# Syntheses and Nonlinear Optical Properties of Polymers Prepared from Chloromethylstyrene

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## SYNOPSIS

The synthesis and characterization of new dyes, prepared in two steps from chloromethylstyrene, and containing azo moieties or stilbene are reported. All synthesized monomers show spectroscopic properties (nuclear magnetic resonance, ultraviolet) in accordance with the attempted structure. These monomers have been copolymerized with styrene and the nonlinear optical properties of the new compounds and those of previously described polymeric imines have been studied via second harmonic generation. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Because of their numerous applications, the nonlinear optical properties of inorganic and organic materials and chiefly of organic polymers have been given increasing attention.[1] The best material seems to be organic polymers or copolymers, the structure of which is a polymer backbone bearing a spacer linked to the nonlinear species. The systems based on polymethacrylate or polystyrene have been previously studied. They can be synthesized either by means of a copolymerization reaction of a functional monomer or by a chemical modification of a polymer. Organic dyes with a spacer and a nonlinear species, linked to a methacrylic skeleton have been synthesized and copolymerized with methyl methacrylate.[2-8] Chemical modifications of polymers have been studied less: Iodomethylated polystyrene, prepared from a nucleophilic substitution of chloromethylated polystyrene reacts with the "Red-One" dye and gives a grafted product[9] with a moderate yield. Poly(4-hydroxystyrene) has also been modified with 4'-(4N nitrophenylazo)(N-ethyl)(2-hydroxyethyl)aniline[10,11] or with various azo compounds,[12] and, recently, similar reactions have been described with poly(methacryloyl chloride).[13] We have pre-

viously reported the syntheses of organic dyes for nonlinear optics, prepared in two easy steps from chloromethylstyrene and copolymerized with styrene.[14,15] In this work, we report new syntheses of organic dyes from chloromethylstyrene **1a** (commercial name: vinyl benzyl chloride) commercially available in a mixture of *meta* and *para* isomers in the ratio 3/2 or from a pure *para* isomer of chloromethylstyrene now also commercially available. These monomers or their corresponding polymers allow a great number of nucleophilic substitution reactions.[16,17] In this report are described the preparations of dyes, their copolymerizations, and measurements of their nonlinear optical parameters.

## EXPERIMENTAL

### Materials

Chloromethylstyrene **1a** (mixture *meta,para*, ratio 3/2; Dow Chemical) and 4-chloromethylstyrene **1b** (Kodak) were purified by vacuum-distillation. Phenol-4-hydroxybenzaldehyde and 4-nitrophenylacetic acid (Janssen Chemicals) were used without further purification.

### Instrumentation

^{1}H-NMR spectral data were obtained on a Bruker WP 300 spectrometer (deuterated chloroform was

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used as solvent). Ultraviolet-visible (UV-Vis) spectra were recorded with an Hitachi 1100 apparatus. The glass transition temperatures and melting points were recorded with a DSC 92 Setaram. The molecular masses of the copolymers were measured with a Knauer apparatus by using $10^3$-$10^4$-$10^5$ Å columns and polystyrene standards. Tetrahydrofuran (THF) was used as the solvent. Microanalyses were performed at the Service Central d'Analyse, Vernaison, France.

## Syntheses of the Monomers

4-(4' Hydroxyphenylazo)nitrobenzene **2a** ($R$ = $NO_2$) was prepared by reaction of a 4-nitroaniline, nitrous acid, and phenol according to the procedure described by Mc Culloch and Bailey.[12] 4-(4' hydroxyphenylazo)cyanobenzene **2b** ($R$ = CN) and 4-(4' hydroxyphenylazo)trifluoromethylbenzene **2c** ($R$ = $CF_3$) were synthesized with a similar procedure, respectively, using as starting amine 4-cyanoaniline and 4-trifluoromethylaniline.

4-[(Vinylbenzyloxy)-4'-phenylazonitrobenzene] **3a** ($R$ = $NO_2$) was prepared through a nucleophilic substitution of chloromethylstyrene: 2.43 g (0.01 mol) of a **2a** was dissolved in 60 mL of anhydrous dimethylformamide (DMF) with 0.24 g (0.01 mol) of sodium hydride, and after 1 h of stirring, 1.525 g of **1a** (0.01 mol) in 5 mL of DMF was added and

the mixture was heated at 80°C for 7 h. Dye **3a** was obtained after pouring into 100 mL of water. The product was filtered and dried under vacuum, and the yield was close to 75%. A similar method was used for the syntheses of the monomers **3b** ($R$ = CN) and **3c** ($R$ = $CF_3$).

Aldehyde **5a** or **5b** was prepared by reaction of **1a** or **1b** with 4-hydroxybenzaldehyde using a previously described method.[18,19]

4-(Vinylbenzyloxy)-4' nitrostilbene **6b**, a new dye, was synthesized by reaction of **1b** with 4-nitrophenylacetic acid and piperidine as a catalyst. A 250 mL, three-necked, round-bottomed flask (fitted with a magnetic stirrer and reflux condenser) was charged with 4-nitrophenylacetic acid (16.65 g; 0.092 mol) and piperidine (7.4 g; 0.092 mol) and was heated for 1 h between 80 and 90°C. Aldehyde **5b** (21.9 g; 0.092 mol) and 2,6-di-*tert*-butyl-4-methylphenol (0.2 g; 0.0009 mol) were added; the mixture was then heated at 120–130°C for 4 h, the water being distillated during the reaction. Then, the mixture was dissolved in 100 mL of chloroform and washed with 3 × 20 mL of NaOH 1$N$. The solution was dried with anhydrous sodium sulfate and the chloroform was removed under vacuum. Dye **6b** has been purified after dissolution in chloroform and precipitation with pentane.

The procedure was similar to that used with the monomer **1a**[14] (mp 183°C). The elemental analyses

**Table I  Elemental Analyses and Melting Point (mp) of Monomers**

| Monomers | mp[a] | Elemental Analyses | | | | |
|---|---|---|---|---|---|---|
| | | C[b] | H[b] | N[b] | O[b] | F[b] |
| **3a** ($C_{21}H_{17}N_3O_3$) | 124 and 139 | 70.14 | 4.88 | 11.36 | 13.08 | |
| | | (70.19) | (4.73) | (11.70) | (13.37) | |
| **3b** ($C_{22}H_{17}N_3O$) | 146 and 165 | 77.50 | 5.23 | 12.63 | 4.74 | |
| | | (77.88) | (5.01) | (12.39) | (4.72) | |
| **3a** ($C_{22}H_{17}N_2OF_3$) | 118 and 130 | 68.85 | 4.65 | 7.42 | | 14.86 |
| | | (69.10) | (4.45) | (7.33) | | (14.92) |
| **6a** ($C_{23}H_{19}NO_3$) | 146 and 156 | 77.00 | 5.50 | 4.00 | 13.50 | |
| | | (77.30) | (5.32) | (3.92) | (13.44) | |
| **6b** ($C_{23}H_{19}NO_3$) | 183 | 77.15 | 5.40 | 3.98 | 13.46 | |
| | | (77.30) | (5.32) | (3.92) | (13.44) | |
| **8a** ($C_{22}H_{18}N_2O_3$) | 84 | 73.44 | 4.92 | 7.99 | 13.70 | |
| | | (73.70) | (5.00) | (7.80) | (13.40) | |
| **8b** ($C_{23}H_{18}N_2O$) | 111 | 81.47 | 5.00 | 8.34 | 5.02 | |
| | | (81.66) | (5.30) | (8.30) | (4.73) | |
| **8c** ($C_{23}H_{18}NOF_3$) | 77 | 72.17 | 4.73 | 3.80 | | 14.20 |
| | | (72.44) | (4.72) | (3.67) | | (14.96) |

[a] mp was determined by differential scanning calorimetry (DSC).
[b] Found (calcd) values.

## Table II   UV-vis Absorptions (nm) and Values of the Molar Coefficients $\varepsilon$ (L/mol cm)

| Dyes | $\lambda_{max}$ | $\varepsilon$ |
|------|------|------|
| 3a | 380 | 18,200 |
| 3b | 365 | 18,000 |
| 3c | 355 | 17,000 |
| 6a | 380 | 29,300 |
| 6b | 375 | 41,800 |
| 8a | 370 | 28,750 |
| 8b | 320 | 21,900 |
| 8c | 280 | 15,300 |

and melting points of dyes 3a,b, and c, 6a and b, and 8a,b, and c are given in Table I, the UV absorptions in Table II, and $^1$H NMR in Table III.

### Syntheses of the Copolymers 9a and 9b

Dye 3a, 3b or 3c (0.0028 mol) was dissolved in 5 mL of chlorobenzene and mixed with 0.0252 mol of styrene ( molar proportion dye/styrene 10/90) with 1‰ in weight of di-tert-butylperoxide. After the tube was degassed and sealed, the mixture was heated at 120°C for 3 days. Then, the copolymer 9a or 9b was precipitated with methanol and purified by dissolving in THF and precipitation with methanol. The yields of these reactions were close to 45%. The characterization (NMR) of these copolymers show that dye 3c with the $CF_3$ group in the para position was not incorporated.

### Syntheses of the Copolymers 10a and 10b

A similar procedure was used for the copolymerization reaction of the stilbenic dye 6a or 6b. The

monomer 6a or 6b (1 g; 0.0028 mol) was dissolved in 10 mL of chlorobenzene and mixed with styrene (2.6 g; 0.025 mol) and 3.6 mg of azobisisobutyronitrile (AIBN) as initiator (1‰ in weight). The mixture was placed in a glass tube, sealed under nitrogen, and heated at 75°C for 20 h. The copolymer 10a or 10b was obtained with a yield of 45% and was purified by dissolving in chloroform and precipitated by methanol.

### Syntheses of the Copolymers 11a, 11b, and 11c

The copolymers 11a, 11b, and 11c were synthesized by heating a mixture of the monomers 8a, 8b, and 8c with styrene (molar proportions 10/90). A total of 1 g of dye 8a (0.0028 mol) and 2.62 g of styrene (0.0252 mol) were dissolved in benzene (3 mL) with AIBN (3.6 mg, 1‰ in weight) and placed in a sealed tube and heated for 72 h. After dissolving the product in chloroform and precipitation with methanol, the copolymer 11a was obtained with a 60% yield. A similar method was used for the syntheses of 11b and 11c, and the yields were close to 60%.

The copolymers 9a and 9b, 10a and 10b, and 11a, 11b, and 11c were characterized. Molecular masses and glass transition temperatures of the copolymers are given in the Table IV. The main characteristics of their $^1$H-NMR spectra are given in Table V, and the proportions of incorporated dye have been calculated by the measurement of the $CH_2O$ peak area in the $^1$H-NMR spectra.

### Preparation of Thin Films

Thin films of 9a, 9b, 10a, 10b, 11a, 11b, and 11c were obtained by spin-coating solutions in

## Table III   NMR Peaks of Dyes 3a, b, and c; 6a and b; and 8a, b, and c

| | $^1$H-NMR, $\delta$ in ppm[a] | | | | | |
|---|---|---|---|---|---|---|
| Monomers | Aromatics | CH=CH | $CH_2$=CH | CH=$CH_2$ | $CH_2O$ | Aromatics and CH=N |
| 3a | 8.7–7 (m) | | 5.8, 5.3 (2d) | 6.8 (m) | 5.10 (s) | |
| 3b | 8–7 (m) | | 5.8, 5.3 (2d) | 6.8 (m) | 5.10 (s) | |
| 3c | 8.7–7 (m) | | 5.8, 5.3 (2d) | 6.8 (m) | 5.10 (s) | |
| 6a | 8–7 (m) | 8.3 (d)–8.2 (d) | 5.8, 5.2 (2d) | 6.8 (m) | 5.15 (s) | |
| 6b | 8–7 (m) | 8.3 (d)–8.2 (d) | 5.8, 5.2 (2d) | 6.8 (m) | 5.15 (s) | |
| 8a | | | 5.8, 5.3 (2d) | 6.7 (m) | 5.10 (s) | 8.4–7 (m) |
| 8b | | | 5.8, 5.3 (2d) | 6.7 (m) | 5.10 (s) | 8.4–7 (m) |
| 8c | | | 5.8, 5.3 (2d) | 6.7 (m) | 5.10 (s) | 8.4–7 (m) |

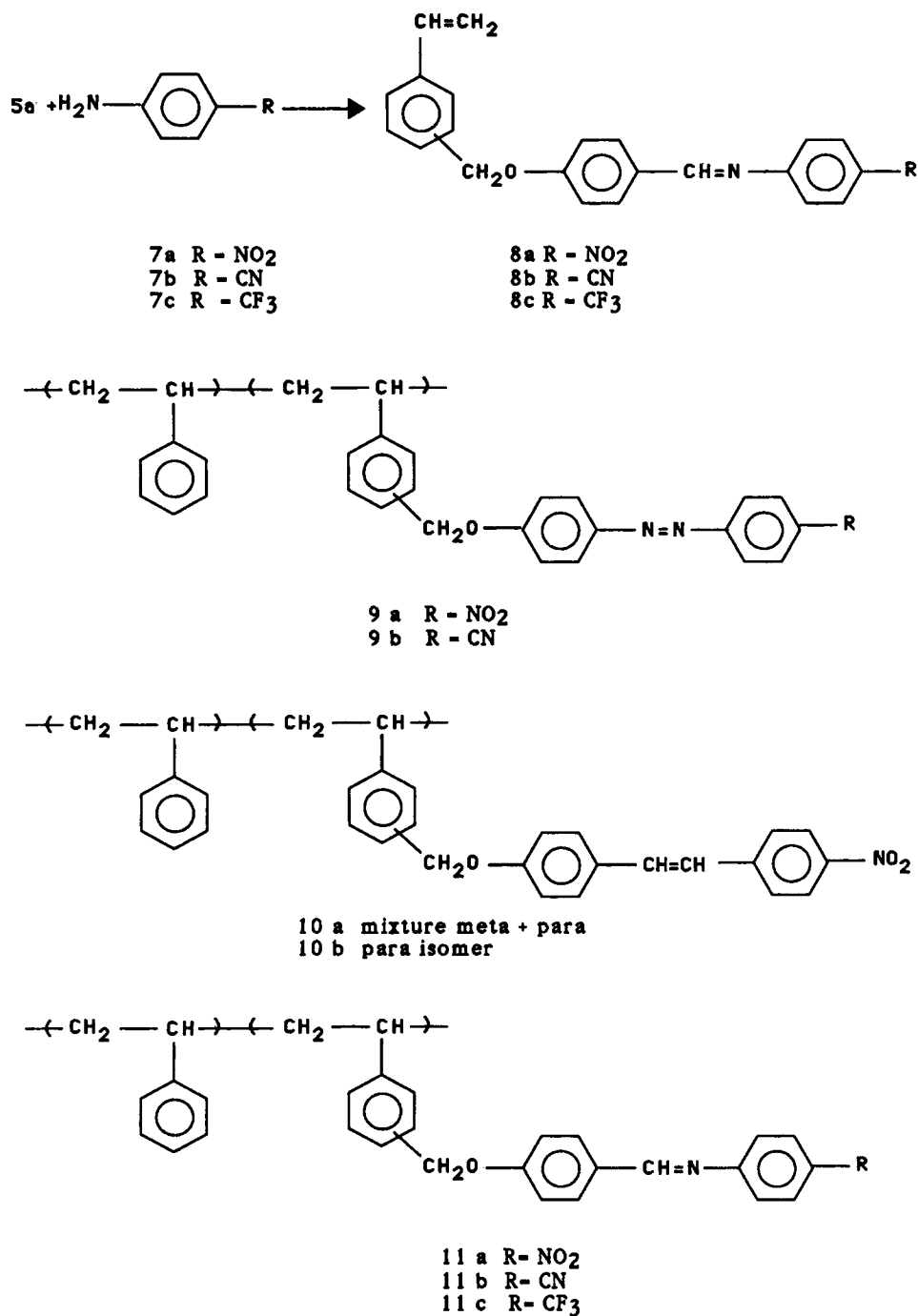[a] m = multiplet; d = doublet; s = singlet.
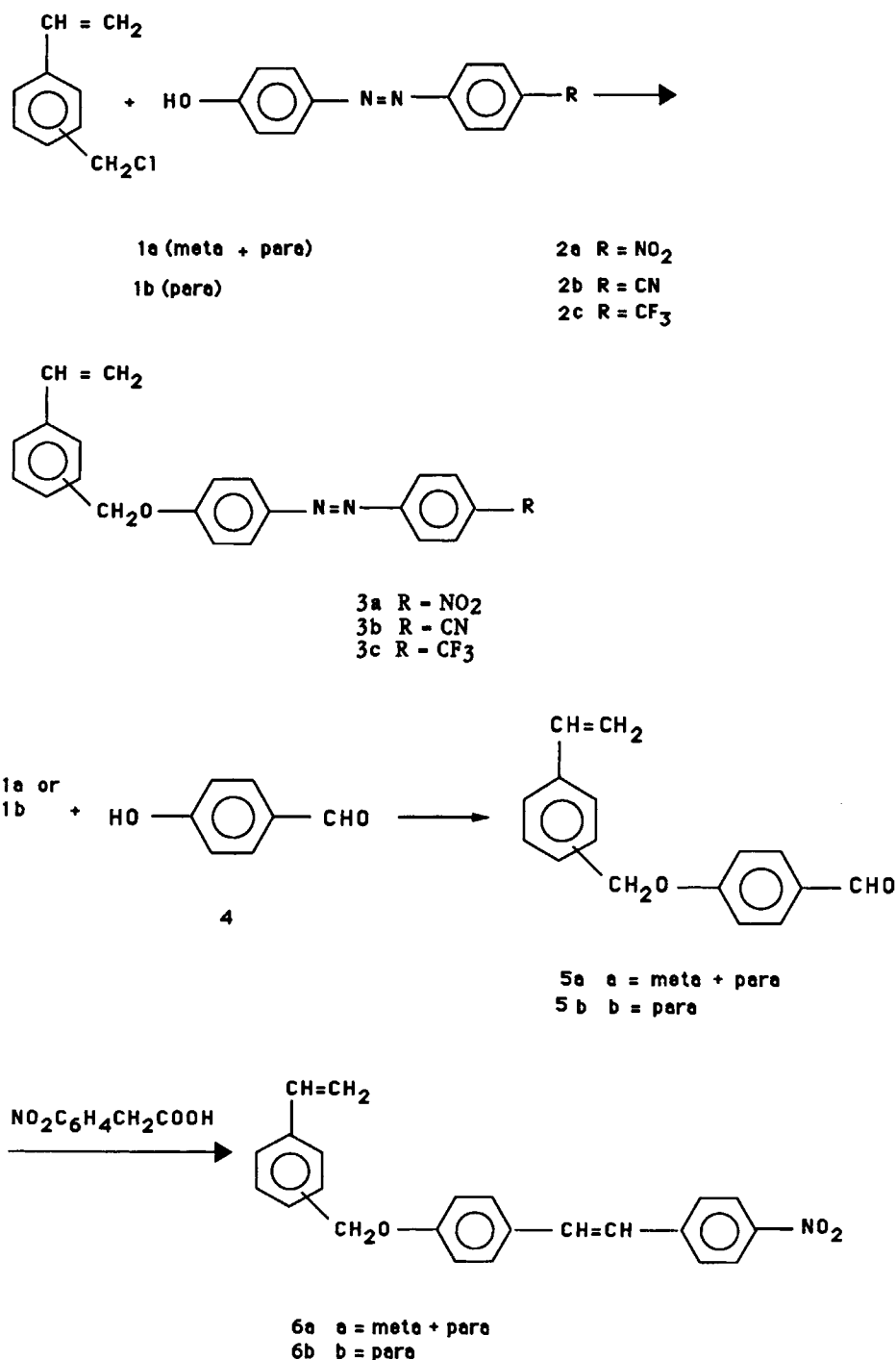
**Scheme 1**

chloroform ($\gg$ 120 g/L) on glass substrates ($n$ $\gg$ 1.51 at 0.6328 $\mu$m and 1 mm thickness) and dried at 80°C for 1 h under vacuum to evaporate the residual solvent.

We made an optical characterization by exciting the guided modes of the structure glass/polymer/

air through an LiNbO$_3$ prism using an HeNe laser ($\lambda$ = 0.6328 $\mu$m) or a white source and a monochromator. The analysis of the M lines in the reflected light (ATR method) gives—after a numerical treatment of the measured effective indexes[20]—the refractive indexes ($s$ and $p$ according to the laser po-

CH=CH₂

5a  +H₂N—⬡—R ⟶  (structure)  CH₂O—⬡—CH=N—⬡—R

7a  R - NO₂          8a R - NO₂
7b  R - CN           8b R - CN
7c  R - CF₃          8c R - CF₃

—(CH₂—CH)—(CH₂—CH)—  (with pendant CH₂O—⬡—N=N—⬡—R)

9 a  R - NO₂
9 b  R - CN

—(CH₂—CH)—(CH₂—CH)—  (with pendant CH₂O—⬡—CH=CH—⬡—NO₂)

10 a  mixture meta + para
10 b  para isomer

—(CH₂—CH)—(CH₂—CH)—  (with pendant CH₂O—⬡—CH=N—⬡—R)

11 a  R- NO₂
11 b  R- CN
11 c  R- CF₃

**Scheme 2**

larization) and the film thickness. The as-deposited guides exhibit the well-known optical characteristics of polystyrene films[21]: They are isotropic (noncentrosymmetric) with a low dielectric constant, $n \gg 1.60$ and they have an excellent transparency with low optical losses (some dB cm$^{-1}$ at 0.6328 $\mu$m) and thicknesses ranging from 1–4 $\mu$m.

**Nonlinear Optical Properties**

To induce the nonlinear properties of the thin polymer films, they were oriented by corona-poling at a temperature above the $T_g$. We established a 5–10 kV voltage between a tungsten needle and a metallic plane electrode during 0.5 h (Fig. 1) and then cooled

**Table IV  Molecular Masses, Glass Transition Temperature, and Yields ($Y$) of the Copolymers 9a and b, 10a and b, and 11a, b, and c**

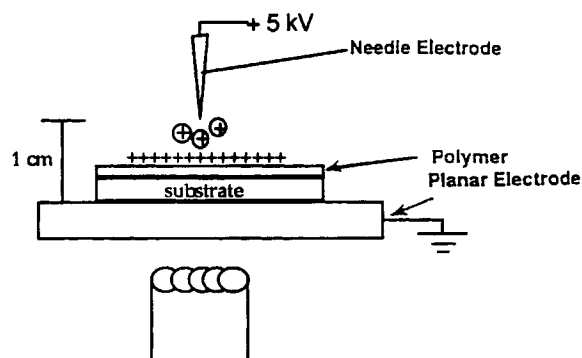| Copolymers | $M_w$ ($10^{-3}$) | $M_n$ ($10^{-3}$) | $M_w/M_n$ | $T_g$ (°C) | $Y$ (%) |
|---|---|---|---|---|---|
| 9a | 7.2 | 4.1 | 1.7 | 90 | 40 |
| 9b | 58 | 18 | 3.2 | 100 | 50 |
| 10a | 39 | 18 | 2.2 | 62 | 40 |
| 10b | 40 | 11 | 3.6 | 115 | 50 |
| 11a | 20 | 14 | 1.4 | 93 | 60 |
| 11b | 140 | 35 | 4 | 100 | 70 |
| 11c | 40 | 22 | 1.8 | 105 | 60 |



**Figure 1**  Corona-poling configuration.

the sample, maintaining the high voltage to freeze the orientation. In some cases, the polymer films became white and turbid and underwent degradation of their optical and guiding characteristics. This phenomenon may be caused by decomposition under the electric field[22] and can be avoided by poling at lower temperature or voltage when possible. Oriented layers are uniaxial with the $c$-axis perpendicular to the substrate plane and a birefringence of typically 0.020–0.030 at 0.6328 $\mu$m: They belong to the $\infty mm$ symmetry group. Refractive index typical values are given in Table VI.

The nonlinearities were studied via second harmonic generation by transmission through the guiding layers. When an intense laser light at frequency $\omega$ propagates in a nonlinear medium, the electric field generates a nonlinear polarization that gives rise to harmonic components at frequencies $2\omega$, $3\omega$, . . . and several nonlinear effects. In the case of materials with second-order nonlinearities, we can detect in the transmitted light a component at frequency $2\omega$ (Fig. 2) that depends on the incidence angle and light polarization. The nonlinear polarization components for the second harmonic gen-

eration in terms of the electric field at $\omega$ can be written as

$$P_h^{nl}(2\omega) = 2 \cdot \varepsilon_0 \cdot d_{hij} E_i (\omega) \cdot E_j (\omega)$$

where $d_{hij} = \frac{1}{2}\chi_{hij}^{(2)}$ the nonlinear susceptibility tensor at $2\omega$ at which nonzero elements depend on the symmetry conditions in the material.[23]

If we assume that the samples belong to the $\infty mm$ symmetry group with the $c$-axis perpendicular to the substrate plane, the transmitted light at $2\omega$ is $p$-polarized for both $s$- and $p$-polarizations of the incident light. Applying the boundary conditions of the electromagnetic fields in Maxwell's equations for the studied structure, we deduce the general expression of the intensity of the transmitted $p$-polarized second harmonic light[24]:

$$I(2\omega,\theta) = A \cdot t_\omega^4 \cdot T_{2\omega} \cdot t_0^2 \cdot [n_{2\omega}^2 - n_\omega^2]^{-2}$$
$$\times d^2(\theta) \cdot I^2(\omega) \cdot \sin^2\Psi(\theta)$$

where $\theta$ is the incidence angle on the sample; $I(\omega)$, the intensity of the incident laser light; $t_\omega$, $T_{2\omega}$, and $t_0$, the Fresnel-like transmission coefficients; $n_\omega$ and $n_{2\omega}$, the refraction indexes at $\omega$ and $2\omega$; $A$, a constant depending on the unity system; $d(\theta)$, the appropriate nonlinear coefficient; and $\Psi(\theta) = [2\prod d/\lambda]$ ·

**Table V  Percentage of Incorporated Dye in the Copolymers Calculated from $^1$H-NMR**

| Copolymers | $\delta$ in ppm $-CH_2O-$ | Percentage of Dye |
|---|---|---|
| 9a | 4.9–5.1 | 10 |
| 9b | 4.9–5.1 | 10 |
| 10a | 4.8–5.0 | 11 |
| 10b | 4.8–5.0 | 11 |
| 11a | 4.9–5.1 | 13 |
| 11b | 4.8–5.0 | 12 |
| 11c | 4.8–5.0 | 11 |

**Table VI  Refractive Indexes $s$ and $p$ After Poling ($\lambda$ = 0.6328 $\mu$m)**

| Copolymers | $n_s$ | $n_p$ |
|---|---|---|
| 9a | 1.610 ± 0.001 | 1.632 ± 0.001 |
| 9b | 1.615 ± 0.002 | 1.656 ± 0.004 |
| 10a | 1.608 ± 0.002 | 1.628 ± 0.003 |
| 10b | 1.610 ± 0.001 | 1.635 ± 0.001 |
| 11a | 1.605 ± 0.002 | 1.623 ± 0.003 |
| 11b | 1.604 ± 0.001 | 1.633 ± 0.001 |
| 11c | 1.590 ± 0.001 | 1.606 ± 0.002 |

**Table VII   Experimental Nonlinear Coefficients $d_{33}$**

| Copolymers | $d_{33}$ (pm/V) |
|:---:|:---:|
| **9a** | 8.1 ± 0.9 |
| **9b** | 9.3 ± 1.2 |
| **10a** | 6.5 ± 0.3 |
| **10b** | 9.0 ± 3.0 |
| **11a** | 6.0 ± 1.1 |
| **11b** | 4.9 ± 0.3 |
| **11c** | 2.5 ± 0.2 |

$[n_{2\omega} \cdot \cos \theta_{2\omega} - n_\omega \cdot \cos \theta_\omega]$, the angular dependence of $I(2\omega)$ due to the interference between the bound and free wave at $2\omega$.

The expression of $d(\theta)$ depends on the incident laser light polarization and on the symmetry conditions. For an $\infty mm$ material, the nonlinear susceptibility tensor presents only two nonzero different elements, $d_{31}$ and $d_{33}$.

## RESULTS AND DISCUSSION

Syntheses of dyes with spacers for nonlinear optics generally require several steps. By using chloromethylstyrene as starting monomers, we have prepared azo dyes **3a**, **3b**, and **3c**, imine dyes **8a**, **8b**, and **8c**, and stilbenic dyes **6a** and **6b** in two steps from commercial products by using a nucleophilic substitution reaction.

The copolymerization reaction was carried using a molar proportion dye/styrene of 10/90 and the reactivities of the dyes are various: (a) Azo dyes **3a**, **3b**, and **3c** are difficult to copolymerize with styrene. The heating of a mixture of monomers using benzene as a solvent with AIBN as initiator did not provide copolymers. The thermal reaction, by heating a mixture of monomers at 100°C during 2 days also failed and gave only a poor yield of oligomers. Therefore, we employed the di *tert*-butylperoxide as an initiator at 120°C with the chlorobenzene as a solvent. The half-life time of this peroxide is longer at 120°C than those of AIBN in the same solvent at 70°C and its efficiency seems to be higher. The isobutyronitrile radicals are generally less reactive than are the radical fragments encountered in the decomposition of most peroxides.[25]

Azo dyes **3a** ($R = NO_2$) and **3b** ($R = CN$) in these experimental conditions have been copolymerized, but azo dye **3c** ($R = CF_3$) could not be incorporated in a copolymer with styrene. (b) Contrary to the azo dyes, the copolymerization of imines

**8a**, **b**, and **c** and stilbenic dyes **6a** and **b** is easy with AIBN as the initiator. The determination of dye in the copolymer can be calculated by the measurement of the area due to the $-CH_2O$ peak, in the $^1$H-NMR, and comparison with the areas of aromatic peaks. The results are given Table V. In spite of a great analogy between the $^1$H-NMR spectrum of polystyrene and the spectra of our copolymers in which the styrene units are in great proportions, we can easily observe the $CH_2O$ peak bond for the dyes.

Experiments on thin films have been carried out using a pulsed YAG-laser at $\lambda = 1.064$ $\mu$m. With an $s$-polarized light, the $d_{31}$ values can be directly calculated by comparison with the already-known coefficient $d_{11} = 0.5$ pm/V of a quartz crystal[21-24,26] with respect to the absorption in the different materials. By correlation of the obtained value in the analysis of the data set with a $p$-polarized light, the value of the $d_{33}$ coefficient has been calculated.[26] The experimentally determined ratio $d_{33}/d_{31}$ for each copolymer agrees approximately with the theoretical predicted value of 3,[27] but with a great dependence in the value used for the chromatic dispersion. Unlike the already published works, we observe no fast initial decay of the second harmonic coefficients, and in a majority of cases, more than 70% of the initial value can still be found 1 month after poling. This slow decay could be due to the rigid polymer side chains. All compounds present similar linear optical properties, but the copolymers **11b** ($R = CN$) and **9a** and **b** (including azo dyes **3a** and **b**) seem to be more sensitive to the poling process (Table VI). The numeric results summarized in Table VII give $d_{33}$ and the fluctuation observed between the different samples for each material. The copolymer **10b** including a pure *para* unit of nitrostilbene (dye **6b**)
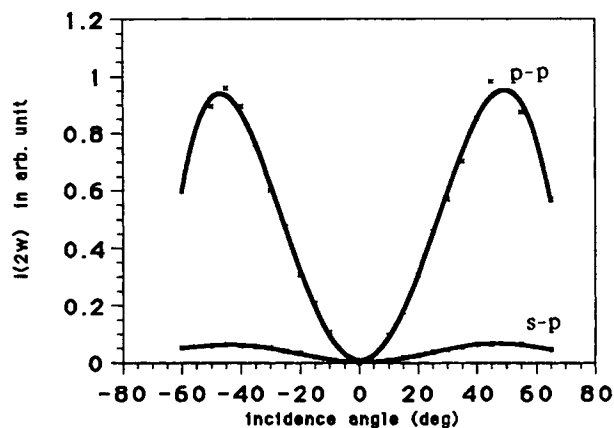


**Figure 2**   Experimental second harmonic intensity for a poled polymer film.

presents higher values of $d_{33}$ compared with copolymer **10a**; it seems that many physical properties of chloromethylstyrene derivatives are improved when the para isomer is used instead of a mixture of *meta* and *para* isomers: The values of the glass transition temperature and the dielectrical constants are generally also higher.[28] These results compare favorably with inorganic materials such as $KH_2PO_4$ and quartz crystals ($d_{ij}$ 10–20 times smaller) or $LiNbO_3$ and $LiTaO_2$ ($d_{ij}$ 1–2 times smaller). The obtained nonlinear susceptibilities are similar to those of poled organic monomeric glasses such as $2N$ - $\alpha$ - (methylbenzylamino) - 5 - nitropyridine (NBANP) and 2-$N$-(cyclooctylamino)-5-nitropyridine (CoANP), for which $d_{33}$ = 7.5 pm /V,[26] but they are significantly smaller than those of organic crystals such as $N$-4-nitrophenyl (-L) prolinol (NPP), for which $d_{ij}$ are around 50 pm/V.[29]

Compared with other polymers or copolymers, the measured values of our products are rather good enough (the values are given in pm/V unit; 1 pm/V = 3 × $10^{+9}$ e.s.u.) and many patents or articles give values in e.s.u. × $10^{-9}$; their results must be divided by three to compare with our values.[30] Polystyrene was chloromethylated and the resulting modified polymer reacts with-nitro-4'-hydroxyazobenzene to give a product a structure similar to those of copolymer **9a**.[31] The values of $d_{33}$ are (in pm/V) 3, 1.5, 1.6, and 1.4 for a polymer including, respectively, 15, 25, 34, and 45% of NLO species.[31] The observed value is 8.1 pm/V for the copolymer **7a** prepared from a mixture of *para* and *meta* isomers of chloromethylstyrene. Various NLO species grafted on to methacrylic skeletons are copolymerized with methyl methacrylate or homopolymerized. The $d_{33}$ values (in pm/V) depend on the percentages of incorporated dyes in the copolymer and are in the range of 1–30 pm/V[30]: The highest values were observed for two homopolymers and are in the range of 50 pm/V. Azo dyes grafted onto poly (4-hydroxystyrene) have also been measured and are relatively low (1.1 and 1.4 pm/V) or similar to our values (8.1 pm/V).[12] Finally, Hayashi et al. synthesized homopolymers or copolymers of vinylchromophore monomers from pure *para*-chloromethylstyrene and the highest $d_{33}$ were observed for the homopolymers.[22]

## CONCLUSION

(a) Chloromethylstyrene, in a mixture of *meta* and *para* (60/40), grafted with an NLO species, and copolymerized with styrene (molar

proportions 10/90), gives products with $d_{33}$ coefficients in the range of 2.5–9.3 pm/V.

(b) These results might be improved by using pure *para*-chloromethylstyrene instead of a mixture of *meta* and *para* isomers.

(c) The properties of polymers for NLO might also be improved by using generally a higher proportion of dye in the copolymer.

We have obtained goods results with only 10% of dyes incorporated into the copolymer. In the near future, we shall try to prepare new copolymers of styrene with modified *para*-chloromethylstyrene in higher proportions.

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