Halogenated high index polymer coating

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Introduction: high index materials

What is high index materials?

Antireflective coating

With a higher RI, the material can be thinner
High refractive index polymers (HRIPs) compared with inorganic counterparts

Why polymeric high index materials over inorganic high index materials?

- Mechanical flexibility
- Lightweight
- Impact resistance
- Processability
- Dying ability
- Low cost
Refractive indices of polymers ranges from 1.3 – 1.7

Polymer has a much lower upper limit of RI compared with inorganic material
Recent progress in high refractive index polymers

**Sulfur containing polyimides**

Example:

![Sulfur containing polyimides](image)

RI = 1.769

**Phosphorous containing high-n polymers**

Example:

![Phosphorous containing high-n polymers](image)

RI = 1.750-1.755

**Polyphenylquinoxalines**

Example:

![Polyphenylquinoxalines](image)

RI = 1.728-1.795

These newly developed HRIPs involve complicated synthesis processes, and yet still didn't achieve a RI higher than 1.8
A substituent with a high molar refraction and low molar volume will increase the RI of a polymer.

### Table 1. Comparison of molar refraction of selected substituents

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$R_m/(cm^3\text{mol}^{-1})$</th>
<th>Substituent</th>
<th>$R_m/(cm^3\text{mol}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.100</td>
<td>C ≡ C</td>
<td>2.398</td>
</tr>
<tr>
<td>C</td>
<td>2.418</td>
<td>C = C</td>
<td>1.733</td>
</tr>
<tr>
<td>O (in OH)</td>
<td>1.524</td>
<td>4-membered ring</td>
<td>0.400</td>
</tr>
<tr>
<td>O (in C = O)</td>
<td>2.211</td>
<td>Phenyl</td>
<td>25.463</td>
</tr>
<tr>
<td>O (in ether)</td>
<td>1.643</td>
<td>Naphthyl</td>
<td>43.000</td>
</tr>
<tr>
<td>Cl</td>
<td>5.967</td>
<td>S(S - H)</td>
<td>7.691</td>
</tr>
<tr>
<td>Br</td>
<td>8.865</td>
<td>S(S - S)</td>
<td>8.112</td>
</tr>
<tr>
<td>I</td>
<td>13.900</td>
<td>PH3</td>
<td>9.104</td>
</tr>
</tbody>
</table>

**Strategy:** incorporate iodine directly into the polymer chain to increase RI.
Design HRIPs

To incorporate iodine into polymer

Find a polymer that can lock down iodine

P4VP can form CTC with iodine

Poly(4-vinyl pyridine) (P4VP)

P4VP-I$_2$ Charge transfer complex (CTC)
Preparation of P4VP thin film by using Initiated chemical vapor deposition (iCVD)

Reaction mechanism proposed for iCVD polymerization

**gas phase reactions**

\[
i(g) \xrightarrow{k_i} 2R \cdot (g) \quad (1)
\]

**gas-to-surface processes**

1. primary radical adsorption:
   \[
   R \cdot (g) \xrightarrow{k_{R,ad}} R \cdot (ad) \quad (2)
   \]
2. monomer adsorption:
   \[
   M(g) \xrightarrow{k_{M,ad}} M(ad) \quad (3)
   \]

**surface reactions**

1. initiation:
   \[
   R \cdot (ad) + M(ad) \xrightarrow{k_i} M_1 \cdot (ad) \quad (4)
   \]
2. propagation:
   \[
   M_n \cdot (ad) + M(ad) \xrightarrow{k_p} M_{n+1} \cdot (ad) \quad (5)
   \]
3. termination:
   \[
   M_n \cdot (ad) + M_m \cdot (ad) \xrightarrow{k_t} M_{n+m} \cdot (ad) \quad (6)
   \]
   \[
   M_n(ad) + M_m(ad) \quad (6)
   \]
4. primary radical termination:
   \[
   M_1 \cdot (ad) + R \cdot (ad) \xrightarrow{k_{t,R}} M_1(ad) \quad (7)
   \]
5. primary radical recombination:
   \[
   R \cdot (ad) + R \cdot (ad) \xrightarrow{k_{r,R}} R_2(ad) \quad (8)
   \]

[Diagram of polymerization process with reactions and mechanisms annotated]
iCVD vs. PVD

**iCVD:**
- Conformal
- Fast deposition rate
- Low cost
- Room temperature
- Scale up
- Coat on flexible substrate

**Sputtering:**

**Evaporation:**

**PVD:**
- Light of sight deposition
- Small deposition range
- Expensive
- Slow deposition rate
- High vacuum requirement
- High temperature

[Diagram of iCVD process]

[Diagram of Sputtering process]

[Diagram of Evaporation process]

Preparation of P4VP-I\textsubscript{2} Charge transfer complex (CTC)

A charge-transfer complex (CTC) is an association of two or more molecules, in which a fraction of electronic charge is transferred between the molecular entities.

Dark environment

30° C

Iodine hexane solution

P4VP coated wafer

\[
\text{P4VP} + \text{I}_2 \rightleftharpoons \text{P4VP-I}_2
\]
Effective halogen incorporation confirmed by FTIR

The peak shift in P4VP-I$_2$ can be attributed to electron redistribution to the I$^{6+}$ acceptor in CTCs.

RI can be fine-tuned by controlling CTC % in the polymer film via copolymerization with monomers that inert to halogen compounds.

The FTIR results demonstrated the formation of charge transfer compounds between P4VP and iodine.
The RI of P4VP-I\(_2\) is tunable by altering the iodine solution treatment time.

The maximum achievable refractive index for P4VP-I\(_2\) is higher than 2.0+

Thermal stability needs further improvement.

ICI and IBr are stronger Lewis acids compared with iodine, and can form more stable CTC with P4VP.

After 24hrs environmental stability test at 20°C:
The refractive index of P4VP-I\(_2\) decreased by 7.9%.
P4VP-IBr high index films

The RI of P4VP-IBr is tunable by altering the IBr vapor treatment time.
P4VP-IBr is more thermally stable and has a lower extinction coefficient than P4VP-I₂.

After 24hrs environmental stability test at 20°C:
The refractive index of P4VP-I₂ decreased by 2.6%
P4VP-ICI high index films

After 24hrs environmental stability test at 20°C:
The refractive index of P4VP-I₂ decreased by 0.41%

P4VP-ICI is more thermally stable than both P4VP-IBr and P4VP-I₂.
The extinction coefficient of P4VP-ICI in visible wavelength range is negligible.

By increasing the degree of ionization of the prepared CTC, the stability of P4VP-IX is greatly improved
Absorption of halogenated polymer films

Negligible absorption in visible range (T>99.8%)

P4VP-ICI and P4VP-IBr has negligible absorption in visible wavelength range
A new generation of halogenated high index polymers exhibit higher refractive index (2.1+), lower average extinction coefficient compared with P4VP-I2, and remains stable up to 250°C.
Conclusion

1. Developed a series of halogenated polymer thin films with high refractive indices (n = 1.58 - 2.0+) and outstanding optical transparency prepared via vapor deposition followed by a halogen vapor treatment.

2. The P4VP-I\textsubscript{2} complex is demonstrated to have an RI of 2.0 and is transparent above a wavelength of 600nm. In another formulation, P4VP complexed with ICl achieved an RI up to 1.77, while still retaining the outstanding optical transparency throughout visible range.

3. The RI of the halogenated polymer can be fine-tuned from 1.58 to 2.0 by controlling the concentration of CTC in the polymer film via copolymerization with monomers that are inert to halogen compounds.

4. A new generation of halogenated high index polymers exhibit higher refractive index and lower extinction coefficient compared with P4VP-I\textsubscript{2}, and remains stable until 250°C.
Appendix