

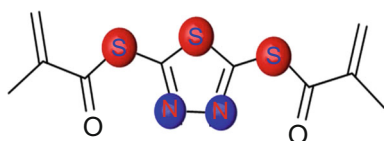
Preparation of 2,5-bis(methylallyl thioester)-thiadiazole with high refractive index and its coatings

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Abstract New high refractive index monomer of 2,5-bis(methylallyl thioester)-thiadiazole (BMATETDZ) containing thioester and thiadiazole was synthesized by a one-step condensation reaction with methyl acryloyl chloride and 2,5-dimercaptothiadiazole (DTD). N–N=C, C=O, and C–S with high molar refraction groups were introduced into the structure of BMATETDZ. FTIR and ¹H NMR were used to characterize the molecular structure of BMATETDZ. The refractive index of BMATETDZ was 1.661. The coatings of poly(2,5-bis(methylallyl thioester)-thiadiazole) (C-PBMA-TETDZ) on polyethylene terephthalate (PET) film were prepared by photopolymerization under UV irradiation. The C-PBMA-TETDZ coatings exhibited better comprehensive properties with high refractive index, high hardness, good adhesive force, excellent thermal stability, and high transparency in range of 200–900 nm.

Graphical Abstract



Film Type	Refractive Index
BMATETDZ	1.661
C-PBMA-TETDA	1.652

Keywords High refractive index, Thioester and thiadiazole polymer, Organic coatings, Properties

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Introduction

Optical materials are used in a wide range of applications and categorized into inorganic and polymer optical materials.^{1–3} Compared with inorganic, polymer optical materials may have many advantages and disadvantages. The disadvantages include low refractive index and poor thermal stability, which limit their commercial application.⁴

The properties of polymer optical materials are determined by refractive index, transparency and thermal stability. In particular, the refractive index of synthesized monomer is the key to attain excellent performance of optical materials. Introducing high molar refraction or low molar volume of groups into the polymers, such as benzene ring, fused ring or other aromatic ring can improve refractive index effectively.⁵ But the molar ratio of such functional groups need to be controlled in the process of preparation. Another way to improve the refractive index is using halogen elements such as Cl, Br, and I. Minns synthesized polymethyl methacrylate using bromine or iodine generation as carbazole side chain, and the refractive index of carbazole side chain containing Br and I was 1.74 and 1.77, respectively.⁶ The pollution of halogen elements limited their application. Papers have reported that added high refractive index inorganic nanoparticle, such as TiO₂ ($n = 2.7$), ZrO₂ ($n = 2.10$), amorphous silicon ($n = 4.23$), PbS ($n = 4.20$) and ZnS ($n = 2.36$) in organic-inorganic nanometer compounds can improve the dispersion of optical nanoparticles.^{7–9} Shobha and his co-workers synthesized poly-ferrocenes polymers which possessed high refractive index ranging from 1.60 to 1.74.¹⁰ However, the size of inorganic nanometer particle was difficult to disperse uniformly, limiting its application.

More recently, S atoms as additives are being utilized to obtain high Abbe number.^{11,12} Kim and

his co-workers synthesized thioacrylate and thiourthane acrylate monomers with the refractive indices of 1.623 and 1.577.¹³ Matsuda et al. synthesized S-[2-(phenylthio) ethyl] thiomethacrylate sulfur-containing monomer, the homopolymers of which had a refractive index of 1.649.¹⁴ The sulfur contained in the molecular structure can improve the refraction index of monomer. The current focus of most high refractive index monomer and polymer research is aimed at complicated methods and expensive reagents, which often require complex multistep synthetic routes.

In this paper, new polymers containing thioester and dithiazole with high refractive index have been synthesized to improve physical properties in optical film coating applications. The homopolymerization coating of the monomer is prepared by photopolymerization under UV irradiation. The optical properties, mechanical properties, and thermal stability of coating film using the synthetic monomer are measured.

Experimental methods and materials

Material and sample preparation

2,5-dimercapthiadiazole (DTD, AR) and methacryloyl chloride (MAC, AR) were obtained from McLean Reagent Company (China) and utilized as the monomers. Triethylamine (AR) or potassium hydroxide (AR) was used as acid-binding agent, hydroquinol (AR) was used as inhibitor, triethyl benzyl ammonium chloride (TEBAC, AR) was used as phase transfer catalyst, and acetone (AR) was utilized as solvent. These reagents were supplied by Sinopharm Chemical Reagent Co., Ltd., (China). Irgacure 907 was supplied by BASF (Germany) and utilized as photoinitiator. Polyethylene terephthalate (PET, thickness 188 μm) was used as the standing of the coatings and manufactured by Hefei Lucky Science and Technology Industry Company (China).

When 2,5-bis(methylallyl thioester)-thiadiazole (BMATETDZ) was synthesized, a 500 mL glass reactor, which equipped with an agitator, a condenser (Allihn type), separating funnel and a nitrogen inlet, was placed in ice-bath. The compositions of all prepared samples with their corresponding designation are tabulated in Table 1. DTD, TEBAC, hydroquinol, and 150 mL acetone were added to the 500 mL glass reactor. After stirring for 10 min, triethylamine or 10% KOH aqueous solution was also added to the glass reactor. MAC and 50 mL acetone were added in a 100-mL beaker, and the solution was obtained. The solution of MAC was dripped slowly to the glass reactor over 30 min and continued to react 2–3 h with stirring. At the end of the reaction, the mixture in the glass reactor separated into two layers, the organic layer was collected and successively washed by 10% of dilute hydrochloric acid, 10% sodium bicarbonate solution, and distilled water, respectively. Then the

light yellow oily products were obtained by vacuum distillation and anhydrous calcium chloride drying technology. The needle crystal of 2,5-bis(methylallyl thioester)-thiadiazole (BMATETDZ) was obtained after recrystallization with petroleum ether.

In order to further study the properties of BMATETDZ, the coatings of the poly(2,5-bis(methylallyl thioester)-thiadiazole) (C-PBMATETDZ), which were coated on polyethylene terephthalate (PET) film, were prepared by photopolymerization under UV irradiation. 10 g BMATETDZ, 0.15 g irgacure 907, and 15 mL acetone were added into a 50 mL beaker, and the viscous liquid was obtained after being stirred for 20 min. The viscous liquid was coated on the transparent PET film (thickness, 188 μm) with coating machine (K202, RK, England), and then it was put into the UV-curing box (ZXD-800, Weigert UV Equipment Co., Ltd., China) with the wavelength of 360 nm for 30 s and dried in vacuum drying oven for 24 h at 40°C.

Characterization

In this paper, Fourier transform infrared spectroscopy (FTIR, Nicolet 67, Thermo Nicolet, USA) and nuclear magnetic resonance (NMR, VNMR600, Agilent, USA) were utilized for structural analysis of BMATETDZ. An Abbe refractometer (AR4, Kruss, Germany) was used to measure the refractive index of BMATETDZ and PET. A film thickness gauge with the wavelength of 550 nm (F20-UV, Defelsko, USA) was employed to test the thickness and refractive index of C-PBMATETDZ. A UV/VIS/NIR spectrophotometer (UV-CARY5000, Agilent, USA), which was employed in the wavelength range of 200–900 nm at a resolution of 4.0 cm^{-1} , was used to acquire the transmittance of C-PBMATETDZ. In order to study the mechanical and thermodynamic properties of C-PBMATETDZ, the thermal gravimetric analyzer (TGA, NETZSCH, 209F3, Germany) was employed to analyze the thermal stability with heating from 30 to 900°C at 2°C/min under a nitrogen atmosphere. The hardness was tested by the coating hardness tester (QHQ - type A, Deman, China) according to ISO 15184-2012, and the adhesive force of C-PBMATETDZ was measured by cross-cut tester (BYK, Germany) according to ISO 2409-2013.

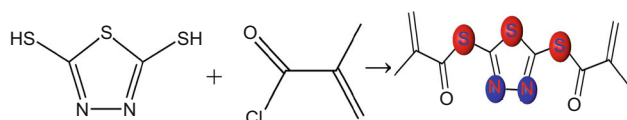
Results and discussion

Synthesis of BMATETDZ

The molar refractions of atoms and organic groups are summarized in *Chemical Handbook Basic*.¹⁵ The molar refraction of N-N=C, C=O, S-C, and C=C groups was 3.446, 2.21, 7.97, and 1.73, respectively. These groups had considerably high molar refraction. In this paper, 2,5-bis(methylallyl thioester)-thiadiazole (BMA-

Table 1: Composition and nomenclature of all prepared samples

Sample	MAC (g)	DTD (g)	TEBAC (g)	Hydroquinol (g)	Triethylamine (g)	KOH (g)
1	13	7.5	0.12	0.01	12.6	–
2	15.6	7.5	0.12	0.01	15.2	–
3	18.2	7.5	0.12	0.01	17.7	–
4	20.8	7.5	0.12	0.01	20.2	–
5	23.4	7.5	0.12	0.01	22.6	–
6	13	7.5	0.12	0.01	–	70
7	15.6	7.5	0.12	0.01	–	84
8	18.2	7.5	0.12	0.01	–	98
9	20.8	7.5	0.12	0.01	–	112
10	23.4	7.5	0.12	0.01	–	125

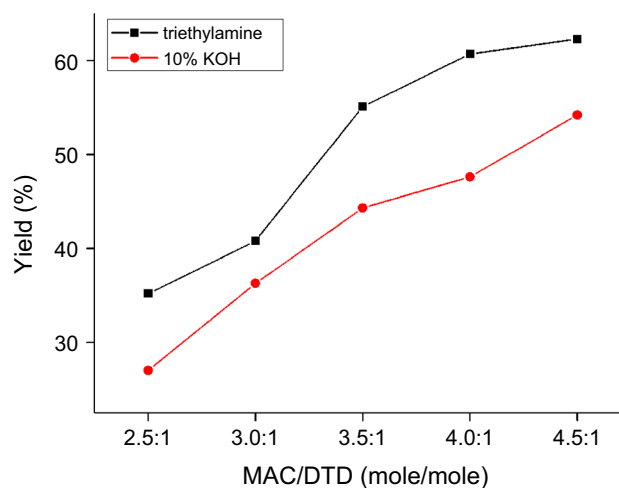
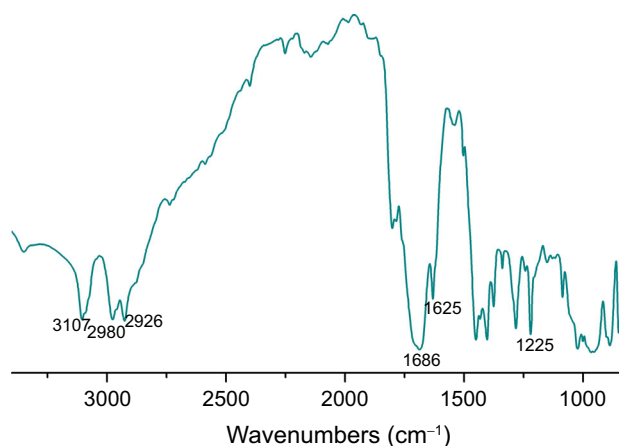
**Scheme 1: Reaction and molecular structure of BMA-TETDZ**

TETDZ), whose molecular structure contained N=N(C), C=O, C-S, and C=C groups, was synthesized by a one-step condensation reaction using 2,5-dimercaptothiadiazole (DTD) and methacryloyl chloride (MAC) as raw materials. The reaction and molecular structure of 2,5-bis(methylallyl thioester)-thiadiazole are shown in Scheme 1.

The effects of different mole ratio of MAC/DTD and the type of acid-binding agent on the yield of BMATETDZ are shown in Fig. 1. The yield of BMATETDZ using triethylamine as acid-binding agent was higher than that of using 10% KOH solution as acid-binding agent. The reasonable explanation was that methacryloyl chloride could react with water in the KOH solution. The yield of BMATETDZ increased rapidly when the mole ratio of MAC/DTD was lower than 3:1, but increased slowly when the mole ratio of MAC/DTD was higher than 3:1. As a result, the triethylamine was selected as acid-binding agent, and the mole ratio of MAC/DTD was kept at 4.5:1 when BMATETDZ was synthesized.

FTIR of BMATETDZ

The structure of 2,5-bis(methylallyl thioester)-thiadiazole (BMATETDZ) was characterized by FTIR spectroscopy in Fig. 2, and the characteristic absorption peaks at 1686, 1625, 2980, and 2926 cm^{-1} were attributed to the thioester group, carbon-carbon double bond, and C-H stretching vibration, respectively. There was no peak at 2500 cm^{-1} which proved that sulfhydryl group had completely reacted. The absorption peaks between 1500 and 1250 cm^{-1} were caused by the thiadiazoles ring.

**Fig. 1: Effects of MAC/DTD mole ratio and acid-binding agent type on BMATETDZ yield****Fig. 2: FTIR spectrum of BMATETDZ**

^1H NMR of BMATETDZ

The nuclear magnetic resonance (^1H NMR) of BMATETDZ is shown in Fig. 3. As shown in Fig. 3,

the signals which resonated at 5.63, 5.78 ppm were attributed to the hydrogen on the allyl double bond, and the signals at 1.93 ppm were assignable to methyl. The results of FTIR spectroscopy and the ¹H NMR spectrum indicated that 2,5-bis(methylallyl thioester)-thiadiazole (BMATETDZ) was successfully synthesized.

Optical properties of BMATETDZ and C-PBMATETDZ

In the study, an Abbe refractometer was utilized to observe the refractive index of BMATETDZ and PET, and a film thickness gauge with the wavelength of 550 nm was utilized to investigate the thickness and the refractive index of C-PBMATETDZ. The thickness and refractive index of C-PBMATETDZ were obtained by analyzing the path difference of reflected light between film and coatings under the condition of known thickness and refractive index of PET. The optical properties of BMATETDZ and C-PBMATETDZ are shown in Table 2. The color of BMATETDZ and C-PBMATETDZ was near colorless, and the refractive index of BMATETDZ, C-PBMATETDZ, and PET was 1.661, 1.652 and 1.663 at

20°C, respectively. The C-PBMATETDZ was coated on PET film with the thickness of 188 μm by photopolymerization under UV irradiation, and the thickness of coating was 2 μm. The refractive index of C-PBMATETDZ was lower than that of BMATETDZ. An acceptable explanation was that single bond possessed a lower molar refraction than that of the carbon-carbon double bond.

UV/VIS/NIR spectrophotometer was used to acquire the transmittance of C-PBMATETDZ/PET. The transmittance curve of C-PBMATETDZ/PET is shown in Fig. 4. The largest transmittance of C-PBMATETDZ/PET was 83% in the range of 200–900 nm. The transmittance of PET (thickness, 188 μm) was 86%. It was obvious that the transmittance of the C-PBMATETDZ was high.

Mechanical and thermodynamic properties of C-PBMATETDZ

Mechanical properties of C-PBMATETDZ are shown in Table 3. The hardness of C-PBMATETDZ was 3H, and the adhesive force of C-PBMATETDZ was grade 2.

The TGA curve of C-PBMATETDZ under nitrogen at a heating rate of 10°C /min is shown in Fig. 5, and the 5% weight loss decomposition temperature of C-PBMATETDZ was 387°C. The coating showed high thermal stability presumably due to the existence of the crosslinking structure.

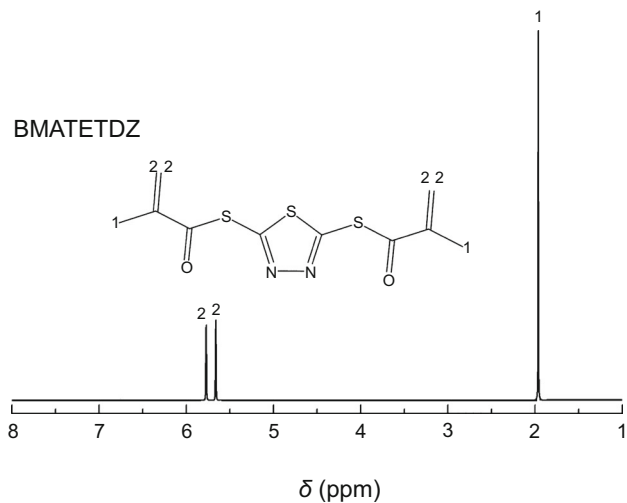


Fig. 3: ¹H NMR spectrum of BMATETDZ

Table 2: Optical properties of BMATETDZ and C-PBMATETDZ

Type	Color	Refractive index	Thickness (μm)
BMATETDZ	Near colorless	1.661	—
C-PBMATETDZ	Near colorless	1.652	2
PET	Transparency	1.663	188

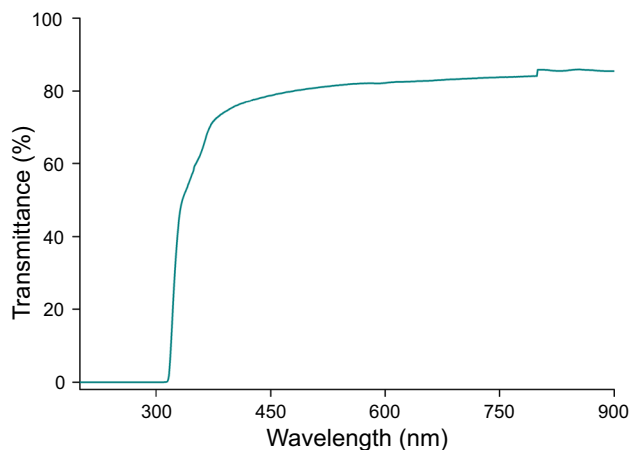


Fig. 4: Transmittance curve of C-PBMATETDZ and PET film

Table 3: Mechanical properties of C-PBMATETDZ

Coating type	Hardness	Adhesive force
C-PBMATETDZ	3H	Grade 2

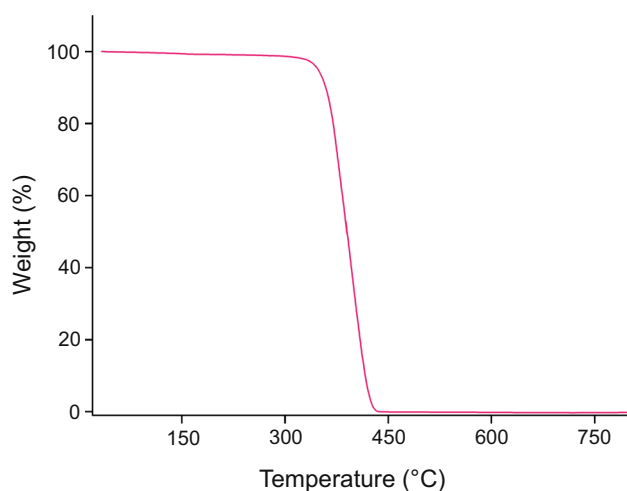


Fig. 5: TGA of C-PBMATETDZ

Conclusions

2,5-bis(methylallyl thioester)-thiadiazole (BMA-TETDZ) containing thioester and dithiazole with high refractive index was successfully synthesized. N=N(C), C=O, and C-S of high molar refraction group in the structure of BMATETDZ improved the refractive index effectively. The refractive index of 2,5-bis(methylallyl thioester)-thiadiazole (BMATETDZ) and its coating (C-PBMATETDZ) was 1.661 and 1.652, respectively. C-PBMATETDZ exhibited higher transparency in the visible spectra, high hardness of 3H, good adhesive force of grade 2 and high thermal stability of 5% weight loss decomposition temperature at 387°C.

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