproduced with permission from ref 67. Copyright 2008 Royal Society of Chemistry.
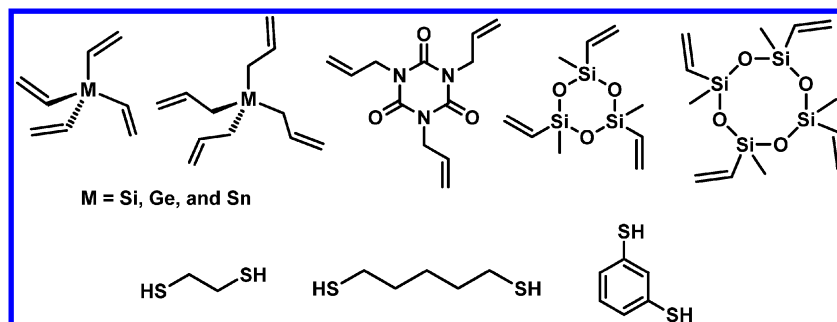

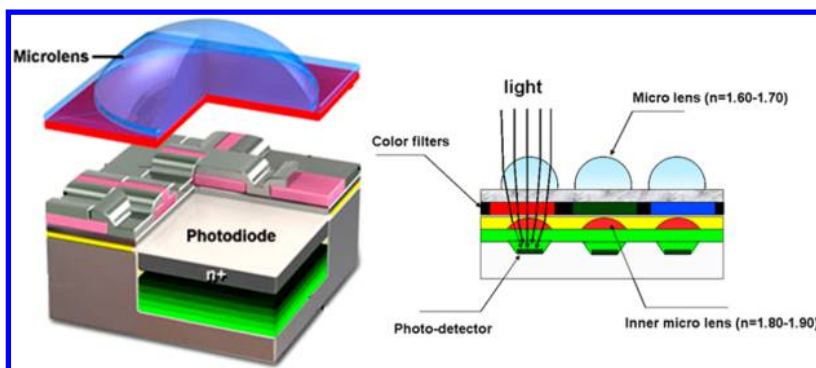**Figure 5.** Chemical structures of vinyl and thiol monomers.

Figure 8. Microlens array in CMOS image sensor device. Reproduced from URL: http://www.olympusmicro.com/primer/digitalimaging/cmosimagesensors.html.

wt % (n = 1.625)) (Figure 7). To reduce the reflection by adjusting the phase of light, the optical thickness (physical thickness × refractive index) was designed to be $0.25l_0$, $0.5l_0$, and $0.25l_0$ (l_0 = 550 nm) for the three-layered structure. An average reflection of less than 0.5% in the visible range was obtained, which was significantly lower than that of 5% for BK7.

A three-layered AR coating was also reported based on the hybrid films, prepared from colloid SiO_2 (n = 1.29), a titania content of 50 wt % (6TP50: n = 1.86), and 10 wt % (6TP10: n = 1.71) for the first, second, and third layers, respectively, and revealed a reflectance of less than 0.7% in the visible range. This report shows potential optical applications of a film with a tunable refractive index.[69]

Microlens for CMOS Image Sensor (CIS). A complementary metal−oxide−semiconductor (CMOS) image sensor is a device which converts an optical image into an electrical signal. Figure 8 shows the pixel in a CMOS image sensor consisting of microlens, color filter, and photodiode. The pixel sizes have been steadily decreased from more than 10 μm to less than 1 μm within a decade. Recently, the increasing densities of assembly to decrease the size of devices are very crucial in CMOS image sensors in which a microlens is employed to collect the light. The analogue image is collected by the lenses, and a photodiode converts this image to a digital one. Several millions of microlenses are placed under the camera lens of smartphones and digital cameras.

The polymeric materials for microlenses have received much attention due to their simple fabrication process, low cost, and flexibility. To fabricate such film with a thickness of few micrometers, high-n polymers with n > 1.8 are desired. Many high-n photosensitive coatings have been reported using hybrid techniques. Recently, Ueda et al. reported a high-n PI and titania (TiO_2) nanocomposite with a n value greater than 1.80.[34] The good photolithographic characteristics were realized based on the photoresist system using poly(amic acid), silica-modified TiO_2 nanoparticles, and a photobase generator (Scheme 4). The scanning electron microscopy (SEM) shows monophase morphology of the nanocomposite membrane and the photolithographic PI pattern (Figure 9).

A positive-tone photosensitive PI (PSPI) coating for the lens layer in a CMOS image sensor was also reported by Tomikawa et al.[13] The PSPI is characterized by its high-n (1.80 at 633 nm), good optical transparency in the visible region (>85% at 400−700 nm), and high sensitivity to i-line (365 nm).

An inner lens may be replaced by a waveguide to shorten the light path and preventing an undesirable crosstalk effect

Scheme 4. Photoresist System Based on Poly(amic acid), Silica-Modified TiO_2 Nanoparticles, and a Photobase Generator
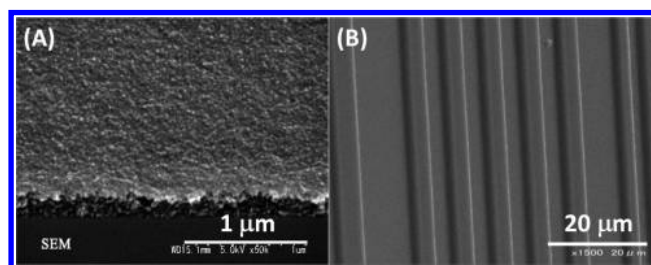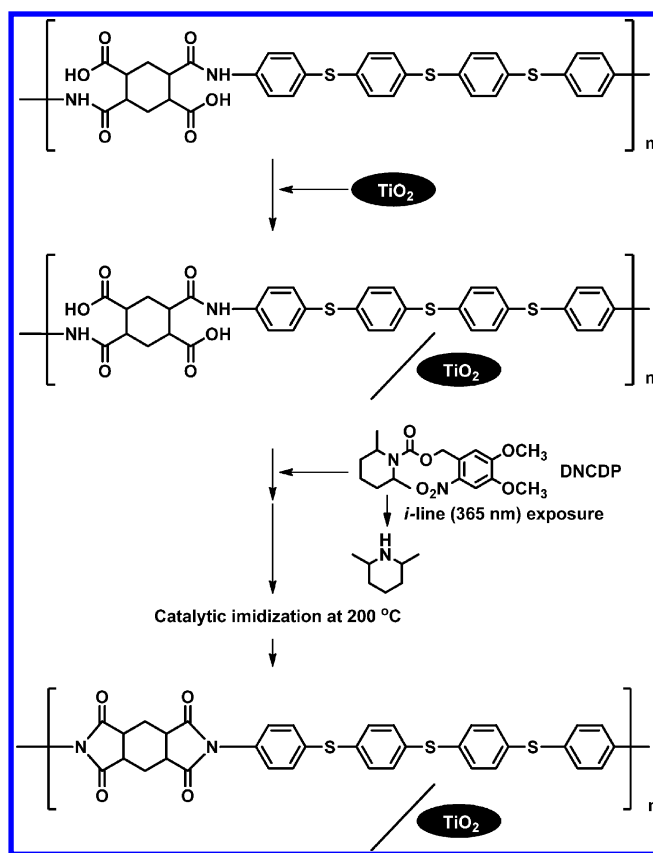

Figure 9. SEM images of (A) PI−TiO_2 (55:45 w/w) nanocomposite film and (B) negative photosensitive PI pattern (film thickness: 1.0 μm). Reproduced after modification with permission from ref 34.
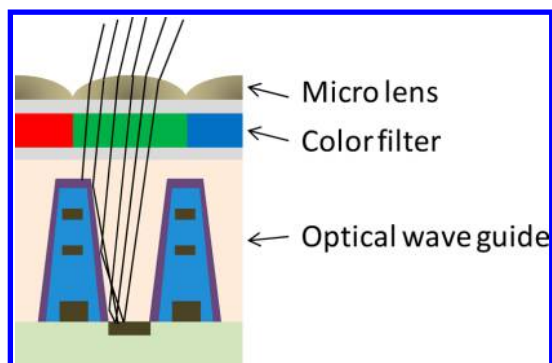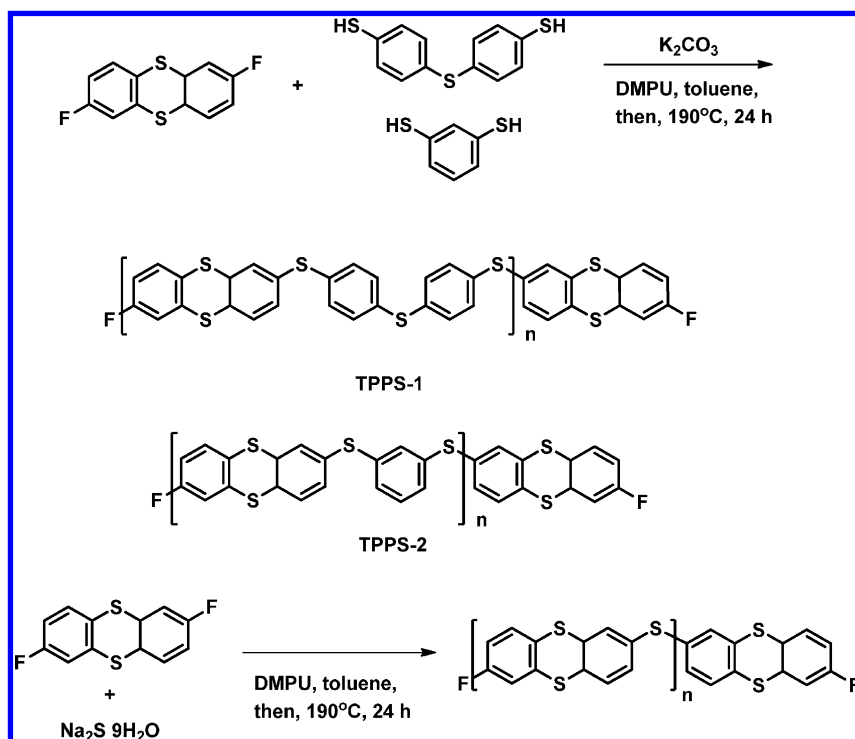
Figure 10. CMOS image sensors with optical waveguides.

between different optical devices (Figure 10). The fabrication of the optical waveguide is much easier than that of a microlens array, in which a photosensitivity is no longer necessary for the high-n materials. However, a very high-n exceeding 1.8 as well as a good transparency and high thermal stability are desired for the materials.[74] Quite recently, Ueda and co-workers reported the synthesis of thianthrene-based poly(phenylene sulfide)s (TPPS) with high-n values reaching 1.8.[75] TPPSs have been prepared from 2,7-difluorothianthrene and dithiols, including 4,4-thiobisbenzenethiol, m-benzenethiol, or sodium sulfide nonahydrate by the aromatic nucleophilic substitution reaction. They showed excellent thermal stabilities, such as relatively high glass transition temperatures in the range of 143−147 °C, 5 wt % weight-loss temperatures over 430 °C, a high transparency in the visible region, and low birefringence in the range of 0.0037−0.0039. An n value exceeding 1.8 is in the highest class among the polymeric materials without nano-composites (Scheme 5).

■ ENCAPSULANTS FOR LED

Light-emitting diodes (LEDs) based on GaN semiconductors are expected to replace traditional incandescent and fluorescent lighting, achieving a lower cost per lumen. However, it is still difficult to commercialize high-brightness LEDs (HBLEDs). The technical problems exist in the relatively low light extraction efficiency (LEE) of the HBLEDs, mainly caused by the mismatch of the n values between the inorganic LED dies (GaN, $n = 2.5$) and the organic encapsulants (epoxy or silicone, $n \sim 1.5$). Figure 11 shows the relationship between the escape

Figure 11. Escape cone of an LED without and with encapsulation (a) and light extraction efficiency ratio for GaN and GaP as a function of the encapsulant refractive index. Reproduced with permission from ref 76. Copyright 2008 American Institute of Physics.
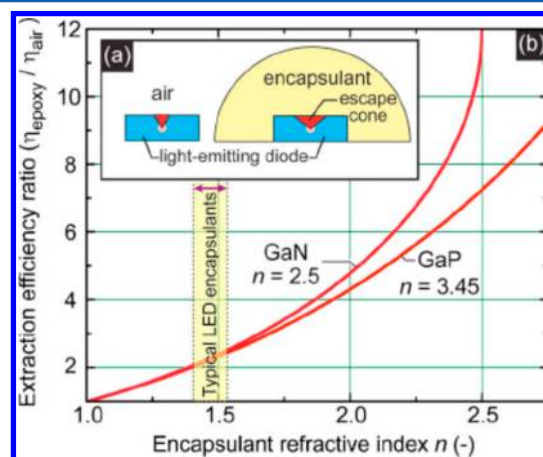
cone of an LED without and with encapsulation and the light-extraction efficiency ratio for GaN and GaP as a function of the n value of encapsulant.[76] The angle of the light escape cone for

Scheme 5. Synthesis of TPPS

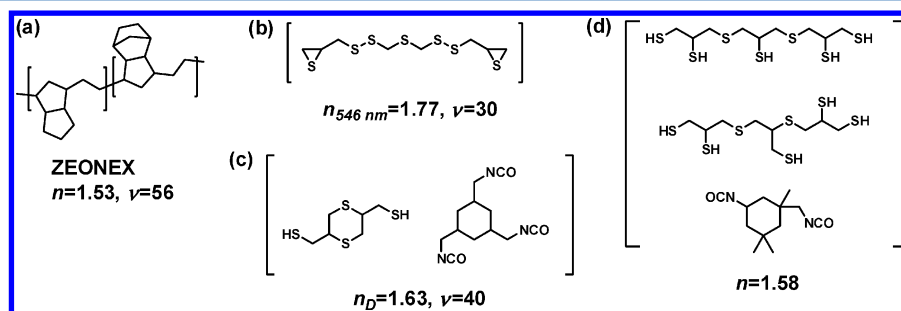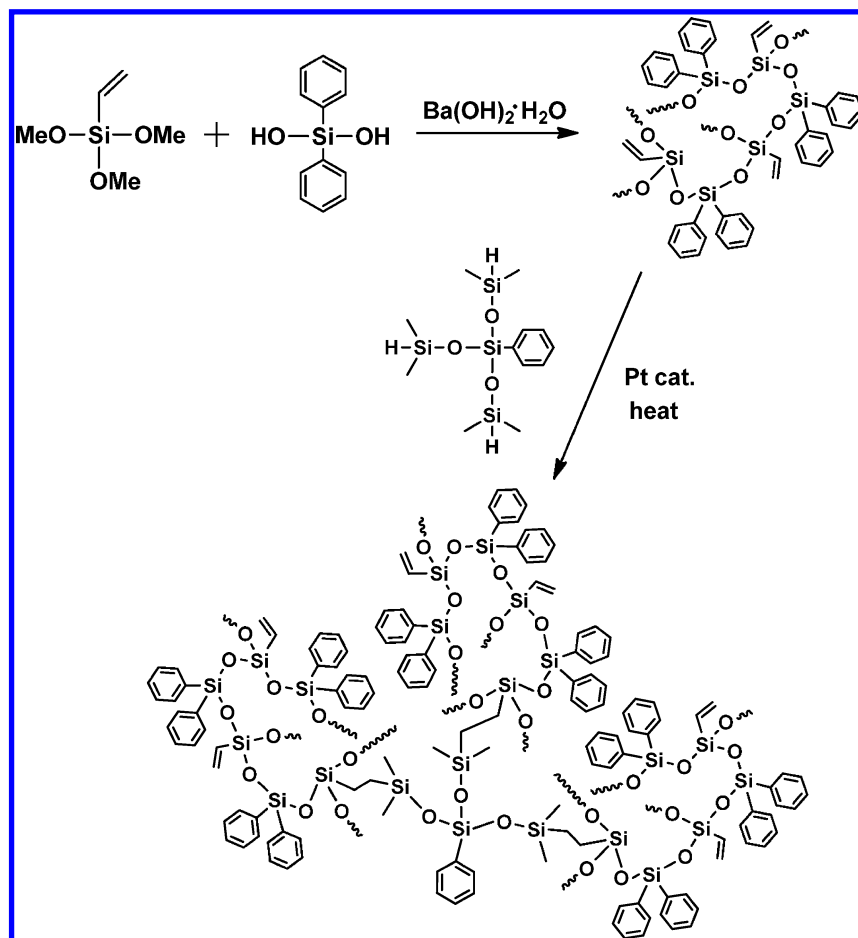**Scheme 6. Synthesis of Phenyl Hybrimer**

Figure 12. Chemical structure and refractive index values of (a) ZEONEX developed by Nihon Zeon, (b) episulfide,[3] (c) polyisocyanates,[5] and (d) polythiols.[4]

the semiconductor—air interface is very small due to the high-n contrast. On the other hand, encapsulants, represented by silicone and epoxy, reduce the refractive index contrast, resulting in a larger light escape cone as shown in Figure 11. Furthermore, as the n value of the encapsulant increases, the calculated LEE rapidly increases (Figure 11b), which motivates the development of encapsulants with higher n values ($n > 1.6$) with a thickness of few millimeters compared to typical silicones or epoxies. The surfactant-coated TiO$_2$-nanoparticle-loaded epoxy encapsulant was reported by Mont et al., which had an n value of 1.67 at 500 nm, significantly higher than that of a conventional epoxy ($n = 1.53$). Theoretical light-extraction enhancements greater than 50% were achieved.[77]

Chau et al. reported a nanocomposite from epoxy and acetic acid-modified TiO$_2$ nanoparticles. The modified TiO$_2$ nano-

particles were easily incorporated into the epoxy matrix without aggregation of particles. The n value range of the transparent hybrid films is 2.18—2.38, making them good candidates for LED encapsulation.[78] Zhou et al. reported a one-component high-n epoxy encapsulant for LEDs via a low-temperature and fast cure processing.[79] It displayed an n value of 1.60 and good optical transparency. Epoxy-based polymers for an LED encapsulant provided stable light emission at the junction temperatures up to 120 °C. However, in some recent LEDs, the device reliability and lifetime are more required even at over 150 °C.[80] To meet such requirements, a transparent and thermally stable phenyl hybrimer with a high-n value ($n = 1.56$) was developed for LED encapsulation through siloxane networks by a hydrosilylation reaction with a cross-linker and Pt catalyst.[81] In particular, it has a good thermal stability against

coloration after aging even at 200 °C, inducing long lifetime of a LED encapsulant (Scheme 6).

Quite recently, phenyl-based polysiloxanes with high-*n* values have been reported. Indeed, thermally stable phenoxyphenyl and phenylthiophenyl silicones showed *n* values of 1.60 and 1.62 at 633 nm, respectively.[82] These liquid dispensed encapsulants were highly thermostable, showing little change in their optical properties after heating in air at 200 °C for 7 weeks. In addition, they were also only slightly changed after cycling between 210 and 85 °C for over 6 months.

■ HIGH-*n* THERMOPLASTIC LENSES

Thermosets and thermoplastics with high-*n* and high-*ν* values have attracted significant interest because of their potential

Table 5. High-*n* and High-*ν* Polymers

| Polymer	S(%)[a]	n_{av}[b]	ν_D[c]	ref.
P16	32	1.620	38.5	86
P17	28	1.582	38.6	87
P18	29	1.59	43	88
P19	23	1.59	42.9	15
P20	29	1.61	44.5	15
P21	30	1.62	40.2	15
P22	37	1.64	42.1	15
P23	37	1.631	38.0	91
P24	52	1.686	48.6	16
P25	64	1.7800	-	94

[a]Sulfur content. [b]Average refractive index measured at 589 nm. [c]Abbe's number.

**Scheme 7. Synthesis of Poly(DSDT-DVS)**
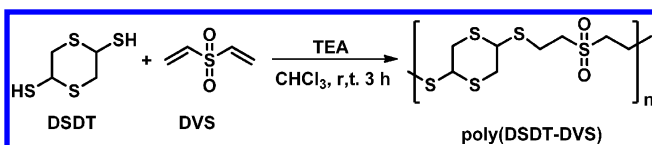
application to many optical materials as described in the Introduction. Thermosets possessing both high-*n* and high-*ν* values have been reported in patents, including poly[ethylene glycol bis(allylcarbonate)] (CR-39)[83] and resins prepared from
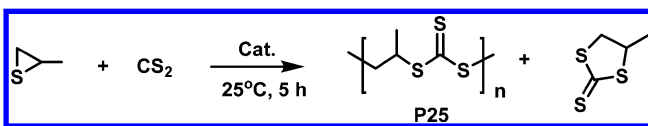
Scheme 8. Synthesis of Poly(BMMD-DVS) and Poly(BMMD-BVSM)
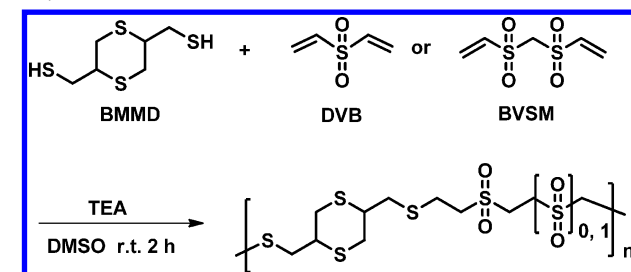
Scheme 9. Synthesis of Copoly(BMMD-CHDA-DVB)
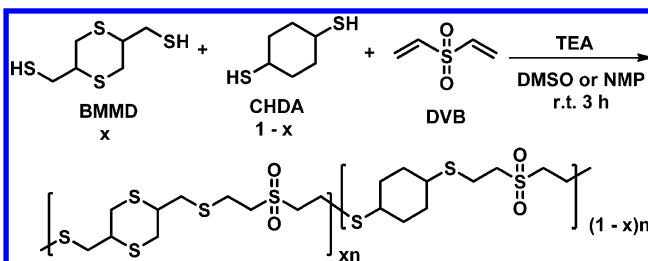
Scheme 10. Synthesis of Polytrithiocarbonate

episulfides,[3] polythiols,[4] and polyisocyanates.[5] Other optical polymers could be synthesized by the radical polymerization of 2,5-bis(2-thia-3-butenyl)-1,4-dithiane and the polyaddition of oligo[2,5-bis(thiomethyl)-1,4-dithiane] and di- or triisocyanates[84] and episulfide-type copolymers[85] (Figure 12). On the other hand, only a few examples of thermoplastics with high-*n* and high-*ν* values have been investigated in detail. The higher *ν* values correspond to a lower dispersion of the refractive index.[23] In general, there is a trade-off relationship between *n* and *ν* values; that is, the higher *n*, the lower *ν*.[22] Early studies of high-*n* polymers with high-*ν* values have been reported by Okubo et al. and Matsuda et al. (Table 5). Actually, sulfur-containing polymers, such as poly(thiourethane)s[86] (**P16**) and poly(thiomethacrylate)s[87] (**P17**), were reported. All of the polymers exhibited *n* values (1.570−1.678) and *ν* values (31.0−38.5). In addition, sulfur-containing poly(methacrylate)s were reported in a patent (**P18**).[88]

Recently, Ueda and co-workers developed new series of polymers containing alicyclic and sulfone units as well as a sulfur atom in order to improve the *n* and *ν* values at the same time as shown in Table 5.[15] These (metha)acrylates having sulfur-containing alicyclic structures, such as 2-[2-{exo-3,5-dithiatricyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl}-ethyloxycabamoyl]ethyl methacrylate (**P19**), 2-{exo-3,5-dithiatricyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl}ethyl methacrylate (**P20**), 2-{exo-3,5-dithiatricyclo-[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl}ethyl acrylate (**P21**), and 2-{exo-3,5-dithiatricyclo-[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl}ethyl thiomethacrylate (**P22**), exhibited high transparencies (<400 nm), high-*n* values in the range of 1.592−1.640 (at 589 nm), and high-*ν* values in the range of 40.2−44.5.

To obtain high-*ν* polymers, an alicyclic group was focused on, which is also known to show a *n* value higher than an

Scheme 11. Synthesis of Poly(TCDSH-DVS) and Poly(BSMD-VSTCD)
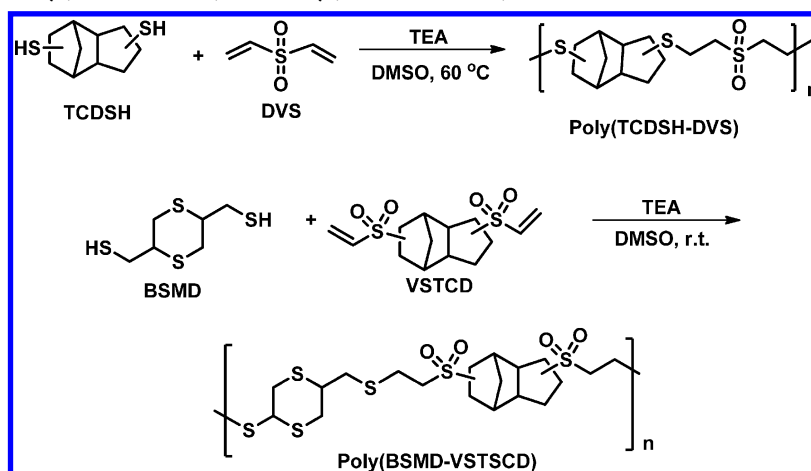
aliphatic moiety,[89,90] and a sulfonyl ($-SO_2-$) group, leading to a high transparency and a low refractive index dispersion due to its very low molecular dispersion. Thus, polymers with a high sulfur content show a high-n and a relatively low-ν values (<40), due to a high atomic refraction ([R] = 7.80) and high atomic dispersion ([ΔR] = 0.22) of the sulfide unit. Whereas, a sulfone has a low [ΔR] of 0.07 for [R] of 9.76, and thus the PES containing both sulfide and sulfone groups exhibits high-n and high-ν values. These consideration prompted a promising design concept of the introduction of sulfur, sulfonyl, and alicyclic units at the same time for producing a high-n and high-ν polymer. Indeed, poly(thioether sulfone) (**P24**) with a high n value of 1.686 at 589 nm and a high ν_D value of 48.6 among the thermoplastics poly(DSDT-DVS) could be prepared by the Michael polyaddition of 2,5-disulfanyl-1,4-dithiane (DSDT) with divinyl sulfone (DVS) (Scheme 7).[16] The transparent, tough, flexible, and amorphous poly(DSDT-DVS) film exhibited a good thermal stability with a 5% weight loss temperature of 275 °C in nitrogen. Unfortunately, poly(DSDT-DVS) gets colored above 150 °C in air, which is probably due to the presence of thermally unstable thioacetal units.

Novel two thermoplastic poly(thioether sulfone)s (PESs) with high-n and high-ν values were prepared by the Michael polyaddition of 2,5-bis(sulfanylmethyl)-1,4-dithiane (BMMD) with divinyl sulfone (DVS) or bis(vinylsulfonyl)methane (BVSM) (Scheme 8).[92] Poly(BMMD-DVS) and poly-(BMMD-BVSM) exhibited high n values of 1.6512 and 1.6461 and high ν values of 42.6 and 43.1, respectively, as thermoplastics. The coloration of the resulting polymers did not occur even at 200 °C due to the absence of thioacetal units.

Only one remaining issue of poly(BMMD-DVS) is its semicrystalline nature which may raise another problem in optical device applications, although the crystallization is sluggish during a normal cooling process. The random copolymerization generally results in amorphous formation of polymers by disturbing the structural symmetry. Thus, cyclohexane-1,4-dithiol (CHDT) with a high sulfur content (43.25 wt %) and alicyclic units was chosen as a comonomer. Novel poly(thioether sulfone)s were synthesized by the copolymerization of BMMD, CHDT, and DVS (Scheme 9). These polymers exhibited high-n values in the range of 1.6512−1.6022 (at 589 nm), high-ν_D values in the range of 42.6−50.6, a high optical transparency (>400 nm), and perfectly amorphous nature (BMMD <80 mol % to CHDT).[93]

Nakano et al. reported the synthesis of sulfur-rich polymer, polytrithiocarbonate (**P25**), by the copolymerization of episulfide with carbon disulfide as shown in Scheme 10. **P25** possesses a high molecular weight and an n value of 1.7800 at 589 nm; however, it shows a low thermal decomposition temperature around 200 °C and low glass transition temperature of 25 °C.[94]

As described above, PESs are the highest class of thermoplastics with high-n and high-ν values. However, their T_g values were typically low and must be improved to over 100 °C for practical lens applications. The flexible sulfide linkages and alkyl chain in the main chain may cause the low T_g values. One of the most promising strategies to increase the T_g of polymers is the introduction of rigid structures such as polycyclic hydrocarbons.[95]

Thermoplastic poly(thioether sulfone)s, poly(TCDSH/DVS) and poly(BSMD/VSTCD), with high-n and high-ν values have been developed using specially designed monomers, disulfanyltricyclo[5.2.1.0^{2,6}]decane (TCDSH) and bis-(vinylsulfone)tricyclo[5.2.1.0^{2,6}]decane (VSTCD) having the tricyclo[5.2.1.0^{2,6}]decane moiety (Scheme 11). TCDSH and VSTCD could be polymerized with divinyl sulfone (DVS) or 2,5-bis(sulfanylmethyl)-1,4-dithiane (BSMD) to afford corresponding polymers (M_n = 19 300 and 28 400).[96] The transparent, flexible, and amorphous films of poly(TCDSH/DVS) and poly(BSMD/VSTCD) were successfully obtained. They showed a good thermal stability ($T_{d,5\%} \sim 300$ °C) in nitrogen, the T_g values of 74 and 113 °C, high-n values of 1.6052 and 1.6228, and high-ν values of 48.0 and 45.8, respectively. Poly(TCDSH/DVS) and poly(BMMD/VSTCD) with highly balanced thermal and optical properties are promising candidates especially for applications of lens materials.

■ SUMMARY AND OUTLOOK

In this Perspective, the recent progress of high-n polymers over the past decade has been introduced, focusing on the practical strategy to increase the n values of polymers and applications of HRIPs. Significant advancements have been achieved in the development of high-n polymers with a high-ν value and low birefringence. For practical applications, many other properties such as a high transparency, thermal and mechanical properties, the long-term photostability and oxidative stability must be satisfied. To attain these goals, significant efforts are essential.

Advances in optoelectronic technologies have also produced specific applications of high-n polymers. For example, the method for correcting the chromatic aberration of an optical system is based on the combination of glass materials having different dispersion properties, that is, a positive lens with a high-ν and a negative lens having a low ν. However, the range of the optical constant of a usable polymeric lens is limited. Thus, polymers with a higher n values around 1.7, low orientation birefringence Δn (less than 1.0×10^{-3}), and low ν_D (20−30) are required.[97] To reduce the Δn value, the polarizability between the main and side chains should cancel each other. Another application of high-n polymers is a transparent insulating material with a high-n value, which reduces the refraction at the interface between the ITO or SiNx and an insulating layer and enhances the brightness from the backlight of a liquid crystal display. Thus, high-n polymers with very similar n values to those of ITO ($n \sim 2.0$) and SiNx ($n \sim 1.9$) should be developed. The application fields for high-n polymers keep expanding, and property requirements become stricter day by day. Thus, a significant amount of basic and applied researches on high-n polymers should be performed to reveal the fundamental details regarding the molecular design and basic properties and to improve the performance of these materials in terms of their optical properties and long-term stability, such as photostability and oxidative stability.

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Notes

The authors declare no competing financial interest.

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Tomoya Higashihara was born in Kagawa, Japan, and received his B.S, M.S, and Ph.D. degrees from Tokyo Institute of Technology in 2000, 2002, and 2005, respectively, under the supervision of Prof. Akira Hirao. During 2005−2008, he joined postdoctoral researches at University of Massachusetts (UMASS) Lowell, under the supervision of Prof. Rudolf Faust. Then, he returned to the Tokyo Institute of Technology as an Assistant Professor at Prof. Mitsuru Ueda's laboratory in 2008. In 2013, he was promoted to an Associate Professor of Innovative Flex Course for Frontier Organic Material Systems (iFront) at Yamagata University. He published 170 papers/review articles. His research interests include living/controlled polymerization, π-conjugated polymers, polymer solar cells, and high refractive index polymers.

Mitsuru Ueda was born in Fukuoka, Japan, and received his B.S (1970) and M.S (1972) degrees from Chiba University and his Ph.D. (1978) degree from Tokyo Institute of Technology. He joined Yamagata University in 1972 as an assistant professor and was promoted to an associate professor in 1980 and a full professor in 1989. He also joined the University of Alabama during 1977−1978 and IBM Almaden Research Center during 1985−1986. He moved to the Tokyo Institute of Technology in 1999. After the retirement of Tokyo Institute of Technology in 2013, he has become an emeritus professor, a visiting professor at Kanagawa University, a specially appointed professor at Yamagata University, and a distinguished chair professor at National Taiwan University. He published more than 600 papers/review articles. His current research interests are the development of new synthetic methods for condensation polymers, hyperbranched polymers with controlled degree of branch, high refractive index polymers, fuel cell membranes, photosensitive materials for microelectronics, and new advanced resist materials.

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