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# High refractive index polymers: fundamental research and practical applications

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Rapid developments in advanced photonic devices have led to the increasing exploration of high refractive index (high- $n$ ) materials, particularly high-refractive-index polymers (HRIP). High refractive indices have been achieved either by introducing substituents with high molar refractions to make intrinsic HRIPs or by combining high- $n$  nanoparticles with polymer matrixes to make HRIP nanocomposites. For intrinsic HRIPs, aromatic rings, sulfur-containing groups, halogens except fluorine and organometallic moieties are often utilized to increase their refractive indices. However, their upper  $n$  limitation is usually below 1.80. Incorporation of high- $n$  nanoparticles into polymers seems to be a more promising strategy to achieve a refractive index higher than 1.80; however, the obtained organic-inorganic hybrid materials sometimes suffer from poor storage stability, higher optical loss and poor processability. Besides the refractive index, optical dispersion (Abbe number), birefringence and optical transparency are often involved in designing HRIPs for practical optical fabrications. Therefore, research of HRIPs is becoming an interdisciplinary subject. This feature article reviews recent developments in optical HRIPs and their typical applications in high-tech fields.

## 1. Introduction

Achievements of new functions in advanced optical devices are becoming increasingly dependent on the availability of new functional materials.<sup>1–3</sup> Recently, high refractive index polymers (HRIPs) have attracted considerable attention due to their potential applications in advanced optoelectronic fabrications,

such as high performance substrates for advanced display devices,<sup>4</sup> optical adhesives or encapsulants for organic light-emitting diode devices (OLEDs),<sup>5</sup> antireflective coatings for advanced optical applications,<sup>6</sup> photoresists for 193-nm immersion lithography,<sup>7</sup> and microlens components for charge coupled devices (CCD) or complementary metal oxide semiconductor (CMOS) image sensors (CIS).<sup>8</sup>

Typical refractive indices ( $n$ ) of conventional polymers are often in the range of 1.30–1.70.<sup>9</sup> However, in practical applications, for instance, polymer microlens for CMOS image sensor, a higher refractive index (exceeding 1.70, even 1.80) is frequently desired. Again, in high-brightness LED fabrications, the mismatch of the  $n$  values between the semiconductor dies ( $n$ : 2.50~3.50) and the polymer encapsulants ( $n$ : 1.40~1.60) often causes total internal reflection when light travels from the die into

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the encapsulant at certain incident angles, resulting in low light extraction efficiency of the device. The desired  $n$  value of the encapsulant layers is at least 1.80 over the entire visible region and preferably in the range of 1.80–2.50.<sup>5</sup> Since many optoelectronic devices are based on components with high refractive indices, molecular tailoring of conventional polymers is greatly desired. Fortunately, the ever-increasing demands of HRIPs greatly promote extensive research in this field and impressive scientific and technological progress has been achieved in the past decade. For example, an optical polymer with the highest refractive index of 1.76 was reported in 2004 by Nitto Denko Corp., Japan,<sup>10</sup> and polymers with similar or higher refractive index values have been reported since then. However, the upper limitation of the refractive indices of organic polymers which have been reported up to now in the literature is usually below 1.80. Recently, with the rapid development of nano-science and technology, a more effective procedure for preparing HRIPs has been developed. Nanocomposites consisting of highly refractive inorganic nanoparticles and organic polymer matrixes could easily achieve an  $n$  value higher than 1.80. However, such polymer nanocomposites sometimes suffer from storage stability, higher optical loss and poor processability.

In addition to the refractive index, optical dispersion (Abbe number), birefringence and optical transparency, as well as other physical properties are often involved in designing HRIPs for various optical applications. For example, as lenses for ophthalmological application, a high refractive index and a high Abbe number are both required.<sup>11</sup> As photoresists for 193-nm photolithography, a high refractive index and a high optical transmittance to 193-nm ultraviolet light are often demanded simultaneously. Although such various physical properties might be required for different optical applications, the high refractive index value is essentially important. Herein, we review recent progress in HRIP research and development and mainly focus on the methodologies for increasing the refractive index values of polymers. In addition, the applications of HRIPs in some typical areas are introduced.

## 2. Methodologies for developing HRIPs

The Lorentz–Lorenz equation (1) is often used to predict the refractive index of a polymer, which expresses the refractive index ( $n$ ) in terms of the molecular refraction ( $R$ ), molecular weight ( $M$ ), and molecular volume ( $V$ ) of the polymer repeating unit.<sup>12</sup> In equation (1),  $R/M$  can be further termed as molar refraction ( $R_M$ ), which is the sum of atomic and group refraction of the components composing the polymer repeating unit. Similarly,  $M/V$  can be expressed as the reciprocal of molar volume ( $V_M$ ).

$$\frac{n^2 - 1}{n^2 + 2} = \frac{R}{M} \rho = \frac{R}{M} \cdot \frac{M}{V} = \frac{R_M}{V_M} \quad (1)$$

Thus, equation (2) is solved from equation (1).

$$n = \sqrt{\frac{1 + 2(R_M/V_M)}{1 - (R_M/V_M)}} \quad (2)$$

According to equation (2), the introduction of substituents with high molar refractions and low molar volumes can

**Table 1** Molar refractions ( $R_M$ ) of atoms or organic groups

Group	$R_M$	Group	$R_M$
H	1.100	Phenyl (C <sub>6</sub> H <sub>5</sub> )	25.463
C	2.418	Naphthyl (C <sub>10</sub> H <sub>7</sub> )	43.00
Double bond (C=C)	1.733	Cl	5.967
Triple bond (C≡C)	2.398	Br	8.865
O (carbonyl) (C=O)	2.211	I	13.900
O (hydroxyl) (O–H)	1.525	S(thiocarbonyl) (C=S)	7.97
O (ether, ester) (–C–O–)	1.643	S(thiol) (–SH)	7.69
F	0.95	S(dithia) (–S–S–)	8.11

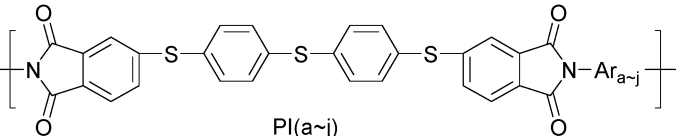
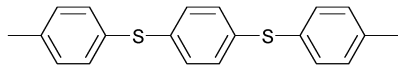
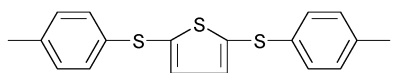
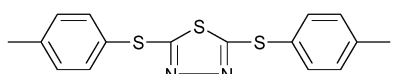
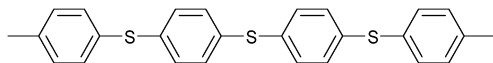
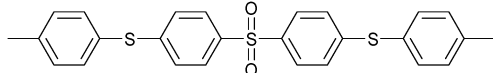
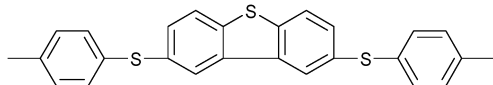
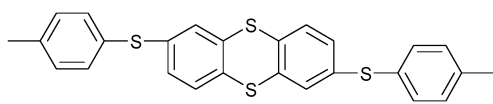
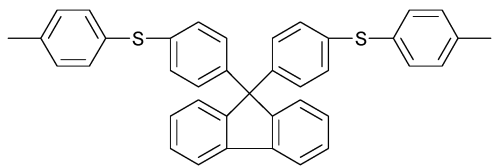
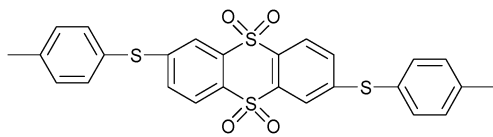
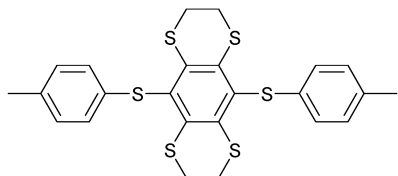
efficiently increase the refractive index of a polymer. Table 1 gives the molar refractions of common atoms or groups.<sup>13</sup> As shown in the right column of Table 1, aromatic rings, halogen atoms except fluorine, and sulfur atoms are effective in increasing the refractive indices of polymers. In addition, metal elements and highly polarizable  $\pi$ -conjugated functionalities are also beneficial for increasing the refractive indices of polymers. In practice, the abovementioned substituents are usually combined into one polymer, whose  $n$  values can often be increased by the synergic effects of the groups.

### 2.1 Sulfur-containing HRIPs

Sulfur-containing substituents including linear thioether and sulfone, cyclic thiophene, thiadiazole, and thianthrene are the most commonly used groups for increasing a polymer's refractive index. Recently, systemic work by Ueda revealed the influence of sulfur groups on the refractive indices and optical dispersion of polymers.<sup>14–23</sup> First, a series of sulfur-containing polyimides (PIs) was developed with the aim of increasing the  $n$  values of polymers. As listed in Table 2, the average  $n$  values ( $n_{av}$ ) are all higher than 1.7200 and increase with an increase in the sulfur content of the PIs. In addition, the flexible thioether or sulfonyl linkages in PIs endow them with a birefringence ( $\Delta n$ ) lower than 0.01. PI-g and PI-j contain sulfur-rich thianthrene and tetra-thiaanthracene moieties in their repeating units, respectively. Thus, they exhibited the highest  $n_{av}$  values. Values exceeding 1.7600 made them among the most refractive polymers in the literature. Although sulfur content is a crucial factor influencing the refractive indices of polymers, it is not the only one. The degree of molecular packing in PIs also affects their  $n$  values. For example, PI-i has a sulfur content of 21.68%, which is higher than that of PI-d. However, the  $n_{av}$  of PI-i (1.7374) is 0.0108 lower than PI-d (1.7482). This is mainly attributed to the looser molecular packing of PI-i caused by the bulky sulfonyl moieties. For the same reason, the fluorene-bridged PI-h exhibited a relatively lower  $n$  value (1.7258) although it had very high aromatic components. Actually, the fluorene moiety has been widely adopted to increase the refractive indices of common polymers. For instance, Takata reported a series of fluorene-modified HRIPs, including poly(arylene thioether)s,<sup>24</sup> polyesters,<sup>25</sup> and poly(thioether ketone)s.<sup>26</sup>

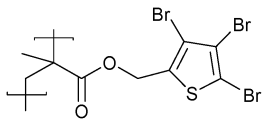
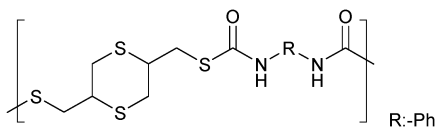
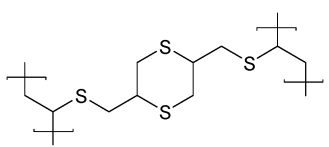
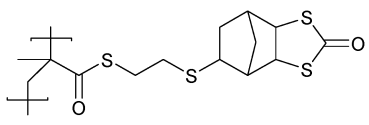
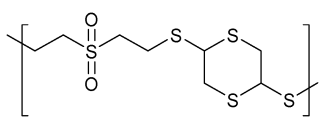
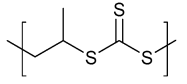
Birefringence is another important parameter for optical polymers. For instance, the high birefringence of one optical polymer often degrades the performance of optical devices that require focusing by lenses or maintaining the polarization state of incident light.<sup>27</sup> The birefringence of one polymer is defined as

**Table 2** Sulfur-containing PIs with high refractive indices<sup>a</sup>

 PI(a~j)					
Ar <sub>a~j</sub>	S <sub>c</sub> (%)	n <sub>TE</sub>	n <sub>TM</sub>	n <sub>av</sub>	Δn
a 	19.25	1.7488	1.7407	1.7461	0.0081
b 	22.98	1.7552	1.7478	1.7527	0.0074
c 	22.93	1.7521	1.7428	1.7490	0.0093
d 	20.48	1.7505	1.7437	1.7482	0.0068
e 	19.81	1.7352	1.7275	1.7326	0.0077
f 	20.53	1.7606	1.7522	1.7578	0.0084
g 	23.20	1.7628	1.7545	1.7600	0.0084
h 	14.96	1.7278	1.7219	1.7258	0.0059
i 	21.68	1.7402	1.7318	1.7374	0.0084
j 	28.48	1.7723	1.7630	1.7692	0.0093

<sup>a</sup> S<sub>c</sub>: sulfur contents; n<sub>TE</sub>: in-plane refractive index; n<sub>TM</sub>: out-of-plane refractive index; n<sub>av</sub>: average refractive index, n<sub>av</sub> = (2 n<sub>TE</sub> + n<sub>TM</sub>)/3; Δn: birefringence, Δn = n<sub>TE</sub> - n<sub>TM</sub>.

**Table 3** Sulfur-containing HRIPs with high Abbe numbers

Polymer	Chemical structure	$n_{589nm}$	$\nu$
polythiomethacrylate		1.6450	31.0
poly(s-alkylcarbamate)		1.6610	32.0
poly(TBD)		1.6780	34.8
polythiomethacrylate		1.6400	42.1
poly(thioether sulfone)		1.6859	48.6
polytrithiocarbonates		1.7800	— <sup>a</sup>

<sup>a</sup> Not reported.

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. The birefringence originates from two main sources: the inherent molecular structure and the processing history of the polymer. It has been well established that the combination of components with high inherent polarizability, rigid-rod morphology, and high orientation often results in the increasing birefringence values of the polymers.<sup>28</sup> On the other hand, the orientations of polymer molecular chains during the melt flow in injection-molding, extrusion or drawing processing also induce the birefringence of the polymer. Obviously, birefringence will be eliminated or reduced as long as the polymer molecular chain orientations are perfectly random.

One effective method to form random molecular orientations in one polymer is to introduce flexible segments or substituents preferably oriented perpendicularly to the polymer main chain.<sup>29</sup> As shown in Table 2, flexible thioether linkages and fluorenyl groups were introduced into PIs to afford the polymers with high  $n$  and low  $\Delta n$  values. For instance, PI-a exhibited a relatively lower  $\Delta n$  value (0.0081) than that of the standard poly(pyromellitic dianhydride-co-4,4'-oxydianiline) (0.0780).<sup>16</sup> The  $\Delta n$  value was further reduced by the introduction of more flexible thioether linkages. PI-d with one more thioether group in

the diamine moiety had lower  $\Delta n$  value (0.0068) than that of PI-a. Furthermore, PI-g achieved the lowest  $\Delta n$  value (0.0059) in the system, which was attributed to the fluorenyl group that was oriented perpendicularly to the polymer main chain. This orientation compensated the inherent birefringence of the polymer.

Very recently, Ueda *et al.* reported several sulfur-containing HRIPs with high Abbe numbers.<sup>30,31</sup> The Abbe number ( $\nu$ ), reflecting the optical dispersion of the refractive index, is a key parameter for optical polymers used in geometrical optics. The high optical dispersion of a polymer, that is a low  $\nu$  value, will limit its application in optical lenses because it causes changes in the focal length and coloration of the image. Conversely, a larger  $\nu$  value means lower optical dispersion, that is, smaller chromatic aberration. The Abbe number is usually expressed in terms of the refractive index ( $n$ ), molecular refraction ( $R$ ), and molecular dispersion ( $\Delta R$ ), as described in equation (3).<sup>32</sup>

$$\nu_D = \frac{6n_D}{(n_D+2)(n_D+1)} \cdot \frac{[R]}{[\Delta R]} \quad (3)$$

It can be concluded from equation (3) that a larger refractive index makes the Abbe number smaller and *vice versa*.

Typically, organic polymers with values of  $n = 1.70$  or higher have an Abbe number lower than 20.0. Therefore, there is an optimum point between the refractive index and the Abbe number. The reported HRIPs with high Abbe numbers are shown in Table 3.

The pioneering work of Matsuda *et al.*<sup>33</sup> and Okubo *et al.*<sup>34,35</sup> concerning HRIPs with high Abbe numbers demonstrated that a condensed sulfur-containing alicyclic ring was beneficial to increasing the Abbe number of a polymer while maintaining its high refractive index. Matsuda *et al.* reported the preparation of thiophene-containing polymethacrylates.<sup>33</sup> As shown in Table 3, brominated poly(thiophene methacrylate) exhibited a refractive index of 1.6450 and an Abbe number of 31.0. Okubo *et al.* prepared a series of HRIPs containing dithiane rings.<sup>34</sup> The developed polymer, based on 2,5-bis(2-thia-3-butenyl)-1,4-dithiane (TBD), showed high  $n$  and  $\nu$  values. In order to further increase the  $n$  and  $\nu$  values of optical polymers, the Ueda Lab developed two series of sulfur polymers, polythiomethacrylates<sup>30</sup> and poly(thioether sulfone)s.<sup>31</sup> The former had a high  $\nu$  value of 42.1, although its  $n$  value was around 1.6400. The latter polymer exhibited excellent combined physical properties, including a high  $n$  of 1.6859, a large  $\nu$  of 48.6, a glass transition of 152 °C, and high optical transparency (>99%) in the visible light region of 400–800 nm. In addition, it could be processed *via* the conventional cast molding procedure, making it a good candidate for advanced optical applications. Recently, a sulfur-rich polymer, polytrithiocarbonate (Table 3) was reported by Nakano and *et al.*<sup>36</sup> It showed an  $n$  value of 1.7800 at 589 nm and a high molecular weight. Although the Abbe number of this polymer was not reported, it might be a promising HRIP with a high Abbe number.

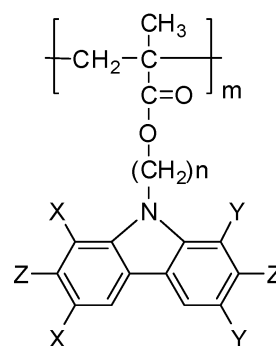
## 2.2 Halogen-containing HRIPs

Halogen elements, especially bromine and iodine, were the earliest utilized components for developing HRIPs. In 1992, Minns and Guadiana reported a series of polymethacrylates containing lateral brominated and iodinated carbazole rings.<sup>37</sup> As shown in Fig. 1, the refractive indices of the polymers ranged from 1.67–1.77 depending on the components and numbers of the halogen substituents, as well as the lengths of methylene spacers.

Although bromination or iodination can increase the  $n$  values of polymers, overloading of the elements often deteriorates their optical properties. On the other hand, recent applications of halogen elements in microelectronic devices have been severely limited by the WEEE Directive and RoHS legislation promulgated by the European Union due to their potential pollution of the environment.<sup>38</sup> Although much attention have not been paid to their applications in photonic devices, there still exists the potential possibility of prohibition in some optical fields, such as the high- $n$  encapsulant for LEDs. Thus, research on halogen-containing HRIPs has progressed slowly in recent years.

## 2.3 Phosphorus-containing HRIPs

Phosphorous-containing groups, such as phosphonates and phosphazenes, often exhibit high molar refractions and good



$$X=Y=-\text{Br}; Z=-\text{H}; n=4; n_{589,3}=1.68$$

$$X=Y=-\text{Br}; Z=-\text{H}; n=6; n_{589,3}=1.67$$

$$X=Y=Z=-\text{Br}; n=4; n_{589,3}=1.74$$

$$X=Y=Z=-\text{Br}; n=6; n_{589,3}=1.72$$

$$X=Y=Z=-\text{Br}; n=6; n_{589,3}=1.72$$

$$X=-\text{I}; Y=-\text{H}; Z=-\text{H}; n=4; n_{589,3}=1.74$$

$$X=Y=-\text{I}; Z=-\text{H}; n=4; n_{589,3}=1.77$$

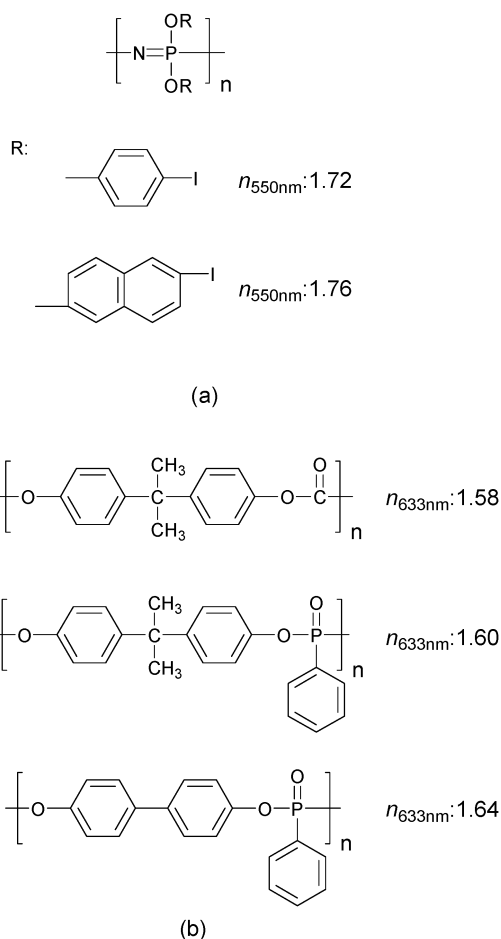
Fig. 1 Structure of halogen-substituted polymethacrylates.

optical transmittance in the visible light region. Thus, phosphorous-containing polymers might be good candidates as HRIPs for optical applications. Noteworthy are the high- $n$  polyphosphazenes developed by Allcock *et al.*<sup>39–41</sup> and polyphosphonates reported by McGrath *et al.*<sup>42,43</sup> Polyphosphazenes contain an inorganic phosphorus–nitrogen backbone, affording dense molecular packing and a high molar refraction of the repeating unit. As illustrated in Fig. 2a, polyphosphazenes containing iodinated aromatic side groups showed  $n$  values higher than 1.70. In addition, the films exhibited good optical transparency with maximum absorption wavelengths of around 270–280 nm.<sup>39</sup> Very recently, Allcock developed cyclo-triphosphazenes with sulfur-containing side chains.<sup>41</sup> The synergic effects of the sulfur substituents and  $-\text{P}=\text{N}-$  repeating units endowed the material with high refractive indices and low optical dispersions.

Polyphosphonates have chemical structures analogous to polycarbonates. However, their refractive indices are obviously increased by the phosphorus moiety, as evidenced by Fig. 2b. In addition, polyphosphonates exhibited good melt stability, good optical transparency, and good fire retardancy. Thus, they are suitable for casting into plastic lenses for customer use.

## 2.4 Organometallic HRIPs

Metal elements usually have large specific gravity and low solubility in organic solvents and colors. Thus, they have not been suggested for developing HRIPs in spite of being able to endow polymers with extreme high  $n$  values. However, in recent years, organometallic components have proven to be effective in



**Fig. 2** Phosphorus-containing HRIPs. (a) polyphosphazenes and (b) polyphosphonates.

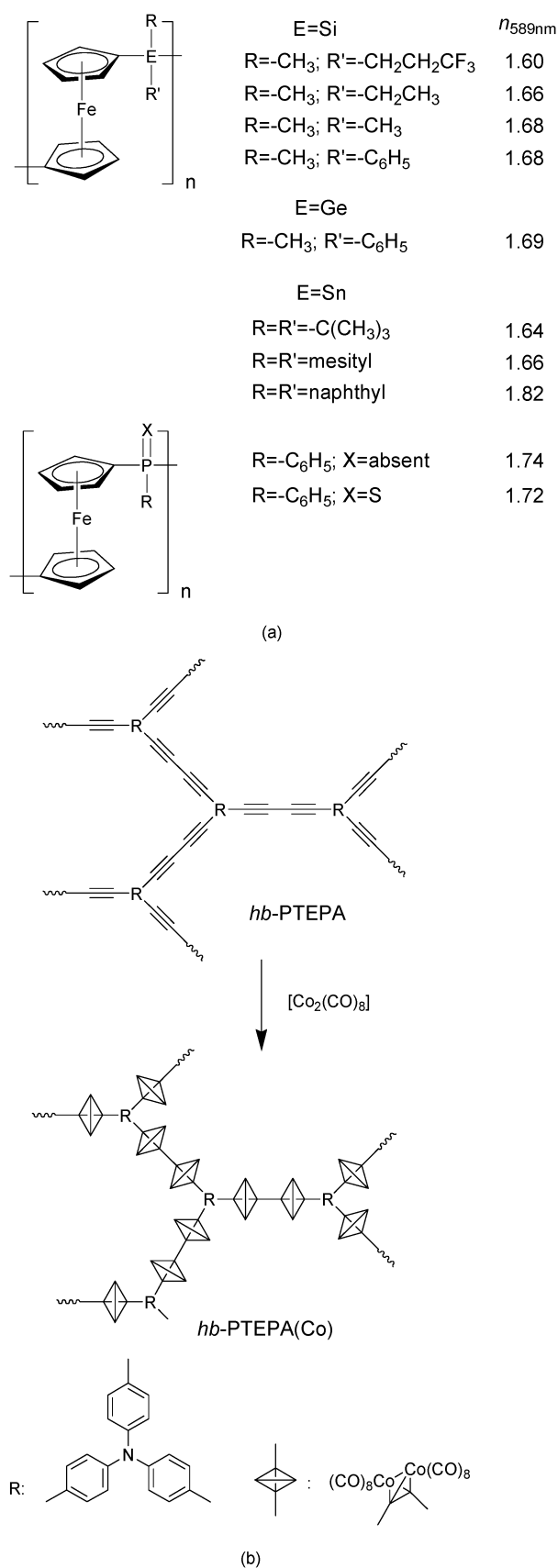
developing HRIPs with good film formability and relatively low optical dispersion.

Manners *et al.* reported a series of high- $n$  metallopolymers, including polyferrocenylsilanes<sup>44</sup> and polyferrocenes.<sup>45</sup> The polyferrocenes, embedded with different spacer elements and substituent groups, are shown in Fig. 3a. Polymers containing phosphorous spacers and phenyl side chains showed unusually high  $n$  values ( $n = 1.74$  and  $n = 1.72$ ). In addition, they exhibited moderate optical dispersion between organic polymers and inorganic glasses. Thus, they might be good candidates for all-polymer photonic devices.

Tang *et al.* reported a cobalt-containing hyperbranched polydiyne (Fig. 3b), which showed refractive indices as high as 1.713–1.813 in the long wavelength region.<sup>46</sup> What is more, the polymer films showed good patternability by simple irradiation with UV light. The  $n$  values of the polymers could be tuned to a large extent up to 0.048. The UV-cured polymer films exhibited a large Abbe number ( $\nu = 35.5$ ) in the near-IR region.

## 2.5 Hybrid techniques for developing HRIPs

Hybrid techniques have been adopted to develop HRIPs since the 1990s. Early work which deliberately studied high- $n$  inorganic-organic hybrid nanocomposites was reported by Weibel *et al.* in 1991.<sup>47</sup> In recent years, with the rapid development of



**Fig. 3** Organometallic HRIPs. (a) polyferrocenes and (b) Co-containing Polydienes.

nanoscience and nanotechnology, research on high- $n$  nanocomposites has progressed rapidly. In contrast to the intrinsic HRIPs mentioned above, hybrid techniques which combine an organic polymer matrix with highly refractive inorganic nanoparticles could achieve much higher  $n$  values. The factors affecting the refractive index of a high- $n$  nanocomposite include the characteristics of the polymer matrix, nanoparticles, and the hybrid technology between inorganic and organic components.

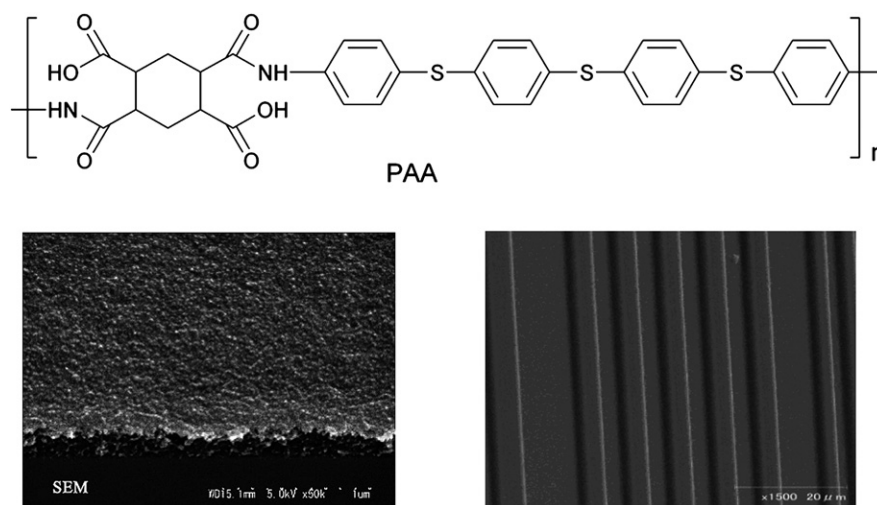
In theory, one can choose any polymer as the matrix of a high- $n$  nanocomposite. However, polymers with inherent high  $n$  values are more suitable to act as the matrix. The refractive index of a nanocomposite can be approximately estimated by the equation  $n_{\text{comp}} = \phi_p n_p + \phi_{\text{org}} n_{\text{org}}$ ,<sup>48</sup> where  $n_{\text{comp}}$ ,  $n_p$ , and  $n_{\text{org}}$  stand for the refractive indices of the nanocomposite, nanoparticle, and organic matrix, respectively.  $\phi_p$  and  $\phi_{\text{org}}$  represent the volume fractions of the nanoparticles and organic matrix, respectively. Thus, it can be concluded from the equation that, in order to achieve a definite  $n_{\text{comp}}$  value with a definite type of nanoparticle, the higher the value of  $n_{\text{org}}$ , the lower the value of  $\phi_p$ . This is important for the design of HRIP nanocomposites for optical applications because an overload of nanoparticles often increases the optical loss and decreases the processability of the nanocomposites.

On the other hand, the choice of nanoparticle is often influenced by its size and surface characteristics. In order to achieve good optical transparency and avoid Rayleigh scattering of the nanocomposite, the diameter of the nanoparticle should be below 25 nm.<sup>49</sup> In addition, the direct mixing of nanoparticles with the polymer matrix facilitates the aggregation of nanoparticles. Thus, in practice, the surface of nanoparticles is often modified in order to fit the mixing process. The most commonly used nanoparticles for HRIPs include TiO<sub>2</sub> (anatase,  $n = 2.45$ ; rutile,  $n = 2.70$ ),<sup>50</sup> ZrO<sub>2</sub> ( $n = 2.10$ ),<sup>51</sup> amorphous silicon ( $n = 4.23$ ), PbS ( $n = 4.20$ ),<sup>52</sup> and ZnS ( $n = 2.36$ ).<sup>53</sup>

Polyimides (PIs) are often utilized as the matrix to combine with high- $n$  nanoparticles due to their inherent high- $n$  nature. Thus, a low number of nanoparticles might be used to achieve

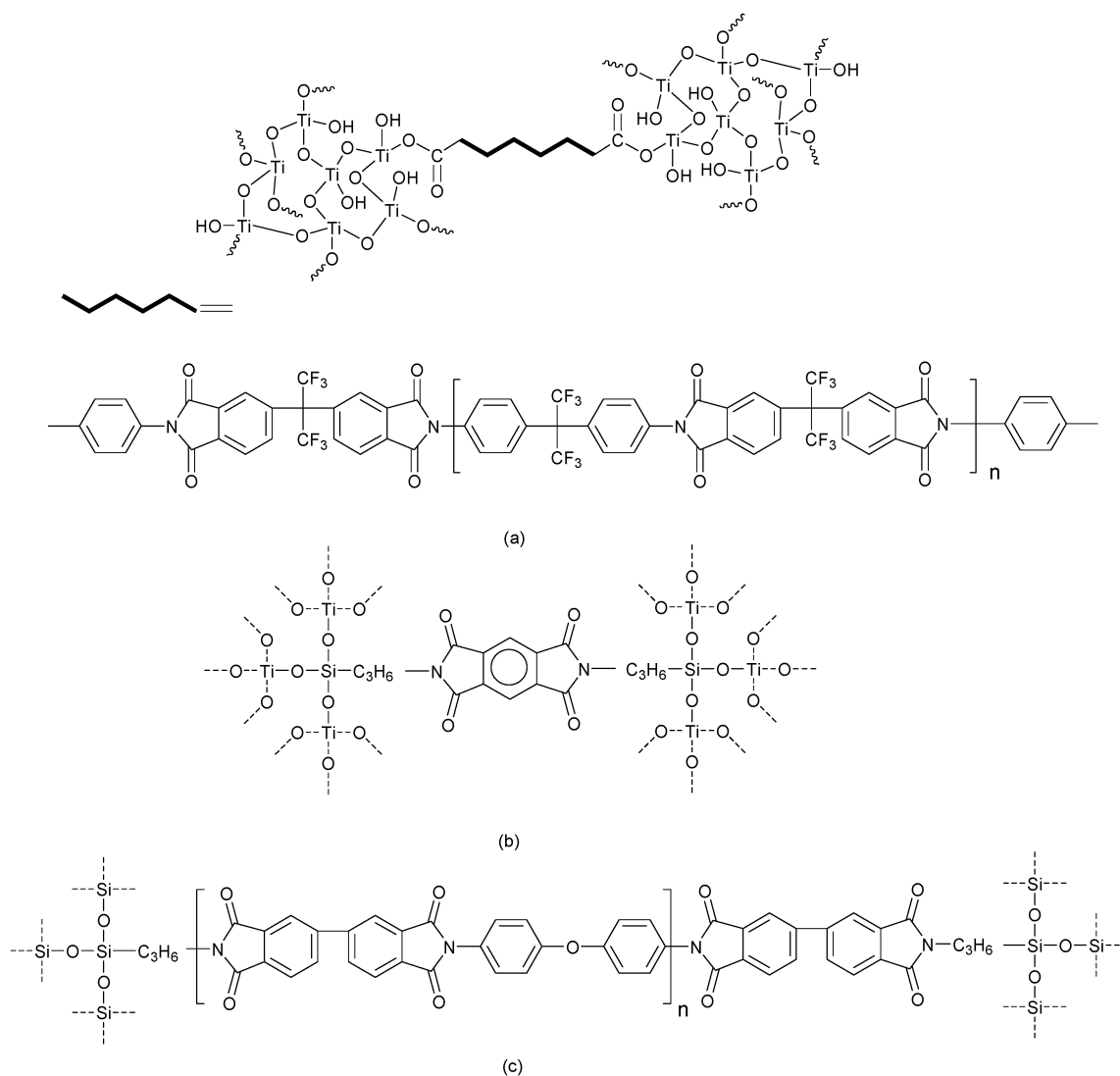
high  $n$  values. Ueda *et al.* reported a series of optically transparent sulfur-containing PI-TiO<sub>2</sub> nanocomposites.<sup>54</sup> The aim of the work is to develop an outer or inner microlens array for CMOS image sensors. Thus, a refractive index higher than 1.80, high optical transparency, low birefringence and high thermal stability are the basic concerns in designing the material. In addition, in order to form a microlens by the photolithography process, the nanocomposite should exhibit good photolithographic characteristics. Therefore, a semi-alicyclic polyimide precursor, poly(amic acid) (PAA) (Fig. 4), was chosen as the matrix and a silica-modified TiO<sub>2</sub> nanoparticle as the filler. TiO<sub>2</sub> is a nontoxic, thermally and environmentally stable nanoparticle; thus, it has been widely used in high-tech fields. However, the surface chemistry of the TiO<sub>2</sub> nanoparticle is rather complex and quite dependent on the synthetic method and on the crystalline state.<sup>55</sup> Thus, in practice, the surface of the TiO<sub>2</sub> nanoparticle is often functionalized by grafting substituents. In Ueda's experiments, the surface of an anatase TiO<sub>2</sub> nanoparticle was modified by silica so as to improve its affinity with PAA. A homogeneous mixture was easily achieved by a mechanical stirrer. The nanocomposite film exhibited good uniformity, as evidenced by the SEM image shown in Fig. 4. The PAA-titania film had good transparency to the  $i$ -line (365 nm) of a high-pressure Hg lamp, and thus a fine negative pattern with a resolution of 4  $\mu\text{m}$  was successfully printed on the nanocomposite film by the direct patterning technique of PAA using a photo base generator.<sup>56</sup>

Chang and Chen developed a series of titania-PI hybrid optical materials.<sup>57</sup> In their earlier work, high- $n$  aminoalkoxysilane-capped pyromellitic dianhydride (PMDA)-titania hybrid optical films (Fig. 5b)<sup>58</sup> and poly(BPDA-ODA)/silica hybrid optical films (Fig. 5c)<sup>59</sup> were prepared *via* the sol-gel process. By a new route, they developed a PI-titania nanocomposite using soluble fluorinated PI as the matrix, as illustrated in Fig. 5a. First, a soluble PI containing carboxyl endcaps (6FDA-6FpDA-COOH) was prepared. Then the end groups underwent an esterification reaction with titanium butoxide to form organic-inorganic bonding. After hydrolysis, condensation and thermal



**Fig. 4** Chemical structure of PAA and SEM picture of PI-TiO<sub>2</sub> nanocomposite (bottom left); SEM image of PI-TiO<sub>2</sub> pattern (bottom right). Reproduced with permission from ref. 54. © 2008 American Chemistry Society.





**Fig. 5** High-*n* polyimide nanocomposites. (a) PI(6FDA-6FpDA-COOH)-titania nanocomposite, (b) Aminoalkoxysilane capped PMDA-titania nanocomposite and (c) PI(BPDA-ODA)-Silica nanocomposite.

curing, optically transparent nanocomposite film was obtained. The hybrid films exhibited a tunable refractive index, from 1.571 to 1.993. Chang and coworkers also reported soluble-PI/Titania hybrid films, whose refractive indices reached 1.82 with a TiO<sub>2</sub> load of 40 wt%.<sup>60</sup>

The other high-*n* polymers, such as polythiourethane (PTU), have been incorporated with TiO<sub>2</sub>,<sup>61</sup> ZnS,<sup>53</sup> or PbS<sup>62</sup> to develop nanocomposites. Yang *et al.* systemically investigated the influence of the abovementioned nanoparticles on the refractive indices of PTU.

Common polymers such as epoxy,<sup>63,64</sup> poly(methyl methacrylate) (PMMA),<sup>65,66</sup> poly(urethane-methacrylate),<sup>67</sup> poly(vinylpyrrolidone),<sup>68</sup> and poly(acrylic acid)-graft-poly(ethylene glycol methacrylate)<sup>69</sup> have also been utilized as the matrix to prepare high-*n* nanocomposites. However, in order to achieve high *n* values, a relatively large amount of high-*n* nanoparticles are usually used.

### 3. Leading-edge applications of HRIPs

The driving force of rapid developments in HRIPs comes from the ever-increasing demands of advanced optoelectronic

fabrications. It has been well established that the performance of optoelectronic devices, such as cover layers for optical disks, diffraction gratings, molded microlenses, flat panel displays, planar waveguides, image sensors, photonic circuits, and high-brightness light-emitting diodes (LEDs) can be improved by applying high-*n* coatings.<sup>70,71</sup> In this section, we review the recent leading-edge materials and applications of HRIPs in advanced optical fields.

#### 3.1 Microlens for CMOS image sensor (CIS)

The microlens array is an important optical element for information processing, optoelectronics, optical communications, and three-dimensional displays.<sup>72,73</sup> The polymeric microlens is particularly attractive because of its flexibility, simple fabrication process, and low cost. Recently, applications of the high-*n* polymeric microlens in CMOS image sensor (CIS) fabrication have attracted much attention. In contrast to the well-utilized CCD (charge coupled device) image sensor, CIS is occupying more of the digital market due to its lower power consumption,

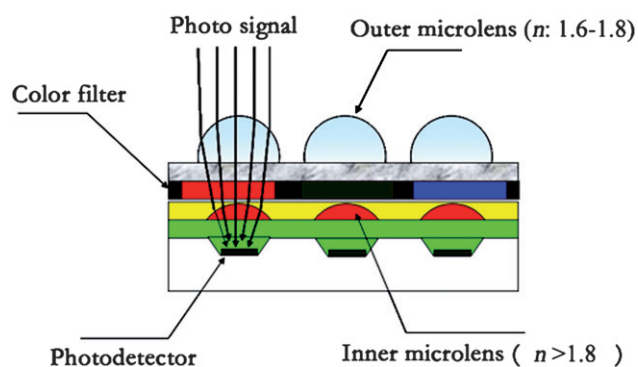


Fig. 6 Microlens array in CMOS image sensor device.

smaller size, easy-to-achieve mass-production, and lower cost. However, the relatively lower sensitivity of CIS to CCD limits its application in fields where image quality is the primary requirement. An improved procedure is to apply a high- $n$  microlens array on the photodetector in CIS so as to concentrate the optical signals and thus increase the sensitivity of the device (Fig. 6).

As mentioned in section 2.5, Ueda reported a high- $n$  PI-Titania nanocomposite with a refractive index higher than 1.80.<sup>54</sup> The hybrid system could be fabricated into a microlens by the standard photolithography process. Recently, Toray Ind. Inc.

reported a positive-tone photosensitive PI coating for the lens layer in CIS.<sup>74</sup> The photosensitive PI (PSPI) is characterized by its high  $n$  (1.80 at 633 nm), good optical transparency in the visible light region (>85% at 400–700 nm wavelength), and high sensitivity to the  $i$ -line (365 nm).

### 3.2 Photoresists for 193-nm immersion lithography

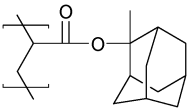
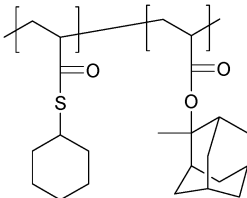
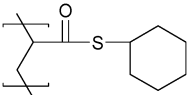
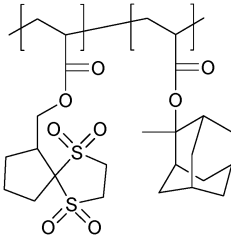
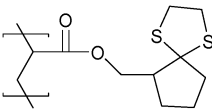
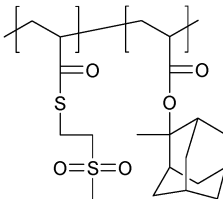
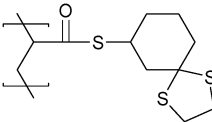
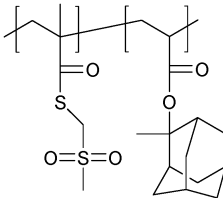
The 193-nm immersion lithography process is considered the most promising technology to achieve integrated circuit manufacture at the 65-nm and 45-nm node. The corresponding materials are the key factors which determine the achievement of the new lithography technique.<sup>75</sup>

High-refractive-index fluids and photoresists are among the most important materials in 193-nm immersion lithography.<sup>76</sup> Advances in high- $n$  fluid and resist design could extend the technology to the 32-nm node or below.<sup>77</sup> In the design and development of high- $n$  photoresists, the work of the scientists at the University of Queensland and SEMATECH is particularly noteworthy.<sup>78–82</sup> Their design of high- $n$  photoresists are based on the Lorentz–Lorenz equation with the aid of quantitative structure-property relations (QSPR) analysis. The QSPR model was used to accurately predict the refractive index of a photoresist at 193 nm. The prediction reveals the following results: (1) aromatic groups lead to high absorbance at 193 nm, thus should be absent in 193-nm photoresists; (2) thioethers result in significant increases in the refractive index compared to non-sulfur

Table 4 High- $n$  photoresists for 193-nm immersion lithography from ref. 79 and 80

polymer	$n_{193\text{nm}}$	polymer	$n_{193\text{nm}}$
	1.81		1.70
	1.74		1.76
	1.90		1.80
	1.88		1.90

**Table 5** High-*n* photoresists for 193-nm immersion lithography from ref. 83

polymer	<i>n</i> <sub>193nm</sub>	polymer	<i>n</i> <sub>193nm</sub>
	1.73		1.78
	1.84		1.74
	1.84		1.82
	1.94		1.81

analogues; (3) cyclic compounds have refractive index approximately 0.1 higher than linear analogues.<sup>79</sup> Based on these criteria, a series of aromatic-free cyclic-thioether-containing polymers was developed, as shown in Table 4. All photoresists usually exhibit *n* values in the range of 1.70–1.90 at 193 nm. In order to achieve a higher *n* value (>1.90) of the photoresist so as to bridge the gap between the 45-nm and 32-nm half-pitch nodes, nanotechnology has been investigated.<sup>81</sup>

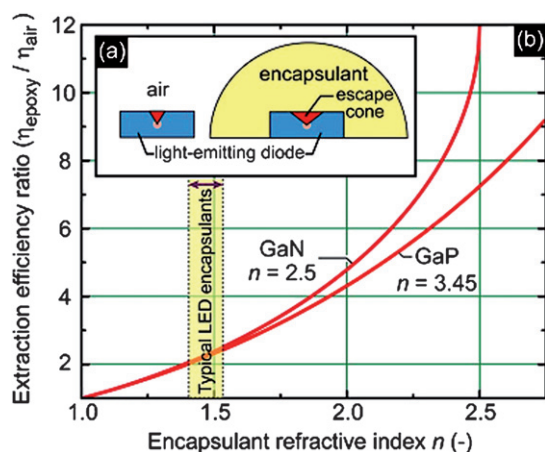
Another important system of sulfur-containing photoresists for 193-nm lithography was demonstrated by Willson *et al.*, as illustrated in Table 5.<sup>83</sup> The thioester or sulfone moieties endowed the photoresists with high *n* values and low absorbance at 193 nm. Fine 110-nm line and space patterns were successfully produced by the photoresist systems.

### 3.3 Encapsulant for LED

Light-emitting diodes (LEDs) are thought to be the most promising solid-state light source for general lighting and have the potential to replace traditional incandescent bulbs and fluorescent lamps.<sup>84</sup> Although LEDs are already extensively

used in outdoor displays, traffic signals and back lighting in liquid-crystal displays nowadays, high-brightness LEDs (HBLEDs) are still difficult to manufacture. The technical hurdles lie in the relatively low light extraction efficiency (LEE) of HBLEDs, mainly coming from the mismatch of the refractive indices between inorganic LED dies (GaN, *n* = 2.5) and the organic encapsulants (epoxy or silicone, *n* = ~1.5). Mont *et al.* reported on the relationship between the LEE ratio of LEDs and the encapsulant refractive index, as presented in Fig. 7.<sup>85</sup> As the refractive index of the encapsulant increases, the LEE ratio increases rapidly. If an encapsulating resin with an index higher than 1.80 can be achieved, the LEE will be greatly enhanced.

As an encapsulant for HBLEDs, high refractive indices, high optical transparency, and a long-term ultraviolet light and thermal stability are basically required. Obviously, common optical polymers cannot fulfill the requirements. The high-*n* nanocomposite seems to be a promising solution to address the problem. Mont *et al.* reported a high-*n* epoxy-TiO<sub>2</sub> encapsulant.<sup>86</sup> In order to reduce the optical scattering of the nanocomposite, the surface of TiO<sub>2</sub> nanoparticles were modified with a surfactant as so to improve their compatibility with an epoxy



**Fig. 7** (a) Escape cone of an LED without and with encapsulation. (b) Light-extraction efficiency ratio for GaN and GaP as a function of the encapsulant refractive index. Reprinted with permission from ref. 85. © 2008 American Institute of Physics.

matrix. The epoxy-TiO<sub>2</sub> encapsulant exhibited an  $n$  value of 1.67 at 500 nm, significantly higher than that of conventional epoxies ( $n = 1.53$ ). Theoretical light-extraction enhancements larger than 50% were achieved.

Chau *et al.* reported a nanocomposite from epoxy and acetic acid-modified TiO<sub>2</sub> nanoparticles. The modified TiO<sub>2</sub> nanoparticles were easily incorporated into the epoxy matrix without particle agglomeration. The  $n$  values of the transparent hybrid films were in the range of 2.18–2.38, making them good candidates for LED encapsulation.<sup>87</sup> Zhou *et al.* reported a one-component, low-temperature, and fast cure high- $n$  epoxy encapsulant for LEDs.<sup>88</sup> The system had an  $n$  value of 1.60 and good optical transparency.

### 3.4 Coatings for long-period fiber gratings (LPFGs)

Recently, long-period fiber gratings (LPFGs) have been widely used as sensors for the detection and monitoring of temperature, strain, refractive index, and other parameters in environmental analysis.<sup>89</sup> When sensitive material has a lower refractive index than that of the fiber cladding, the sensitivity of the LPFG response will be limited. In order to enhance its sensitivity, a high- $n$  coating has to be deposited. This idea was first proposed by Tatam *et al.* in 2002.<sup>90</sup> The presence of a high- $n$  coating on an LPFG will induce strong changes in the field distribution of the cladding modes along the periodic structure.

Pilla *et al.* systemically studied the influence of high- $n$  coatings on the sensitivity enhancements of LPFGs.<sup>91–93</sup> They used  $\delta$ -form syndiotactic polystyrene (sPS,  $n = 1.58$ ) as the high- $n$  coating. It was found that the utilization of a high- $n$  coating induced a significant enhancement of the device sensitivity to the refractive index of the external medium.

## 4. Summary and outlook

In this article, we have reviewed a variety of methodologies for developing HRIPs and their typical applications in advanced optical fabrications. Generally speaking, with regard to HRIPs,

the achievement of a high refractive index is essentially a chemistry issue. However, the further functionality of HRIPs in order to meet the practical requirements of advanced optical fabrications makes the research an interdisciplinary subject. In addition to the parameter of the refractive index, the other parameters, including birefringence, Abbe number, and optical transparency in the specific spectrum range are often taken into consideration in practice. Thus, HRIPs with special functionalities might have a brighter future.

Several developing trends in functional HRIPs might be concluded from the recent reports in the literature. Processable polymers with high refractive indices and high transparency might be highly desired for future HBLEDs. Polymer (micro)lenses with high refractive indices and high Abbe numbers might find wider applications in future industrial or customer uses. Polymers with high refractive indices, low or zero birefringence and low optical loss are ideal waveguide materials for future optical fiber communication. Photosensitive high- $n$  polymers make it possible to fabricate semiconductor components at 45-nm or lower nodes. In addition, high- $n$  polymers with high-refractive-index modulation via photoreaction have attracted wide attention in volume holographic recording.<sup>94,95</sup> They might be good candidates for future memories.

Undoubtedly, nanotechnology is still the most effective way to achieve all of the goals mentioned above. However, how to achieve a concordant nanocomposite system is an on-going issue. Also, it is important to develop a new high- $n$  polymer matrix. It might become a hot topic in polymer chemistry in the future.

## Acknowledgements

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