Preparation of polymeric non-linear optical materials from chloromethylstyrene

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Three new dyes have been synthesized in two steps by the reaction of 4-hydroxybenzaldehyde with commercial chloromethylstyrene followed by reaction with *p*-substituted anilines. Three Schiff bases have been copolymerized with styrene and the refractive index of the resulting films has been measured.

(Keywords: non-linear optics; chloromethylstyrene; Schiff bases; refractive index)

Introduction

The development of polymeric non-linear optical materials is an area of intense investigation because of their wide applications in the fields of optical communication and information processing technologies[1]. While inorganic materials such as $LiNbO_3$ have been used[2], growing evidence indicates that organic materials composed of Π electron chromophores hold considerable promise. These organic materials bearing electron donor and acceptor groups separated by conjugated nuclei can be dispersed[3] in glassy polymers or liquid crystalline polymers[4–6]. However, the best way is the preparation of an organic dye incorporated in a macromolecule either by means of a modification reaction of a polymer or by a copolymerization reaction of the dye with a comonomer. Functionalized polystyrenes such as polyiodomethylatedstyrene or polyhydroxystyrene react with 'Red-1 dye'[7], with 4-(4-nitrophenylazo) (*N*-ethyl)(2-hydroxyethyl) aniline[8] and with various other chromophores[9]. Organic dyes with methacrylic and acrylic skeletons have been recently synthesized using relatively difficult procedures. These products, with a spacer (aliphatic chain with a hetero atom such as nitrogen or sulphur) between the dye and the methacrylic or acrylic unit, have been copolymerized with methacrylic or acrylic comonomers[10–13]. In this paper we report an easy synthesis of organic dyes for non-linear optics, in two simple steps, from chloromethylstyrene or vinylbenzylchloride (VBC, I) and their copolymerizations with styrene in order to study the optical properties of the resulting thin films. Commercially available VBC is a mixture of *meta* and *para* isomers (ratio 3/2), the separation of which is difficult[14]. Consequently the prepared copolymers were terpolymers. This paper describes the preparation of dyes (*Scheme 1*) and their subsequent copolymerization.

Experimental

Characterization and measurements. Molecular masses were measured using Knauer apparatus and Ultrastyragel columns (10^3, 10^4 and 10^5 Å) in tetrahydrofuran as solvent at 20°C. Elemental analyses were performed by the Service Central d'Analyse, CNRS, Vernaison (France). The glass transition temperatures (T_gs) and melting points of the starting dyes were measured with a DSC 101 Setaram (sample mass 10–15 mg, heating rate 10°C min^{-1}). ^1H n.m.r. spectra were recorded with a Bruker AM 300 at 300 MHz and at 300 K with 10% (w/v) $CDCl_3$ solutions. U.v. spectra were recorded with an Hitachi 1100 apparatus in chloroform as a solvent. The refractive index was measured[15] using the optical waveguide technique by determining the synchronous angles for the prism coupled mode excited at $\lambda = 0.6328$ nm.

Materials. VBC (I) was obtained from Dow Chemical Corp. and was purified by vacuum distillation. The 4-hydroxybenzaldehyde, 4-nitroaniline, 4-trifluoromethylaniline, 4-cyanoaniline and 4-methyl-2,6-ditertbutylphenol used were commercially available and were used without further purification.

Preparation of 3,4-vinylbenzyloxybenzaldehyde(II). This aldehyde was prepared by heating a mixture of I and 4-hydroxybenzaldehyde according to a previously described procedure (m.p. $\approx$ 40°C)[16].

Preparation of Schiff bases (III a, b and c). A typical run is described for the synthesis of dye III a ($R = NO_2$). Aldehyde II (23.8 g, 0.1 mol) was dissolved in anhydrous benzene (100 ml) with *p*-toluenesulphonic acid (50 mg) as catalyst in a 250 ml three-necked round-bottomed flask bearing a Dean–Stark trap and reflux condenser. Then 4-nitroaniline (13.8 g, 0.1 mol) was added. After complete elimination of water the benzene solution was evaporated under vacuum, and the solid Schiff base dissolved in chloroform. The solution was filtered to eliminate the catalyst, and the dye precipitated with petroleum ether. Dye III a (yellow) was purified by means of recrystallization with chloroform and petroleum ether (yield ~85%). The procedures and yields were similar for the synthesis of dyes III b and c.

Characteristics of dyes III a, b and c (u.v. and ^1H n.m.r. spectra, elemental analyses and melting points) are given in *Table 1*.

Preparation of terpolymers IVa and b. Dye III a (1 g, 0.00279 mol) was mixed with styrene (1.16 g, 0.011 mol) and azobisisobutyronitrile (AIBN, 8 mg) as initiator (3 wt%). The mixture was placed in a glass tube, sealed

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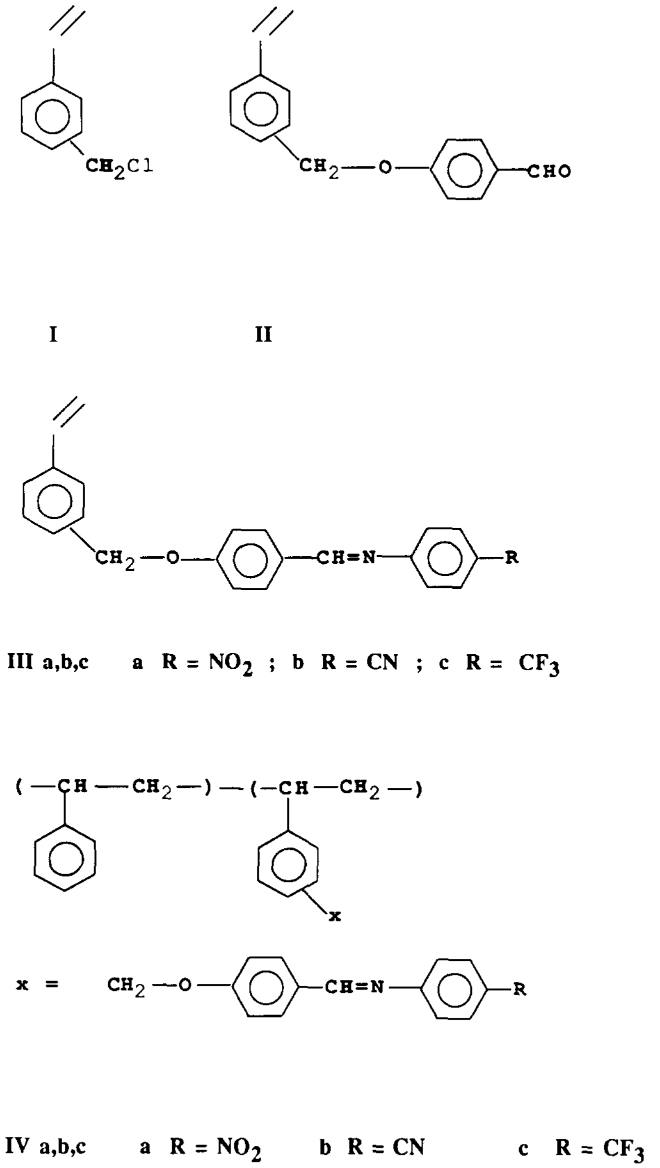

Scheme 1

Table 1 Physical properties of dyes III a, b, c

Elemental analyses(%)				
III a (R = NO_2, m.p. = 84°C)				
Exp.	C 73.44	H 4.92	N 7.99	O 13.70
Calc.	C 73.70	H 5.00	N 7.80	O 13.40
III b (R = CN, m.p. = 111°C)				
Exp.	C 81.47	H 5.00	N 8.34	O 5.02
Calc.	C 81.66	H 5.30	N 8.30	O 4.70
III c (R = CF_3, m.p. = 77°C)				
Exp.	C 72.17	H 4.73	N 3.80	F 14.20
Calc.	C 72.40	H 4.70	N 3.67	F 14.95
U.v. spectra				
	λ_{max} (nm)			ε
III a	260			32000
	370			29000
III b	245			28700
	320			19000
III c	255			19500
	280			12300
^1H n.m.r. spectra[a]				
III a, b and c	CH_2O 5.2 (S), $-CH=CH_2$ 5.3, 5.8(2d), $CH=CH_2$, aromatic H and CH=N 6.6–8.6 (m)			

[a] The chemical shifts are similar for III a, b and c

Table 2 Molecular masses, T_gs and λ_{max} values from u.v. spectra for copolymers IV a, b and c

	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	T_g (°C)	λ_{max} (nm)
IV a	13000	18000	1.38	94	265
IV b	53000	205000	3.87	99	250
IV c	21500	37300	1.73	107	250

under nitrogen and heated at 75°C for 72 h. Copolymer IV a was obtained after dissolving in chloroform and precipitation with petroleum ether (yield 65%).

Similar molar proportions of dyes III b and styrene were used for the preparation of IV b but the duration of the copolymerization was only 3 h (yield 70%).

Preparation of terpolymer IV c. Dye III c (1 g, 0.00262 mol) and styrene (1.1 g, 0.010 mol) were dissolved in benzene (3 ml) with AIBN (8 mg). The mixture was placed in a sealed tube and heated for 72 h. After dissolving the product in chloroform and precipitation with methanol terpolymer IV c was obtained (1.25 g, yield 60%).

Terpolymers IV a, b and c were characterized by g.p.c., T_g measurements and u.v. spectra (*Table 2*).

Results and discussion

Syntheses of dyes with spacers for non-linear optics generally require several steps. By using chloromethylstyrene we have built a polymeric chain with a benzyloxy group as a spacer linked to a substituted phenyl group by an imine function. We have previously reported various syntheses of pure isomers of *o*-, *m*- and *p*-chloromethylstyrene[17] but as the reactivity rates of *meta* and *para* are equal[18] we used the commercial product rather than the pure isomer for this study. The copolymerizations of dyes III a, b and c with styrene have given relatively high molecular masses (*Table 2*) and the observed T_gs are in the range of 94–107°C, By using a molar proportion of dye to styrene of 20%, the results of microanalyses (nitrogen, oxygen or fluorine) show that 30% of the dyes have been incorporated. As in i.r. spectroscopy, a weak peak at 1690 cm^{-1} is observed for the three copolymers (carbonyl function) as partial hydrolysis of the imine occurs during the purification step. Syntheses of similar polymeric dyes could also be carried out by the reaction of 4-hydroxybenzaldehyde with poly(VBC) followed by the reaction of 4-substituted aniline, and copolymerization of the dyes with methyl methacrylate could give products with higher molecular masses and higher T_gs.

The incorporation of dyes III a, b and c in a copolymer with styrene does not decrease the 'filmability' compared to polystyrene[19]. Copolymers IV a, b and c have been dissolved in chloroform (1 g in 50 ml) and thin films have been prepared by means of spin-coating. The thickness of these films is ~1 μm and the refractive index of copolymers IV a, b and c are, respectively, 1.634, 1.633 and 1.614. The room temperature breakdown field for our samples was found to be $>4 \times 10^8$ V m^{-1} which is high enough to allow efficient poling by an electric field. Studies of electro-optical properties are now being carried out. The product, $\beta\mu$, of the hyperpolarizability coefficient β by the molecular dipole moment μ of these dyes could be improved by using another spacer and other double bonds between the aromatic nuclei (azo bond or carbon–carbon double bond) and other electron-withdrawing substituents[20].

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