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Tatsuhito Matsuda[a]; Yasuaki Funae[a]; Masahiro Yoshida[a]; Tetsuya Yamamoto[a]
[a] Tsukuba Research Laboratory, Nippon Shokubai Co. Ltd. Tsukuba, Ibaraki, Japan

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HIGH INDEX OPTICAL MATERIALS PREPARED BY COPOLYMERIZATION OF NOVEL BIFUNCTIONAL THIOMETHACRYLATES

Tatsuhito Matsuda,* Yasuaki Funae, Masahiro Yoshida,
and Tetsuya Yamamoto

Tsukuba Research Laboratory
Nippon Shokubai Co. Ltd. Tsukuba
Ibaraki 305-0856, Japan

Key Words: Optical Material, Crosslinking Agent, Bifunctional Thiomethacrylate, High Refractive Index, Impact Resistance

ABSTRACT

Optical materials, such as ophthalmic lens, are thermosetting resins, which require crosslinking agents. An optical resin, having a high refractive index, is usually produced by radical copolymerization in which high index crosslinking monomers are significantly important. We provide here the resins prepared by radical polymerization of novel bifunctional thiomethacrylates as high index crosslinkers.

INTRODUCTION

In recent years, transparent synthetic resins having a high refractive index have found increasing applications as optical plastic materials replacing inorganic optical materials because of their light weight and good impact strength, moldability or processability, and dyeability.

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* Author to whom correspondence should be addressed.

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A diethylene glycol bis(allyl carbonate) resin as one example of conventional optical plastic materials has a refractive index of as low as 1.49 to 1.50 [1, 2]. Hence, an eyeglass lens, for example, formed from this resin, has the defect of being large in the thickness of both its center and edge as compared with inorganic optical lenses. When ethylene glycol dimethacrylate was used as a crosslinking agent, the resin obtained showed thermosetting, but refractive index was low because the refractive index of ethylene glycol dimethacrylate homopolymer itself is as small as 1.5 [1].

Kida *et al.* developed a high index bifunctional methacrylate, 3,5-dibromo-bisphenol-A type dimethacrylate [3, 4]. We have developed novel bifunctional thiomethacrylates which are described in the previous paper. They have high refractive indices indeed and are liquid at ambient temperature, so that they are very easy to handle and miscible with a wide variety of monomers.

Ophthalmic lenses are made of thermosetting resins in which bifunctional crosslinking monomers have a great role for various properties of lens. In this sense, bifunctional methacrylates have a good advantage to be able to copolymerize with various other vinyl monomers [5, 6]. Bifunctional thiomethacrylates are also able to be copolymerized with other vinyl monomers. In this paper, we show the examples of copolymerization.

EXPERIMENTAL

Materials

Preparation of 1,2-Bis(methacryloylthio)ethane(1)

A 2L glass flask equipped with a stirrer, a thermometer, a condenser and dropping funnels was charged with 5.36 g (13.8 mmol; 5.2 mol%/dithiol) of trioctylmethylammonium chloride, 0.31 g (5000 ppm/100%Y of product) of p-methoxyphenol and 480 g of chloroform. While the temperature inside of the flask was maintained at less than 10°C, a separately prepared mixture of 25.0 g (0.266 mol; 1 mol eq.) of 1,2-dimercaptoethane and 700.8 g of a 7.5 wt% aqueous solution of potassium hydroxide (0.939 mol of KOH; 3.53 mol eq.) and 66.6 g (0.637 mol; 2.39 mol eq.) of methacryloyl chloride were added dropwise over 20 minutes through a separate dropping funnel. After addition, the mixture was further stirred at the same temperature for 15 minutes and the reaction solution was then separated into two layers. The chloroform layer was washed with a 5 wt% aqueous solution of potassium hydroxide and then with water, and dried over anhydrous sodium sulfate. Chloroform was evaporated to give 52.6 g (0.229 mol; yield 86.1 mol%/dithiol) of 1,2-bis(methacryloylthio)ethane.

The product was purified by distillation at 124-125°C/1.1 torr and its structure was determined by elemental analysis, mass analysis and infrared spectroscopy. Found (%); C 52.39, H 6.09, S 27.57, Calcd. (%); C 52.14, H 6.13, S 27.84, m/e 230 M^+, 1660 cm^{-1} (n C=O), ^{1}H-NMR (δ ppm) 2.0, s, 6H, 2(CH_3), 3.1, s, 4H, SCH_2CH_2S, 5.6, s, 2H and 6.1, s, 2H, 2(CH_2=C).

Preparation of Bis[(2-methacryloylthio)ethyl] Ether(2)

By the same method, as in preparation of the compound (1), the compound (2) was prepared in a yield of 90.2% from 2-mercaptoethyl ether and methacryloyl chloride.

The product was purified by distillation at 133-134°C/1.0 torr and its structure was determined by elemental analysis, mass analysis and infrared spectroscopy. Found (%); C 52.36, H 6.72, S 23.49, Calcd. (%); C 52.53, H 6.61, S 23.37, m/e 274 M^+, 1660 cm$^{-|1}$ (ν C=O), ^{1}H-NMR (δ ppm) 2.0, s, 6H, 2(CH_3), 3.2, t, 4H, 2(CH_2S), 3.7, t, 4H, 2(OCH_2), 5.6, s, 2H and 6.1, s, 2H, 2(CH_2=C).

Preparation of 1,2-Bis[(2-methacryloylthio)ethoxy]ethane(3)

By the same method, as in preparation of the compound (1), the compound (3) was prepared in a yield of 89.3% from 1,2-bis(2-mercaptoethoxy)ethane and methacryloyl chloride.

The product was purified by silica gel column chromatography and its structure was determined by elemental analysis, mass analysis and infrared spectroscopy. Found (%); C 53.51, H 7.04, S 20.12, Calcd. (%); C 52.80, H 6.96, S 20.14, m/e 318 M^+, 1660 cm^{-1} (ν C=O), ^{1}H-NMR (δ ppm) 1.95, s, 6H, 2(CH_3), 3.1, s, 4H, 2(CH_2S), 3.6, s, 8H, 4(OCH_2), 5.55, s,2H and 6.05, s, 2H, 2(CH_2=C).

Preparation of Bis[(2-methacryloylthio)ethoxy]ethyl Ether(4)

By the same method, as in preparation of the compound (1), the compound (4) was prepared in a yield of 84.0% from bis(2-mercaptoethoxy)ethyl ether and methacryloyl chloride.

The product was purified by silica gel column chromatography and its structure was determined by elemental analysis, mass analysis, and infrared spectroscopy. Found (%); C 52.14, H 7.09, S 17.51, Calcd. (%); C 53.01, H 7.23, S 17.69, m/e 362 M^+, 1660 cm^{-1} (ν C=O).

Preparation of Bis-(2-methacryloylthio)ethyl Sulfide(5)

By the same method as in preparation of the compound (1), the compound (5) of was prepared in a yield of 93.1% from 2-mercaptoethyl sulfide and methacryloyl chloride.

The product was purified by distillation at 170-171°C/1.0 torr and its structure was determined by elemental analysis, mass analysis and infrared absorption spectroscopy. Found (%); C 49.40, H 6.38, S 33.37, Calcd. (%); C 49.62, H 6.25, S 33.11, m/e 290 M^+, 1660 cm^{-1} (ν C=O), ^{1}H-NMR (δ ppm) 2.05, s, 6H, 2(CH_3), 2.8, t and 3.15, t, 8H, $SCH_2CH_2SCH_2CH_2S$, 5.6, s, 2H and 6.1, s, 2H, 2(CH_2=C).

Preparation of 1,2-Bis[(2-methacryloylthio)ethylthio]ethane(6)

By the same method as in preparation of the compound (1), the compound (6) of was prepared in a yield of 84.0% from 1,2-bis(2-mercapto-ethylthio)ethane and methacryloyl chloride.

The product was purified by silica gel column chromatography and its structure was determined by elemental analysis, mass analysis and infrared absorption spectroscopy. Found (%); C 47.20, H 6.46, S 36.99, Calcd. (%); C 47.97, H 6.33, S 36.58, m/e 350 M^+, 1660 cm^{-1} (ν C=O).

Preparation of Bis-2-[(2-methacryloylthio)ethylthio]ethyl Sulfide(7)

By the same method as in preparation of the compound (1), the compound (7) of was prepared in a yield of 84.0% from 1,2-bis(2-mercapto-ethylthio)ethane and methacryloyl chloride.

The product was purified by silica gel column chromatography and its structure was determined by elemental analysis, mass analysis and infrared absorption spectroscopy. Found (%); C 47.00, H 6.49, S 38.85, Calcd. (%); C 46.79, H 6.38, S 39.03, m/e 410 M^+, 1660 cm^{-1} (ν C=O).

A Typical Preparation Procedure of Polymerization is as Follows:

A mixture of bis(2-methacryloylthioethyl)sulfide, 25 g, styrene, 20 g, acrylonitrile, 5 g, 2-(2-hydroxy-5-methylphenyl)benzotriazole, 0.05 g, 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine, 0.05 g and 2,2’-azobis(2,4-dimethylvaleronitrile), 0.25 g was cast into a mold consisting of two glass plates and a silicone rubber gasket, and was heated at 50°C for 6 hours, at 60°C for 16 hours and further at 110°C for 2 hours to polymerize the monomer mixture. The obtained resin sheet was colorless and transparent.

Measurement

Refractive Index and Abbe Number

A small piece of a 1.5 mm-thick sheet-like polymer obtained by cast polymerization was measured for a refractive index using an Abbe refractometer, and an Abbe number was found from a dispersion table. The measurement was conducted at 25°C and 60% RH atmosphere.

Total Light Transmittance

A 1.5 mm-thick sheet-like polymer obtained by cast polymerization was measured for an total light transmittance by using a hazemeter in accordance with ASTM D1003-59.

Cutting Processability

A 1.5 mm-thick sheet-like polymer obtained by cast polymerization was cut by a diamond cutter, and defects such as crack, fissure, and fusion of the cut surface that occurred at that time were observed. In case that no defect was observed, we gave “good” as for the evaluation.

Heat Resistance

A 1.5mm-thick sheet-like polymer obtained by cast polymerization was analyzed by thermal mechanical analyzer (TMA) in accordance with JIS K7196. Softening temperature at which a needle began to penetrate into the sheet was regarded as the heat resistance temperature of the sample polymer.

Impact Resistance

Impact resistance was evaluated in accordance with ASTM F659. Namely, a steel ball having a weight of W g was dropped on a sheet sample having a thickness of ca.1.5 mm from a height of H cm, and an unbroken sheet was marked O, while a broken sheet was marked ×.

RESULTS AND DISCUSSION

In order to synthesize a bifunctional thiolcarboxylic acid ester, particularly a bifunctional thiomethacrylate, we adopted a reaction of dimercaptan with methacryloyl chloride. Usually, this reaction is carried out in organic solvent using an organic base such as triethylamine or pyridine as a scavenger for evolved hydrochloric acid [7, 8]. But, in such reactions, a large amount of organic base is needed and a Michael addition of mercaptan to the product occurred in significant amounts. Instead of expensive organic bases, a cheap inorganic base such as potassium carbonate was used (5), but the yield was poor because of its poor contact with the reactant.

In the preparation of bifunctional thiomethacrylate, if we use a base as a hydrochloric acid scavenger, this base also generates thiolate anion (RS^-). This thiolate anion easily adds to α, β-unsaturated ester like bifunctional thiomethacrylate [9]. Therefore, the yield of the desired bifunctional thiomethacrylate should be lowered and a by-product by the Michael addition should be increased.

In this context, we have developed two phase reaction systems of organic and aqueous phases by using a phase transfer catalyst drawn in Scheme 1.

We have expected two effects of phase transfer catalyst (PTC) as follows:

a) To accelerate the reaction by changing the distribution ratio of $RS^- {}^+NR'_4$.

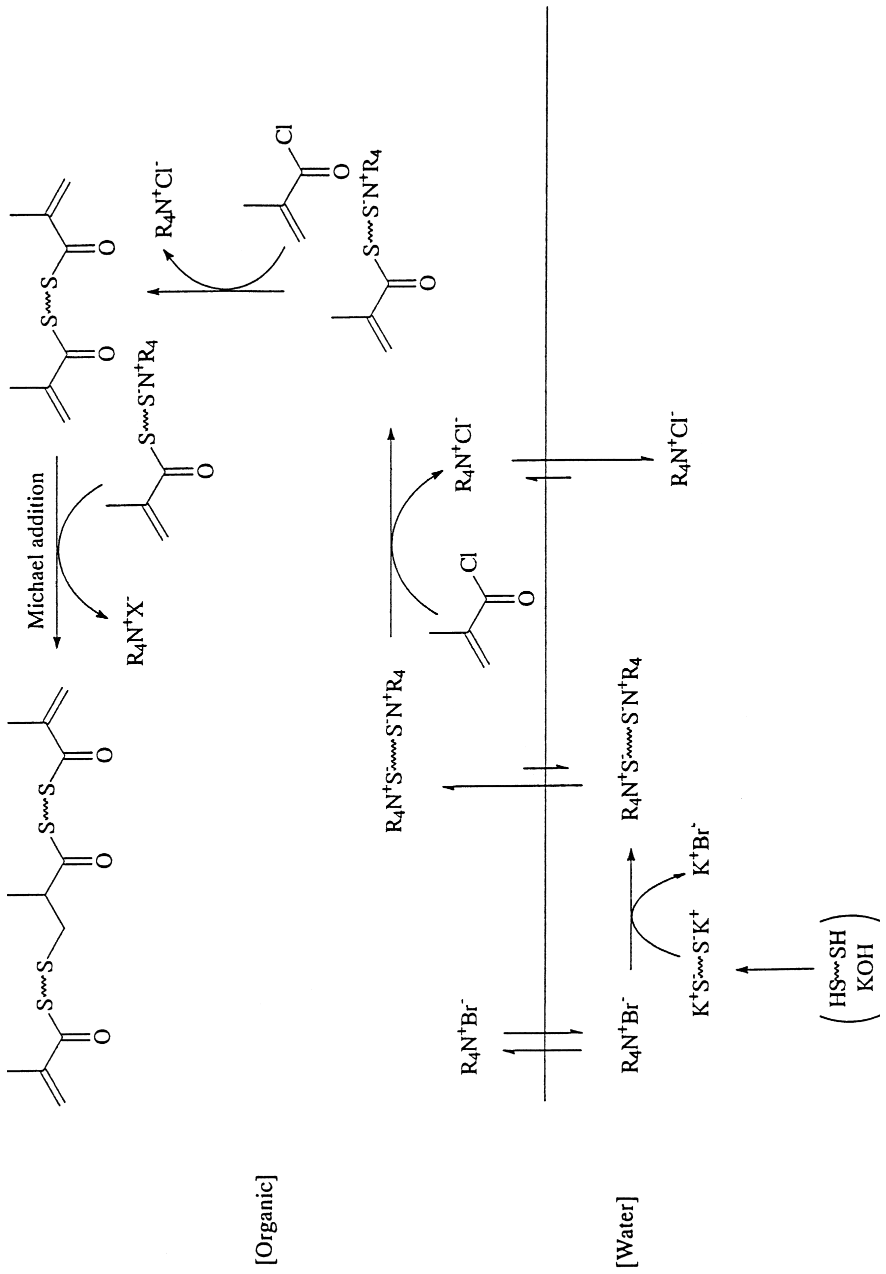
b) To control the nucleophilicity of RS^- by the counter cation (to control the Michael addition reaction).

We examined the reaction by adopting the preparation reaction of 1,2-bis(methacryloylthio)ethane from ethane dithiol (1 mol eq.), methacryloyl chloride (2.4 mol eq.) and potassium hydroxide (3.0 mol eq.).

Effects of Solvent and PTC

The reaction was conducted by dropping methacryloyl chloride to the mixture of the substrate and solvent. After dropping methacryloyl chloride and stirring the reaction mixture for a certain time, the pH of the reaction mixture was measured and the product yield of the desired compound of 1,2-bis(meth-acryloylthio)ethane, was analyzed by an internal standard method using a gas chromatography. The Michael addition by-product (the Michael adduct of half thioester to the desired product) was quantitatively analyzed by a peak area of gas chromatography. The results are summarized in Table 1.

The reaction was found to proceed without PTC (Run 1, 2). In the presence of PTC, a good result was obtained in case of two phase reaction, while the product formation was very small in case of alkaline aqueous one phase reaction. We think that the desired diester product and the Michael adduct by-product were formed as shown below.


[Organic]
[Water]
Michael addition
R4N+X-
R4N+Cl-
R4N+Cl-
R4N+Cl-
S~S-N+R4
S~S-N+R4
Cl
O
R4N+S-~S-N+R4
R4N+S-~S-N+R4
R4N+Br-
R4N+Br-
K+S-~S-K+
K+Br-
HS~SH
KOH

Scheme 1.

TABLE 1. Effects of Solvent and Phase Transfer Catalyst (PTC)

Run No.	Solvent	Yield by gas	chromatography	pH of reaction mixture
	PTC[a]	product diester	by-product[b]	
1	CH_2Cl_2/KOHaq no PTC	21.2%	26.8%	11
2	KOHaq no PTC	42.5%	17.6%	6~7
3	CH_2Cl_2/KOHaq TBAB[c] 5mol%	51.8%	6.3%	11
4	KOHaq TBAB[c] 5mol%	16.1%	1.8%	7

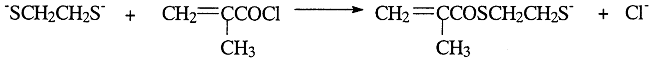
Substrate: $HSCH_2CH_2SH$:methacryloyl chloride:KOH=1.0:2.4:3.0 eq (alkali 7.5%aq)

Organic solvent/water=1.0/2.0, Inhibitor; p-methoxyhydroquinone 5000ppm

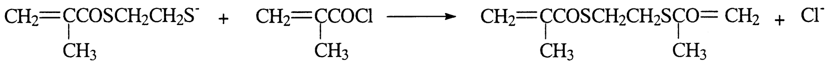
a) phase transfer catalyst

b) Michael adduct

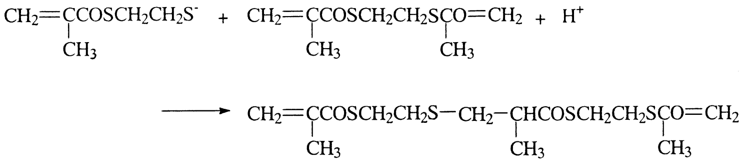
c) tetra-n-butylammonium bromide



$$^{-}SCH_2CH_2S^{-} + CH_2{=}\underset{CH_3}{\underset{|}{C}}COCl \longrightarrow CH_2{=}\underset{CH_3}{\underset{|}{C}}COSCH_2CH_2S^{-} + Cl^{-} \qquad (1)$$



$$CH_2{=}\underset{CH_3}{\underset{|}{C}}COSCH_2CH_2S^{-} + CH_2{=}\underset{CH_3}{\underset{|}{C}}COCl \longrightarrow CH_2{=}\underset{CH_3}{\underset{|}{C}}COSCH_2CH_2S\underset{CH_3}{\underset{|}{C}}O{=}CH_2 + Cl^{-} \qquad (2)$$



$$CH_2{=}\underset{CH_3}{\underset{|}{C}}COSCH_2CH_2S^{-} + CH_2{=}\underset{CH_3}{\underset{|}{C}}COSCH_2CH_2S\underset{CH_3}{\underset{|}{C}}O{=}CH_2 + H^{+} \qquad (3)$$

$$\longrightarrow CH_2{=}\underset{CH_3}{\underset{|}{C}}COSCH_2CH_2S{-}CH_2{-}\underset{CH_3}{\underset{|}{C}}HCOSCH_2CH_2S\underset{CH_3}{\underset{|}{C}}O{=}CH_2$$

Without organic solvent, the hydrolysis of methacryloyl chloride proceeded resulting in lowering the pH of the reaction mixture to 6-7 (Run 2). Furthermore, using PTC in Run 2, the esterification reaction was depressed by a dominance of hydrolysis reaction (Run 4).

Considering the effect of PTC, we recognize that the Michael addition reaction proceeded without PTC, while the Michael addition reaction was depressed in the presence of PTC. This shows that the effect of nucleophilicity control (b) is larger than the effect of the distribution ratio control (a) in Scheme

1. If only the distribution ratio of $RS^{-+}NR'_4$ in the organic phase was increased, the Michael addition reaction was also promoted. Seeing that the esterification reaction proceeds greater than the Michael addition reaction, PTC is thought to control the nucleophilicity of RS^-. This speculation explains the difference of Run 1 and 3.

Effects of Reaction Method

In the discussions described above, we added methacryloyl chloride dropwise to the reaction mixture but the product yield was poor. We examined the dropping method. As shown in Scheme 1, there are two important concerting reactions; diester formation reaction (2) and Michael addition reaction (3). In the method of dropping methacryloyl chloride, supplying a rate of methacyloyl chloride was not enough in resulting in the formation of the Michael adduct. We examined several dropping methods to increase the concentration of methacryloyl chloride.

Method A: dropping methacryloyl chloride into the reaction mixture (Run 3).

Method B: dropping ethane dithiol/potassium hydroxide aqueous solution into the reaction mixture (Run 5).

Method C: dropping methacryloyl chloride and ethane dithiol/potassium hydroxide aqueous solution separately and at the same time into organic solvent (Run 6).

The results are summarized in Table 2.

From Table 2, we found that in method B and C, the Michael addition reaction was depressed and the product selectivity increased. The hydrolysis of methacryloyl chloride was not as significant seeing from the pH of the reaction mixture.

Effects of PTC

We examined the type of PTC and its effects. Table 3 shows the distribution coefficient of several PTCs. In general, halogenated hydrocarbon solvents are preferable to hydrocarbon or aromatic hydrocarbon solvents because of swift phase separation due to the large difference of density. We chose chloroform as a solvent and examined several kinds of PTCs. We dropped methacryloyl chloride and ethane dithiol/pottasium hydroxide aqueous solution simultaneously as shown in the above. The results are summarized in Table 4.

TABLE 2. Effects of Reaction Methods

Run No.	Reaction bottom	Dropping substrates	Yield by gas chromatography		pH of reation mixture
			product diester	by-product	
3	CH_2Cl_2/KOHaq	MACl [a]	51.8%	6.3%	11
5	CH_2Cl_2/ MACl	$HSCH_2CH_2SH$/KOHaq	55.0%	3.0%	11
6	CH_2Cl_2	MACl $HSCH_2CH_2SH$/KOHaq	56.3%	2.5%	11

Substrate: $HSCH_2CH_2SH$:methacryloyl chloride:KOH=1.0:2.4:3.0 eq (alkali 7.5%aq)

Organic solvent/water=1.0/2.0, Inhibitor; p-methoxyhydroquinone 5000ppm

PTC; tetra-n-butylammonium bromide (TBAB) 5 mol%

a) MACl; methacryloyl chloride

TABLE 3. Distribution Coefficient of Various Phase Transfer Catalysts (PTC)

Phase transfer catalyst (PTC)	Distribution coefficient	
	benzene/water	chloroform/water
n-Bu$_4$NBr(TBAB)	6.07 x 10^{-3}	5.26
n-Bu$_4$NHSO$_4$(TBAHS)	0	1.49 x 10^{-2}
BzEt$_3$NCl(BTEAC)	3.52 x 10^{-3}	1.96 x 10^{-2}
Oct$_3$MeNCl(TOMAC)	26.1	56.6

Although the difference of the distribution coefficient of TBAB and TBAHS was more than 300, the result was nearly the same (Run 7, 8). This is because that the counter cation of RS$^-$ was the same form, $^+$NBu-n in both cases and the nucleophilicity control toward RS$^-$ is thought to be the same. This result also tells us that we should consider not only the distribution coefficient of PTC

TABLE 4. Effects of Various PTCs in the Conditions of Simultaneous Dropping of Methacryloyl Chloride and Ethane Dithiol/Potassium Hydroxide Aqueous Solution

Run No.	PTC (mol%)	Yield by gas chromatography		pH of reaction mixture
		product diester(%)	by-product 1)(%)	
7	TBAB 2) (5mol%)	60.7	3.1	11
8	TBAHS 3) (5mol%)	59.0	3.1	11
9	BTEAC 4) (5mol%)	50.2	13.4	5~6
10	BTEAC (10mol%)	61.8	7.8	11
11	TOMAC 5) (5mol%)	67.5	2.0	8
12	TOMAC (10mol%)	68.0	1.7	11

Reaction substrate: HSCH$_2$CH$_2$SH:methacryloyl chloride:KOH=1.0:2.4:3.0 eq (alkali 7.5%aq)

Organic solvent(CHCl$_3$)/water=1.0/2.0, Inhibitor; p-methoxy hydroquinone 5000ppm

1) Michael adduct 2) tetra-n-butylammonium chloride 3) tetra-n butylammonium hydrogensulfate

2) benzyltriethylammonium chloride 5) trioctylmethylammonium chloride

itself but also that of the counter ion exchanged form. Increasing the amount of PTC, diester formation was accelerated more than the Michael adduct formation (Run 9, 10). TOMAC has the largest distribution coefficient of PTC examined and both the reactivity and the selectivity were most excellent in this series. In the case of TOMAC, 5 mol% of catalyst amount seemed to be enough (Run 11, 12).

We optimized the reaction conditions more precisely to obtain some novel bifunctional thiomethacrylates in high yields shown in Table 5. We optimized the molar ratio of the substrates, conducted spontaneous dropping of methacryloyl chloride and dithiol/potassium hydroxide aqueous solution in independent manner, and kept the reaction temperature below 10°C. These monomers are very important and useful monomers for high index crosslinkers for optical plastics.

We picked up some typical bifunctional thiomethacrylates among those and examined the optical properties of their homopolymers. The results are shown in Table 6.

As seen in Table 1, the greater the sulfur content ratio in a molecule became, the larger the refractive index of the homopolymer became. The relationship between the sulfur content ration and the refractive index is shown in Figure 1.

On the other hand, we could not see any relationship between the Abbe number and the sulfur content (Figure 2).

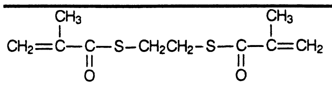
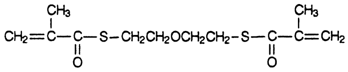
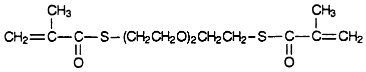
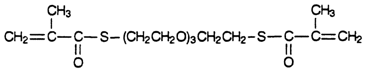
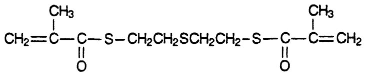
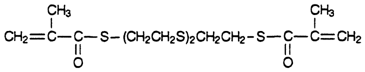
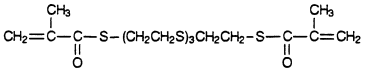
Furthermore, the values of refractive index and Abbe number were approximately the same in case of both thiomethacrylate (BMTEO) and methacrylate (BMETE) if they had the same sulfur content ratio.

As shown in our previous paper [6], the polymer enhanced an excellent impact strength in case that there were four ethylene oxide units between two vinyl groups. Therefore, we tried copolymerization of BMTEO first. The results are shown in Table 7.

We examined copolymerization with acrylonitrile and styrene. As expected, we obtained transparent resins having high refractive index and excellent impact strength durable in the FDA's dropball test. Furthermore, the obtained resins have small specific gravities of 1.16-1.17. However, in the case that we used bifunctional thiomethacrylate as a crosslinker as much as 60 wt%, the impact strength was weakened because the density of crosslinking was too high. However, all resins obtained had a good processability without cracking.

We also examined the same copolymerization on BMETE in which oxygen atom and sulfur atom replaced each other on BMTEO. The results are shown

TABLE 5. Preparation of Novel Bifunctional Thiomethacrylates in the Presence of PTC

Compound	Properties	Yield (%/dithiol)
 $CH_2{=}C(CH_3){-}C({=}O){-}S{-}CH_2CH_2{-}S{-}C({=}O){-}C(CH_3){=}CH_2$	colorless transparent liquid, bp;124-125℃/1.1torr	86.1
 $CH_2{=}C(CH_3){-}C({=}O){-}S{-}CH_2CH_2OCH_2CH_2{-}S{-}C({=}O){-}C(CH_3){=}CH_2$	colorless transparent liquid, bp;133-134℃/1.0torr	90.2
 $CH_2{=}C(CH_3){-}C({=}O){-}S{-}(CH_2CH_2O)_2CH_2CH_2{-}S{-}C({=}O){-}C(CH_3){=}CH_2$	colorless transparent liquid	89.3
 $CH_2{=}C(CH_3){-}C({=}O){-}S{-}(CH_2CH_2O)_3CH_2CH_2{-}S{-}C({=}O){-}C(CH_3){=}CH_2$	colorless transparent liquid	84.0
 $CH_2{=}C(CH_3){-}C({=}O){-}S{-}CH_2CH_2SCH_2CH_2{-}S{-}C({=}O){-}C(CH_3){=}CH_2$	colorless transparent liquid, bp;170-171℃/1.0torr	93.1
 $CH_2{=}C(CH_3){-}C({=}O){-}S{-}(CH_2CH_2S)_2CH_2CH_2{-}S{-}C({=}O){-}C(CH_3){=}CH_2$	colorless transparent liquid	88.7
 $CH_2{=}C(CH_3){-}C({=}O){-}S{-}(CH_2CH_2S)_3CH_2CH_2{-}S{-}C({=}O){-}C(CH_3){=}CH_2$	colorless transparent liquid	82.5

Dithiol:MACl:KOH=1eq:2.4eq:3.5eq, chloroform:water=1:2

phase transfer catalyst: trioctylmethylammonium chloride (TOMAC) 5mol%

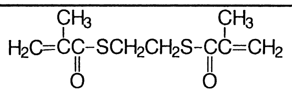
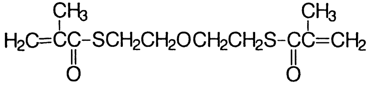
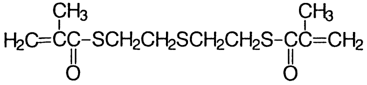
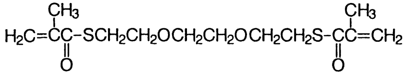
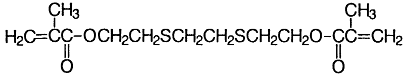
Inhibitor: p-methoxyhydroquinone 5000ppm/product 100mol% yield

Methacryloyl chloride and dithiol/KOHaq. were dropped spontaneously in an independent manner. The reaction temperature was kept below 10℃.

in Table 8. As expected, we obtained the resins having similar properties to those of BMTEO despite the bonding.

In order to obtain higher refractive index optical resins, we examined copolymerization of BMTES which had much more sulfur content ratio in a molecule. The results are shown in Table 9.

TABLE 6. Homopolymer of Bifunctional Thiomethacrylates

Monomer	Refractive index	Abbe number	Entire light transmittance (%)
 $H_2C=\overset{\overset{CH_3}{\vert}}{C}\underset{\underset{O}{\Vert}}{C}-SCH_2CH_2S-\overset{\overset{CH_3}{\vert}}{C}\underset{\underset{O}{\Vert}}{C}=CH_2$ (BMTE)	1.608	34.5	92
 $H_2C=\overset{\overset{CH_3}{\vert}}{C}\underset{\underset{O}{\Vert}}{C}-SCH_2CH_2OCH_2CH_2S-\overset{\overset{CH_3}{\vert}}{C}\underset{\underset{O}{\Vert}}{C}=CH_2$ (BMTEE)	1.593	36.7	92
 $H_2C=\overset{\overset{CH_3}{\vert}}{C}\underset{\underset{O}{\Vert}}{C}-SCH_2CH_2SCH_2CH_2S-\overset{\overset{CH_3}{\vert}}{C}\underset{\underset{O}{\Vert}}{C}=CH_2$ (BMTES)	1.616	36.5	92
 $H_2C=\overset{\overset{CH_3}{\vert}}{C}\underset{\underset{O}{\Vert}}{C}-SCH_2CH_2OCH_2CH_2OCH_2CH_2S-\overset{\overset{CH_3}{\vert}}{C}\underset{\underset{O}{\Vert}}{C}=CH_2$ (BMTEO)	1.569	39.8	92
 $H_2C=\overset{\overset{CH_3}{\vert}}{C}\underset{\underset{O}{\Vert}}{C}-OCH_2CH_2SCH_2CH_2SCH_2CH_2O-\overset{\overset{CH_3}{\vert}}{C}\underset{\underset{O}{\Vert}}{C}=CH_2$ (BMETE)	1.572	40.2	92

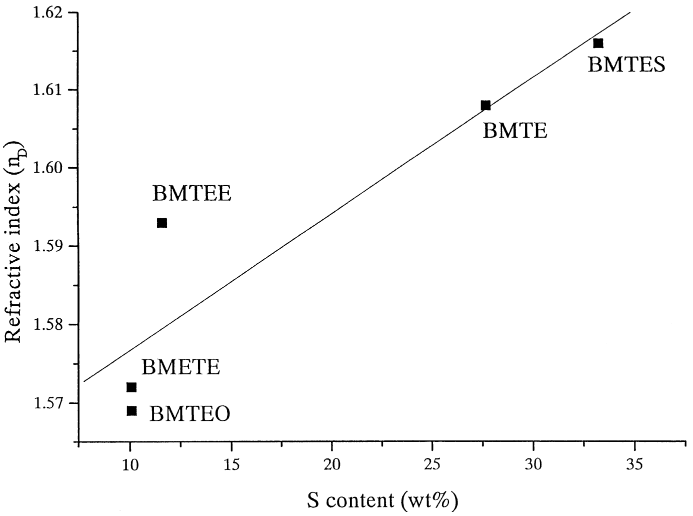


Figure 1. Relationship between Refractive Index and Sulfur Content.

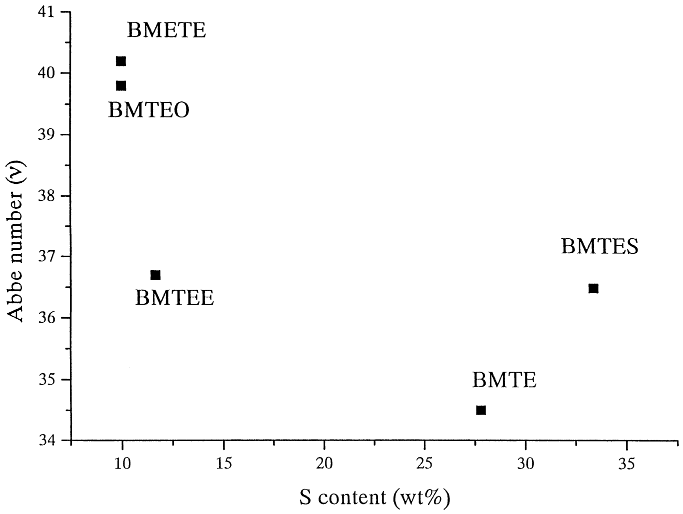


Figure 2. Relationship between Abbe Number and Sulfur Content.

As summarized in Table 9, we could obtain transparent resins having high indices of approximate 1.6 although the impact strength was a little weakened compared with the resins from BMTEO and BMETE. We found that the impact strength could be recovered by adding more acrylonitrile as a soft segment, but in that case the heat resistance was weakened. We should consider the appropriate composition in order to balance the total performance. For instance, we should consider copolymerization with other monomers. We also found in Table 4 that all resins had light weight with small specific gravity and good processability.

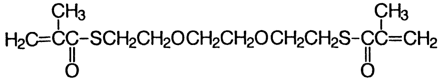
CONCLUSION

Bifunctional thiomethacrylate prepared from dithiol and methacrylol chloride was successfully carried out by potassium hydroxide aqueous solution in the presence of PTC. This reaction is stepwise and esterification and Micheal addition reaction are concerted. PTC catalyst is effective to control both distribution coefficient and nucleophlicity of thiolate anion resulting in dominating esterification reaction. We provide some novel bifunctional thiomethacrylates

TABLE 7. Resins Prepared by Copolymerization of Bis(2-methacryloylthioethoxy)ethane(BMTEO)

Monomer (weight ratio)	Refractive index/Abbe number	Heat resistance (℃)	Impact resistance			Processability	Specific gravity
			127	100	80 (cm)		
BMTEO/AN/St							
50/10/40	1.574/37.0	90.0	○	—	—	good	1.16
50/20/30	1.566/35.9	88.0	○	—	—	good	1.16
60/10/30	1.570/35.0	73.0	×	×	○	good	1.17

BMTEO:



$$H_2C{=}\underset{\underset{O}{\|}}{\overset{CH_3}{\overset{|}{C}}}C{-}SCH_2CH_2OCH_2CH_2OCH_2CH_2S{-}\underset{\underset{O}{\|}}{C}\overset{CH_3}{\overset{|}{C}}{=}CH_2$$

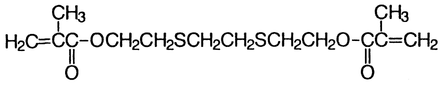
AN: acrylonitrile

St: Styrene

TABLE 8. Resins Prepared by Copolymerization of Bis(2-methacryloylthio)ethane(BMETE)

Monomer (weight ratio)	Refractive index/Abbe number	Heat resistance (℃)	Impact resistance 127	100	80 (cm)	Processability	Specific gravity
BMETE/AN/St							
50/10/40	1.574/39.9	92.0	○	—	○	good	1.16
50/20/30	1.564/39.3	87.0	○	—	○	good	1.17

BMETE:



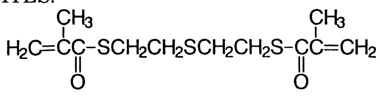
$H_2C{=}\underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}}C{-}OCH_2CH_2SCH_2CH_2SCH_2CH_2O{-}\underset{\underset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}{=}CH_2$

AN: acrylonitrile St: Styrene

TABLE 9. Resins Prepared by Copolymerization of Bis(2-methacryloylthio)ethyl Sulfide(BMTES)

Monomer (weight ratio)	Refractive index/Abbe number	Heat resistance (℃)	Impact resistance			Processability	Specific gravity
			127	100	80 (cm)		
BMTES/AN/St							
50/10/40	1.595/33.4	75.0	×	○	○	good	1.17
50/20/30	1.587/35.6	50.5	○	—	—	good	1.17
60/10/30	1.599/34.8	110.0	×	×	○	good	1.20

BMTES:



$H_2C{=}\overset{CH_3}{\underset{}{C}}\underset{\underset{O}{\|}}{C}{-}SCH_2CH_2SCH_2CH_2S{-}\underset{\underset{O}{\|}}{C}\overset{CH_3}{C}{=}CH_2$

AN: acrylonitrile

St: Styrene

which are very important and useful monomers for high index crosslinkers for optical plastics.

We provided transparent resins having high refractive index by using good copolymerizable crosslinking thiomethacrylates which had high refractive indices of 1.6 and larger. This is significant in the meaning that we showed the prospect to fabricate excellent optical materials, particularly lens, having light weight, high refractive index, large Abbe number and excellent impact strength by examining monomer composition in detail.

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