

# Structure–activity relationship of new NLO organic materials based on push–pull azodyes

## 4. Side chain polymers

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### Abstract

Several new polymeric materials containing push–pull azobenzene derivatives in the side chains were synthesized by polymer-analogous reactions involving the coupling of the diazonium salts of 4-substituted anilines with a preformed polymer, poly(*N*-methacryloyl-*N'*-phenylpiperazine). The second harmonic generation properties of these glassy macromolecular materials were investigated in order to understand the influence of the chromophore chemical structure on dipole orientability and stability of orientation. The results thus obtained were compared with those of analogous guest–host systems and a lack of chromophore mobility was highlighted for the side chain polymers. The use of a short flexible spacer should probably improve the NLO performance. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Structure–activity relationship; Push–pull azobenzenes; Nonlinear optical organic materials

### 1. Introduction

In recent years much attention has been devoted to polymeric materials with nonlinear optical properties for electrooptical and photorefractive applications [1–5]; several reviews summarize structures and orientation methods [6–9].

In spite of the ease of synthesis and characterization, dispersions of NLO-active chromophores in polymer matrices are generally considered to be unsuitable for applications, due to the fast isotropization rate, the plasticizing effect of the guest chromophores that lowers the glass transition temperature ( $T_g$ ), and the possibility of phase separation at high dye loading. Anchoring the chromophores to a polymer chain should prevent many of these problems. Accordingly, many studies have been devoted to side-[10–15] and main-chain [16–25] NLO-active polymers.

In amorphous polymers, the second order nonlinear optical properties are generally developed through orientation of molecular dipoles with an electric poling. A high  $T_g$  value is a prerequisite for long-term stability of the polar order and so, of the NLO properties. Other factors such as hydrogen

bonding and other specific interactions, very likely play an important role in the relaxation processes that lead to a randomization of the dipoles distribution.

Recently, we have undertaken an investigation aimed at the study of the relationship between chemical structure of the dipole and its orientation behavior in a polymer matrix. Several high dipole moment azobenzenes, having different shape and hydrogen bonding properties, were synthesized and their second order hyperpolarizabilities ( $\beta$ ) were measured [26]. These chromophores were then dispersed in poly(*N*-methacryloyl-*N'*-phenylpiperazine) (PMPP), in order to prepare guest–host systems, whose orientational behavior was investigated on thin films after corona poling; second harmonic generation (SHG) was used as an analytical tool [27].

In the present paper we report on the synthesis, molecular characterization and NLO-behavior of a series of methacrylic polymers derived from PMPP (Fig. 1) and bearing in the side chain the same chromophoric structures used in the formulation of guest–host systems.

The comparison with the behavior of the chromophores physically dispersed in the matrix is intended to highlight what influence a short, rigid spacer can have on the polar order and on its dynamics, and how this effect depends on the chemical structure of the chromophore.

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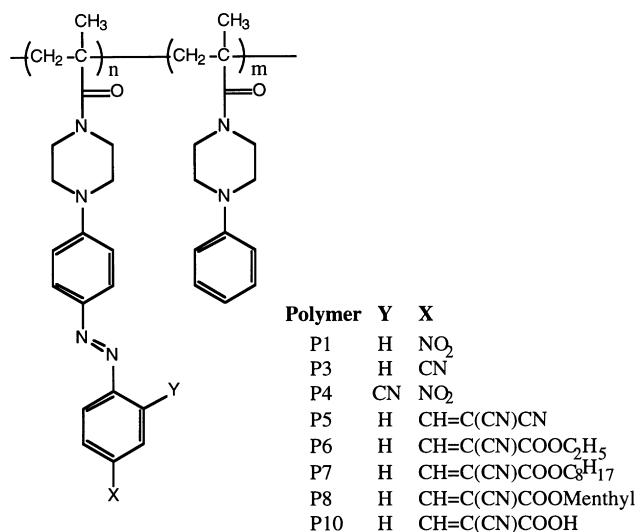


Fig. 1. Polymer structures.

The orientation of the polymer systems were calculated from the SHG data of a fundamental wavelength of 1542 nm.

## 2. Results and discussion

### 2.1. Preparation and characterization of polymers

Two polymerizable azo dyes were prepared by coupling of the diazonium salts of 4-nitroaniline and 2-cyano-4-nitroaniline with *N*-methacryloyl-*N'*-phenylpiperazine (Fig. 2). The attempts to polymerize these monomers, at temperatures varying between 60 and 90°C, and in the presence of either AIBN or BPO up to 5% (in moles) as

free radical initiators, failed. Only a small amount of oligomeric material was recovered when the polymerization was carried out in the presence of anionic initiators, such as *n*-BuLi and C<sub>6</sub>H<sub>5</sub>Li. Radical copolymerization experiments with (–)-menthyl methacrylate afforded low yield of polymeric products constituted exclusively by poly((–)-menthyl methacrylate).

These results and the parallel failure of polymerization of *N*-methacryloyl-*N'*-phenylpiperazine and its hydrochloride [27] were thought to arise more from steric hindrance of the *N,N*-dialkylmethacrylamide, than from the reactivity of nitro or *N,N*-dialkylaniline groups towards free radicals.

Finally, the desired polymer structures were synthesized by reacting PMPP, obtained through a polymer-analogous reaction from poly(methacryloyl chloride) [27], with suitable aromatic diazonium salts (Table 1). To the best of our knowledge, this is one of the first examples for these kind of polymer-analogous reactions [28]. All polymer samples were assumed to have the same average polymerization degree of the starting poly(methacryloyl chloride), having  $\overline{DP}_n = 530$ , under the reasonable assumption that no chain scission occurred in the reaction conditions [27].

<sup>1</sup>H NMR spectroscopy did not give satisfactory results in the determination of polymer composition because of the poor solubility of some of these materials. Therefore, the chemical compositions were evaluated by UV–Vis spectroscopy, assuming the azobenzenes to have the same molar extinction coefficients as the corresponding low molecular weight dyes [26,27]. The rather low extent of functionalization (Table 1) must be very likely attributed to the precipitation of the polymeric material during the coupling reaction.

By these routes, azobenzene groups bearing different electron withdrawing groups, such as 4-nitro (P1), 4-cyano (P3), 2-cyano-4-nitro (P4) and 4-(2-cyanovinyl) (P5–P10) were attached to the polymer chain. Samples

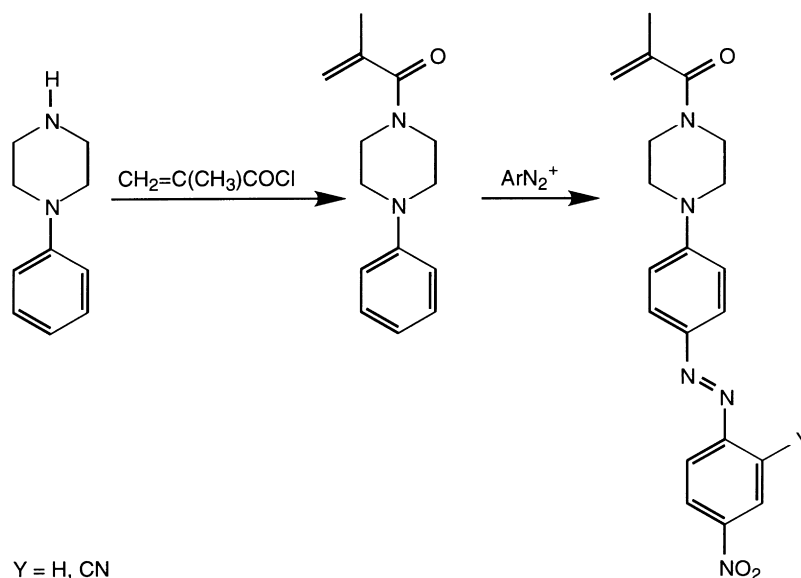


Fig. 2. Reaction scheme adopted for the synthesis of polymerizable push–pull azobenzene derivatives.

Table 1  
Characterization of copolymer samples

Polymer sample	Yield <sup>a</sup> (%)	Functionalization <sup>b</sup> (%)	$T_g^c$ (°C)	$T_g^d$ (°C)	$T_{d1}^c$ (°C)	$T_{d2}^c$ (°C)
P1	67	33	109	115	–	230
P3	71	24	115	113	–	263
P4	34	12	113	122	–	212
P5	53	25	109	118	212	255
P6	73	22	120	121	168	210
P7	73	32	95	99	210	263
P8	64	18	114	112	–	245
P10	48	17	111	108	192	233

<sup>a</sup> Evaluated as  $100 \times (\text{moles of monomeric units in the recovered material})/(\text{moles of monomeric units in the starting material})$ .

<sup>b</sup> Content of aromatic units as evaluated by UV spectroscopy.

<sup>c</sup> By DSC.

<sup>d</sup> By DMTA.

P5–P10 were differentiated by the presence of cyano (P5), carboxyethyl (P6), carboxyethyl (P7), carboxyethyl (P8) and carboxyl (P10) groups in 2-position of the 2-cyanovinyl substituent.

In none of the cases differential scanning calorimetry (DSC) analysis evidenced the presence of melting endotherms, in accordance with the absence of crystalline patterns in the X-ray diffractograms. Dynamic-mechanical thermal analysis (DMTA) and DSC gave consistent results for the location of glass transition temperatures, and no further transition was detected by DMTA. This result confirms that the relaxations recorded 20–30°C below the  $T_g$  in the DMTA plots of structurally analogous guest–host systems in the region have to be associated with guests' movements [27].

In all DSC and thermogravimetric analyses exothermal transitions at 210–260°C ( $T_{d1}$ , Table 1) were recorded, attributable to the decomposition of the azo chromophore. Polymers containing cyanovinyl-substituted chromophores were characterized by an additional decomposition transition ( $T_{d2}$ ), about 40°C lower than  $T_{d1}$ , which is likely connected more to decarboxylation than to denitration reactions.

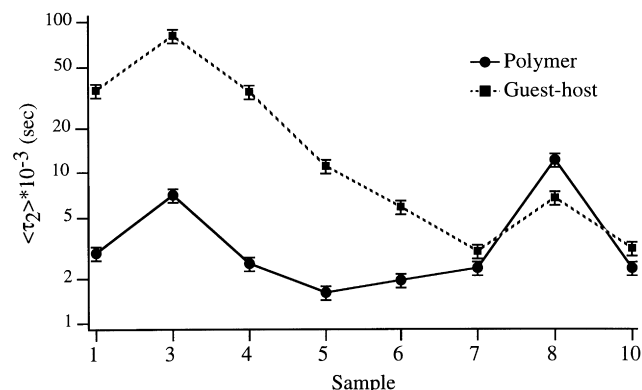


Fig. 3. Average relaxation times of the side chain polymers and of the corresponding guest–host systems at 30°C. Lines between data points are only a guide for the eyes. Logarithmic scale is given for a better comparison of the two data sets.

## 2.2. Nonlinear optical properties

The polymer films were oriented by the corona poling technique. The samples were heated above the glass transition temperature (130°C) for 30 min and then cooled down slowly, including an annealing stage at 90°C, to room temperature.

The SHG signal decay after switching off the poling field was fitted by a biexponential function, derived from the Kohlrausch–Williams–Watts (KWW) function:

$$\chi^{(2)}(t) \propto (I_{\text{SHG}})^{1/2} = A_1 \exp[-t/\tau_1] + A_2 \exp[-(t/\tau_2)^{b_2}]$$

as elsewhere reported for similar guest–host systems [27].

All the systems showed  $\tau_1$  values, the faster decay rate constant, in the 10–20 s range. This process has been attributed to the neutralization of surface charges; indeed no fast decay can be detected in contact electrodes poling [29] as well as in corona poling when a surface discharge stage is used immediately after the poling process [30].

Our attention was therefore focused on the slower relaxation process, which is directly related to dipole reorientation in the sample. In order to compare different polymer systems, the average relaxation times  $\langle \tau_2 \rangle$  were calculated according to Wang [31,32] (Fig. 3)

$$\langle \tau_2 \rangle = \int_0^{\infty} dt \exp -(t/\tau_2)^{b_2} = \frac{\tau_2}{b_2} \Gamma(b_2^{-1})$$

where  $\Gamma$  is the gamma function.

Second order nonlinear susceptibilities were measured on these films at 30°C, with Maker fringes experiments. From these data an order parameter, proportional to  $\langle \cos^3 \Theta \rangle$ , where  $\Theta$  is the tilt angle between chromophores molecular axis and the normal to the film, was calculated. A detailed description of this method is reported elsewhere [27]. The values of average relaxation times ( $\langle \tau_2 \rangle$ ), second order nonlinear susceptibilities ( $d_{33}$ ), local field factors ( $f_\omega$  and  $f_{2\omega}$ ), second order molecular hyperpolarizabilities of structurally analogous low molecular weight compounds ( $\beta^{1542}$ ), and order parameters ( $\langle \cos^3 \Theta \rangle$ ) are summarized in Table 2.

All polymer samples exhibited a rather poor stability of

Table 2  
NLO characterization of copolymer samples

Polymer sample	$\langle\tau_2\rangle \times 10^{-3}$ (s) <sup>a</sup>	$d_{33}$ (pm/V) <sup>a</sup>	$f_{\omega}$ <sup>b</sup>	$f_{2\omega}$ <sup>b</sup>	$\beta^{1542}$ ( $10^{-40}$ m <sup>2</sup> V <sup>2</sup> ) <sup>c</sup>	Order parameter (a.u.) <sup>d</sup>
P1	2.9	0.87	1.54	1.48	137	0.10
P3	7.1	0.63	1.53	1.48	104	0.13
P4	2.5	4.08	1.63	1.54	344	0.42
P5	1.6	1.62	1.57	1.48	164	0.19
P6	1.9	1.62	1.54	1.47	132	0.28
P7	2.3	2.31	1.54	1.48	141	0.25
P8	12.1	3.12	1.53	1.48	172	0.51
P10	2.3	0.48	1.53	1.49	< 130 <sup>e</sup>	> 0.11

<sup>a</sup> Estimated error:  $\pm 10\%$ .

<sup>b</sup> Estimated error:  $\pm 2\%$ .

<sup>c</sup> Estimated error  $< \pm 10\%$ .

<sup>d</sup> Estimated error  $< \pm 25\%$ .

<sup>e</sup> No direct data available, value estimated to be lower than that of the model compound for P6.

the polar order, up to one order of magnitude lower than that of analogous guest–host systems, and quite low orientability (Fig. 4). The polymer P4, whose chromophore is characterized by the highest molecular hyperpolarizability, exhibited a good orientation behavior, even though P3 (cyano substituted azobenzene) showed the best stability of SHG. For the polymers P5–P10, all containing a cyanovinyl group, the orientability and the stability of the SHG grew almost linearly with the alkyl content in the chromophore. The bad orientation in presence of a carboxylic acid group (P10), when compared to analogous esters, confirmed the results obtained for guest–host systems [27].

The ratios between the order parameters and the  $\langle\tau_2\rangle$  of the side chain polymers and those of the corresponding guest–host systems are plotted in Fig. 5. The comparison of polymer samples with the corresponding guest–host systems [27], highlighted a dramatic loss of both orientability and stability for the rigid rod chromophore structures, whereas this effect is less pronounced when cyanovinyl groups are present.

Only for the 2-cyano-4-nitro substituted chromophore (P4) the loss in orientability was not so dramatic as the one in stability of orientation. Here, the deviation from the rod shape seems to have increased the dipole mobility

during the poling, allowing better orientation than for P1 or P3, whereas at room temperature reorientation phenomena look similar.

It is worth to notice that the behavior of P10, with a carboxylic acid group, did not differ much from those of P1 and P3; when chromophores with analogous substituents were used in the guest–host systems, a gap of almost an order of magnitude was observed.

In all cases the poling procedure was much less effective for dipoles rigidly connected to the methacrylic polymer than for guest–host systems. This behavior has to be attributed to the limitation of the dipoles moments; this arises from the crowded environment around the polymer chain, but also from the piperazine-mediated coupling of the motions of side and main chains.

### 3. Experimental section

#### 3.1. Materials

*p*-Amino- $\alpha$ -cyanocinnamitrile, ethyl *p*-amino- $\alpha$ -cyanocinnamate, octyl *p*-amino- $\alpha$ -cyanocinnamate, (–)-menthyl *p*-amino- $\alpha$ -cyanocinnamate, *p*-amino- $\alpha$ -cyanocinnamic acid

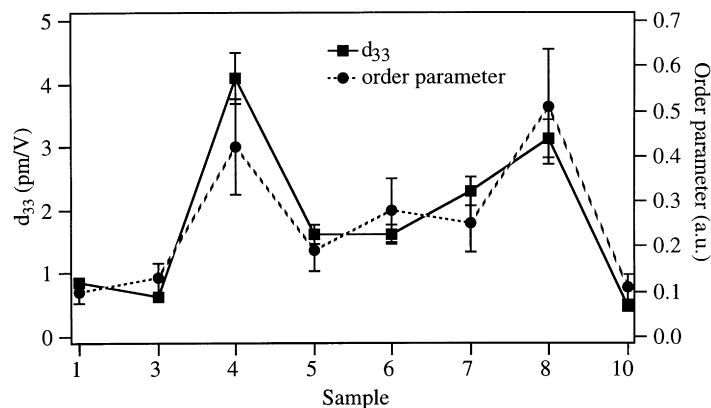


Fig. 4. Second order nonlinear susceptibilities ( $d_{33}$ ) and order parameters for the side chain polymers. Lines between data points are only a guide for the eyes.

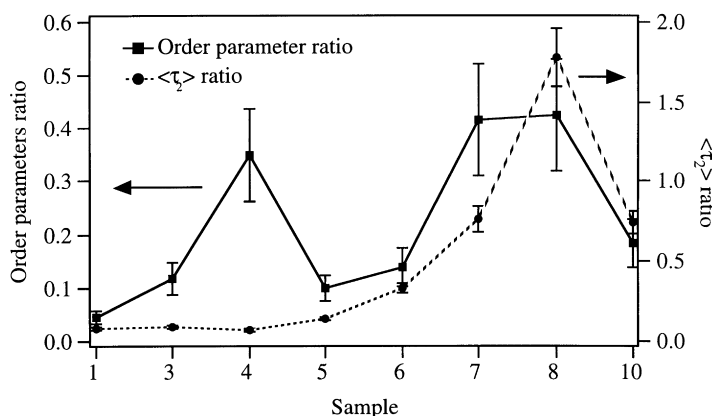


Fig. 5. Ratios of the order parameter and  $\langle \tau_2 \rangle$  values of guest–host systems and side chain polymers. Lines between data points are only a guide for the eyes.

and poly(*N*-methacryloyl-*N'*-phenylpiperazine) (PMPP) were synthesized as already reported [26,27]. 2,2'-Azobisisobutyronitrile (AIBN) and benzoylperoxide (BPO) were recrystallized from ethanol. *N*-methylpyrrolidinone (NMP) was distilled at 40°C at 1 mm Hg on CaH<sub>2</sub>.

### 3.2. Polymer synthesis

A solution of 1.0 g (14 mmol) of NaNO<sub>2</sub> in 3 ml of water was slowly added to a solution of 14 mmol of electron-poor aniline in 70 ml of acetic acid, cooled just above the freezing point. The solution was warmed up to room temperature and stirred for 20 min; then the temperature was lowered to 7–8°C and 3.2 g (14 mmol) of PMPP dissolved in 10 ml of acetic acid was added; the color turned to red-violet. The solution was warmed up to room temperature and stirred for 5 h, then 300 ml of water was added and pH was brought to 6 by addition of NaHCO<sub>3</sub>; the precipitate was filtered, dissolved in 15 ml NMP and reprecipitated in diethyl ether; the collected solid was extracted for 12 h in a Soxhlet extractor with diethyl ether to eliminate any trace of NMP; colored polymer products were obtained after vacuum drying, with functionalization ranging between 12 and 33% (Table 1).

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  = 6.5–8.3 (aromatic protons), 0.6–4.2 ppm (aliphatic protons). The UV–Vis extinction coefficients were assumed the same as for the model compounds [26,27].

**P1:** (KBr pellet):  $\nu$  = 3100–3000 (aromatic  $\nu$ CH), 2970–2840 (aliphatic  $\nu$ CH), 1620 ( $\nu$ C=O), 1600 and 1515 (aromatic ring vibrations +  $\nu_a$ NO<sub>2</sub>), 1340 ( $\nu_s$ NO<sub>2</sub>), 1230 (aniline aliphatic  $\nu$ C–N), 860 and 825 cm<sup>-1</sup> (aromatic  $\delta$ C–). UV–Vis (NMP):  $\lambda_1$  = 478 nm;  $\lambda_2$  = 266 nm.

**P3:** (KBr pellet):  $\nu$  = 3100–3000 (aromatic  $\nu$ CH), 2970–2840 (aliphatic  $\nu$ CH), 2224 ( $\nu$ nitrilic CN), 1625 ( $\nu$ C=O), 1597 and 1505 (aromatic ring vibrations), 1230 (aniline aliphatic  $\nu$ C–N), 846 and 825 cm<sup>-1</sup> (aromatic  $\delta$ C–). UV–Vis (NMP):  $\lambda_1$  = 440 nm;  $\lambda_2$  = 274 nm.

**P4:** (KBr pellet):  $\nu$  = 3100–3000 (aromatic  $\nu$ CH), 2980–2860 (aliphatic  $\nu$ CH), 2223 ( $\nu$ nitrilic CN), 1620

( $\nu$ C=O), 1600 and 1525 (aromatic ring vibrations +  $\nu_a$ NO<sub>2</sub>), 1365 (aniline aliphatic  $\nu$ C–N), 1340 ( $\nu_s$ NO<sub>2</sub>), 1230 (aniline aliphatic  $\nu$ C–N), 840 and 825 cm<sup>-1</sup> (aromatic  $\delta$ C–). UV–Vis (NMP):  $\lambda_1$  = 532 nm;  $\lambda_2$  = 290 nm.

**P5:** (KBr pellet):  $\nu$  = 3100–3000 (aromatic  $\nu$ CH), 2970–2860 (aliphatic  $\nu$ CH), 2226 ( $\nu$ nitrilic CN), 1621 ( $\nu$ C=O), 1600 and 1515 (aromatic ring vibrations), 1230 (aniline aliphatic  $\nu$ C–N), 841 and 828 cm<sup>-1</sup> (aromatic  $\delta$ C–). UV–Vis (NMP):  $\lambda_1$  = 443 nm;  $\lambda_2$  = 280 nm.

**P6:** (KBr pellet):  $\nu$  = 3100–3000 (aromatic  $\nu$ CH), 2970–2840 (aliphatic  $\nu$ CH), 2224 ( $\nu$ nitrilic CN), 1722 (ester  $\nu$ C=O), 1625 (amide  $\nu$ C=O), 1600 and 1505 (aromatic ring vibrations), 1365 (aniline aromatic  $\nu$ C–N), 1230 (aniline aliphatic  $\nu$ C–N), 845 cm<sup>-1</sup> (aromatic  $\delta$ C–). UV–Vis (NMP):  $\lambda_1$  = 438 nm;  $\lambda_2$  = 273 nm.

**P7:** (KBr pellet):  $\nu$  = 3100–3000 (aromatic  $\nu$ CH), 2960–2860 (aliphatic  $\nu$ CH), 2222 ( $\nu$ nitrilic CN), 1723 (ester  $\nu$ C=O), 1630 (amide  $\nu$ C=O), 1597 and 1505 (aromatic ring vibrations), 1370 (aniline aromatic  $\nu$ C–N), 1230 (aniline aliphatic  $\nu$ C–N), 843 cm<sup>-1</sup> (aromatic  $\delta$ C–). UV–Vis (NMP):  $\lambda_1$  = 436 nm;  $\lambda_2$  = 273 nm.

**P8:** (KBr pellet):  $\nu$  = 3100–3000 (aromatic  $\nu$ CH), 2970–2840 (aliphatic  $\nu$ CH), 2223 ( $\nu$ nitrilic CN), 1719 (ester  $\nu$ C=O), 1625 (amide  $\nu$ C=O), 1598 and 1504 (aromatic ring vibrations), 1370 (aniline aromatic  $\nu$ C–N), 1231 (aniline aliphatic  $\nu$ C–N), 844 cm<sup>-1</sup> (aromatic  $\delta$ C–). UV–Vis (NMP):  $\lambda_1$  = 438 nm;  $\lambda_2$  = 272 nm.

**P10:** (KBr pellet):  $\nu$  = 3100–3000 (aromatic  $\nu$ CH), 2970–2840 (aliphatic  $\nu$ CH), 2224 ( $\nu$ nitrilic CN), 1705 (acid  $\nu$ C=O), 1630 (amide  $\nu$ C=O), 1597 and 1505 (aromatic ring vibrations), 1370 (aniline aromatic  $\nu$ C–N), 1230 (aniline aliphatic  $\nu$ C–N), 846 cm<sup>-1</sup> (aromatic  $\delta$ C–). UV–Vis (NMP):  $\lambda_1$  = 445 nm;  $\lambda_2$  = 276 nm.

### 3.3. Physicochemical measurements

IR spectra were recorded with a NICOLET 5SXC FT-IR spectrometer on KBr pellets. UV spectra were recorded by a Perkin–Elmer Lambda 9 spectrometer. <sup>1</sup>H NMR spectra were recorded on a Bruker 300 MHz spectrometer on

DMSO- $d^6$  solutions; tetramethylsilane (TMS) was used as an internal standard. DSC analysis was performed under nitrogen atmosphere at an heating rate of 10°C/min by a Mettler TA 4000 calorimeter, equipped with a DSC 30 low temperature cell. DMTA was performed at an heating rate of 2°C/min by a Polymer Laboratories Thermal Analysis dynamico-mechanical analyser working in bending mode and equipped with a low temperature cell.

### 3.4. Film preparation

Appropriate amounts of polymer were dissolved in freshly distilled NMP to give 20% w/w solutions; after filtration, to remove undissolved particles (Teflon filter with porosity 0.45  $\mu\text{m}$ ), films were prepared by spin coating the solutions on ITO-coated glass slides for SHG measurements or on quartz slides for refractive index measurements. The slides were placed in a vacuum oven at 80°C for three days in order to remove any residual solvent; the film thickness was measured with a profilometer Alphastep.

Films were also prepared by solution casting on brass slides for bending mode DMTA analysis or on glass slides: the latter ones were used for preparation of DSC samples.

### 3.5. Optical measurements

The refractive indices of the thin films were measured as elsewhere described elsewhere [27,33,34].

The second harmonic generation experimental set-up is described in detail in Refs. [14,27]; it involved a Q-switched Surelite Nd:YAG laser ( $\lambda = 1.064 \mu\text{m}$ , frequency up to 10 Hz, 8.5 mJ per pulse), pumping a methane Raman cell with output at 1.542  $\mu\text{m}$ . The beam intensity was measured performing a Maker fringes reference experiment with a quartz crystal (110) ( $d_{11} = 0.4 \text{ pm/V}$  [35]). The sample holder was mounted on a computer controlled goniometer stage with possibility of temperature control of  $\pm 0.1^\circ\text{C}$ . The corona poling technique was used to orient the dipoles, using a 6.5 kV potential difference between the needle and the sample, placed at a constant distance of 2 cm. The poling experiments were performed by measuring the SHG growth at a fixed angle ( $35^\circ$ ), with the following temperature profile: heating to 130°C; 30 min isotherm; cooling down to 90°C at 1°C/min; 30 min isotherm; cooling down to room temperature at 1°C/min.

## 4. Summary and conclusions

Several new methacrylic polymers containing high-dipole chromophores in the side chains were prepared in good yield by diazonium ion coupling reaction on a preformed polymer. On the other hand, attempts of direct polymerization of methacryloyl derivatives of push–pull azobenzene failed. The order parameters calculated from the nonlinear susceptibilities, and the kinetic analysis of

SHG decay allowed to study the chromophores orientability.

Two factors have been used to influence the molecular mobility: variation of (a) the dipole flexibility, and (b) the state of the chromophore, i.e. freely dispersed or chemically linked.

In all cases, the measurements showed the orientability and the stability of the polar order to be much lower in the side chain polymers than in the guest–host systems; moreover, flexible structures showed better results than rigid ones. The better orientability of cyanovinyl than rigid rod chromophores, of P4 versus P1 and P3 and the good effect of alkyl chains and carboxylic acid are examples of this trend. An opposite behavior was previously observed for guest–host systems.

The occurrence of two opposite trends for the same chromophore structures suggest the physical state of the dipole to be more important than its substitution pattern; an optimum result could possibly be obtained in an intermediate mobility range. The chromophore needs to have a certain rotational freedom above the  $T_g$ , while the coupling with the main chain movements has to be effective at room temperature; a good compromise could probably be achieved, e.g. by the use of a short flexible spacer and a moderately rigid dipole.

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