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NOVEL THIOPHENE METHACRYLATES FOR MATERIALS OF HIGH REFRACTIVE INDEX

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Key Words: Thiophene Methacrylate, High Index Monomer, Optical Material

ABSTRACT

Authors designed the monomers having hetero-aromatic rings in their structures as optical materials of high refractive index. Among various hetero-aromatics, we noticed thiophene has a large atomic refraction. We synthesized novel mono- and bi-functional thiophene methacrylate derivatives. Their homopolymers had high refractive indices indeed and are promising for optical materials.

INTRODUCTION

Materials used as optical members such as lenses, prisms, optical wave-guides and disc substrates are required to be colorless and transparent. Especially, in the case of lenses for spectacles, transparent synthetic resins are extending a range of their applications as materials that replace inorganic optical materials because they are lightweight and excellent in impact resistance, processability, and dye-

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ability. Various characteristics are required to be transparent synthetic resins as optical materials. Of these, the refractive index is quite important [1-3]. For example, transparent synthetic resins having high refractive index, when used as lenses, can be rendered thinner than materials having low refractive index to give the same focal distance. The use of thin lenses contributes to reducing the volume of space occupied by lenses in optical assemblies, which can advantageously make an optical apparatus lightweight and small-sized. The Abbe number is also important for plastic lenses [1-3]. Larger Abbe number means lower dispersion, that is, smaller chromatic aberation. Generally speaking however, a material having high refractive index usually has small Abbe number. Whereas, sulfur-containing aromatic methacrylates have high refractive indices and larger Abbe numbers [4]. A typical sulfur-containing aromatic is thiophene. Sulfur atom has a large atomic refraction as well as bromine [5]. Aromatic ring also has a large molecular refraction. Therefore, we thought that thiophene which is a sulfur-containing hetero-aromatic ring is a good candidate as a component of a high index monomer. On the other hand, methacrylate is easy to polymerize and transparent suitable for optical material. We designed and synthesized novel mono- and bi-functional methacrylate derivatives which have a thiophene moiety in their structures. There have been a few such methacrylatesreported so far. T. Miyazaki *et al.* reported α-methylstyrene having a benzothiazole ring [6, 7]. R. K. Khanna *et al.* reported a polymer having pendant thiophene group [8, 9]. L. Gargallo *et al.* reported some properties of thienylmethyl methacrylate polymer [10-12].

EXPERIMENTAL

Preparation of 2-(Bromomethyl)dibromothiophene

2-(Hydroxymethyl) thiophene 25.7 g, 0.225 mol and tetrachloromethane 100 ml were placed in a 300 ml flask equipped with a stirrer, thermometer, cooler, and dropping funnel. Under stirring, bromine 73.8 g, 0.462 mol was added dropwise and the reaction mixture was kept stirring for 4 days at 50-55°C. After that, bromine 30.8 g, 0.194 mol was further added and the reaction mixture was kept stirring for 1 day at the same temperature. The reaction was monitored by GC and identified by GC-MS. Analyzing the reaction products by GC, 2-(bromomethyl) dibromothiophene was formed in 84% yield. After purification by silica gel chromatography, 2-(bromomethyl)dibromothiophene 37.9 g, 0.113 mol was obtained (yield 50.4%).

2-(Hydroxymethyl)thiophene 25.7 g, 0.225 mol of and tetrachloromethane 100 ml were placed in a 300 ml flask equipped with a stirrer, thermometer, cooler, and dropping funnel. Under stirring, bromine 161.7 g, 1.013 mol was added dropwise, and the reaction mixture was kept stirring for 1 day at room temperature. The reaction was monitored by GC and identified by GC-MS. Analyzing the reaction products by GC, 2-(bromomethyl)tribromothiophene was formed in 82% yield. After evaporation of the solvent, the reaction products were purified by recrystallization from petroleum ether to obtain 60.4 g, 0.146 mol of 2-(bromomethyl)tribromothiophene (yield 65.0%).

Synthesis of 2-(Methacryloyloxymethyl)thiophene

2-(Hydroxymethyl)thiophene 10 g, 0.088 mol, triethylamine 16.1 g, 0.16 mol, chloroform 100 ml, and phenothiazine 0.010 g were placed in a 300 ml flask equipped with a stirrer, a thermometer, a cooler and a dropping funnel. Under stirring, methacryloyl chloride 12.5 g, 0.12 mol was added dropwise for 20 minutes at 20-30°C. Then, the reaction mixture was kept stirring for 2 hours at the same temperature. The reaction mixture was washed with water, dil.HCl aq., water, $NaCO_3$ aq., then water. The organic layer was dried by anhydrous Na_2SO_4, then chloroform was evaporated to obtain the crude product, which was purified by distillation *in vacuo* to obtain 2-(methacryloyloxymethyl)thiophene 10.9 g, 0.060 mol. The analytical data is summarized in Table 3. B.p. 87-88°C/1.5-2.0 Torr. Yield 68%. Elemental analysis: C; calcd. 59.32, obsd. 59.41 H; calcd. 5.53, obsd. 5.50 S; calcd. 17.59, obsd. 17.72 MS:m/e 182(M^+), ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.30 1H, 7.10 1H, 6.97 1H; (thiophene ring H), 6.14 1H, 5.57 1H; (CH_2=), 5.33 2H; (-CH_2-), 1.95 3H; (CH_3-), IR spectrum: shown in Figure 1.

Synthesis of 2-(Methacryloyloxymethyl)dibromothiophene

2-(Bromomethyl)dibromothiophene 38.0 g, 0.114 mol, potassium methacrylate 13.9 g, 0.112 mol, dimethyl sulfoxide 200 ml, and phenothiazine 0.02 g were placed in a 300 ml flask equipped with a stirrer, thermometer, and cooler. The temperature was raised to 55-60°C, and the reaction mixture was stirred for 5 hours. Then, the reaction mixture was poured into 1000 ml of 0.3N HCl aq. and extracted by 200 ml of diethyl ether three times. The ether layer was washed with water, NaOH aq., and water, then dried with anhydrous Na_2SO_4. After evaporation of ether, the resulting product was distilled *in vacuo* to obtain 21.1 g, 0.062 mol of 2-(methacryloyloxymethyl)dibromothiophene. (Yield

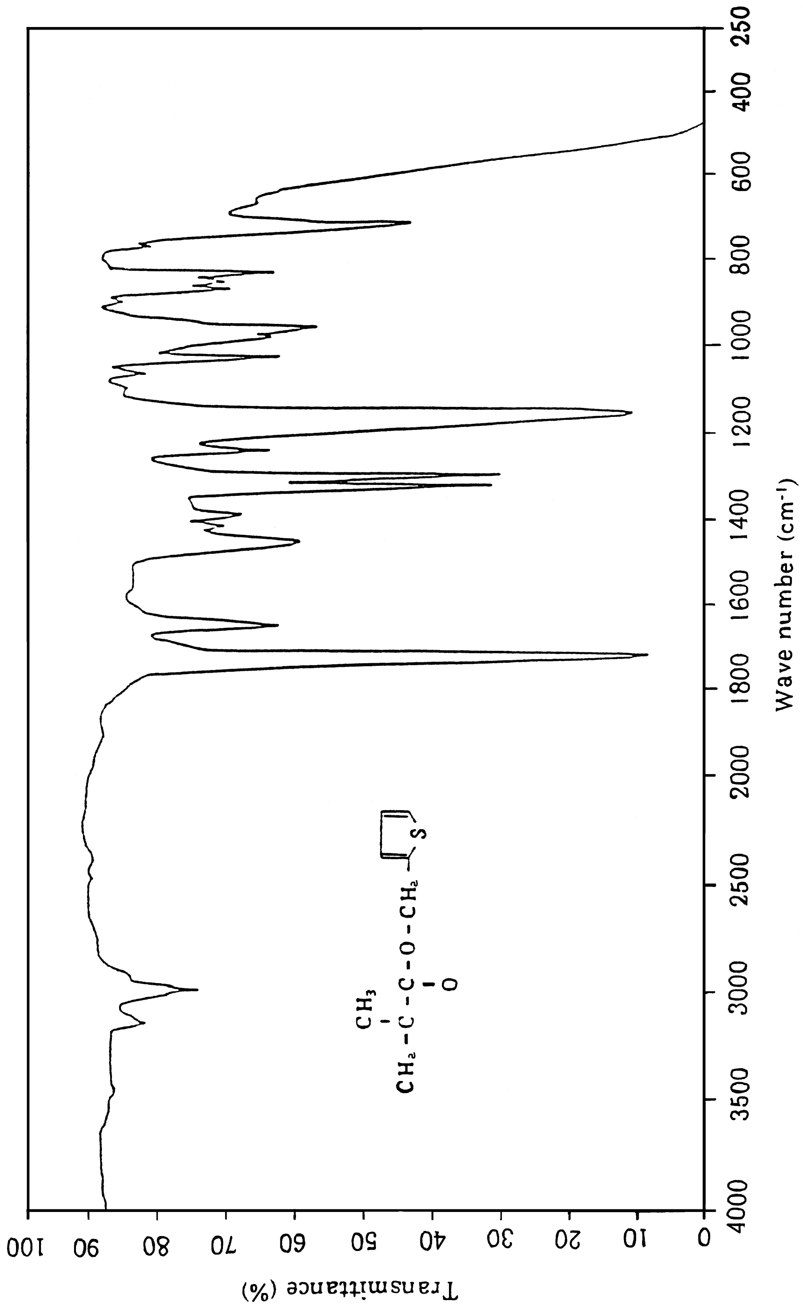


Figure 1. IR spectrum of 2-methacryloyloxymethylthiophene.

55.4%) b.p.; 113-114°C/0.8-1.0 Torr. 3,4-dibromo isomer: 3,5-dibromo isomer: 4,5-dibromo isomer = 18.7:48.4:32.9. The isomers were separated by a column chromatography. The analytical data is summarized in Table 3. IR spectrum; shown in Figure 2.

Synthesis of 2,5-Bis(methacryloyloxymethyl)-3,4-dibromothiophene

2,5-Bis(bromomethyl)-3,4-dibromothiophene 71.3 g, 0.167 mol, tetrachloromethane 500 ml, tetra-n-butylammonium bromide 1.61 g, 5.0 mmol, and phenothiazine 0.1 g were placed in a 1 l flask equipped with a stirrer, thermometer, cooler, and dropping funnel. The temperature was kept at 25-30°C, and 149.7 g, 0.400 mol of 33.2 wt% potassium methacrylate aqueous solution was added dropwise for 105 minutes. Then, the reaction mixture was stirred for 15 hours at 55-60°C. The resulting organic layer was washed with water and dried with anhydrous Na^2SO^4. After evaporation of tetrachloromethane, 54.8 g, 0.125 mol of the crude 2,5-bis(methacryloyloxymethyl)-3,4-dibromothiophene was obtained (yield 74.9%). The product was purified by recrystallization with methanol. The analytical data is summarized in Table 3. The IR spectrum is shown in Figure 3. The ^{1}H NMR spectrum is shown in Figure 4 and ^{13}C NMR spectrum is shown in Figure 5.

Polymerization

2-(Methacryloyloxymethyl)thiophene (10 g) and 2,2'-azobis(2,4-di-methylvaleronitrile) (0.05 g) were cast into a mold consisting of two glass plates and a silicone rubber gasket. The sheet was maintained at 50°C for 6 hours, at 60°C for 16 hours, at 90°C for 1 hour. The resulting resin sheet was colorless and transparent. The refractive index was found to be 1.582 and the Abbe number was 37.5.

Measurement

Refractive Index and Abbe Number

A small piece of 1.5 mm thick sheet-like polymer obtained by cast polymerization was subjected to measurement of a refractive index using an Abbe's refractometer, and an Abbe number was found from a dispersion table (13).

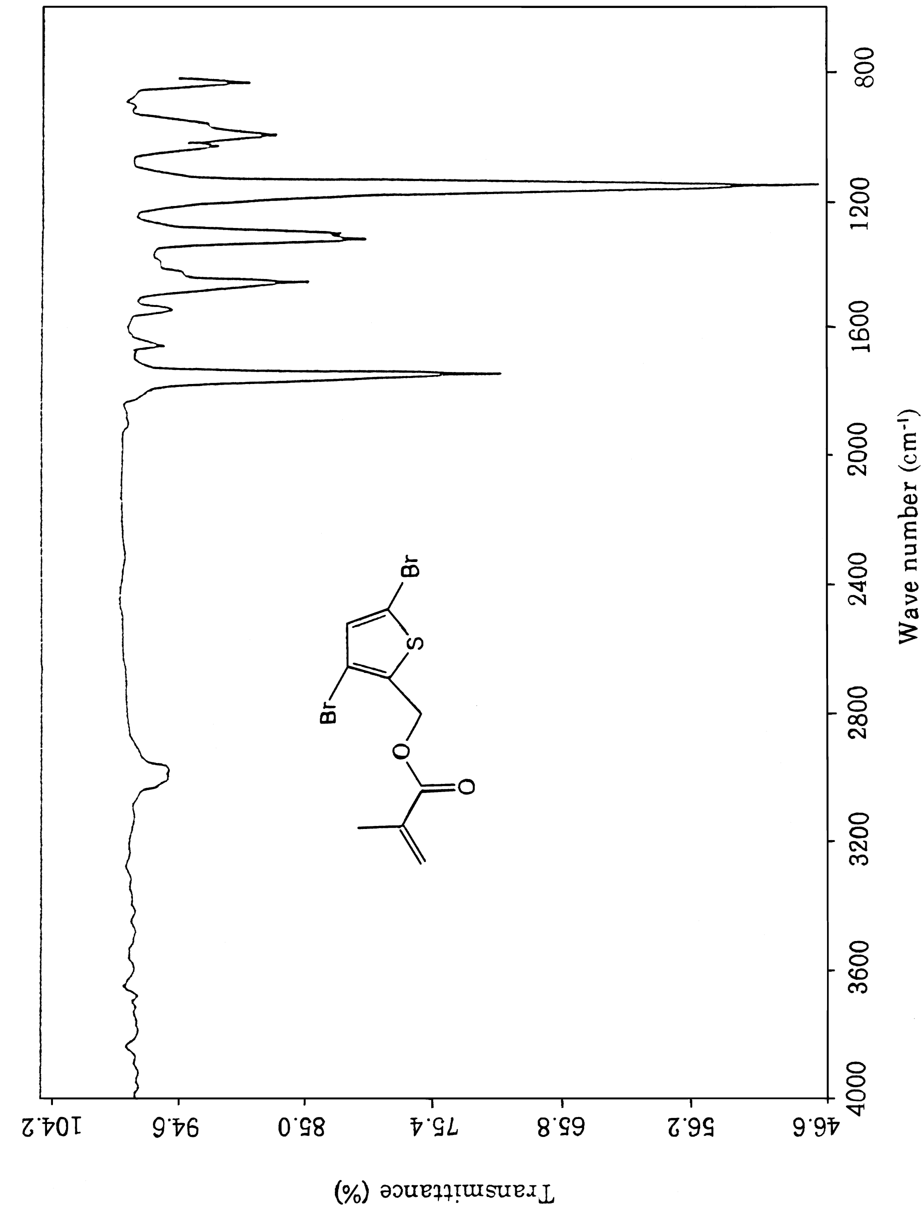


Figure 2. IR spectrum of 2-(methacryloyloxymethyl)dibromothiophene.

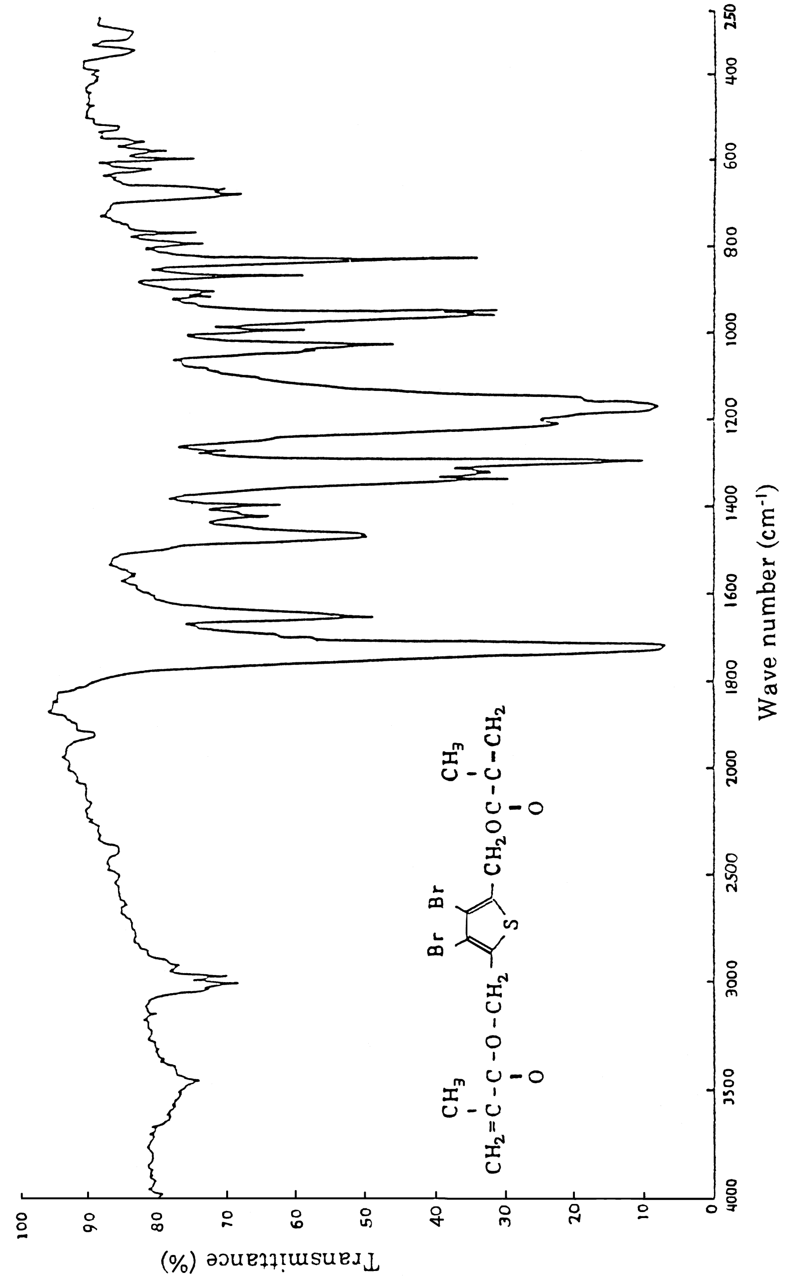


Figure 3. IR spectrum of 2,5-bis(methacryloyloxymethyl)dibromothiophene.

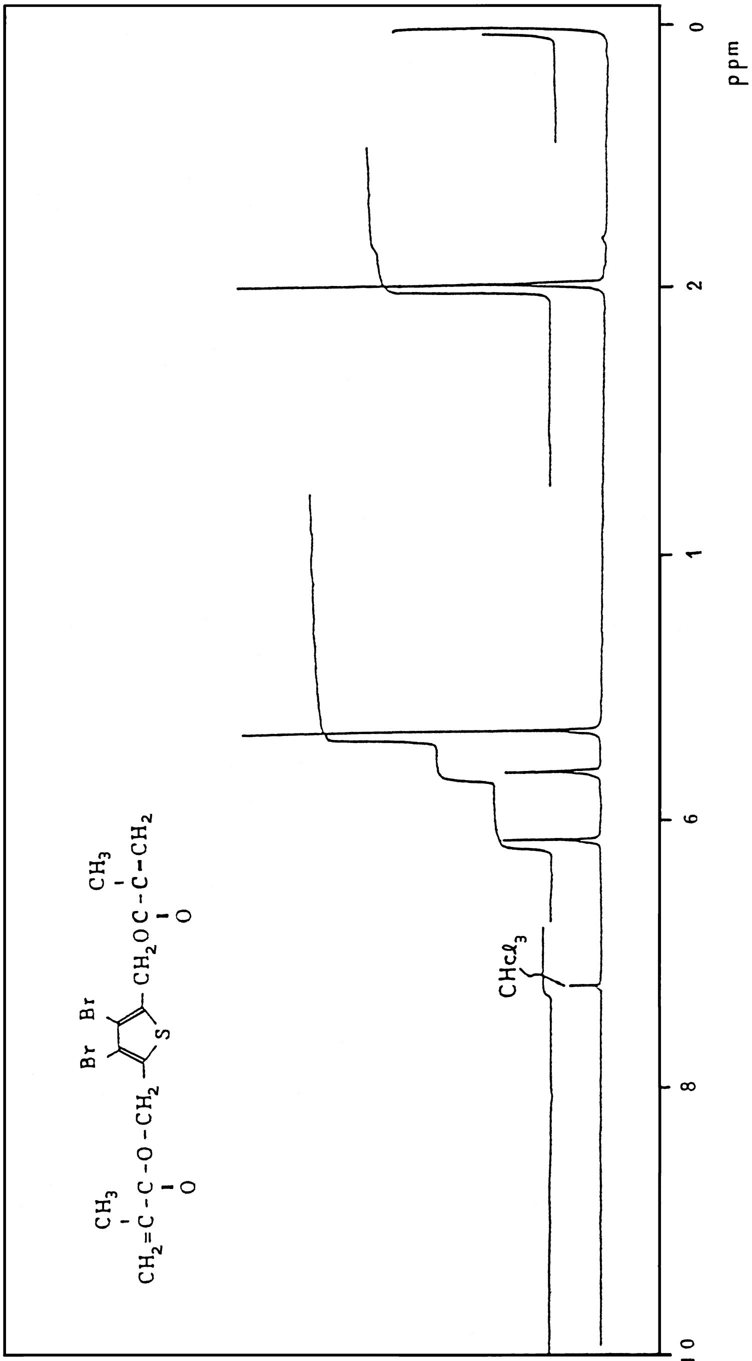


Figure 4. [1]H-NMR spectrum of 2,5-bis(methacryloyloxymethyl)dibromothiophene.

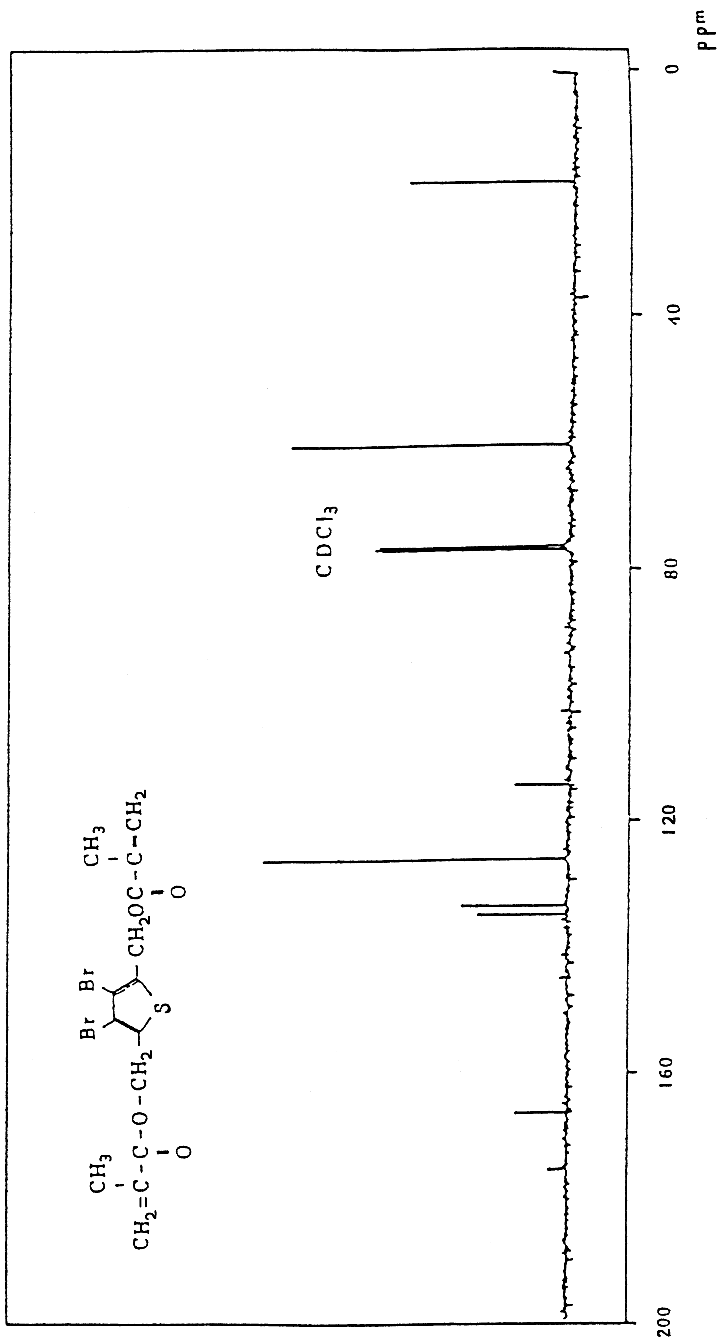


Figure 5. [13]C-NMR spectrum of 2,5-bis(methacryloyloxymethyl)d-bromothiophene.

RESULTS AND DISCUSSION

In designing high refractive index plastic lenses, we use the Lorenz-Lorentz Equation 1, which shows the relationship between refractive index and molecular structure.

$$\frac{n_D^2 - 1}{n_D^2 + 2} = \frac{[R_D]}{M} \cdot \rho = \frac{[R_D]}{V} \tag{1}$$

n_D: refractive index, M: molecular weight, ρ : density

V: molecular volume, R_D molecular refraction

Equation 2 is solved on n_D

$$n_D = \sqrt{\frac{1 + 2[R_D]/V}{1 - [R_D]/V}} \tag{2}$$

Dispersion, which is also significant optical property, is usually expressed by Abbe number described as the following Equation (3).

$$\upsilon_D = \frac{6\, n_D}{(n_D^2 + 2)(n_D + 1)} \cdot \frac{[R_D]}{[\Delta R]} \tag{3}$$

$$[\Delta R] = [R_F] \quad [R_C]$$

Although detailed discussions are given in the literature [14-17], larger density, larger molecular refraction, and smaller molecular volume lead to larger refractive index seeing from Equations 1 and 2. For such examples, aromatic ring, halogen atoms except fluorine, sulfur atom and heavy metal atoms are effective on increasing refractive indices. However, heavy metal atoms have defects of large specific gravity, low solubility toward organic compounds and coloring. Seeing from Equation 3, larger refractive index makes the Abbe num-

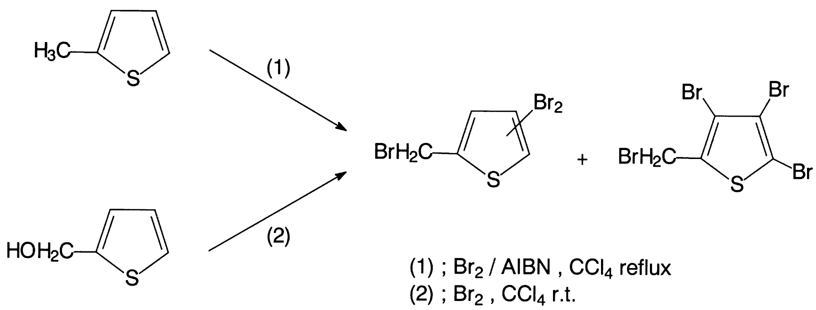
TABLE 1. Effects of Induced Group on Refractive Index and Abbe Number

Group,Atom	Refractive index	Abbe number
aromatic ring	++	−−
aliphatic chain	−	+
aliphatic ring	±	+
condensed aliphatic ring	+	+
bromine	++	± or −
sulfur	+	± or −
fluorine	−	±

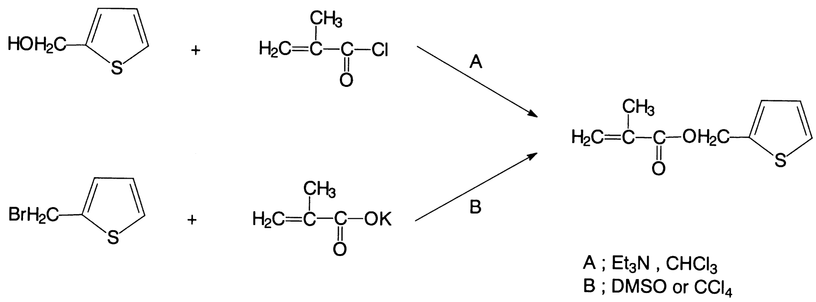
++ ; very effective + ; effective ± ; non- effective
−− ; very anti- effective − ; anti-effective

ber smaller in general. Therefore, there is the optimum point between refractive index and Abbe number. The effect on refractive index and Abbe number is summarized in Table 1.

We have looked into sulfur atom, bromine atom, and aromatic ring. In this paper, we describe the optical material using sulfur containing aromatic methacrylate, i.e., thiophene methacrylate derivatives. Methacrylate is very convenient for copolymerization and has advantage in a wide variety of compositions. Brominated thiophene is thought to be a moiety of very high refractive index. There are two routes to synthesize brominated thiophene (Scheme 1).



Scheme 1.



Scheme 2.

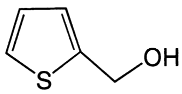
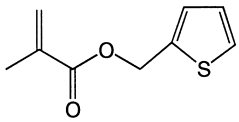
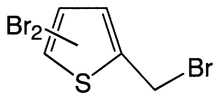
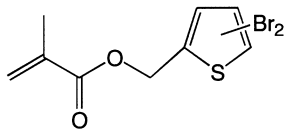
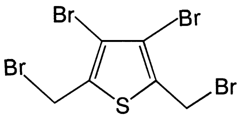
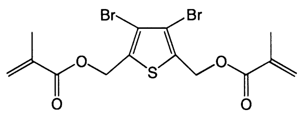
Radical bromination of 2-methylthiophene is easy to ocurr, but is very difficult to control. By-products such as dibromomethyl tribromothiophene are inevitable. On the other hand, bromination of 2-hydroxymethylthiophene is easier to control.

We propose two synthetic routes for thiophene methacrylate in Scheme 2. Route A shows the synthesis of the reaction of methacryloyl chloride and 2-hydroxymethylthiophene. Route B shows the synthesis of the reaction of potassium methacrylate and 2-bromomethyl thiophene. Route B is suitable for brominated thiophene methacrylate because brominated 2-bromomethyl-thiophene is easily synthesized by bromination of 2-hydrox-methylthiophene in Scheme 1 (Table 2). Isomers of dibromothiophene meth-acrylate could not be separated by distillation and were isolated by column chromatography. Analytical data of thiophene methacrylates are summarized in Table 3.

We examined the refractive index and Abbe number of the homopolymers of the thiophene methacrylates. In the case of 2,5-bis(methacryloyloxmethyl)-3,4-dibromthiophene, we obtained the refractive index by extrapolation of the data of different composition coplymers with styrene. As expected, the polymers from the thiophen methacrylate monomers exhibit high refractive index and large Abbe number (Table 4). They are promising candidates for high index lens monomers.

By using such novel thiophene methacrylates, we conducted coplymerization with various compositions. The results are summarized in Table 5. In the case of copolymerization of 2,5-bis(-methacryloyloxymethyl)thiophene (TMDMA) and benzyl methacrylate (BzMA), the transparent polymer having high refractive index (1.570) and high Abbe number (37) was obtained. When

TABLE 2. Synthesis of Thiophene Methacrylates

Thiophene	Method	Methacrylate	Yield(%)
	A		68.3
	B		55.4
	B		74.9

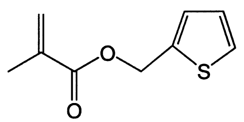
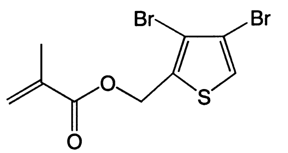
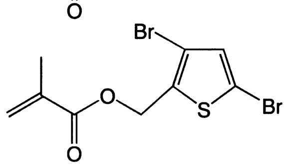
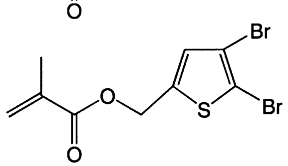
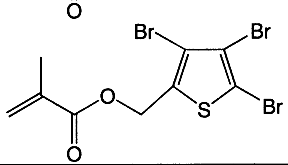
we used styrene (St) and S-benzylthio methacrylate (BzTMA) instead of BzMA in this case, the refractive index increased from 1.570 to 1.599 without any decrease of the Abbe number. Furthermore, we incorporated brominated thiophene (di)methacrylates or brominated methacrylates in the monomer composition. We obtained high index transparent polymer materials of n_D 1.582-1.611 and υ 33-40.

In order to apply these materials as optical materials, there may be many other properties required but we are sure that we can afford promising candidates of high refractive optical materials in this paper.

CONCLUSION

Authors afford novel mono- and bi-functional thiophene methacrylate derivatives which can be copolymerized with styrene or other vinyl monomers to obtain high refractive index optical materials such as lenses.

TABLE 3. Analytical Data of Thiophene Methacrylates

Thiophenemethacrylate	b.p (℃/ Torr)		Elemental analysis(%) C	H	S	Br	MS(m/e⁺)	¹H NMR σ (ppm)		
								7.30	1H	
								7.10	1H	thiophene ring
	87~88	calcd.	59.32	5.53	17.59			6.97	1H	
	/1.5~2.0	obsd.	59.41	5.50	17.72		182M$^+$	6.14	1H	-CH_2=
								5.57	1H	
								5.33	2H	-CH_2-
								1.95	3H	-CH_3-
								7.20	1H	thiophene ring
	113~114	calcd	31.79	2.37	9.43	47.00	338 M$^+$	6.16	1H	-CH_2=
	/0.8~1.0	obsd.	32.88	2.29	9.08	47.43	340	5.61	1H	-CH_2-
							342	5.23	1H	
								1.95	3H	-CH_3
								7.00	1H	thiophene ring
	113~114	calcd.	31.79	2.37	9.43	47.00	338 M$^+$	6.16	1H	CH_2=
	/0.8~1.0	obsd.	32.70	2.41	9.10	47.09	340	5.61	1H	
							342	5.23	1H	-CH_2-
								1.95	3H	-CH_3
								6.90	1H	thiophene ring
	113~114	calcd.	31.79	2.37	9.43	47.00	338 M$^+$	6.16	1H	CH_2=
	/0.8~1.0	obsd.	32.92	2.50	9.13	46.99	340	5.61	1H	
							342	5.23	1H	-CH_2-
								1.95	3H	-CH_3
							416 M$^+$	6.16	1H	CH_2=
	126~127	calcd.	25.80	1.68	7.65	57.22	418	5.61	1H	
	/0.8	obsd.	26.71	1.50	7.87	56.31	420	5.21	1H	-CH_2-
							422	1.95	3H	-CH_3

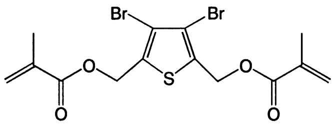
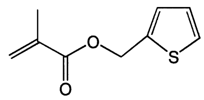
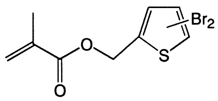
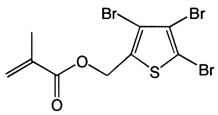
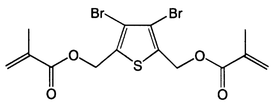
								6.17		CH_2=
								5.63		
								5.32		$-CH_2-$
							436 M^+	1.96	2H	$-CH_3$
							438	166.7	2H	C=O
	74.0(mp)	calcd.	38.38	3.22	7.32	36.48		135.6	4H	thiophene ring
		obsd.	38.49	3.20	7.67	36.80		134.1	6H	olefin
							^{13}C NMR	126.8		
								127.6		
								60.6		$-CH_2-$
								18.3		$-CH_3$

TABLE 4. Refractive Index and Abbe Number of Thiophene Methacrylate Homopolymer

Monomer	Polymer: Refractive index	Polymer: Abbe number
	1.582	37.5
	1.630	33.0
	1.645	31.0
	1.599 [a)]	34.7

a) This value was obtained by extrapolation of the data plotted with several different compositions of copolymer with styrene.

TABLE 5. High Index Optical Material Composed of Thiophene Methacrylate

Monomer composition (wt%)		Refractive index	Abbe number	Entire light transmittance (%)
TMMA/Br_4BMEPP 70/30	(a)	1.585	35	90
Br_2TMMA/EGDMA 70/30	(a)	1.594	39	91
Br_2TMMA /BzMA/Br_4BMEPP 60/20/20	(a)	1.611	33	90
TMDMA/BzMA 40/60	(b)	1.570	37	91
Br_2TMDMA/BzMA 50/50	(b)	1.583	36	90
TMMA/Br_2DTEMA /EGDMA 30/50/20	(a)	1.582	37	90
TMDMA/BzTMA/St 30/40/30	(a)	1.599	33	91

(a):initiator 2,2'-Azobis(isobutyronitrile)(0.2wt%)/1,1'- Azobis(cyclohexane-1-carbonitrile)(0.1wt%)

(b):initiator 2,2'-Azobis(isobutyronitrile)(0.5wt%)

TABLE 5. Continued

TMMA; 2-Methacrlyoloxymethylthiophene
Br_4BMEPP; 2,2-Bis(3,5-dibromo-4-methacrlyoloxyethoxyphenyl)propane
Br_2TMMA; 2- Methacrlyoloxymethyl-dibromothiophene
EGDMA; Ethylene glycol dimethacrylate
BzMA; Benzyl methacrylate
TMDMA; 2,5-Bis(methacryloyloxymethyl)thiophene
Br_2TMDMA; 2,5-Bis(methcryloyloxymethyl)-3,4-dibromothiophene
Br_2DTEMA; 2-Tricyclo[5.2.1.$0^{2,6}$]-3,4-dibromodecylthioethylmethacrylate
BzTMA; S-Benzylthiomethacrylate
St; Styrene

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