

SYNTHESIS AND PROPERTIES OF TRANSPARENT THIODIGLYCOL DIMETHACRYLATE COPOLYMER RESINS*

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Abstract The title compound, thiodiglycol dimethacrylate (TDGDMA), was synthesized from thiodiglycol and methacryloyl chloride by phase transfer catalysis reaction, and its structure was confirmed by FTIR and ¹H-NMR analyses. TDGDMA possesses good polymerizability to produce a homopolymer resin with excellent transparency ($T\%$, 90), moderate refractivity (n_d^{20} , 1.55), lower dispersivity (Abbe's number, 50.6) and higher glass transition temperature (T_g , 119 °C). Through copolymerization with styrene (St) or styrene-4,4'-bismethacryloyloxydiphenylsulfone (BPSDMA), many properties of the copolymer such as refractive index, Abbe's number, strength, onset wavelength in the UV region and density were significantly modified. A copolymer resin with balanced properties between refractive index and dispersion was produced at the weight ratio of TDGDMA:St:BPSDMA (25:50:25), where n_d^{20} and Abbe's number are 1.5815 and 36.5, respectively.

Keywords Thiodiglycol dimethacrylate, Phase transfer catalysis, Optical resin, Copolymerization

INTRODUCTION

Optical resins have been developed rapidly in recent years for their wide applications as optical elements such as lenses for eyeglasses and cameras because of their advantages such as light weight, resistance to spalling and dyeability in comparison with inorganic optical glasses^[1–5]. However, the refractive index of the currently widely used resins, for example, poly(ethylene glycol) bisallylcarbonate (CR-39) and polymethyl-methacrylate (PMMA) is 1.50 or less^[1]. Generally, plastic materials for optical products are strongly required to exhibit high refractive index and low dispersion (with less chromatic aberration). To achieve this aim, sulfur and halogen (except fluorine), especially the former, are preferably incorporated in the polymer structure according to the molecular design principle^[6]. Polymers containing sulfur have the properties of high refractive index, lightweightness while retaining low dispersion^[7–13]. The heat-stability of these polymers is significantly better than that of resins containing halogens.

The most convenient and effective way to prepare such a kind of resin is to combine sulfur-containing compounds with double bond-bearing compounds to obtain monomers that can be polymerized under free radical initiation. Some methods have been developed to create sulfur-containing monomers, among which phase transfer catalysis (PTC) has shown more prominent features in synthesizing double-bond containing monomers from alcohols, phenols or thiols and unsaturated acyl halides, such as methacryloyl chloride (MC)^[14–16]. By this method, a product with high yield, light color and good polymerizability can generally be synthesized at lower temperature. This is rather crucial for the fabrication of colorless optical resins, because most of the final monomers are usually liquid with high molecular weight and sensitive to polymerization during the later purification process such as distillation under reduced pressure^[14].

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Thiodiglycol (TDG), a product of mustard gas hydrolysis, and its derivatives have been used in many fields for different purposes. Ioan *et al.* reported recently that segmented polyurethane has been synthesized by using TDG as a chain extender^[17]. Specific refractive index increments were determined by the Lorenz-Lorentz, Vogel and Gladstone-Dale equations and the corresponding group contributions to the molar refraction and to the molar volume were quantified. An optical resin obtained from copolymerization of thiodiglycol diacrylate and styrene (50:50) was patented with refractive index as high as 1.618 and Abbe's No. 42^[18]. The refractive index, however, might be overestimated if not given mistakenly, because this value is far larger than one can predict according to molecular design principle. In this paper, thiodiglycol dimethacrylate (TDGDMA) was synthesized from thiodiglycol (TDG) and MC by PTC reaction at low temperature ($< 10^{\circ}\text{C}$). Its homo- and copolymer resins were then prepared by casting the monomer or monomer mixture in glass molds. The resins obtained are transparent and colorless. Some basic properties relating to optical applications were characterized.

EXPERIMENTAL

Materials

Methacryloyl chloride (MC), prepared from methacrylic acid and SOCl_2 in the presence of LiCl , was purified by distillation three times, b.p.: $95\text{--}99^{\circ}\text{C}$, $n_d^{20} = 1.4458$. Triethylbenzyl ammonium chloride (TEBA) was prepared from triethylamine and benzyl chloride in 1,2-dichloroethane and was recrystallized from 1,2-dichloroethane/anhydrous ethanol. Thiodiglycol (TDG) was synthesized from Na_2S and chloroethanol as described in the literature^[19]. All other A.R. reagents and solvents were used as received.

Synthesis of TDGDMA by PTC Reaction^[14]

In a three-necked 1000 mL round-bottomed flask equipped with a mechanical stirrer, a thermometer and a dropping funnel, 20 g KOH, 150 mL H_2O , 2.8 g TEBA, 12.9 mL TDG and 50 mL CH_2Cl_2 were introduced. While vigorously stirring and maintaining the temperature at $0\text{--}5^{\circ}\text{C}$ with ice/water bath, 25 mL MC in 50 mL CH_2Cl_2 was added dropwise to the above solution within 1–1.5 h. After continuous stirring at 1.5°C for 0.5–1 h, the dichloromethane layer was separated off and washed with 10% NaHCO_3 , then washed with distilled water until neutral. After drying with CaCl_2 and distilling off the solvent, the liquid product was filtered to obtain the colorless and transparent TDGDMA. Yield 70%, $n_d^{20} = 1.4918$, $v_d = 54.8$. Molecular structure:



Preparation of Transparent Resins

Monomers, 0.3% (by monomer weight) AIBN and 0.2% bis(2-ethylhexyl) hydrogenphosphate (mold-release agent) were mixed together, degassed, prepolymerized at 60°C until all the solids were dissolved. The mixture was cooled and degassed until no bubbles evolved, then poured into the glass molds. After curing in an oven at 45°C for 10 h, the temperature was gradually increased to 100°C at a rate of $5\text{ K}/0.5\text{ h}$. 2 h later, the oven was turned off to decrease the temperature to 30°C . The molds were then emptied to obtain a transparent resin with a thickness of $3 \pm 0.2\text{ mm}$.

Characterization

The analytical instruments and conditions are as following: Bruker IFS66V FTIR spectrometer, using NaCl plate and measured at reduced pressure; Varian FT-80A NMR spectrometer, CDCl_3 as solvent; Shimadzu UV3100 UV-Vis-NIR spectrometer, air as reference; W2S-1 refractometer, α -bromonaphthalene as contact media and measured at 20°C ; PE DSC 7 Series Thermal Analysis System, 10 K/min .

The impact strength was measured according to the Charpy method without notch and averaged from 5 parallel measurements. The density ρ was measured in water at 20°C by a balance and calculated according to:

$$\rho = \frac{W_S \cdot \rho_H}{W_S - W' + W_C}$$

Where W_s , W' , W_C and ρ_H represent the weight of sample (0.5–1 g) in air, in water, of copper thread and the water density, respectively. The measured density of PMMA and polystyrene is in agreement with the literature. The saturated water absorption ratio (R_{wa}) was defined as the weight increase ($W_H' - W_s$) to the initial weight (W_s) after the sample was immersed in aqueous solution at 20°C for 4 days (weight W_H'). The Yellow Index (Y) is defined as

$$Y = 1 - \frac{T_{450}}{T_{650}}$$

where T_{450} and T_{650} represent the absorbance at 450 and 650 nm, respectively^[20].

RESULTS AND DISCUSSION

Elucidation of the Structure of TDGDMA

The FTIR spectrum of TDG is consistent with its standard spectrum and shows a broad absorption band at 3200–3500 cm^{-1} which is assigned to the stretching vibration of OH. After esterification with MC, accompanying the disappearance of the OH band, some new absorption bands appear at 1718.8, 1637, 3104.8 and 1377.4 cm^{-1} which correspond to the COO, C=C, =CH₂ and CH₃ groups, respectively. In the ¹H-NMR spectra of TDG (Fig. 1a), the mono peak at $\delta = 2.24$ is assigned to OH, while the triple peaks at $\delta = 2.77$ and 3.78 ($J = 5.6$) which present the AB type characteristic are assigned to the CH₂ groups connected with S and OH, respectively. Ha:Hb:Hc = 1:2:2. Figure 1(b) shows that accompanying the disappearance of the OH mono peak there appear three mono peaks at $\delta = 1.95$, 5.59 and 6.10 in the TDGDMA spectrum which are assigned to CH₃ and the two unsymmetrical hydrogen atoms of =CH₂, respectively. Influenced by the COO group, the CH₂ resonance peak shifted to lower magnetic field, $\delta = 4.33$. The chemical structure of TDGDMA was therefore confirmed.

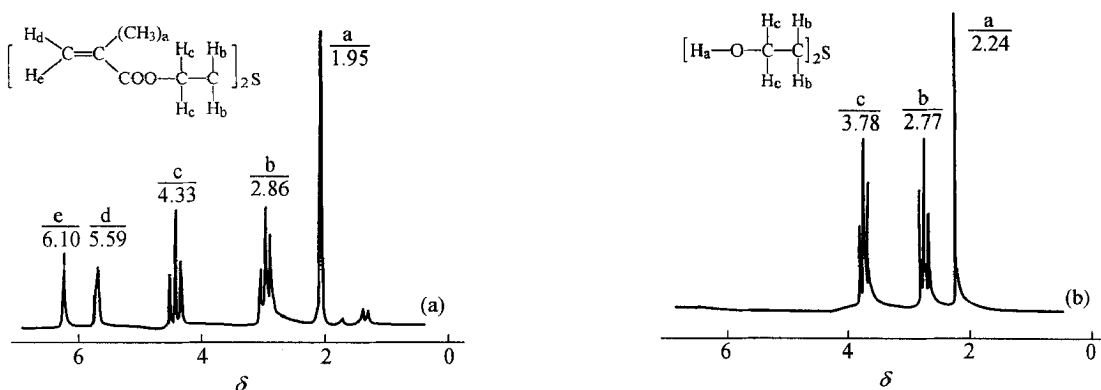


Fig. 1 ¹H-NMR spectra of TDG (a) and TDGDMA (b) together with their chemical structures

TDGDMA Homopolymer Resin

TDGDMA is a liquid ester having good solubility with other double bond containing monomers like styrene (St) or methyl methacrylate (MMA). Therefore, the effectiveness of homopolymerization and copolymerization of TDGDMA is excellent, and the obtained products are thermosetting resins due to the presence of two double bonds in the molecule. The refractive index of TDGDMA homopolymer resin, is $n_d^{20} = 1.55$, much higher than 1.50 for CR-39 or PMMA, while the dispersion of the index is still smaller, Abbe's number $v_d = 50.6$. The reflectance r on one side can be calculated from the Fresnel equation:

$$r = (n - 1)^2 / (n + 1)^2$$

where r is one side reflectance and n is the refractive index. Hence, the total mirror reflectance on the two sides of the resin is 9.3%, which means that the highest transmittance is 90.7%. Spectroscopy measurement from ultra violet, visible to near infrared region showed that the transmittance at 400–1100 nm is about 90% (Fig. 2),

proving that the transparency of the resin is excellent. It is worth mentioning that the transparency of the resin can be improved further if the ordinary glass molds are replaced with optical grade glass molds. The stronger absorptions at 1738 (and 1698) and 1186 nm are attributed to the first and second overtone bands of C—H expansion vibration, respectively, whilst the sharp absorption at 1622 nm is assigned to the overtone of the CH₂ groups which connect to the ester groups^[15, 21]. The light below 330 nm is absorbed totally by the 3mm thick resin. This property is especially important for eyeglasses to eliminate the UV light harmful to human eyes. The other merits include high surface hardness, as well as good heat-resistance as shown in Fig. 3 for the DSC measurement, from which the glass transition temperature was found, $T_g = 119^\circ\text{C}$. The very small deformation in thermal mechanical analysis (TMA) proves further that the resin has rather good ability to resist deformation at higher temperature. The main weakness of the resin is its low impact strength (Charpy unnotched impact strength $0.53 \text{ kJ} \cdot \text{m}^{-2}$), which is caused by the highly crosslinked structure and may be improved via copolymerization with other monoalkenyl monomers, for example, St.

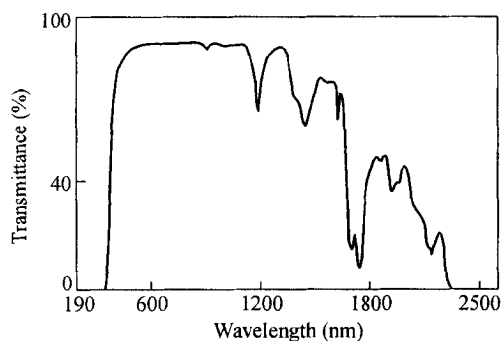


Fig. 2 Transmittance spectrum of TDGDMA homopolymer resin with a thickness of 3 mm

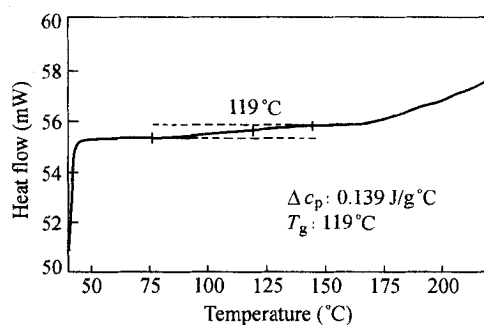


Fig. 3 DSC curve of TDGDMA homopolymer

TDGDMA-St Copolymer Resins

Most of the properties of a homopolymer resin, such as refractive index, dispersion and strength *etc.*, can be adjusted via copolymerization with other monomers to meet the different requirements in variable situations. The homopolymer of TDGDMA possesses higher Abbe's number but lower refractive index, while conventional polystyrene (PS) resin has lower Abbe's number but higher refractive index. Through the copolymerization of TDGDMA and styrene (St), however, a property balance between the refractive index and the dispersion can be expected. Figure 4 shows that the refractive index of the copolymer resins (1.55–1.59) lies between that for the homopolymers, and decreases linearly with the increasing of TDGDMA. It is in good accord with theoretical calculation according to either the weight ratio of the components or the Lorentz equation:

$$R = (n^2 - 1)M/[n^2 + 2]\rho$$

where R is the mole refractivity and ρ is the density of the copolymer^[6]. The Abbe's number of the copolymer resins, on the other hand, was obviously improved. Better comprehensive properties were achieved at a TDGDMA weight ratio of 50%, where n_d^{20} and v_d are 1.57 and 36, respectively. Though the refractive index of the copolymer is slightly lower than that of PS, the dispersion is effectively reduced. Meanwhile, the impact strength at this ratio was also greatly improved as compared with TDGDMA homopolymer resin as shown in Table 1. Some other data listed in Table 1 prove that TDGDMA-St copolymer resins have rather good transparency, low density and water absorption (the R_{wa} of PMMA is 0.5% under the same measuring conditions). Along with increasing the TDGDMA content, the onset wavelength of the copolymer resins in UV region moves toward longer wavelength, which is beneficial for eliminating the injury of human eyes by UV light if this kind of resin is used as eyeglass material.

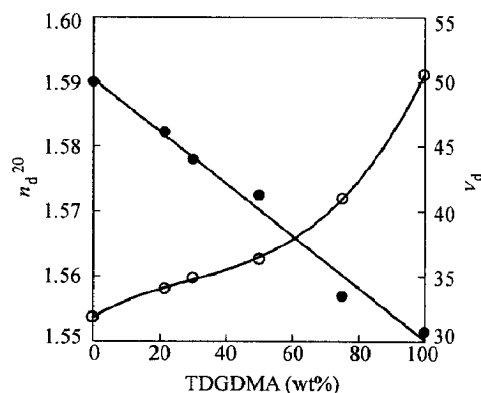


Fig. 4 Variation of refractive index (n_d^{20} , filled circle) and Abbe's number (v_d , open circle) of TDGDMA-St copolymer resins as a function of TDGDMA amount

Table 1. Properties of TDGDMA-St copolymer resins

TDGDMA (wt%)	ρ (g/cm ³)	R_{wa} (wt%)	IPS ^a (kJ/m ²)	Hardness ^b 550 nm	T (%)	UVs ^c (nm)
0(PS)	1.062	0.04	3.00	HB	81.54	308
30	1.100	0.17	3.50	HB	88.17	297
50	1.140	0.27	3.20	HB	88.14	298
75	1.220	—	2.30	—	—	—
100	1.275	0.12	0.53	1H	89.36	330

^a Charpy unnotched impact strength; ^b Pencil hardness; ^c Onset wavelength in UV region

TDGDMA-St-BPSDMA Three-Component Copolymer Resins

Some properties like refractive index and dispersion of the TDGDMA-St copolymer resins can be further modified by introducing the third alkenyl monomer. 4,4'-Bismethacryloyloxydiphenylsulfone (bisphenol-S dimethylmethacrylate, BPSDMA) has been successfully copolymerized with styrene to obtain transparent resins that exhibit prominent high refractivity and surface hardness^[22]. BPSDMA also has good copolymerizability with TDGDMA as testified by transparency measurements (Table 2). Table 2 also lists some other major properties of the TDGDMA-St-BPSDMA three-component copolymer resins. The refractive index and Abbe's number can be adjusted in a wide region. It is worth noting that at weight ratio of TDGDMA:St:BPSDMA (25:50:25) the n_d^{20} (1.5815) is close to that of polycarbonate (PC, 1.5840), while the v_d (36.5) is much higher than PC (30). This suggests that the refractive index and the dispersion of the TDGDMA-St copolymer resins can be well balanced by introducing BPSDMA.

Table 2. Properties of TDGDMA-St-BPSDMA three-component copolymer resins

TDGDMA [*] (wt%)	n_d^{20}	v_d	ρ (g/cm ³)	R_{wa} (wt%)	Hardness	T (%) 550 nm	γ	UVs (nm)
0	1.5952	31.1	1.147	0.19	2H	—	—	—
25	1.5815	36.5	—	0.18	1H	86.62	0.103	304
50	1.5735	42.5	1.193	0.17	1H	82.92	0.102	305
70	1.5633	44.6	1.24	0.16	1H	90.02	0.119	308
100	1.5515	50.6	1.275	0.12	1H	89.36	0.052	330

^{*} BSSMA/St = 1/2 (wt%)

CONCLUSION

Through phase transfer catalysis reaction TDGDMA containing two double-bonds has been successfully produced from TDG with enough purity for either homo- or copolymerization to fabricate optical resins. The homopolymer resin of TDGDMA shows a moderate refractivity and lower dispersivity, as well as higher glass

transition temperature and heat distortion temperature. By copolymerizing with styrene or styrene-BPSDMA, many properties of the copolymers such as refractive index, Abbe's number, strength, onset wavelength in the UV region and density can be modified to a great degree. At an appropriate ratio of the three monomers such as TDGDMA:St:BPSDMA (25:50:25 by weight), a resin with promising balance of refractivity and dispersivity can be achieved.

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