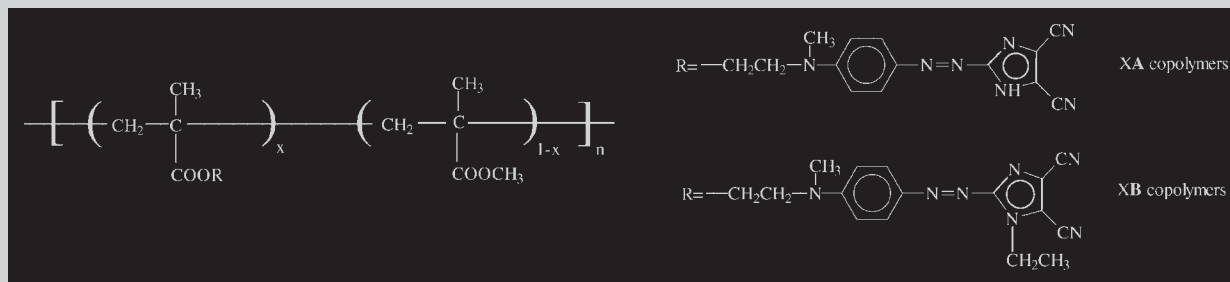


Summary: Two series of methacrylate copolymers were prepared, based on two new nonlinear optically (NLO) active chromophores 2-[4-(*N*-methacryloyloxyethyl-*N*-methylamino)phenylazo]-4,5-dicyanoimidazole (chromophore **A**) and 1-ethyl-2-[4-(*N*-methacryloyloxyethyl-*N*-methylamino)phenylazo]-4,5-dicyanoimidazole (chromophore **B**). Second order NLO properties of the two series of copolymers (**A** or

B as monomer and methyl methacrylate as the comonomer) were investigated by SHG procedures at the fundamental wavelength 1368 nm; d_{33} values in the range 0.2–3.3 pm · V⁻¹ were obtained, depending on the chromophore and on its molar content. The dependence of d_{33} on the molar content of chromophore was investigated in the two cases.



Polymethacrylate Copolymers Containing 4,5-Dicyanoimidazole-Based Chromophores and their Nonlinear Optical Behavior

Antonio Carella,¹ Roberto Centore,^{*1} Pierluigi Riccio,¹ Augusto Sirigu,¹ Alessia Quatela,² Christian Palazzesi,² Mauro Casalboni²

¹Dipartimento di Chimica, Università degli Studi di Napoli “Federico II”, Via Cinthia, 80126 Napoli, Italy
E-mail: roberto.centore@unina.it

²Dipartimento di Fisica, Università di Roma “Tor Vergata”, Via della Ricerca Scientifica 1, 00133 Roma, Italy

Received: March 25, 2005; Revised: May 5, 2005; Accepted: May 10, 2005; DOI: 10.1002/macp.200500112

Keywords: imidazole; nonlinear; optics; polymers; SHG; Synthesis

Introduction

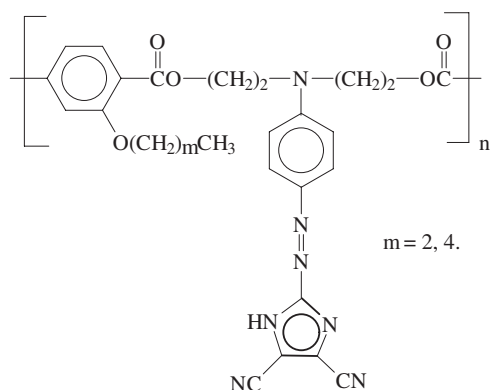
It is well known that second order nonlinear optical (NLO) performances of chromophore containing organic materials are strongly dependent, for a given chromophore, on the way the NLO active units are connected to the organic matrix, e. g. guest-host systems or covalent NLO polymers.^[1,2] In the case of polymers containing the chromophore units covalently attached to the chain (NLO polymers), the density number of chromophores, the mobility of chromophore units and the glass transition temperature (T_g) of the polymer are relevant features affecting the degree of poling and, therefore, NLO performances.^[1,2] We have reported in a recent paper^[3] the synthesis and NLO characterization of two terephthalate homopolyesters con-

taining a new 4,5-dicyanoimidazole based chromophore, having the formula given in Scheme 1.

In this paper we report on the synthesis and the characterization of the two series of methacrylate copolymers given in Scheme 2.

As compared with terephthalate homopolyesters (Scheme 1), in the case of **XA** polymers we have varied the way the chromophore is covalently anchored to the polymer chain, while in **XB** polymers modifications have also been introduced within the chromophore. In particular, the introduction of an ethyl group on N¹ of imidazole affects the shape of chromophore and (mostly) its capability of hydrogen bonding.

Copolymers were prepared starting from two new NLO active chromophore-monomers, 2-[4-(*N*-methacryloyloxy-

Scheme 1. Chemical diagram of polymers described in ref.^[3]

ethyl-*N*-methylamino)phenylazo]-4,5-dicyanoimidazole (**A**) and its *N*-ethyl derivative 1-ethyl-2-[4-(*N*-methacryloyloxyethyl-*N*-methylamino)phenylazo]-4,5-dicyanoimidazole (**B**), as shown in Scheme 3.

Thermal and optical characterization of chromophores was performed. Thin films of copolymers were obtained by spin-coating and oriented by corona poling technique. NLO activity of poled films was estimated by means of direct comparison with quartz reference sample and the dependence of activity on chromophore content is discussed.

Discussion

The NLO activity of the two chromophores as determined by the electric field induced second harmonic generation (EFISH) technique is reported in Table 1. Owing to the absorption features of chromophores and to the wavelength of the working laser (1.907 μm), the reported values may be considered free from resonance enhancement. Both chromophores show a fair NLO activity ($\mu_{\text{g}} \cdot \beta$ is well higher than the value 580×10^{-48} esu measured, in the same experimental conditions, for the reference chromophore DR1, see ref.^[2]). In particular, the $\mu_{\text{g}} \cdot \beta$ value measured for **B**

results to be lower than that obtained for **A** and this is probably due to the electron donor character of the alkyl group attached to the nitrogen of the imidazole ring.^[4]

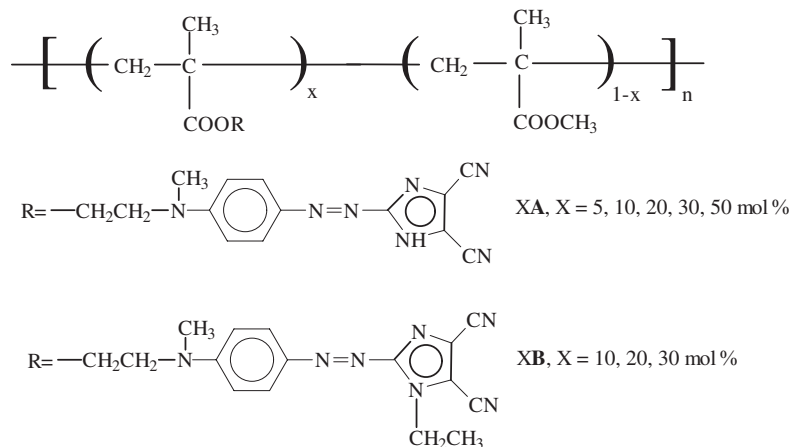
The thermal stability of the two chromophores is moderately good, with decomposition temperature (T_{d}) close to 250 $^{\circ}\text{C}$.

All the synthesized copolymers are amorphous, as shown by X-ray diffraction analysis and requested for materials for applications in second order nonlinear optics. The amorphous behavior is maintained also upon annealing the copolymers for 1 h 10 $^{\circ}\text{C}$ below their T_{g} . The thermal stability of all the copolymers is fairly good, with decomposition temperatures close to 300 $^{\circ}\text{C}$ (see Table 2).

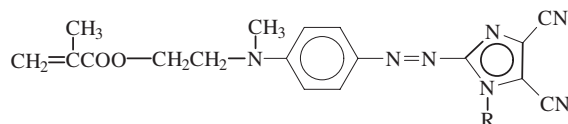
As Table 2 shows, the trend of T_{g} with chromophore loading is evident in the two series of copolymers: the higher the composition in chromophore, the higher the T_{g} of the polymer.

This feature, shown graphically in Figure 1, is probably related to the high rigidity of the chromophoric units.

XA copolymers show a higher T_{g} as compared with XB copolymers having the same loading: in the first class of copolymers, the presence in the heterocycle of both acceptor and donor (N–H) sites of hydrogen bonding leads to a considerable enhancement of rigidity of the whole polymer system. NLO activity of the poled XA copolymers increases initially with increasing chromophore molar content; d_{33} coefficient reaches a maximum and then diminishes by further increase of the chromophore concentration (see Figure 2). This behavior has been previously observed in NLO side-chain polymers (as well as in guest-host type systems)^[5] and has been qualitatively explained.^[1,2,6] At the beginning, an increasing chromophore molar content produces an increment of the d_{33} value. However, it causes a reduction of the mean distance among chromophores in the polymer matrix with an enhancement of (dipolar) chromophore-chromophore interactions. This effect, favoring a locally centrosymmetric arrangement of the active units, reduces the efficiency of the poling process.



Scheme 2. Chemical diagram of polymers investigated.



R = H chromophore **A**

R = CH₃CH₂ chromophore **B**

Scheme 3. Chemical diagram of chromophores.

We remark that for the two terephthalate homopolyesters shown in Scheme 1, having $T_g = 152\text{ }^\circ\text{C}$ ($m = 2$) and $131\text{ }^\circ\text{C}$ ($m = 4$) we measured, under the same experimental conditions of the present work, a d_{33} value of 2.0 and $1.8\text{ pm} \cdot \text{V}^{-1}$ respectively.^[3] That NLO activity is lower than the maximum ($3.3\text{ pm} \cdot \text{V}^{-1}$, $X = 15$) we have obtained for **XA** copolymers, which are based on the same chromophore but less tightly bounded to the polymer chain. In fact, in polymers of Scheme 1, any movement of chromophore units, as a whole, can only be accomplished through conformational changes in the polymer chain, while this is not the case in **XA** copolymers. This consideration gives an additional indication that increasing the density number of chromophores and thereby reducing their mobility reduces the NLO activity basically by reducing the poling efficiency.

Comparing in Table 1 and Figure 2 the NLO activity of the two series of copolymers, it should be noted that **B** based copolymers always have a higher d_{33} value than **A** based ones for similar chromophore concentration. This aspect is not due to the different NLO activity of the two chromophores (actually $\mu_g \cdot \beta$ of **A** is higher than that of **B**, see Table 1). Instead, it might be a geometry effect related to the ethyl group alkylating the imidazole ring of **B** that might act as a spacer, setting the chromophores in the polymeric matrix at longer mean distance and therefore helping the poling process; in fact, with an ethyl group on N¹ atom of the imidazole ring, the shape of chromophore is more oblate than prolate ellipsoid.^[1,2,6] The introduction, in a possible next step, of bulkier substituent groups than ethyl could result in a still more efficient orientation process.

Table 1. Characterization of chromophores.

	$T_d^{\text{a)}$	$\lambda_{\text{max}}^{\text{b)}$	$\mu_g \cdot \beta^{\text{c)}$
	$^\circ\text{C}$	nm	10^{-48} esu
A	249	459	1000
B	236	496	800

^{a)} Decomposition temperature taken as the temperature corresponding to 5% weight loss in the thermo-gravimetric run ($10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$, air atmosphere).

^{b)} Measured in CHCl_3 .

^{c)} EFISH technique, DMF, $1.907\text{ }\mu\text{m}$.

Table 2. Characterization of copolymers.

Copolymer	$X^{\text{a)}$	$T_g^{\text{b)}$	$T_d^{\text{b)}$	$\eta_{\text{inh}}^{\text{c)}$	d_{33}
		$^\circ\text{C}$	$^\circ\text{C}$	$\text{dL} \cdot \text{g}^{-1}$	$\text{pm} \cdot \text{V}^{-1}$
5A	4	138	288	0.47	0.2
10A	8.9	146	283	0.12	1.1
20A	15	159	278	0.23	3.3
30A	27	170	278	0.30	1.0
50A	50	182	280	0.42	0.7
10B	8	131	290	0.27	1.4
30B	29.5	138	279	0.20	3.0
50B	42	149	276	0.18	1.7

^{a)} Actual content of chromophore in the polymer (mol-%) measured by ^1H NMR analysis.

^{b)} Decomposition temperature taken as the temperature corresponding to 5% weight loss in the thermo-gravimetric run ($10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$, air atmosphere).

^{c)} Measured at $25\text{ }^\circ\text{C}$ in $0.5\text{ g} \cdot \text{dL}^{-1}$ DMF solution.

Conclusion

By comparative analysis of results from the present and a preceding paper,^[3] we have shown that for the given chromophore unit, 2-[4-(*N*-alkyl-*N*-alkylamino)phenylazo]-4,5-dicyanoimidazole, side chain polymethacrylates having the chromophore attached to the chain by an ethylene bridge (Scheme 2) reach higher d_{33} values than polycondensates (terephthalate polyesters, Scheme 1) in which the chromophore is directly attached to the chain. Within polymethacrylate copolymers, second order NLO response can be further increased by increasing the lateral bulkiness of the chromophore.

Experimental Part

The synthesis of the two chromophores is schematized in Scheme 4 and 5.

N-Methyl-*N*-(2-methacryloyloxyethyl)aniline (**A**₁)

N-Methyl-*N*-(2-hydroxyethyl)aniline (10 g, 60.1 mmol) was mixed with 10 mL pyridine (0.122 mol). Methacrylic anhydride (13.26 g, 86.1 mmol) were slowly added to the solution cooled in an ice-water bath. 4-(*N,N*-Dimethylamino)pyridine had been previously added in catalytic amount. The system is left under stirring in the dark for the first 30 min in the ice-water bath and subsequently at room temperature for 24 h. The organic layer was then extracted twice with chloroform ($2 \times 100\text{ mL}$), washed with water and dried over anhydrous Na_2SO_4 . The solvent was then removed under reduced pressure, obtaining a yellow oil. Yield: 90%.

^1H NMR (CDCl_3): $\delta = 1.86$ (s, 3H), 2.93 (s, 3H), 3.59 (t, 2H, $J = 5.2\text{ Hz}$), 4.27 (t, 2H, $J = 5.2\text{ Hz}$), 5.48 (s, 1H), 6.00 (s, 1H), 6.68 (m, 3H), 7.18 (m, 2H).

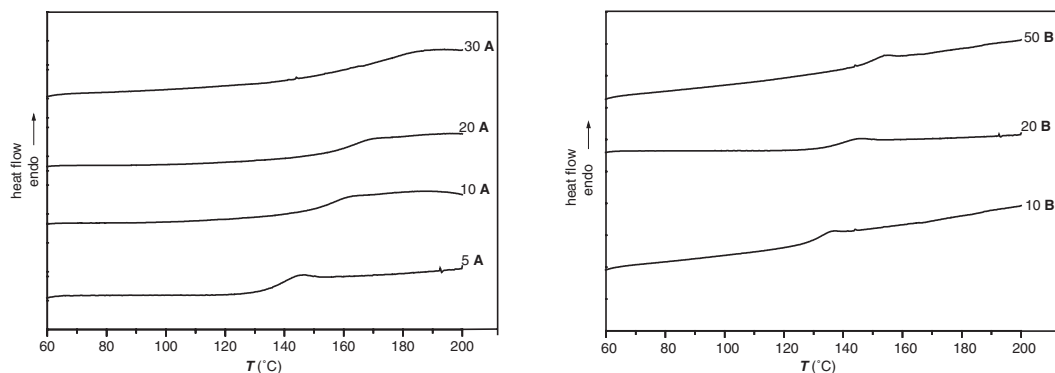


Figure 1. DSC thermograms (heating run) for the two series of synthesized copolymers.

Chromophore A

2-Amino-3,4-imidazoledicarbonitrile (1.823 g, 13.7 mmol) was placed in a flask containing 10 mL H₂O and 3.5 mL 37% HCl. The suspension was cooled to 0–5 °C in an ice-water bath. A solution of NaNO₂ (1.030 g, 14.93 mmol) in 10 mL water was added dropwise to the suspension under stirring. Stirring at low temperature was continued for 30 min after the addition of the nitrite solution.

Separately, a water-ethanol solution containing sodium acetate (3.857 g, 0.047 mol) and *N*-methyl-*N*-(2-methacryloyloxyethyl)aniline (3 g, 13.7 mmol) was prepared. Then the suspension containing the diazonium salt was rapidly added to it under stirring. Immediately the color of solution turned to red and in few seconds, a red-brown precipitate of the azo compound formed. This compound was collected by filtration and then recrystallized from DMF/H₂O, obtaining pure **A** as violet lamellar crystals. Yield: 65%.

¹H NMR (DMSO-*d*₆): δ = 1.79 (s, 3H), 3.12 (s, 3H), 3.86 (t, 2H, *J* = 4.8 Hz), 4.32 (t, 2H, *J* = 5.2 Hz), 5.62 (s, 1H), 5.93 (s, 1H), 6.98 (d, 2H, *J* = 9.2 Hz), 7.81 (d, 2H, *J* = 9.4 Hz).

C₁₈H₁₇N₇O₂: Calcd. C 59.66, H 4.45, N 27.06; Found C 59.13, H 4.70, N 26.36.

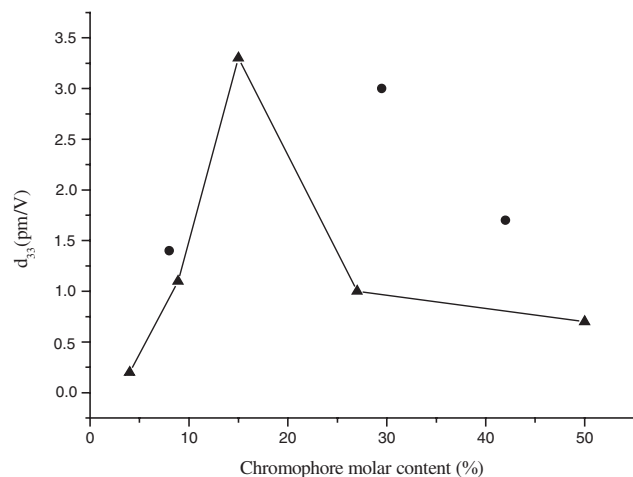


Figure 2. NLO d_{33} coefficient as a function of the chromophore molar content in **XA** (triangles) and **XB** (circles) copolymers. Line is guide for the eye.

Compound B1

The synthesis of **B1** was analogous to that for **A**, except that in this case *N*-methyl-*N*-(2-hydroxyethyl)aniline was used instead of *N*-methyl-*N*-(2-methacryloxyethyl)aniline. Yield: 66%.

¹H NMR (DMSO-*d*₆): δ = 3.12 (s, 3H), 3.60 (s, 4H), 6.90 (d, 2H, *J* = 8.8 Hz), 7.78 (d, 2H, *J* = 8.8 Hz).

Compound B2

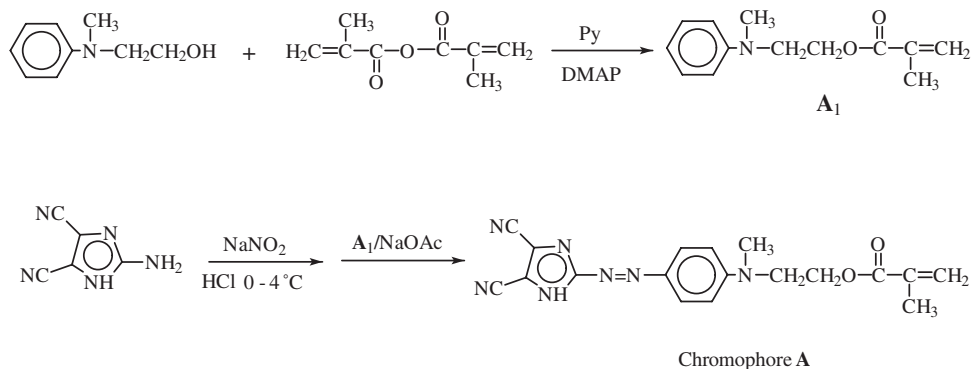
B1 (2.70 g, 9.14 mmol) was dissolved in 25 mL DMSO. 2.53 g K₂CO₃ (18.28 mmol) and finally 1.39 g bromoethane were added to the DMSO solution. The system was kept under magnetic stirring for 24 h. The inorganic part was then filtered off and the resulting solution was slowly poured in 80 mL water under magnetic stirring. A violet solid formed that was recovered by filtration after 15 min of stirring. Yield: 53%.

¹H NMR (DMSO-*d*₆): δ = 1.43 (t, 3H, *J* = 7.4 Hz), 3.14 (s, 3H), 3.61 (s, 4H), 4.45 (q, 2H, *J* = 7.4 Hz), 4.8 (s broad, 1H), 6.91 (d, 2H, *J* = 9.2 Hz), 7.84 (d, 2H, *J* = 9.2 Hz).

Chromophore B

B2 (2 g, 6.18 mmol) was dissolved in 15 mL *N*-methyl-2-pyrrolidone (NMP) under a slight heating. Pyridine (1.1 g, 13.9 mmol) and 3.053 g methacrylic anhydride (19.8 mmol) were then added to the solution. The system was kept under stirring in the dark at 50 °C for the first 6 h and then at the room temperature for 48 h. At this point thin layer chromatography (TLC) of the reacting system showed the absence of the starting material. The solution was poured in 200 mL methanol-water solution 9:1 (v/v) and the formation of a violet solid occurred. The solid was recovered by filtration, dissolved in dichloromethane and washed with water. The organic layer was recovered and dried on anhydrous Na₂SO₄ and the solvent removed under reduced pressure. The resulting solid was purified by liquid-solid chromatography, using florisil (60–100 mesh) and chloroform as eluent. Yield: 30%.

¹H NMR (CDCl₃): δ = 1.50 (t, 3H, *J* = 7.4 Hz), 1.83 (s, 3H), 3.13 (s, 3H), 3.76 (t, 2H, *J* = 7.8 Hz), 4.33 (t, 2H, *J* = 7.8 Hz), 4.47 (q, 2H, *J* = 7.4 Hz), 5.50 (s, 1H), 5.99 (s, 1H), 6.77 (d, 2H, *J* = 9.3 Hz), 7.92 (d, 2H, *J* = 9.3 Hz).



Scheme 4. Synthesis of A.

MS: $m/z = 392.28$ ($M + H^+$, 100%); M calcd. for $C_{20}H_{21}N_7O_2$: 391.43.

Copolymers

Methacrylate chromophores were used in polymerization reactions with comonomer methyl methacrylate to synthesize side-chain copolymers. Various copolymers were synthesized in the two classes with different chromophore compositions as shown in Scheme 2. The copolymers were synthesized according to the same procedure^[5b] with yields ranging from 40 to 84%. As an example we report the synthesis of copolymer 20A.

20A

A (0.800 g, 2.2 mmol) and 0.94 mL of freshly distilled methyl methacrylate (8.8 mmol) were dissolved in a glass vial in 2.75 mL of DMF so that the total molarity of the resulting solution is 4 M. 2,2'-Azobisisobutyronitrile (AIBN) was added as radical initiator in 0.5 mol-%. After three freeze-thaw cycles the vial was sealed under vacuum and brought to 75 °C. The reaction was allowed to proceed at this temperature for 48 h. The reacted mixture was then poured drop-wise into 100 mL of methanol under stirring. The formation of the solid orange copolymer occurred (eventually, the precipitation process can be helped by adding few drops of an aqueous solution

of $CaCl_2$). The solid was filtered off, dissolved in 20 mL of chloroform (DMF, in the case of copolymer containing 50A) and finally precipitated in 100 mL of methanol.

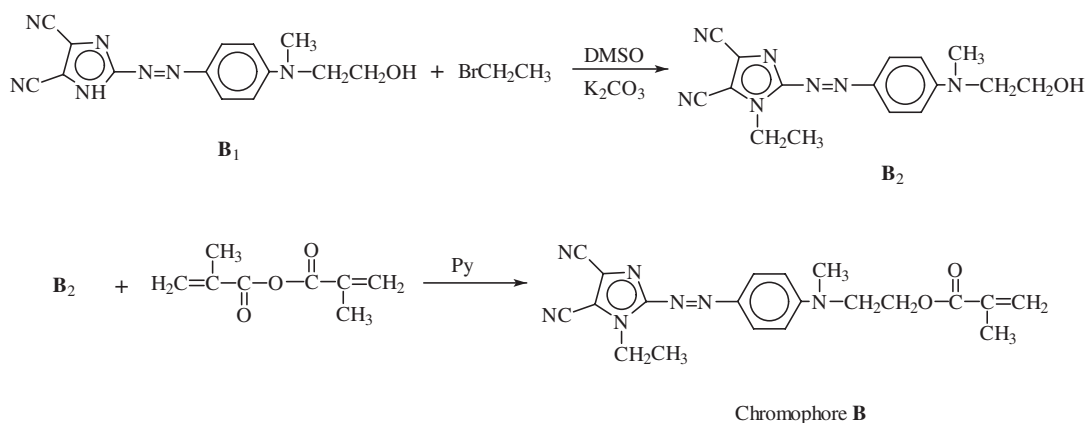
For all the copolymers, 1H NMR spectra showed the expected resonances in the proper intensity ratio.

Physico-Chemical Characterization

The thermal behavior of the compounds was studied by DSC (Perkin-Elmer DSC-7, nitrogen atmosphere, scanning rate $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$), temperature controlled polarizing microscopy (Zeiss microscope, Mettler FP5 microfurnace) and thermogravimetric analysis (TA instruments, air, $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$). 1H NMR spectra were recorded with a Varian XL 200 spectrometer. X-ray diffraction patterns of copolymers were recorded on a flat film camera, using Ni filtered CuK_α radiation. The mass spectrum of B was recorded with a MALDI TOF DE-PRO apparatus on a α -cyano-4-hydroxycinnamic acid matrix. Inherent viscosity (η_{inh}) of copolymer solutions at 25 °C was measured with an Ubbelohde viscometer in DMF solutions (concentration was $0.5\text{ g} \cdot \text{dL}^{-1}$).

NLO Characterization

The second order optical nonlinearity of chromophores was determined by EFISH technique, measuring the $\mu_g \cdot \beta$ dot product of the chromophores, where μ_g stands for the ground



Scheme 5. Synthesis of B.

state permanent dipole moment and β for the (vector) quadratic hyperpolarizability of the molecule. The light source was a Q-switched Nd:Yag laser whose emission at 1.064 μm was shifted to 1.907 μm by stimulated Raman scattering in a high pressure hydrogen cell. The measurements were calibrated relative to a quartz wedge: the experimental value of $d_{11}^{\text{quartz}} = 1.2 \times 10^{-9}$ esu at 1.064 μm was extrapolated to 1.1×10^{-9} esu at 1.907 μm .

A detailed description of the experimental apparatus is given elsewhere.^[7] Measurements were performed in DMF solution.

NLO Measurements

NLO characterization was carried out by performing SHG measurements on 0.2 μm thick films that were deposited on BK7 Corning glass slides by spin-coating. For this purpose, appropriate amounts of the polymers were dissolved in NMP and the resulting solutions filtered on 0.2 μm Teflon[®] filters. The spinner was an SCS P.6204, operating at a rate of 1000 rpm for 30 s at room temperature. Residual solvent was removed by keeping the films at 100 °C for 4 h. Orientation of dipoles was achieved by means of a standard high-temperature high-voltage corona poling set-up in a controlled atmosphere box (dry nitrogen),^[8,9] with a gold wire biased with +7 kV (+6 kV for XB polymers to avoid surface damage) across a 1 cm gap normal to the film. The HV generator was grounded at the heating stage, and the poling current was monitored in order to control the process and to perform a uniform poling procedure for both series of samples.

NLO characterization was carried out by using a Brilliant Q-switched Nd:YAG laser (10 Hz repetition rate, 5 ns pulse duration, 400 mJ per pulse) equipped with a Solid State Raman Shifter CRS-14 providing the operating beam wavelength at 1368 nm (P-polarized). The second harmonic (SH) signal was detected immediately after poling and corrected taking into account sample thickness and refractive index (measured using an Alphastep 200 profilometer and a Brewster angle technique), respectively.^[10] The actual angle between laser beam and sample normal vector was taken into account as well. The nonlinear coefficient d_{33} of samples was evaluated for comparison with a Maker fringes reference experiment^[11,12] obtained on a quartz crystal slab^[13] for suitable range of angles. The d_{33} values estimated by this method are affected by an error of about 25%.

Poling was made by heating the sample up to a temperature 10 °C below the polymers' T_g with the electric field on. This temperature was maintained for 30 min under electric field, after which the sample was cooled down to room temperature at a rate of 1 °C · min⁻¹ rate. The poling field was switched off when sample attained room temperature.

In addition, absorption spectra of the films before and immediately after poling were performed in order to inde-

pendently estimate the dipoles orientational order through the decrease of the absorption coefficients.^[14] Values around 30% were estimated for the orientational order parameter. A twin sample was treated, without applying electric field, with the same thermal cycle of the poled one in order to verify possible chromophores damage which results in a decrease of absorbance.^[14]

Acknowledgements: We thank the European Community (Sixth Framework Programme) for financial support within the ODEON project. Thanks are due to Dr. Alain Fort of IPCMS-GONLO (Strasbourg, France) for help in EFISH measurements, and to CIMCF of Università di Napoli "Federico II" for NMR and MS facilities.

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