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Behavior under UV irradiation of new polymers with photocrosslinkable and NLO groups prepared from chloromethylstyrene

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Summary

In this paper, the syntheses of two styrene-based monomers bearing either an optical active group, Dispersed Red 1, or a photocrosslinkable cinnamate group are described. The study of their copolymerizations with maleic anhydride and the characterizations of the copolymers are given. Polymer materials with exposure to UV curing light, 254 nm, exhibit a photobleaching process. This feature can be used in the preparation of channelized wave-guide using photomask methods.

Introduction

It is well known that grafted polymers with second-order non linear optical (NLO) groups are now of great technological interest for use in highbandwidth electrooptic polymer modulators (1). The main advantage of these polymers is the high concentration of NLO groups and a relatively high glass transition temperature (Tg) that can be achieved. The electro-optic performances of these materials are due to a Pockels effect. It is necessary to pole the NLO groups under high electric field and at a temperature above the Tg, in order to observe the electro-optic effect. But the main problem in these materials is the slow relaxation of NLO chromophores. Several solutions can be used to overcome this drawback. First, it is possible to reduce the relaxation by using a material (2) with a high Tg. Another way to stabilize the orientation during the poling process, is to crosslink the polymers containing NLO groups (3,4) after the poling. In a previous paper we have described the synthesis of methacrylate polymers with both NLO and photocrosslinkable active side groups (5). We present here another type of copolymers based on the copolymerization of maleic anhydride and two monomers prepared from chloromethylstyrene, one of which includes a NLO group (Dispersed Red 1, monomer **1a**) and the other a photocrosslinkable cinnamate group (monomer **1b**). Polymeric materials with NLO chromophores have been already prepared from chloromethylstyrene (6) but without any crosslinkable group. Unfortunately, monomers **1a** and **1b** do not undergo copolymerization under free radical conditions and moreover the direct grafting, by phase transfert catalysis, of the NLO group on a poly[1-(chloromethylphenyl)-ethylene] leads to crosslinked polymer.

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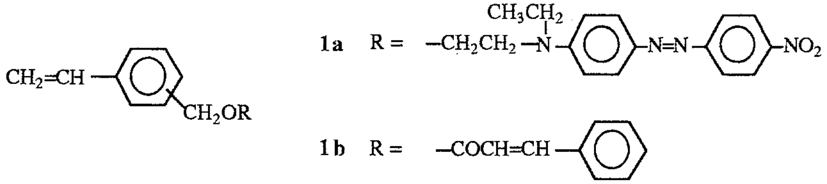


So we used a third monomer which is necessary to allow the copolymerization between monomers **1a** and **1b**. With these two electron donor monomers an electron acceptor monomer has been chosen such as maleic anhydride to performe alternated copolymerization (7). The synthesis and copolymerization of these monomers and study of the behavior of copolymers under 254 nm UV irradition is described.

Experimental

Instrumentation : ^{1}H NMR (200MHz) spectra data were obtained on a Bruker AC200 spectrometer; UV-visible spectra were taken on a Cary 2300 Varian spectrophotometer. The thermal measurements (Tg) were carried out with a Perkin Elmer DSC 4 (40 K.min^{-1}, under nitrogen) and a TGA device from Du Pont 2000 (5K.min^{-1}, under nitrogen). Weight average molecular weights (Mw) of the copolymers were determined with a Spectra-Physic Winner Station equipped with two PL Gel columns, 5µm mixed D (300*7,5mm) using tetrahydrofuran as eluent (1mL. min^{-1}) and with poly(methylmethacrylate) as standards. Films were made by spin coating solutions (100g.L^{-1} in 1,1,2-trichloroethane) onto silica glass. Acceleration and speed parameters were chosen to yield a film thickness (0,3µm) leading to an absorbance between 1 and 2 DO.Irradiations were accomplished with a PROLABO (ref 14313-005) medium pressure quartz mercury lamp, used without a filter and emitting from 240 to 300 nm with an intensity of 1,2 mW.cm^{-2} at 254 nm. The distance between sample and lamp is 5 cm.

Material : Chloromethylstyrene (CMS) (*m* - and *p* - mixture) was purchased from TCI. Dispersed Red 1, from Aldrich, was purified by column chromatography on silica gel with toluene as eluent. Maleic anhydride, cinnamic acid, tetrabutylammonium hydrogen sulfate (TBAH) and tetrabutylammonium bromide (TBAB), were used without purification, and 2,2'-azoisobutyronitrile (AIBN), recrystallized from methanol, were purchased from Aldrich .

Monomers synthesis :

Monomer **1a**: A 500 mL three-necked flask containing 260 mL of toluene and 20g (6.36.10^{-2}mol) of DR1 was heated at 75°C to dissolve the DR1. Then, 2.16g (6.36.10^{-3}mol) of TBAH, 10g (6.56.10^{-2}mol) of CMS and 50 ml of 20 M sodium hydroxide solution were added dropwise. The mixture was stirred for 18 h at 75°C. The crude product was dissolved in dichloromethane. The organic layer was washed with water until neutral and dried over Na_2SO_4. The crude monomer was purified by crystallization from cyclohexane. Yield 16g (60%);

m.p = 80°C. ; ^{1}H NMR ($CDCl_3$): δ (ppm) = 1.3 (t, $-CH_2-\underline{CH_3}$, J = 6.4Hz); 3.6 (q,$-\underline{CH_2}CH_3$,); 3.7 (m, $-CH_2CH_2-$); 4.6 (s for each isomer, $-O-\underline{CH_2}-Ar$); 5.25 (d, $=\underline{CH_2}$ cis, J_{cis}= 10.6Hz); 5.76 (d, $=\underline{CH_2}$ trans, J_{trans}= 17Hz); 6.71 (dd, $-C\underline{H}=$); 6.78 (d, $Ar\underline{H}-N-$, J = 8.5Hz); 7.32 (m, H arom CMS), 7.90 (m, $Ar\underline{H}-N=N-\underline{H}Ar-$); 8.3 (d, $Ar\underline{H}-NO_2$, J = 8.5Hz). Intensity ratio: 3: 2: 4: 2: 1: 1: 1: 2: 4: 4: 2.

Monomer **1b**: This monomer was prepared, according to the procedure described in ref 8, by using potassium cinnamate and CMS. Then 8g ($4.3.10^{-2}$ mol) of potassium cinnamate, prepared from cinnamic acid and potassium hydroxide in methanol, 5.49g ($3.6.10^{-2}$ mol) of CMS and 1.16g ($3.6.10^{-3}$ mol) of TBAB were vigorously stirred 24h at 30°C, in 100 mL of DMF. After cooling the mixture was filtered and the organic layer was dissolved in 300 mL of dichloromethane, washed with water and dried (Na_2SO_4) under vacuum at 60°C. Yield 7.21g (76%).

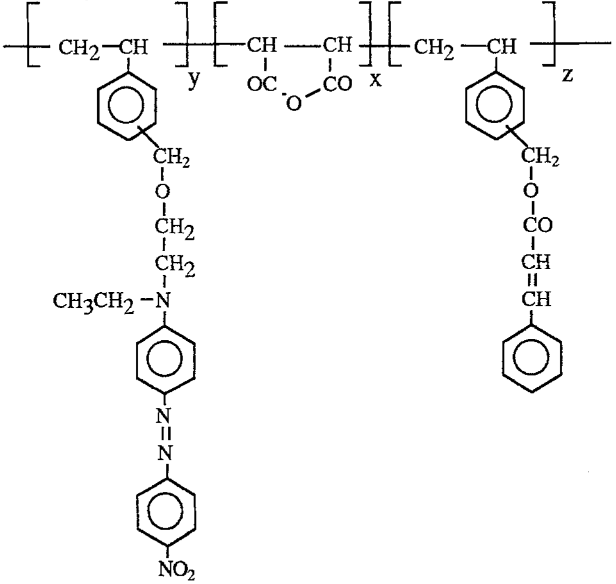
IR (KBr, cm^{-1}): 1450, 1580, 1640, 1710 ; ^{1}H NMR ($CDCl_3$): δ (ppm) = 5.32 (s for each isomer, $-O-\underline{CH_2}-Ar$); 5.35 (d, $=\underline{CH_2}$ cis, J_{cis} = 13Hz); 5.85 (d, $=\underline{CH_2}$ trans, J_{trans}= 18Hz); 6.57 (d, $-\underline{CH}=$, cinnamic group, J = 15.4 Hz); 6.8 (dd, $-\underline{CH}=$, styrenic group); 7.5 (m, ArH); 7.82 (d, $-\underline{CH}=$, cinnamic group). Intensitiy ratio 2: 1: 1: 1: 1: 9: 1.

Synthesis of copolymers : The initial compositions of monomers feed are given in Tab.1. Copolymerizations were performed in glass tubes which were filled with the monomers mixture (total weight 1g : one part, in molar ratio, of maleic anhydride for one part of styrenic monomers mixture), 1,4-dioxane (10mL) and AIBN (10% -mol) in a N_2 atmosphere. Then the tubes, containing a magnetic stirrer, were degassed and sealed under N_2 atmosphere, and put in a oil bath during 6h at 80°C. After cooling to room temperature, the solution was poured into a large excess of methanol and the copolymer was recovered by filtration. The copolymer was then purified by repeated precipitation from 1,4-dioxane into methanol until the methanol layer became colorless and dried under vacuum at 40°C. The compositions of the copolymers were determined by ^{1}H NMR and are given in Tab.1 where x, y and z are, respectively, the mole fractions of maleic anhydride, monomer **1a** and **1b** .

Results and discussion

Polymerization and characterization

The reaction using phase transfert catalysis seemed to be a good way to prepare functionalized monomers from chloromethylstyrene. We have copolymerized monomers **1a** and **1b** with maleic anhydride. The general formula for the copolymers are given in scheme 1. The composition of monomer feed and the copolymer composition analysis are given in Tab. 1. As expected, the copolymers contain 50% of acceptor moities and 50% of a mixture of donor monomers. Furthermore we observe that the composition of the copolymers is not far from the mole fraction of the initial monomers feed. We used a quite high initiator concentration (10% mole fraction) to obtain good copolymerization yield (from 61 to 85%). The results are in agreement with those of the literature. T. Dreyfus and E. Maréchal (9) have already shown the strong inhibition effect in the radical copolymerization of styrenic monomers with dye molecules bearing nitro and tertiary amine groups and the need to use a relatively high quantity of initiator.



Scheme 1 : Chemical structure of copolymers

Exper No	Monomer feed	Yield (%)	Terpolymer compostion^b	Elemental Analysis Calcd	Elemental Analysis Found	Tg (°C)	Td$_{10}$$^{c)}$ (°C)	Mw$^{d)}$
P1A	x = 0.500 y = 0.500	85	x = 0.50 y = 0.50	%C 65.90 %H 5.30 %N 10.61	66.67 6.15 10.92	112	240	7000
P1B	x = 0.500 y = 0.392 z = 0.108	61	x = 0.50 y = 0.40 z = 0.10	%C 67.07 %H 5.25 %N 8.92	65.84 5.67 9.05	116	250	7900
P1C	x = 0.500 y = 0.261 z = 0.239	73	x = 0.50 y = 0.25 z = 0.25	%C 68.62 %H 5.17 %N 6.51	68.61 5.96 6.99	125	250	9500
P1D	x = 0.500 y = 0.130 z = 0.370	72	x = 0.50 y = 0.14 z = 0.36	%C 70.55 %H 5.08 %N 3.59	69.94 5.48 4.40	134	250	13300

a) Experimental conditions : 1,4-dioxane, 10mol-% AIBN, 6 hours at 80°C; b) determined by ^1H NMR; c) decomposition temperature for a 10wt-% loss.d) PMMA standards

Tab.1. Copolymerization$^{a)}$ of maleic anhydride (x), monomers **1a** (y) and **1b** (z).

However the weight average molecular weights (Mw) are high enough to obtain films with good optical quality and Mw increases from 7000 to 13300 (PMMA standards) when the mole fraction of monomer **1a** decreases from 0.50 to 0.14. On the other hand, Tg of copolymers are higher than 110°C and vary from 112 to 134°C. TGA data show a good thermal stability under nitrogen until 240-250°C which is, in fact, the range of the starting decomposition temperature of the azo chromophore, DR1. The copolymers are soluble in common solvents.

Behavior under 254 nm irradiation.

The purpose of these copolymers structures is to exploit their Pockels effect in a polymer waveguide. Here we test the ability and the efficiency of the photocrosslinking process to hinder the relaxation of the poled NLO groups. Since the cinnamate group can undergo [2+2] photocycloaddition at 254 nm and crosslink the polymer, we hoped that formation of a network would be sufficient to freeze the mobility of the dipolar NLO units. Crosslinking by cinnamate groups seems to be a convenient method for that purpose (10). In this study we try to point out advantages and inconveniences of this photoreactive group when it is used with an azobenzene NLO chromophore.

After irradiation, crosslinking was confirmed by the insolubility of copolymers **P1B**, **P1C** and **P1D** in common organic solvents and the fading effect was observed by the disappearance of the red color. Figures 1a and 1b show the UV-Visible spectra changes during irradiation under 254 nm of copolymer **P1B** and **P1D**. We observe the simultaneous decrease of absorption band of the cinnamate group, (λ_{max}=277nm), and the one of the NLO chromophore (λ_{max} = 477nm) We have verified with copolymer **P1C** the photofading effect and the decrease of both the cinnamate and chromophore absorption bands under 254nm irradiation. From these results, we can conclude that the chromophore degradation, with the crosslinking reaction, occurs in the copolymer at 254 nm irradiation when the films contain both azo-dye and cinnamate groups(10).

The 254nm irradiation has modified the chromophore conjugation and the polymer can not be used as a NLO-active material. Up to now there are two kinds of explanations : the first one considers this photobleaching as a result of a combination of degradation and cis-trans isomerization of the NLO chromophore (11) and the second one reports (12) that the photobleaching process is due to a surrounding polarity modification during the crosslinking process. We are carried out further studies to understand and to explain this photobleaching process. First we will study the behavior of the copolymers **P1B** **P1C** and **P1D** under irradiation at wavelength higher than 300 nm and second we will study the syntheses of new monomers bearing chalcone or furyl acrylate as photosensitive groups which have λ_{max} > 300 nm.

At last, our results have been confirmed by a recent study of M. Kato et al. (13). They were prepared copolymers from methacrylate monomers bearing either the cinnamate group or the DR1 moiety. They observed the same changes in absorbances of the photocrosslinkable moiety and of the azo-dye chromophore, under UV irradiation.

However the fact that the chomophore is irreversibly bleachable can be interesting in the field of integrated optics as a means for making waveguide. By this photobleaching process, the refractive index would be lowered and allow to make channel waveguides by exposure through photomask in a mask aligneras(14). At last and concerning polymeric materials for non linear optic devices we are going to work on thermal crosslinking process with new types of crosslinking groups.

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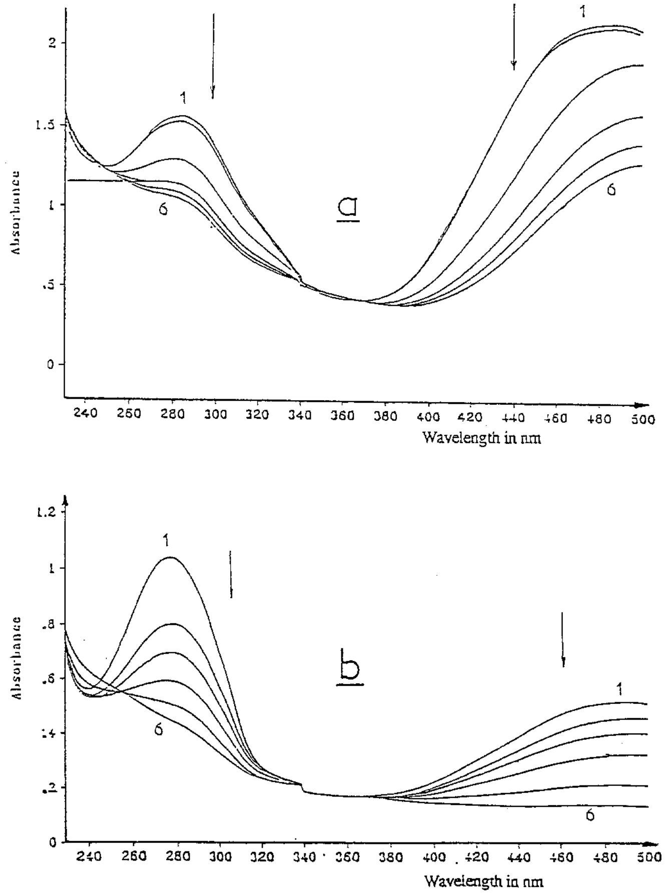

Fig. 1. UV-Vis spectra changes during irradiation upon 254 nm (a) copolymer **P1B** : **-1-** initial; **-2-** Irradiation 0.37 $J.cm^{-2}$; **-3-** 8.3 $J.cm^{-2}$ **-4-** 16.6 $J.cm^{-2}$; **-5-** 20.6 $J.cm^{-2}$; **-6-** 24.7$J.cm^{-2}$; (b) copolymer **P1D**: **-1-** initial ; **-2-** Irradiation 1 $J.cm^{-2}$; **-3-** 3.6 $J.cm^{-2}$; **-4-** 4.3 $J.cm^{-2}$; **-5-** 10 $J.cm^{-2}$; **-6-** 13 $J.cm^{-2}$.

References

1. Teng C, Saturo M G, Findakly T K (1992) Proceed. OFC 92: 333
2. Man H T, Chiang K, Haas D, Teng C C, Yoon H N (1990) Proc. SPIE 1213 Photopolymer Device Physics, Chemistry and Applications: 7
3. Bjorklund G C, Ducharne S, Fleming W, Jungbauer D, Moerner W E, Swalen J D, Twieg R J, Willson C G, Yoon D Y (1991) Materials for Non linear Optics ACS Symposium Series: 455
4. a) Mandal B K, Jeng R J, Kumar J, Tripathy S K (1991) Makromol Chem Rapid Comm 12: 607,b) Mandal B K, Kumar J, Huang J C,Tripathy S K (1991) Makromol Chem Rapid Commun,12: 63 ; c) Mandal B K, Lee J Y, Zhu X F, Chen T M, Prakeenavincha E, Kumar J, Tripathy S K,(1991) Synth. Metals 43: 3143
5. Bosc D, Boutevin B, Granier-Azema D, Rousseau A (1992) Polym Bull 29 : 289
6. Monthéard J P, Boinon B, Zerroukhi A, Le Barny P (1992) J Appl Polym Sci 44 : 1307
7. Ahlheim M, Lehr F (1994) Macromol Chem Phys 195 : 361
8. Iizawa T, Nishikubo.T, Takahashi E (1983) Makromol Chem 184 : 2297
9. a) Dreyfus T, Maréchal E (1975) Bull Soc Chim France 5-6 : 1196; b) Dreyfus T, Maréchal E (1975) Bull Soc Chim France 7-8: 1646
10. Müller H, Müller I, Nuyken O, Strohriegl P (1992) Makromol Chem Rapid Commun 13: 289
11. Chen M, Yu L, Dalton L R, Shi Y, Steier W H (1992) Macromolecules 24: 5421
12. Muller S, Le Barny P, Chastaing E, Robin P, Vairon J P (1992) Mol Eng, 2: 251
13. Kato M, Hirayama T, Matsuda H, Minami N,Okada S, Nakanishi H (1994) Macromol Rapid Commun 15: 741
14. Tomme E V, Van Daele P, Baets R, Möhlmann, Diemeer M B J (1991) J Appl Phys 69 : 6273