Halogenated high index polymer coating

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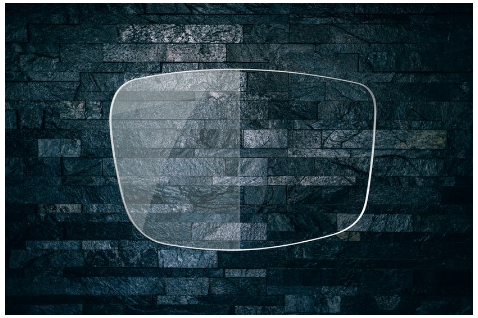
Introduction: high index materials

What is high index materials?

lens

URL: https://techcrunch.com/2021/09/14/apple-brings-macro-low-light-and-cinema-focused-updates-to-the-iphone-13-pro-camera/

Antireflective coating



URL: https://www.zeiss.com/vision-care/int/labs/coating-technologies.html

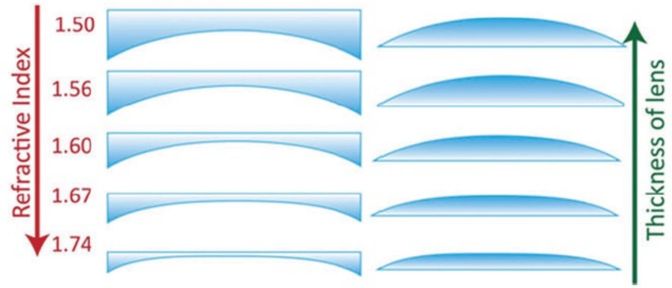
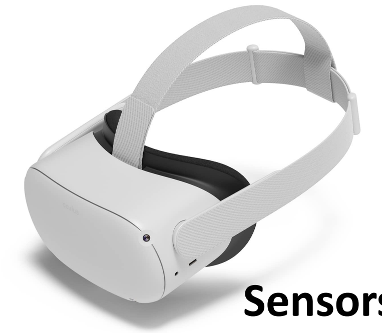


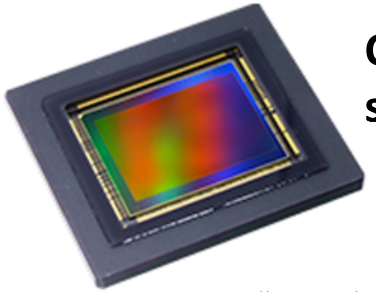
Figure 1. Representation of refractive index *versus* required lens thickness.

https://www.agc.com/en/products/electoric/optical-glass/high-refractive/applications.html



Sensors

URL: https://www.oculus.com/quest-2/



CMOS sensor

URL: https://global.canon/en/

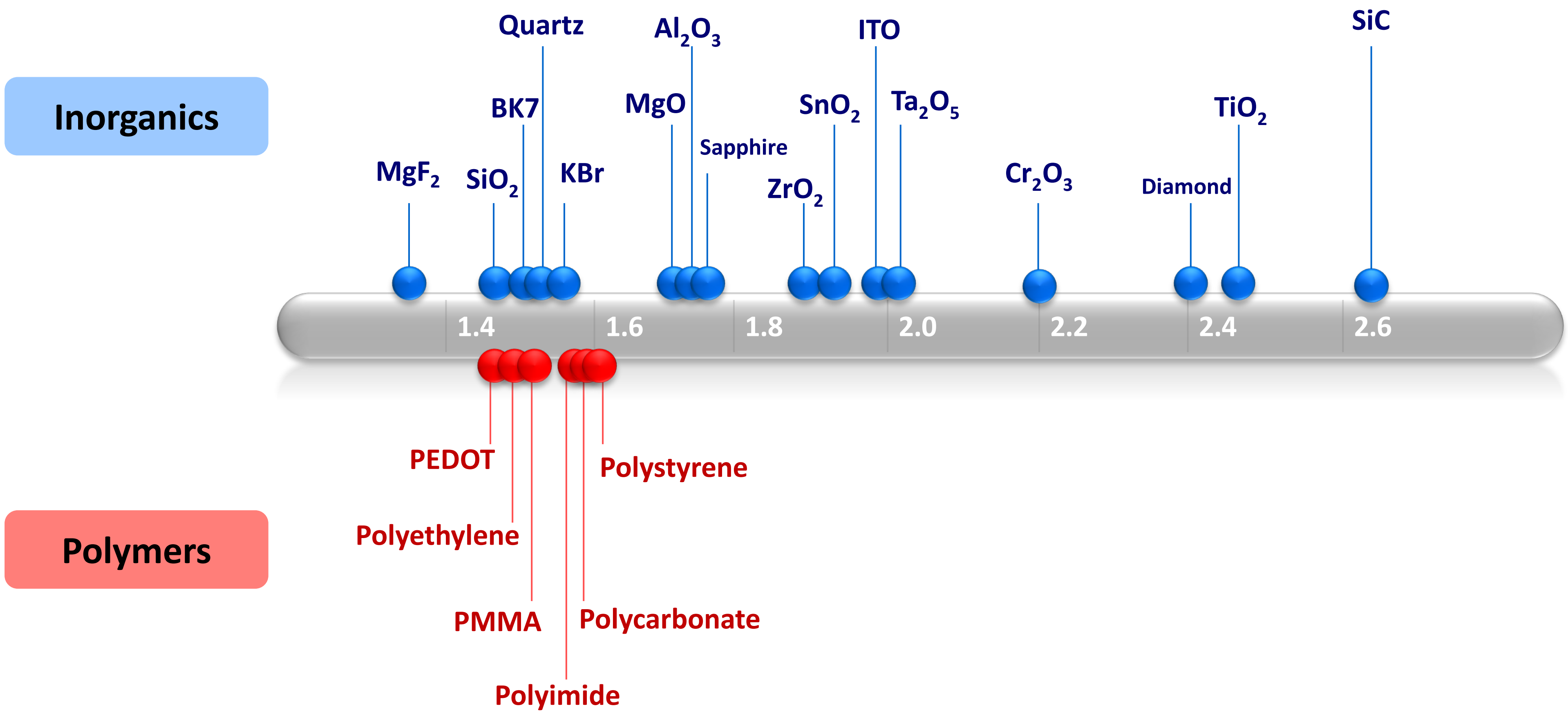
With a higher RI,
the material can be thinner

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

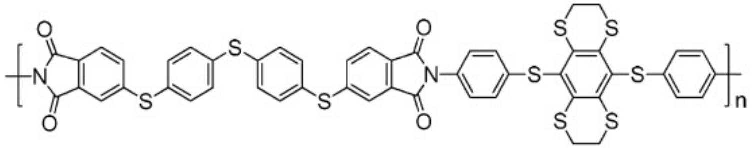
Refractive indices of polymers ranges from 1.3 – 1.7



Polymer has a much lower upper limit of RI compared with inorganic material

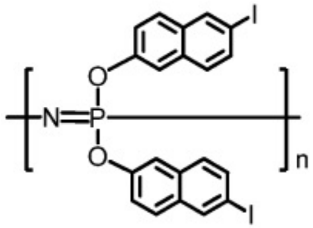
Recent progress in high refractive index polymers

Sulfur containing polyimides

Example: 

RI = 1.769

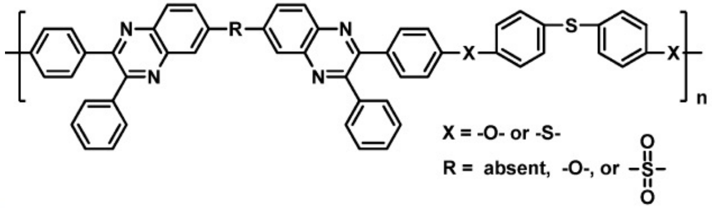
Phosphorous containing high-n polymers

Example: 

RI = 1.750-1.755

These newly developed HRIPs involve complicated synthesis processes, and yet still didn't achieve a RI higher than 1.8

Polyphenylquinoxalines

Example: 

RI = 1.728-1.795

Design HRIPs

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

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

Cause absorption

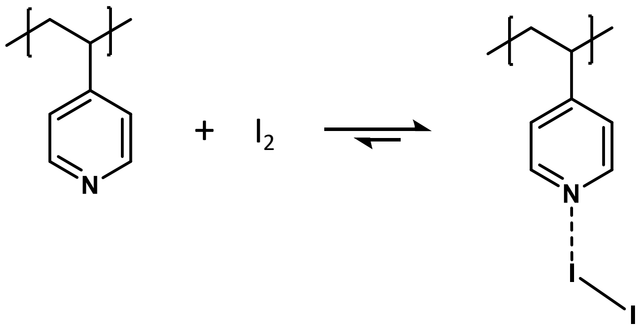
Strategy: incorporate **iodine** directly into the polymer chain to increase RI

Design HRIPs

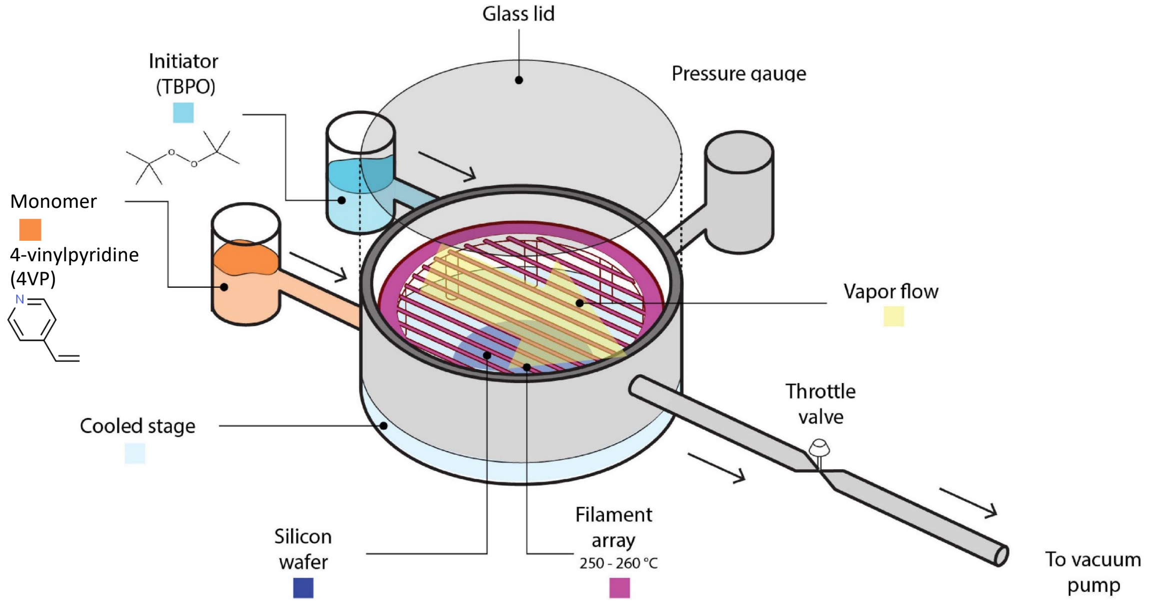
To incorporate iodine into polymer → **Find A polymer that can lock down iodine** → P4VP can form CTC with iodine

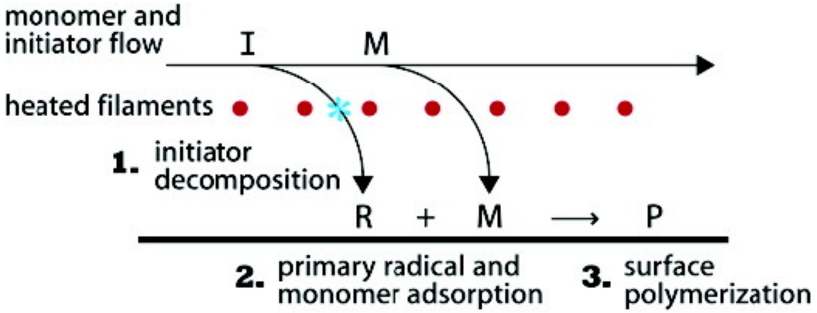
Poly(4-vinyl pyridine) (P4VP)

P4VP-I_2 Charge transfer complex (CTC)



Preparation of P4VP thin film by using Initiated chemical vapor deposition (iCVD)





https://doi.org/10.1002/adem.201700622

Reaction mechanism proposed for iCVD polymerization

gas phase reactions

initiator decomposition: $I(g) \xrightarrow{k_d} 2R\bullet(g)$ **(1)**

gas-to-surface processes

primary radical adsorption: $R\bullet(g) \xrightarrow{k_{ad,R}} R\bullet(ad)$ **(2)**

monomer adsorption: $M(g) \xrightarrow{k_{ad,M}} M(ad)$ **(3)**

surface reactions

initiation: $R\bullet(ad) + M(ad) \xrightarrow{k_i} M_1\bullet(ad)$ **(4)**

propagation: $M_n\bullet(ad) + M(ad) \xrightarrow{k_p} M_{n+1}\bullet(ad)$ **(5)**

termination: $M_n\bullet(ad) + M_m\bullet(ad) \xrightarrow{k_t} M_{n+m}(ad)$ and $M_n(ad) + M_m(ad)$ **(6)**

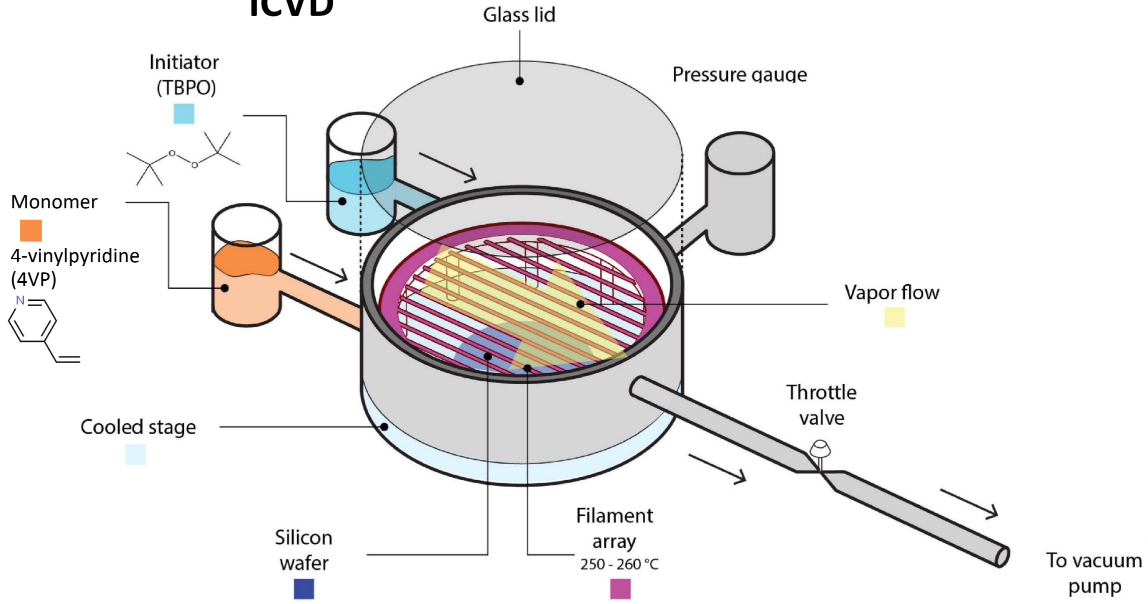
primary radical termination: $M_n\bullet(ad) + R\bullet(ad) \xrightarrow{k_t'} M_n(ad)$ **(7)**

primary radical recombination: $R\bullet(ad) + R\bullet(ad) \xrightarrow{k_t''} R_2(ad)$ **(8)**

https://doi.org/10.1002/adem.201700622

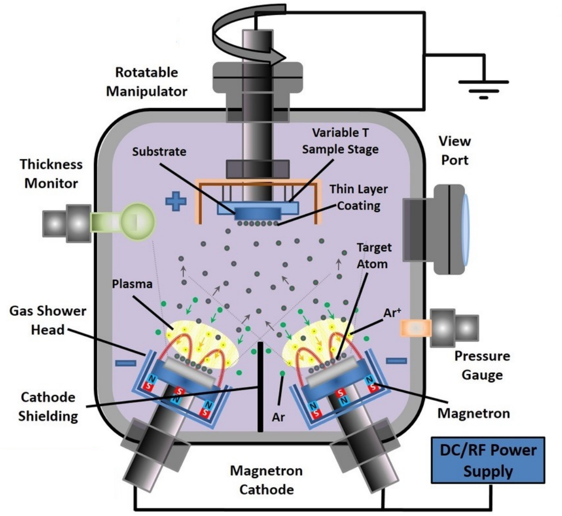
iCVD vs. PVD

ICVD

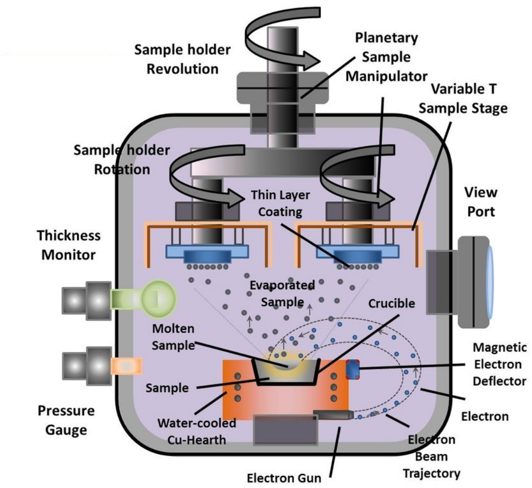


https://doi.org/10.3389/fbioe.2021.670541

Sputtering



Evaporation



https://www.adnano-tek.com/pvd.html

ICVD:

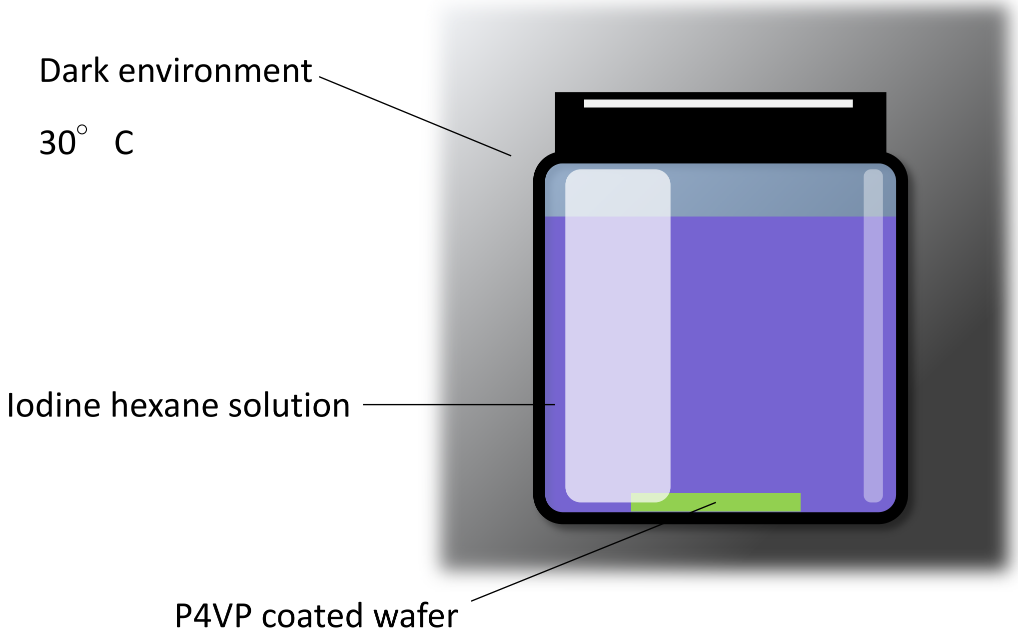
Conformal	Fast deposition rate
Low cost	Room temperature
Scale up	Coat on flexible substrate

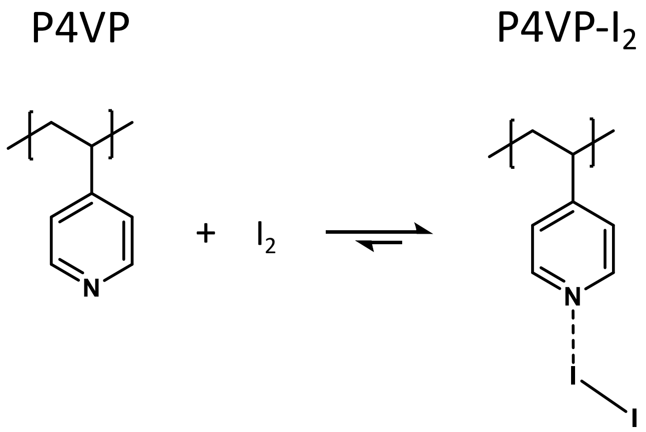
PVD:

Light of sight deposition	Slow deposition rate
Small deposition range	High vacuum requirement
Expensive	High temperature

Preparation of P4VP-I_2 Charge transfer complex (CTC)

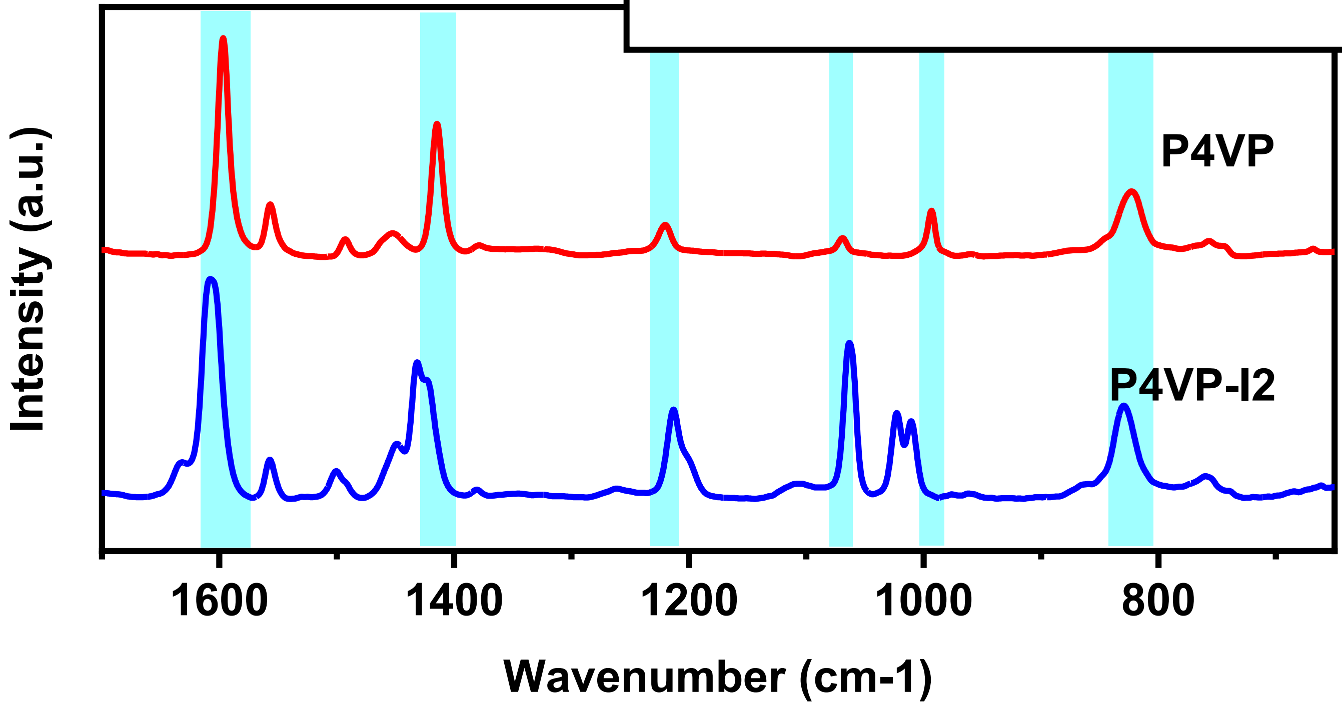
A charge-transfer complex (CTC) is an association of two or more molecules, in which a fraction of electronic charge is transferred between the molecular entities.



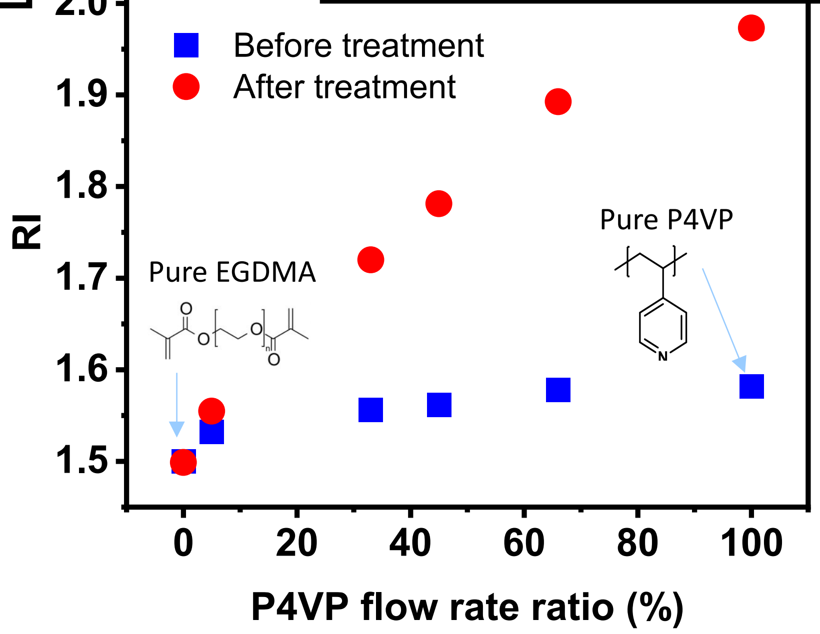


Effective halogen incorporation confirmed by FTIR

The peak shift in P4VP-I_2 can be attributed to electron redistribution to the $I^{\delta+}$ acceptor in CTCs



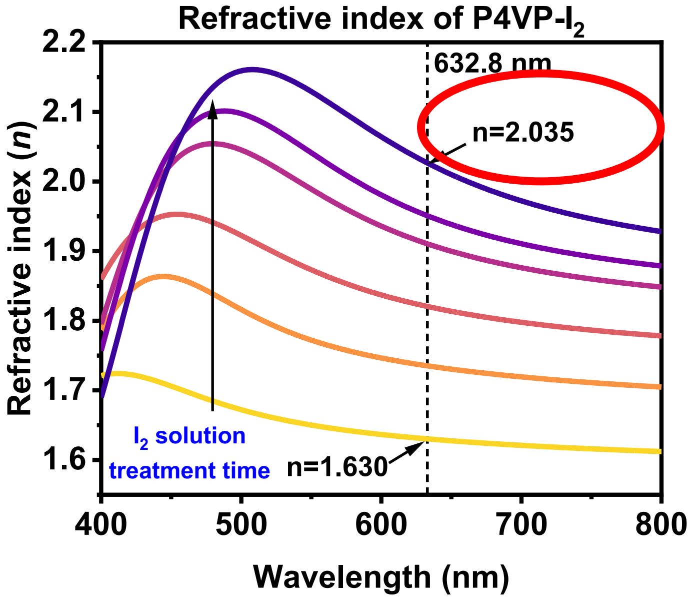
RI can be fine-tuned by controlling CTC % in the polymer film via copolymerization with monomers that inert to halogen compounds

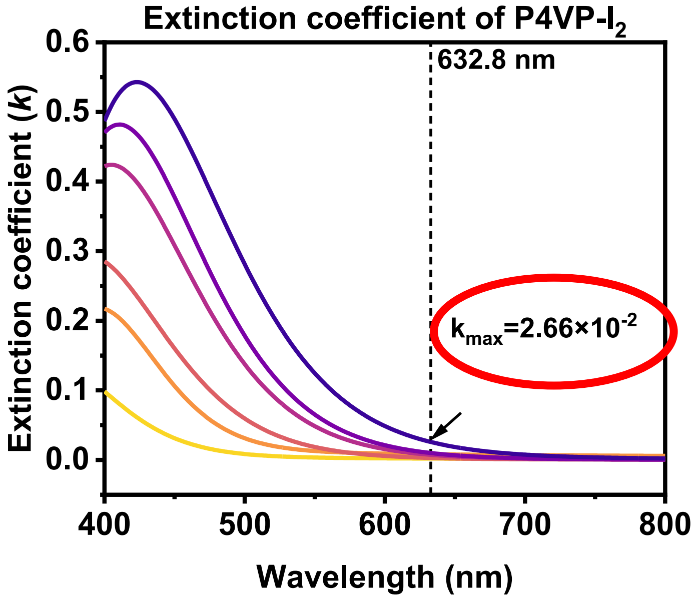


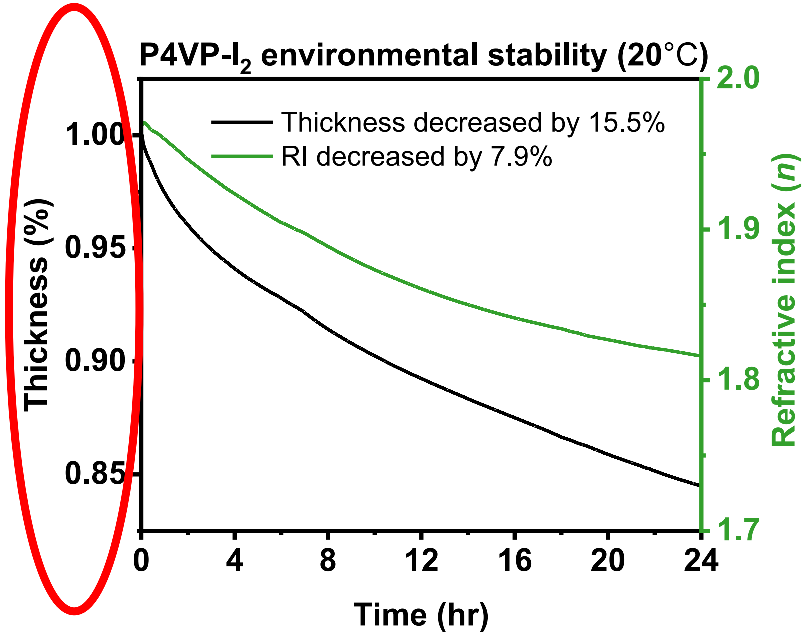
P4VP thin films copolymerized with ethylene glycol dimethacrylate (EGDMA)

The FTIR results demonstrated the formation of charge transfer compounds between P4VP and iodine

P4VP-I_2 high index film





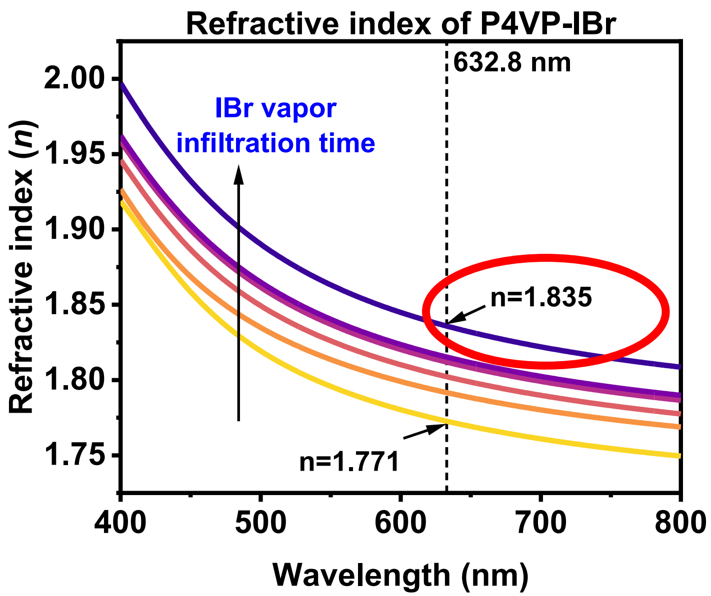


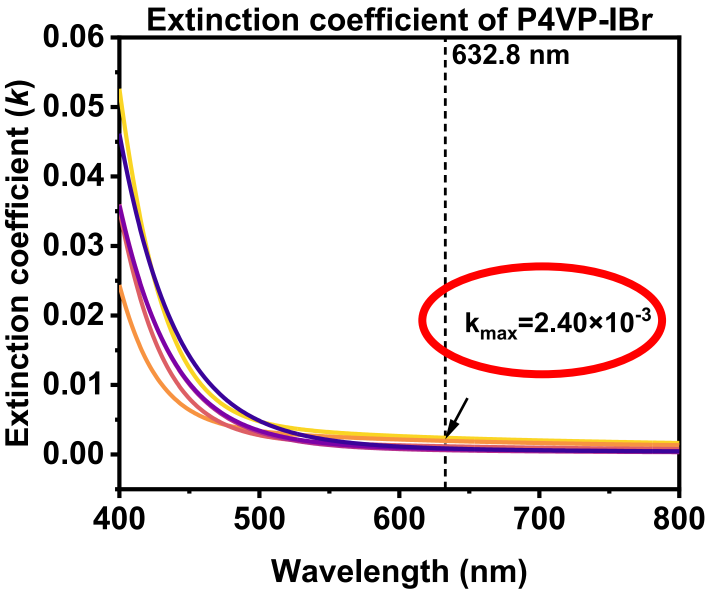
After 24hrs environmental stability test at 20C:
The refractive index of P4VP-I_2 decreased by **7.9%**

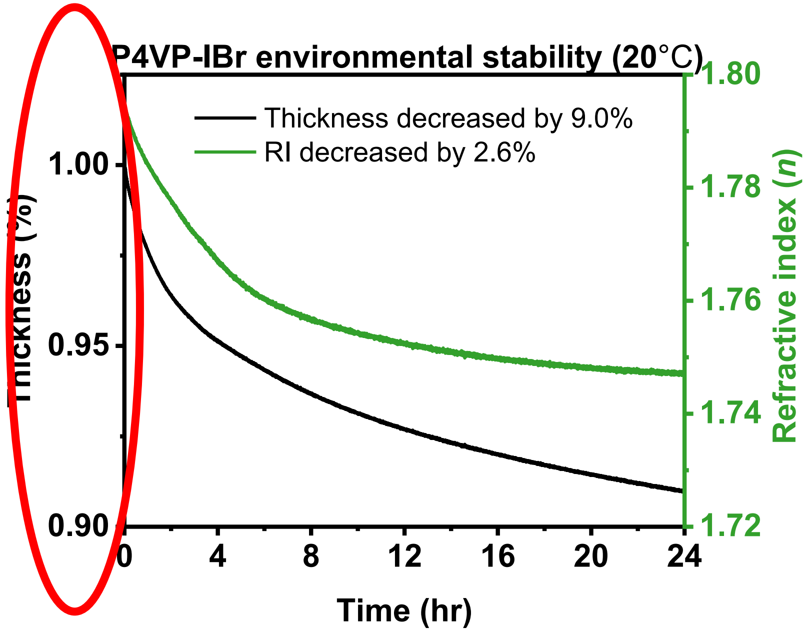
- **The RI of P4VP-I2 is tunable by altering the iodine solution treatment time**
- **The maximum achievable refractive index for P4VP-I_2 is higher than 2.0+**
- **Thermal stability needs further improvement**

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

P4VP-IBr high index films



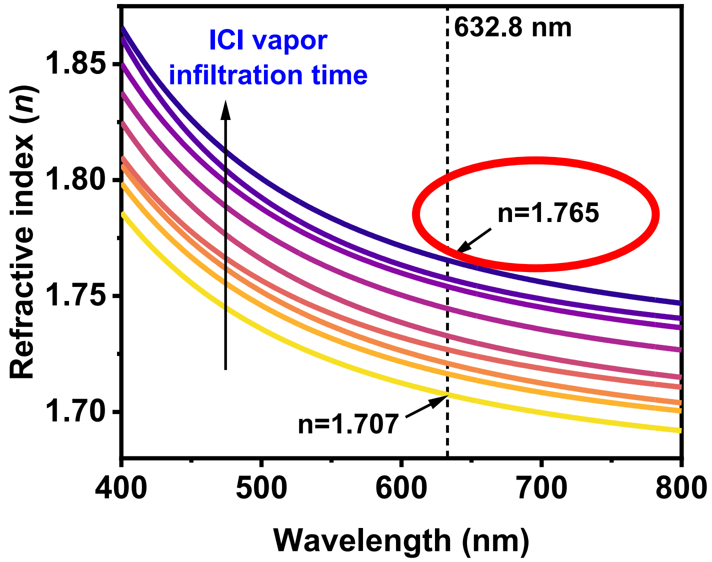


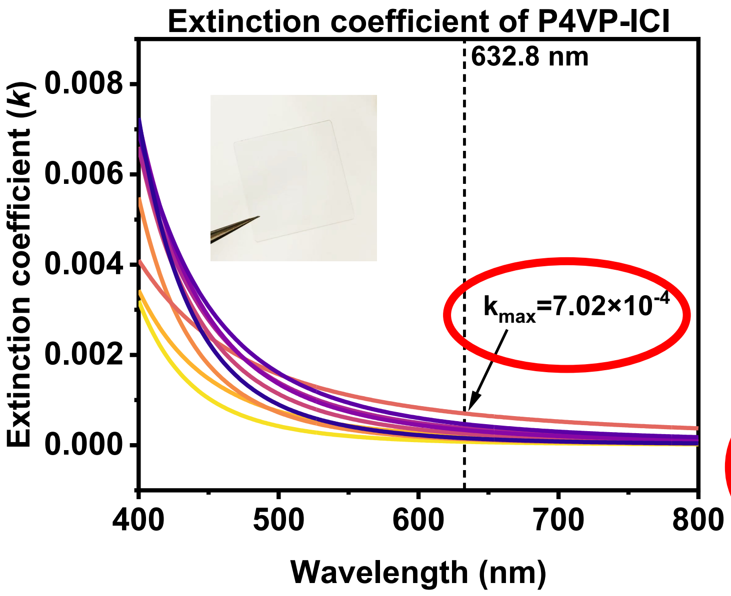


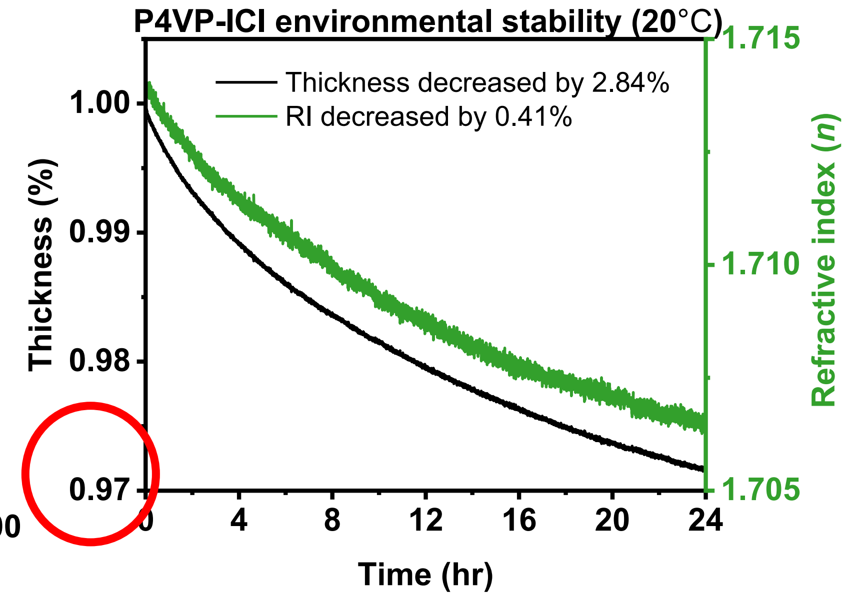
After 24hrs environmental stability test at 20C:
The refractive index of P4VP-I_2 decreased by **2.6%**

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

P4VP-ICl high index films





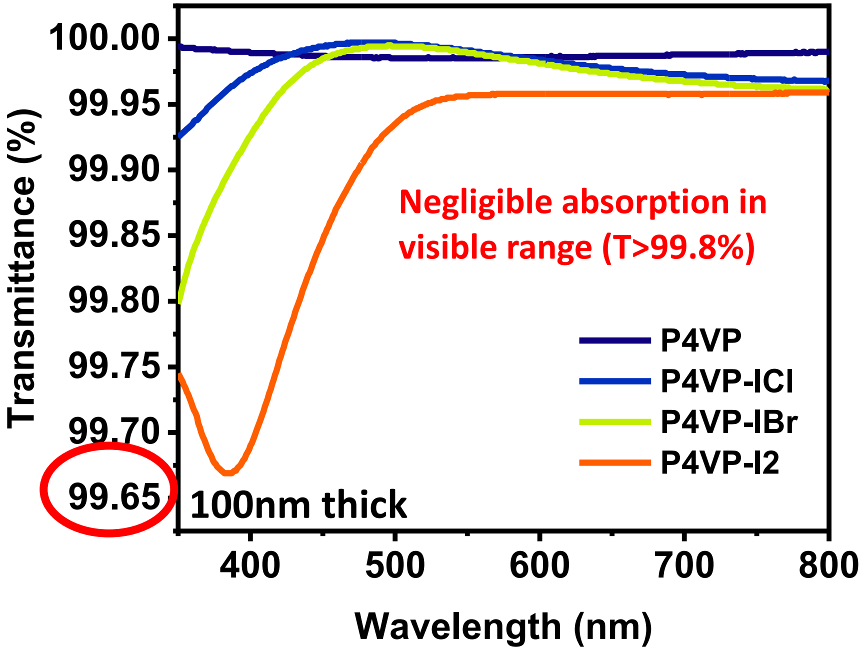


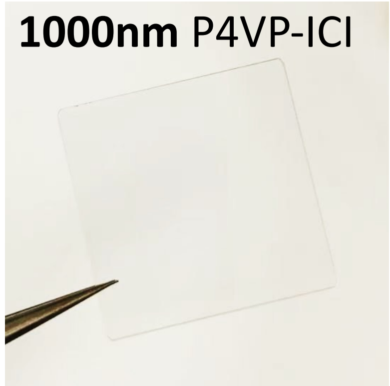
After 24hrs environmental stability test at 20C:
The refractive index of P4VP-I_2 decreased by **0.41%**

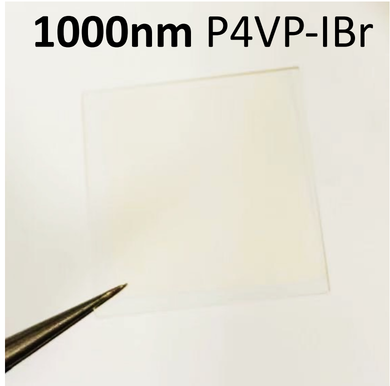
P4VP-ICl is more thermally stable than both P4VP-IBr and P4VP-I2.
The extinction coefficient of P4VP-ICl in visible wavelength range is negligible.

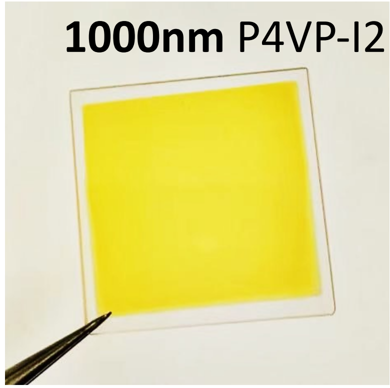
By increasing the degree of ionization of the prepared CTC, the stability of P4VP-IX is greatly improved

Absorption of halogenated polymer films





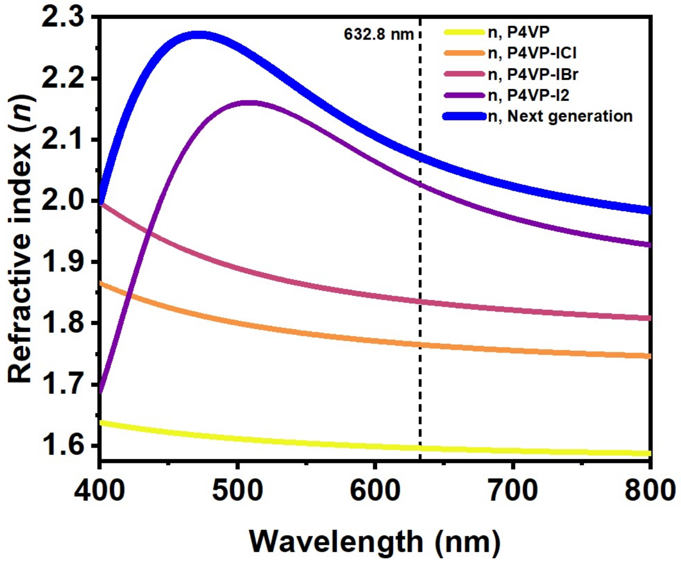




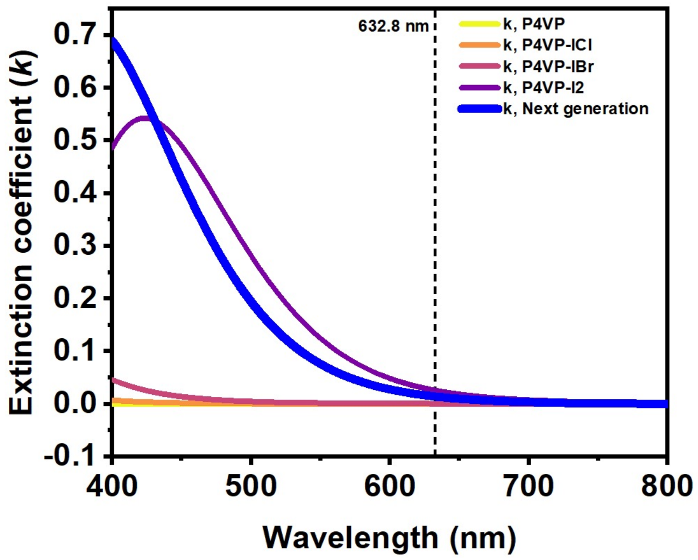
P4VP-ICl and P4VP-IBr has negligible absorption in visible wavelength range

Next generation halogenated high index polymer

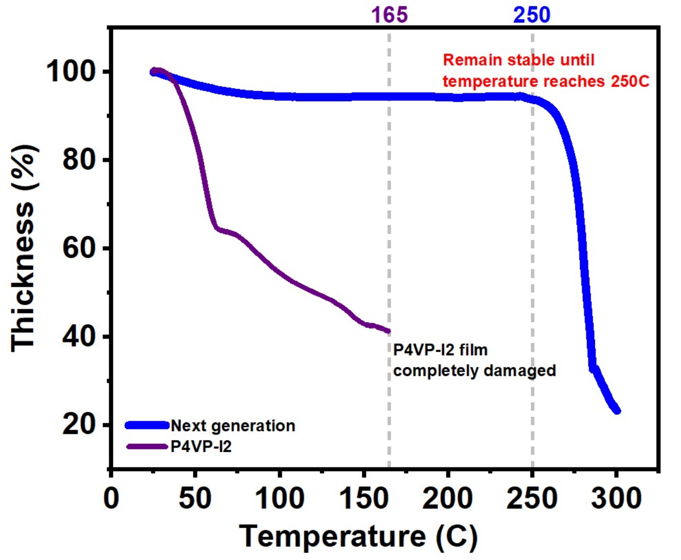
Higher RI



Smaller k



Improved thermal stability



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_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 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_2, and remains stable until 250C.

Appendix