Synthesis of High Refractive Index Polythiocyanurates

Songyan SHI(史　松炎), Yoshihisa ONODERA (小野寺養修),
Yuji SHIBASAKI (芝崎祐二), Yoshiyuki OISHI (大石好行)

Department of Chemistry, Graduate School of Engineering, Iwate University
4-3-5 Ueda, Morioka, Iwate 020-8551, Japan

Abstract: The polythiocyanurates with high molecular weights were successfully prepared by the phase-transfer catalyzed polycondensation of triazinedithiol with activated dibromides. These polymers were soluble in THF and NMP, and readily afforded colorless and transparent cast films. The films of polythiocyanurates exhibited good thermal stabilities such as thermal decomposition temperatures of 320 ˚C in air. A relatively high glass transition temperatures of the polymers were in the range of 112-143 ˚C. The optical transmittance of the films was as high as 80% at 380 nm. The films exhibited high refractive index of 1.730 at D line, which is attributed to the triazine rings and sulfur atoms, and Abbe's number of 18. Furthermore, the film showed the low birefringence of 0.002 at d line. The obtained polythiocyanurates are promising candidates for thermoplastic lenses.
Keywords: polythiocyanurate / phase-transfer catalyzed polycondensation / triazinedithiol / high refractive index / low birefringence / thermoplastic

1. Introduction

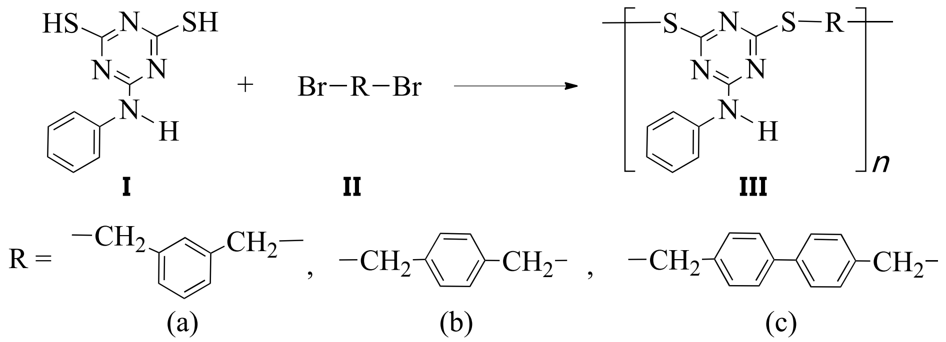
A high refractive index, low birefringence and good thermal solubility, and high optical transparency are the basic concerns in designing optical polymers for high performance components for advanced display devices, various lenses, and optical wave guides.[1] The advantages of polymers are their good proccessability, good impact resistance and lightweight compared to inorganic glasses.

Refractive indices of polymers can be expressed using the Lorentz-Lorenz equation.[2,3] According the equation, the introduction of structure moieties with a high molar refraction and a small molar volume efficiently increases refractive index of the polymers. Sulfur is the most commonly used atom for increasing the refractive index because of its high atomic polarizability and ability to be introduced into polymers. Various sulfur-containing polymers exhibiting high refractive index values have been reported for the optical applications.

Recently, in the image pickup optical system of a camera, thermoplastic lenses have been used instead of optical inorganic glasses. Several thermoplastic lenses with a high refractive index, a low birefringence have been reported such as polyesters. These polymers exhibited a relatively high refractive indices of 1.61-1.64 and a small birefringence of 0.001. Considering their use in thermoplastic lenses, their refractive indices over 1.7 are required. As well as the sulfur atom, heteroaromatic rings such as triazine[4] and pyrimidine[5] is a promising component with a high refractive index due to the higher polarity of the ring, the replacement of benzene units to heteroaromatic rings might be effective for the enhancement of the refractive index.

We now report the synthesis and characterization of polythiocyanurates (**III**) containing sulfur atoms and triazine units prepared by the polycondensation of triazinedithiol (**I**) and activated dibromides (**II**). The polythiocyanurates exhibited excellent optical transparency as high as 80%

over the wavelength of 380 nm, and furthermore afforded high refractive indices of 1.73 and low birefringence values as well as good thermal stability.



(1)

2. Results and Discussion

The phase-transfer catalyzed polycondensation has been preferably used for the synthesis of the polysulfides using dithiols or sodium sulfide as a nucleophilic monomer[6-8]. We had adopted this polymerization method to the synthesis of 1,3,5-triazine-containing polysulfides[4,9] by the polycondensation of triazinedithiols with α,α'-dibromoxylene or 1,10-dibromodecane in the nitrobenzene-aqueous alkaline solution system in the presence of a phase-transfer catalyst. The synthesis of polythiocyanurates (**III**) from 6-anilino-1,3,5-triazine-2,4- dithiol (**I**) and activated dibromides (**II**) was investigated by the two-phase polycondensation [Eq. (1)]. Polycondensation was carried out in a nitrobenzene-aqueous NaOH solution in the presence of cetyltrimethylammonium

Table 1. Synthesis of polythiocyanurates by two-phase polycondensation[a)]

Polymer	Temp. (°C)	Solvent (mL)	Yield (%)	η_{inh} [b)] (dL/g)	M_n [c)]/10^4	M_w/M_n
IIIa	70	5	76	0.82	5.5	2.4
IIIb	70	5	80	0.93	6.2	1.9
IIIc	r. t.	8	81	0.71	5.2	2.8

a) Polymerization was carried out with each monomer (2.5 mmol) in the presence of CTMAB (40 mol%) in nitrobenzene and of 1M aqueous sodium hydroxide (5.1 mL) for 24 h. b) Measured at a concentration of 0.5 g/dL in NMP at 30 °C. c) Determined by GPC on the basis of polystyrene calibration in NMP containing 0.01 wt% LiBr.

bromide (CTMAB, 40 mol%) at r.t. or 70 °C for 24 h. The results are summarized in Table 1.

Three types of colorless polymers **IIIa-IIIc** with high inherent viscosities (η_{inh}) of 0.7-0.9 dL/g and number average molecular weight (M_n) of 50000-62000 were successfully obtained. The chemical structures of polymers **III** were characterized by ^{1}H and ^{13}C NMR and FT-IR spectroscopies.

The solubilities of polymers **III** are summarized in Tabled 2. All polymers were soluble in common organic solvents such as THF, DMF, DMAc and NMP, probably due to the presence of methylene units in the polymer backbone structure.

The thermal decomposition temperature and glass transition temperature (T_g) are quite important considering the thermal process for optical device fabrication. The thermal properties of polymers **III** were investigated by TG and DSC measurements. The results are summarized in Table 3. Polymers **III** showed good thermal stability, a 5% weight loss temperature (T_5) around 320 °C under air atmosphere. The T_g values of polymers **IIIa-IIIc** were in the range of 112-143 °C. Thermoplastic lenses are required to have a relatively high T_g over 110 °C because injection molding is generally carried out around 100 °C higher than the T_gs of the polymers to increase their fluidity in the molten state. Thus, the T_g of thermoplastic polymers processable by injection molding would be suitable at around 120-150 °C. Polymer **IIIc** possessed the highest T_g due to the introduction of the rigid biphenylene units. *m*-Linkages and methylene units contributed to lower T_g of polymer **IIIa.**

Table 2. Solubility[a)] of polythiocyanurates

Polymer	NMP	DMAc	DMF	THF	$CHCl_3$
IIIa	+	+	+	+	-
IIIb	+	+	+	+	-
IIIc	+	+	+	+	-

a) Solubility: +, soluble at room temp.; -, insoluble.

Table 3. Thermal properties of polythiocyanurates

Polymer	T_g[a)] (°C)	T_5[b)] (°C)		T_{10}[c)] (°C)	
		in air	in N_2	in air	in N_2
IIIa	112	319	336	328	343
IIIb	126	320	338	327	347
IIIc	143	316	338	327	345

a) By DSC at a heating rate of 20 °C/min. b) 5% weight loss temperature by TG at a heating rate of 10 °C/min. c) 10% weight loss temperature.

The optical properties of the polymer **III** films with a thickness of 24-33 μm are shown in Table 4. The cutoff wavelengths (λ_{cutoff}) of the polymer **III** films were in the range of 336-338 nm, and the transmittance was as high as 80% at around 380 nm. The refractive indices (n_D) of the polymer **III** films were measured at D line by an Abbe's refractmeter. All the films exhibited high n_D values of 1.7292-1.7304, resulting from the sulfur atoms and the triazine rings with a high molar refraction. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of the polymer **IIIc** film were 1.7383 and 1.7361 at d line, respectively by a prism coupler. The low birefringence (Δn) value of 0.002 was observed for polymer **IIIc** because of its methylene units. The calculated Abbe numbers for polymers **III** were in the range of 18.0-18.2.

Table 4. Optical properties of polythiocyanurates

Polymer	d[a)] (μm)	λ_{cutoff}[b)] (nm)	λ_{80}[c)] (nm)	n_F[d)]	n_D[d)]	n_C[d)]	ν_D[e)]
IIIa	33	338	380	1.7590	1.7292	1.7184	18.0
IIIb	25	336	358	1.7599	1.7304	1.7196	18.1
IIIc	24	336	380	1.7587	1.7303	1.7186	18.2

a) Film thickness. b) Cutoff wavelength. c) 80% transmittance wavelength.
d) Refractive index by Abbe's refractmeter. e) Abbe's number: $n_D= (n_D- 1)/(n_F- n_C)$.

3. Conclusions

A series of polythiocynurates with high molecular weights were successfully prepared by the phase-transfer catalyzed polycondensation. The polythiocyanurates had a high potential as a target material exhibiting a high refractive index of 1.73, high transparency, low birefringence, and relatively high glass transition temperatures of 126-143 °C, and excellent thermal stability. Therefore, the polythiocyanurate is a promising candidate for thermoplastic lenses.

References

[1] H. Higasihara and M. Ueda, *Macromolecules*, **48**, 1915 (2015).
[2] H. A. Lorentz, *Ann. Phys.*, **9**, 641 (1880).
[3] L. V. Lorenz, *Ann. Phys.*, **11**, 70 (1880).
[4] J. J. Kim, Y. Oishi, H. Hirahara and K. Mori, *Kobunshi Ronbunshu*, **56**, 159 (1999).
[5] K. Nakabayashi, T. Imai, M. C. Fu, S. Ando, T. Higashihara and M. Ueda, *J. Mater. Chem. C.*, **3**, 7081 (2015).
(for more regferences goto p107)