

THE SYNTHESIS OF NEW POLED CROSSLINKED POLYMETHACRYLATES AND THEIR SECOND ORDER NONLINEAR OPTICAL PROPERTIES

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ABSTRACT

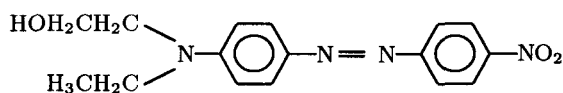
Films were prepared from mixtures of copolymers of 4-nitro-4'-[N-methylacryloyloxyethyl, N'-ethyl] amino azobenzene with glycidyl methacrylate (chromophore content: 6 mol%) and copolymers containing anhydride units, which was obtained by the reaction of 4-nitro-4'-[N-hydroxyethyl, N'-ethyl] amino azobenzene with polymethacryloyl chloride (chromophore content: 25 mol %). During thermal poling process the anhydride reacts with the epoxy group and the resulting crosslinked network structure will stabilize the second harmonic generation in the poled film. The second harmonic generation of the poled film shows a maximum with the variation of composition, this is presumed to be due to the effects of the increasing of concentration, orientation order as well as orientation stability of chromophore groups during crosslinking.

INTRODUCTION

Polymethyl methacrylate (PMMA) functionalized by Disperse Red is one type of nonlinear optical polymers which was known during early investigation. Hill applied 20V/ μm of poling voltage on a Disperse Red functionalized PMMA film and measured the electro-optic coefficient to be about 3pm/V, showing the nonlinear optical (NLO) characteristics comparable with other nonlinear optical materials^[1]. Thereafter its photoinduced birefringence property^[2], photo-recording property^[3], and the effect of photoisomerization on second harmonic generation (SHG) of the poled film^[4], as well as the SHG decay^[5] have been studied. This kind of poled polymer has, to a certain extent, become a model compound in the study of side chain type poled polymers. However, there are few investigations concerning the influence of macromolecular structure, e.g. the changes in chromophore content and the chain structure, on SHG.

The structure relaxation of macromolecules is an intrinsic property and the SHG decay of poled films is unavoidable, and this becomes a big obstacle for the application of poled polymers^[6,7]. Investigations in recent years have shown that measures such as: 1) the synthesis of polymers with high glass transition temperature (T_g)^[8], 2) the forming of crosslinked structure during poling process^[9–11], 3) the generation of interpenetrating polymer networks obtained by sol-gel technique^[12], will favor the orientation stability of poled films and hence reducing the SHG decay. Presently, the crosslinked systems studied are mainly those of epoxy resin^[9], polyurethanes^[10] and polymethacrylates containing cinnamoyl groups^[11], while networks formed between macromolecules are rarely reported, though it is an alternative to obtain IPN-like structure to stabilize the orientation of chromophores in poled polymer films.

In order to study the effects of molecular structure and the chromophore content on SHG, we designed and synthesized two copolymers, i.e. polyglycidyl methacrylate-co-4-nitro-4'-[N-methacryloyloxyethyl, N'-ethyl] amino azobenzene (GMA/MA-DR1) and copolymer containing anhydride units (MA-DR1/MA/MAN) formed by reacting 4-nitro-4'-[N-hydroxyethyl, N'-ethyl] amino azobenzene (Disperse Red 1, DR1) with polymethacryloyl chloride (PMAC1).



DR1

Films were prepared from mixtures of GMA/MA-DR1 and MA-DR1/MA/MAN, after thermal poling the SHG behavior changed and the SHG stability was increased.

EXPERIMENTAL

Testing method and instruments

The ^1H NMR spectra of the synthesized products and monomers were measured using JEOL FX90Q NMR spectrometer. UV-VIS spectra were recorded on a Shimadzu UV-VIS 240 spectrophotometer. Elementary analyses were performed using Perkin-Elmer 204C elementary analyser. The glass transition temperatures were measured on Perkin-Elmer DSC-7C differential scanning calorimeter with temperature rising rate of $20^\circ\text{C}/\text{min}$. FTIR spectra were recorded on Nicolet 250 infrared spectrometer.

The preparation of films and SHG measurement

The polymer dioxane solution was casted on 1 mm thick polished glass plate, after evaporation of the solvent, the plate was vacuum dried for 24h, the thickness of film

obtained was in micrometer range. Poling was performed in a corona poling field, the distance from film surface to the poling electrode was 1 cm, poling temperature was higher than T_g of the polymer. The freezing of orientation was achieved by gradually cooling the film in the poling field. SHG was measured by using 1064nm out-put from a mode-locked Nd:YAG laser as the base frequency, the angle between the incident light and the film surface was 45° . The out-put light passed through a 532 nm filter and IR absorbing isolating glass and was detected by a photo-multiplier with a 3mm thick quartz crystal as the reference. When the film thickness is comparable with the interference length the following relation holds:

$$\chi^{(2)} \propto 2d \propto (I_s^{2\omega}/I_{\text{ref}}^{2\omega})^{(1/2)}$$

in which $\chi^{(2)}$ is the second order non-linear polarizability, d is SHG coefficient measured at 45° incidence, $I_s^{2\omega}$ and $I_{\text{ref}}^{2\omega}$ are the SHG intensity of poled film and quartz crystal, respectively.

Synthesis of material

1. Monomers

(1) α -methacryloylchloride (MACl)

1.5 mol (108 ml) of thionyl chloride were added dropwise into α -methacrylic acid (1mol, 86ml) at 90°C . After 5h of reaction no more HCl was liberated and the unreacted thionyl chloride was distilled off. The α -methacryloylchloride obtained was vacuum distilled to give 50 ml product ($43\text{--}45^\circ\text{C}/25.3\text{ KPa}$).

(2) 4-nitro-4'-[N-methacryloyloxyethyl, N'-ethyl] amino azobenzene (MA-DR1)

0.01 mol of DR1 was dissolved in 15 ml anhydrous tetrahydrofuran (THF) and 0.01 mol of Et_3N was added. During stirring, 5ml of 0.011 M THF solution of MACl was added. After 20 h of reaction at room temperature 75 ml CHCl_3 were added. The mixture was extracted several times with water to remove Et_3N and the acid. The CHCl_3 solution was dried over Na_2SO_4 for 12h, filtered and a purple powder was obtained after the solvent was distilled off. The product was recrystallized in ethanol with a yield $> 90\%$.

Elemental analysis: Calcd. C% 62.66, H% 6.00, N% 14.62

Found C% 61.96, H% 5.96, N% 14.42

^1H NMR (CDCl_3 , δppm): 0.8–1.5 (t, 3H), 1.5–2.1 (t, 3H), 3.1–4.0 (m, 4H),
4.1–4.5 (t, 2H), 5.5–5.7 (s, 1H), 5.9–6.2 (s, 1H),
6.5–6.9 (d, 2H), 7.5–8.0 (m, 4H), 8.0–8.4 (d, 2H)

UV-VIS (λ_{max} in DMF): 498nm

(3) Glycidyl α -methacrylate (GMA)

Potassium methacrylate was mixed with epichlorohydrin at mole ratio of 1:5, appropriate amount of Et_4NBr was added and refluxed under stirring for 6 h. Excess epichlorohydrin was distilled off and the product was obtained by vacuum distillation at 100–103°C/4.0 KPa with 80% yield.

2. Copolymers

(1) Poly {glycidyl methacrylate-co-4-nitro-4' [N-methacryloyloxyethyl, N'-ethyl] amino azobenzene} (GMA/MA-DR1)

A mixture of monomers (GMA:MA-DR1=10:1) was dissolved in 10 ml dioxane in a 25 ml flask, N_2 was bubbled in to expel oxygen, AIBN was then added and the polymerization was carried out at 70°C for 48 h. After precipitated with n-hexane, the polymer was purified at least 3 times by repeatedly dissolved in dioxane and precipitated with n-hexane. The final product was vacuum dried at 60°C with 40% yield.

^1H NMR (CDCl_3 , δ ppm): 0.4–1.6 (m, 50H, $-\text{CH}_3$), 1.6–2.4 (s, 38H, $-\text{CH}_2-$)

$$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ 2.5-3.1 \text{ (d, 28H, } -\text{OCH}-\text{CH}_2\text{)}, \quad 3.1-5.0 \text{ (m)} \end{array}$$

6.7–7.0 (2H), 7.8–8.1 (4H), 8.2–8.5 (2H) (aromatic)

DSC: $T_g=112^\circ\text{C}$

(2) Poly{4-nitro-4'-[N-methylacryloyloxyethyl, N'-ethyl] amino azobenzene-co-methacrylate-co-methacrylic anhydride} (MA-DR1/MA/MAN)

Polymethacryloyl chloride (PMACl) was prepared by similar procedure as described in 1. 10.53 g (5 mmol) of PMACl was dissolved in dry pyridine, 0.9 g (0.25 mmol) of DR1 was added and the reaction was carried out at 100°C for 48 h. After precipitation with methanol the crude product was purified by repeatedly dissolved in THF and precipitated with methanol, the yield was 70%.

FTIR (cm^{-1}): 3400 ($-\text{COOH}$), 1803, 1761 ($-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\overset{\text{O}}{\parallel}\text{C}-$), 1728 ($\overset{\text{O}}{\parallel}\text{C}-\text{OR}$).
 1601, 1587, 1581 ($-\text{NO}_2$), 1422, 1400, 1340($-\text{NO}_2$), 1250, 1125,
 1010, 870, 812.

^1H NMR (d^6 -DMSO, δ ppm): 6.7–7.1, 7.6–8.0, 8.0–8.1 (arom.)

3.6–3.9 ($-\text{NCH}_2-$) 3.9–4.4 [$-\text{C}(\text{O})\text{OCH}_2-$]

2.6–3.6 ($-\text{OCH}_3$, H_2O) 1.4–2.2 ($-\text{CH}_2-$)

0.4–1.4 ($-\text{CH}_3$)

Elemental analysis: C% 59.49; H% 5.79; N% 9.05

DSC: $T_g = 86^\circ\text{C}$

RESULTS AND DISCUSSION

1. Synthesis of copolymers

(1) Synthesis of GMA/MA-DR1 copolymer

During the polymerization process it is desirable to avoid overheating because too high temperature may lead to the ring opening of the epoxy groups in the presence of amine. Fig. 1 shows the ^1H NMR spectrum of GMA/MA-DR1, from the integration it is calculated that $x = 0.06$, $y = 0.94$, and the nitrogen content is 2.31%.

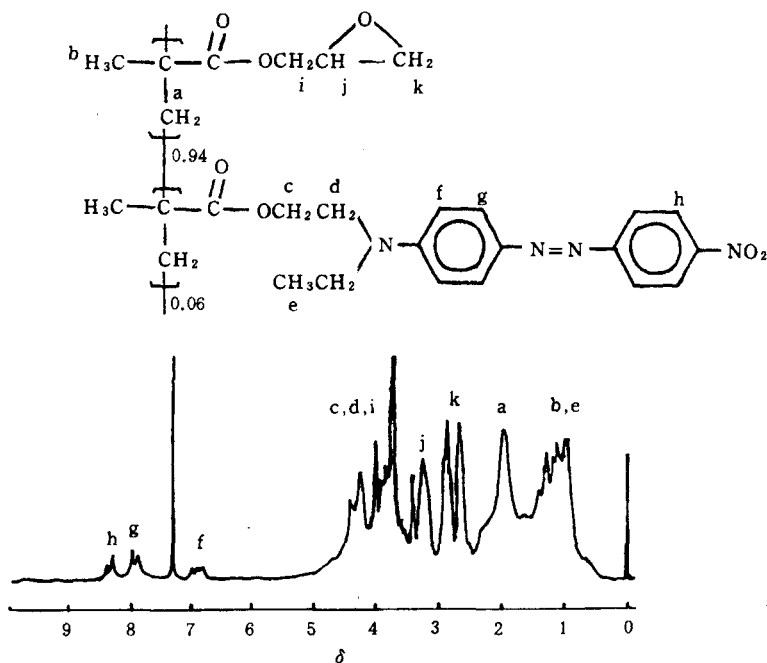


Fig. 1 ^1H NMR spectrum of GMA/MA-DR1

(2) DR1 functionalized PMACl

Reaction between acryl chloride and active hydroxyl group is utilized in the synthesis. This substitution reaction can be completed almost quantitatively, however, the extent of dryness and the after-treatment of the product will greatly influence the structure of the polymer chain. Both ^1H NMR and FTIR spectra imply the existence of anhydride and ester groups in the polymer chain (Fig. 2). The anhydride formation may be an intramolecular reaction that leads to thermodynamically stable six-membered rings in the polymer backbone. These processes are shown as follows:

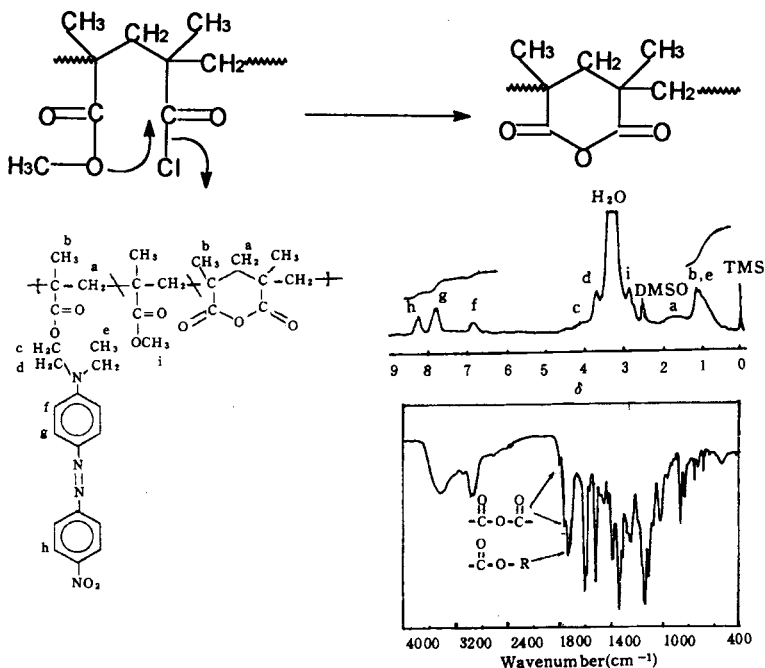
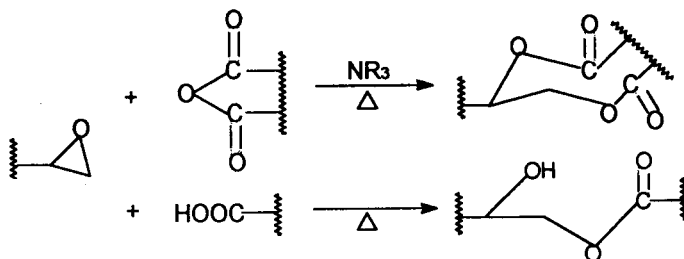


Fig. 2 ¹H NMR and FTIR spectrum of MA-DR1/MA/MAN

From the integrated height of proton in ¹H NMR spectrum it is estimated that the chromophore units amount to about 25 mol% (acid anhydride is regarded as 2 units), its structure could be described as MA-DR1/MA/MAN showing in Fig. 2. In addition, the existence of methacrylic acid units can not be excluded. The elemental composition based on the above mentioned structure is C% 62.56, H% 6.32, N% 8.85, which is close to the result to elementary analysis based on nitrogen content. This is different from the result reported in Ref. [13].

2. Preparation of the blended pre-crosslinked films

Selection of GMA/MA-DR1 with many epoxy groups and MA-DR1/MA/MAN containing anhydride groups allows the reaction of epoxy groups with the acid anhydride to occur at higher temperature (Scheme 1).



Scheme 1

Films prepared from the dioxane solution of the blend of these two copolymers gives crosslinked poled film during thermal poling. The chromophore itself or external amines may serve as catalysts for the ring opening of epoxy groups by acid anhydride. Table 1 lists the formulation of film preparation.

Table 1 Compositions of blended films

Films	GMA/MMA-DR1 (wt %)	MA-DR1/MA/MAN (wt%)	N(wt%)
D	0	100	9.05
D ₁	20	80	7.70
D ₂	40	60	6.35
D ₃	60	40	5.00
D ₄	80	20	3.66
C ₃	100	0	2.31

3. Poling of GMA/MA-DR1 and MA-DR1/MA/MAN blend pre-crosslinked films and SHG measurement

Table 2 gives the poling conditions and results of SHG measurement. C₃ and D are poled at the T_g of the respective copolymer, other films are poled by two poling process.

Table 2 Poling process and SHG of blended films*

Poling process 1		Poling process 2	SHG [(1/f)(I _s ^{2ω} /I _{ref} ^{2ω})]
D	7 kV 100°C 10 min		0.77
D ₁	7 kV 60°C → 12 min	7 kV 90°C 30 min	0.34 → 0.55
D ₂	7 kV 70°C → 10 min	7 kV 100°C 10 min	0.34 → 0.71
D ₃	7 kV 40°C → 10 min	7 kV 90°C 40 min	0.23 → 0.82
D ₄	7 kV 60°C → 15 min	7 kV 100°C 25 min	0.46 → 0.77
C ₃	8 kV 112°C 10 min		0.22

* At the same thickness (about 2 micrometers)
f: A parameter of the measurement system ($f \geq 1$)
→: Means “change to”

SHG detected in process 1 is higher than that detected in process 2. It is clear that from process 1 to process 2 the orientation of chromophore raised. Fig. 3 is a plot of SHG versus the compositions of the poled and crosslinked films.

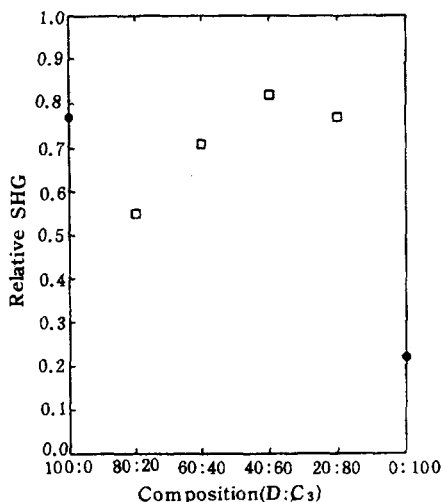


Fig. 3 Relation between SHG intensity and composition of blended films after poling and crosslinking (●: pure, □: blend)

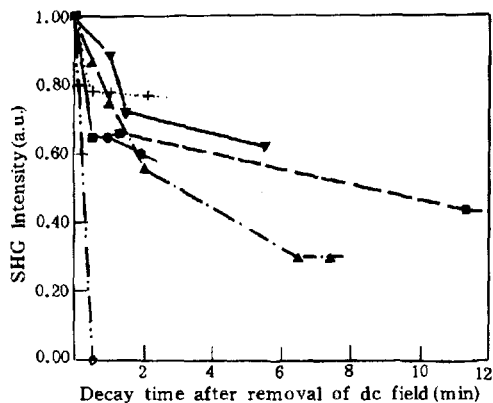


Fig. 4 Decay behavior of SHG signal in blended films at 90°C (●: D; ▽: D₁; ■: D₂; +: D₃; ▲: D₄; ○: C₃)

As the film composition changes from D to C₃, the chromophore concentration decreases whilst the concentration of epoxy group increases. At elevated poling temperature the ring opening of epoxy groups will take place, forming a polymer network due to the crosslinking of macromolecular chains. The crosslinking structure tends to increase orientation stability of the chromophore groups. At a high temperature, the thermal motion of chromophore groups is intense and random, dipoles of chromophore groups are in disorder. The crosslinking structure formed in the poling process will inhibit the thermal motion and increase the orientation order of dipoles of chromophore groups and somewhat causes the contraction of volume which, in turn, increases the chromophore concentration. This effect counteracts with the effect of decreasing of chromophore concentration arising from the change in composition (decreasing of MA-DR1/MA/MAN component). These all have the effects on the SHG of poled film according to the following equation^[14]:

$$I_s^{2\omega} \propto \chi_{zzz}^{(2)} \propto N\beta \langle \cos^3 \theta \rangle E_p$$

$$\Phi = [3\langle \cos^2 \theta \rangle - 1]/2$$

where $N, \beta, \theta, \Phi, E_p$ are the number of chromophore groups in an unit volume, the

first hyperpolarizability, the angle between the long axis of a given dipole and the average direction of orientation of the long axes of dipoles, the orientational order parameter, and the effective intensity of electric field, respectively. As a result, a maximum appears in the plot of SHG versus the composition of the films (Fig. 3).

Fig. 4 shows the SHG decay characteristics of the poled films. For films D₁, D₂ and D₃ the SHG decay of SHG signal is slower than that for films D and C₃ at 90°C, indicating the relative high orientation stability of the chromophore groups. For this kind of crosslinked poled films, the orientation stability of the chromophore groups is determined by two factors, namely the entanglement of the macromolecules and the chemical crosslinking of the reactive groups in the polymers. The latter has greater influence on SHG stability, the SHG decay decreases with the increasing of the extent of crosslinking which limits the thermal motion of the chromophores.

Keywords:

Second order nonlinear optics, Poled polymers, Disperse Red 1, Methacrylate copolymers

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