Polymer Bulletin 29, 289–293 (1992)

Polymer Bulletin

Novel nonlinear optical polymers with crosslinkable functional groups

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Summary

Monomers with non linear optical (NLO) and photocrosslinkable (cinnamate) active side group have been synthetized. The study of their copolymerization has shown that a third monomer is necessary to increase the yield of copolymerization from 9% to 53%. The monomers reactivity ratios were estimated to be close to each other. Glass transition temperatures are relatively high though inherent viscosities of the terpolymer are low.

Introduction

Some organic materials exhibiting large nonlinear optical (NLO) characteristics are currently of great scientific and technological interest. The attraction derives from large non resonant susceptibilities, ultrafast response time, low dielectric constant and high damage threshold (1).

These organic molecules associated with polymers as substrate enable a good electro-optic medium. The strategies for polymer NLO materials began with guest-host systems (2), where NLO dye is dispersed in the solid polymer matrix. The main disadvantage concerns the low solubility of the incorporated molecule. Further works carried out the grafting of the considered dye on monomers (3) or on polymer materials (4). During the last five years a high level of publications raised describing a lot of combinations of processes and materials. Thus, the grafting of a dye molecule with hydroxyl pendant group on a polymer such as poly((methacryloyl chloride)-*co*-(methyl methacrylate)) has been proposed (5). These new polymers have been performed to implement active optical components such as optical phase modulators. The state of art mentioned a high level of performance, low driving voltage (6)($<10V_{RMS}$) and high bandwidth (7) (until 40 GHz). These high electro-optic effects must bring out by signifiant and persistent acentricity of the medium. For that reason, the NLO moiety must be poled to align them as it is possible orthogonally to the optical wave direction .

Up to now, this kind of device undergoes decreasing electro-optic response due to dye dipole relaxations (8). To overcome this previous

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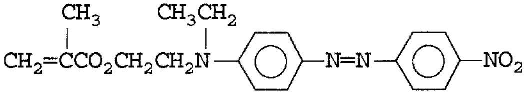
drawback, some authors try to quench the dipole orientations by simultaneous crosslink of the polymer during poling (9).

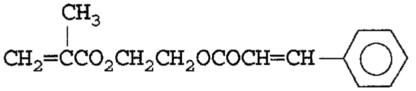
In this paper, we suggest to use a terpolymer poly((methylmethacrylate)-*co*-(dye grafted methacrylate)-*co*-(2-methacryloxyethylcinnamate)), to take advantage of cinnamate groups to photocrosslink the polymer film during or after the poling process.

Experimental

First we have to prepare both functionalized NLO active side group monomer and photocrosslinkable side group monomer. The NLO group is the usual azo dye Dispersed Red 1 (DR1) from Aldrich Chemical. This group is esterified with methacryloyl chloride to give the methacrylate azo dye monomer **1 (MMARED)**. The second monomer, **2 (MMACi)**, is synthetized from commercial 2-hydroxyethylmethacrylate which is esterified with the photocrosslinkable cinnamoyl chloride group (Aldrich Chemical).The structure of the two monomers are given below :



1 (MMARED)



2 (MMACi)

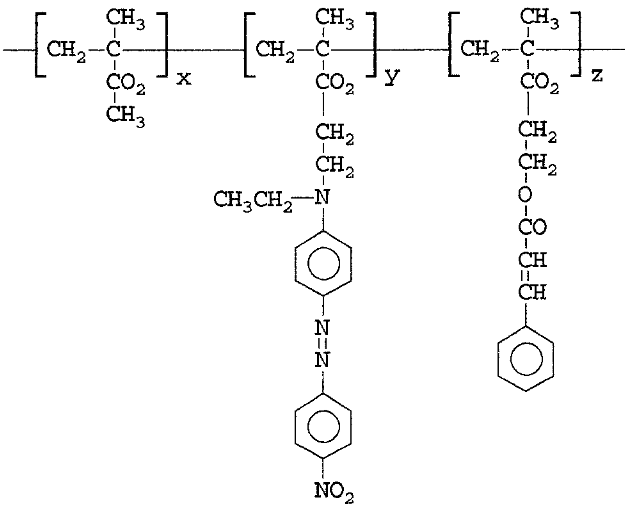
Synthesis of monomer 1 : The methacrylate ester of azo dye Dispersed Red 1 is prepared from 22 g (0.210 mol) of methacryloyl chloride dissolved in chloroform which are added dropwise at room temperature, to a mixture of 60 g (0.191 mol) of azo dye, 15 g (0.191 mol) of pyridine and 400ml of chloroform. After complete addition , the mixture is warmed at 40°C during 24 hours. Then pyridine and chloroform are removed under vacuum. Monomer 1 is purified by column chromatography on silica gel using toluene as eluent: yield: 12.1 g (55%); mp = 93°C; ^1H NMR 200 MHz ($CDCl_3$) : δ = 1.3 (triplet (t), J_{H-H} = 9 Hz, 3H, -$CH_2\underline{CH_3}$), 2 (multiplet (m), 3H, =$C(\underline{CH_3})$), 3.6 (quadruplet (q), J_{H-H} = 9Hz, 2H, -$\underline{CH_2}CH_3$), 3.75 (t, J_{H-H} = 5Hz, 2H, N-$\underline{CH_2}$-CH_2-O), 4.38 (t, J_{H-H} = 5Hz, 2H, N-CH_2-$\underline{CH_2}$-O-), 5.6 and 6.12 (m, 2H, $\underline{CH_2}$=C-), 6.82 (m, 2H, aromatic proton α of tertiary amine), 7.9 (m, 4H, aromatic protons α of azo group), and 8.32 (m, 2H, aromatic protons α of nitro group).

Synthesis of monomer 2 : 16.66 g (0.1 mol) of cinnamoyl chloride were added dropwise to a mixture of 14.3 g (0.11 mol) of 2-hydroxyethylmethacrylate and 8.7 g (0.11 mol) of pyridine in 100 ml of carbon tetrachloride. Then the procedure is the same as described above. After evaporation of the solvent, monomer 2 was purified by column chromatography on silica gel using toluene as eluent: yield: 21 g (73%); IR (KBr): ν $_{C=O}$ 1725 and 1715 cm^{-1}, ν $_{C=C}$ 1640 cm^{-1}; ^1H NMR 200 MHz ($CDCl_3$) : d = 1.95 (m, 3H, $=C(\underline{CH_3})$), 4.4 (m, 4H, $-O\underline{CH_2CH_2}O-$), 5.55 and 6.15 (m, 1H, $\underline{CH_2}=C-$), 6.45 (d, J = 15 Hz, 2H,$-CH=\overline{C}H-$), 7.45 (aromatic protons, m, 5H) and 7.7 (d, J = 15 Hz, 1H,-CH=CH-).

Terpolymerization : The terpolymerization were performed, under an N_2 atmosphere at 65°C during 88 hours, in glass sealed tubes which were filled with monomers mixture, solvent (1,4-dioxane, 10ml) and initiator 2,2'-Azoisobutyronitrile (AIBN) added at 2.10^{-2} mole by mole of monomers. The initial weight of monomers was kept constant and equal to 1 g. After the polymerization, the deep red solution were precipitated into 500 ml of methanol. The polymer was filtered, washed with methanol and dried under reduced pressure at room temperature.

Results and discussion

The general formula of the terpolymers is:



The aim of the study is to incorporate a large quantity of NLO active group, so we have choosen the value of 50% in weight of NLO active group, DR1, in the monomer feed. In a general manner, the weight fraction of DR1 (ω_G) can be given by :

$$[1] \quad \omega_G = \frac{y.M_G}{x.Mx + y.My + z.Mz}$$

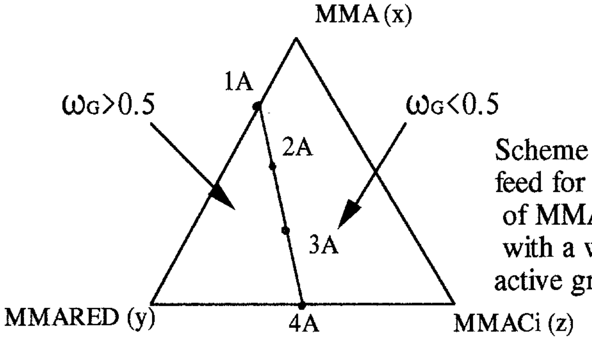
with M_G molecular weight of DR1 (MG = 314), x, y, z were the molar fraction of MMA (Mx = 100 $g.mol^{-1}$), MMARED (My = 382 $g.mol^{-1}$) and

MMACi ($M_z = 260\ g.mol^{-1}$) respectively. With $x + y + z = 1$ [2] and relation [1] we can write the general equation between x and y:

$$[3] \quad y = \omega_G \frac{[\ M_z + x\ (M_x - M_z)\ ]}{[\ M_G - \omega_G\ (M_y - M_z)\ ]}$$

So with $\omega_G = 0.5$, equation [3] can be expressed as :[4] $y = 0.514 - 0.316.x$

From equation [4] and [2] we can calculate four compositions in which the weight concentration of DR1 is 0.5 in the monomer feed. (scheme 1).



Scheme 1 : Composition of monomers feed for the terpolymerization of MMA, MMARED and MMACi with a weight fraction of ONL active group of 0.5.

In table 1 we have reported the mole fraction of monomers feed as well as the terpolymers determined composition and their inherent viscosity and glass transition temperature.

It is interesting to notice that during these polymerizations we did not observe any insoluble polymer.

The results show that monomers MMARED and MMACi copolymerize in low yield (< 10%), exp No 4A, under usual free radical conditions and the use of a third monomer especially methyl methacrylate (**MMA**), is necessary to increase the yield of the copolymerization.

On the other hand, it is very interesting to observe the good agreement of the weight fraction of ONL group in the terpolymer compositon (close to 0.5 in all cases), with that in the monomer feed which is equal to 0.5. That augurs well for high NLO properties and demonstrates that the reactivity monomer ratios are close to each other.

It will be noted that the Tg of the terpolymer increases from 86 to 118 °C when the mole fraction of cinnamoyl group, z, decreases from 0.3 to 0. The Tg values are high though the inherent viscosities are quite low. Thermogravimetric investigations show that all the terpolymers are stable for one hour at a temperature of 150°C and that is a sufficiently high thermostability for the poling process. The NLO properties and the ability to crosslink the polymers and to quench the poled NLO moities are under studies and will be published in a further paper.

Exp No	Monomer feed (ω_G =0.5)	Yield (%)	Analytical results		Terpolymer a) composition	ω_G (exp)	η_{inh} b) (dl.g^{-1})	Tg c) (°C)
			calc	exp				
1A	x = 0.711 y = 0.289 z = 0	66	%C=60.87 %H = 6.64 %N = 8.92 %O=22.73	60.85 7.15 8.43 23.52	x = 0.70 y = 0.30 z = 0.00	0.51	0.123	118
2A	x = 0.5 y = 0.356 z = 0.144	42	%C=63.27 %H =6.33 %N =8.92 %O=21.48	62.35 6.86 8.22 22.4	x = 0.50 y = 0.31 z = 0.18	0.45	0.133	102
3A	x = 0.25 y = 0.435 z = 0.315	53	%C=64.49 %H =6.08 %N =8.92 %O=20.50	63.24 6.7 8.36 21.4	x = 0.28 y = 0.41 z = 0.30	0.49	0.098	86
4A	x = 0 y = 0.514 z = 0.486	9	-	-	-	-	0.045	-

a) determined by ^{1}H NMR and analytical results

b) Inherent viscosity measured at a concentration of 0.5g/l in tetrahydrofuran at 30°C

c) Tg was determined by differential scanning calorimetry (DSC)

Table 1 : Mole fraction of monomers in feed and of terpolymers and physical properties of poly(MMA-*co*-MMARED-*co*-MMACi) terpolymer.

Acknowledgement

Financial support from the "Centre National d'Etudes des Télécommunications "from France Télécom is acknowledged.

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Accepted August 12, 1992 C