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NLO-active polymers containing triazolo-thiadiazole segments

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Abstract

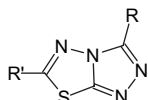
Polymethacrylate and polycondensated polymers based on chromophores containing the *s*-triazolo[3,4-*b*]-thiadiazole heterocycle were synthesized. Chromophore and polymer preparations are described. Second order NLO measurements are reported for polymers and for one functionalized chromophore. The maximum value of second harmonic generation coefficient (d_{33}) measured is 11.5 pm/V at incident laser wavelength of 1368 nm. For the most active polymer, 85% of the initial d_{33} value is retained after 27 days at 80 °C.
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Keywords: Nonlinear optics; Second harmonic generation; Polymer

1. Introduction

In continuation of our studies on new NLO-active chromophores containing electron poor heterocycles [1], we have started studying molecules containing the *s*-triazolo[3,4-*b*]-thiadiazole heterocycle (Scheme 1). This heterocycle has been investigated in biochemistry and has a large spectrum of biological activity [2].

There are several reasons that can suggest this heterocycle as a potentially interesting building block for second order NLO-active chromophores: (a) the high number of electronegative N atoms and the sulphur atom, according to the literature [3], are expected to increase the quadratic molecular NLO response; (b) the planar conformationally blocked geometry of the two fused rings allows good π -electron conjugation; (c) the bent geometry of the bonds in positions 2 and 5 is



Scheme 1.

expected to confer to the chromophore a more oblate ellipsoid shape than prolate which, again, is reported to improve the NLO properties [4]; (d) the easy and low cost nature of the synthetic procedure. Actually, in general, for the heterocycle reported in the scheme above, starting materials are the two carboxylic acids (RCOOH and R'COOH), hydrazine and carbon disulfide, all manipulations being performed in water solution in air [5].

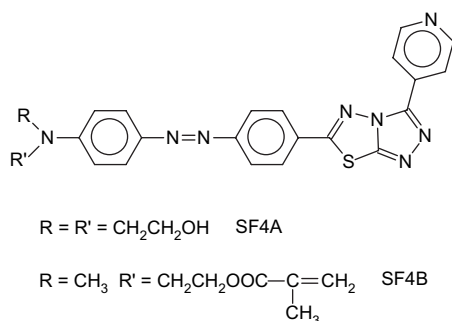
In the present work we describe the synthesis of two chromophores containing this heterocycle, SF4A and SF4B, in which an additional electron poor pyridine group has been attached to the heterocycle from the side of the triazole ring (Schemes 2 and 3).

The diol chromophore SF4A is functionalized for polycondensation and from it the polyurethane PUSF4 was obtained, while SF4B is functionalized for radical polyaddition; from it, methacrylate copolymers PMA10 and PMA20 were prepared.

2. Experimental section

The synthesis of the two chromophores is outlined in Chart 1 below. The fused 1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazole system is obtained by cyclization of *p*-aminobenzoic acid with the triazole-amino-thiol (**I**) in polyphosphoric acid. Although

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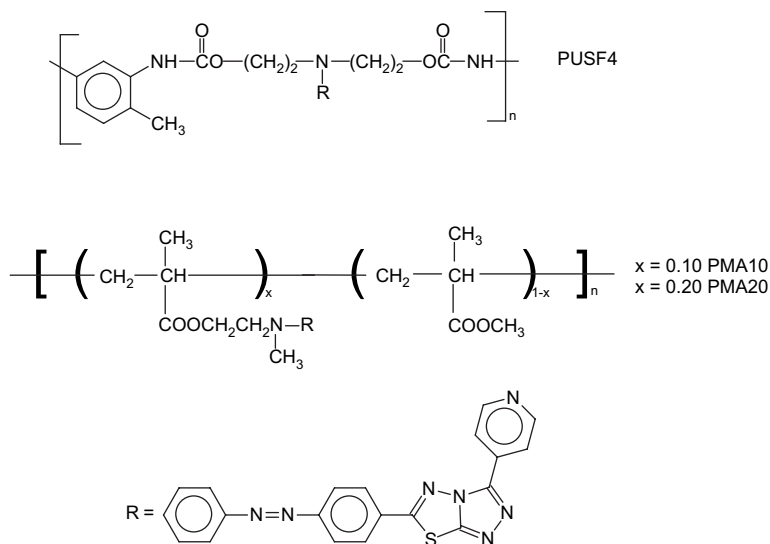
Scheme 2.

compound **(I)** can be easily prepared from isonicotinic acid, hydrazine and carbon disulfide [5b], it is a commercial product and was purchased by Aldrich.

2.1. 2-(4-Aminophenyl)-5-(4-pyridyl)-1,2,4-triazolo-[3,4-b]-1,3,4-thiadiazole (**II**)

3-(4-Pyridyl)-4-amino-5-thiol-1,2,4-triazole (**I**) (3.00 g, 15.06 mmol), 4-aminobenzoic acid (2.065 g, 15.06 mmol) and polyphosphoric acid (~75 g) were stirred at 210 °C for 5 h. Then, the brown paste was poured into water (200 mL) and ice under stirring. A yellow solid formed. After neutralization at pH = 5 with aqueous NaOH, the colour of the product changed from yellow to green. The solid was filtered and washed with aqueous solution of Na₂CO₃ (10% by weight). The green solid was collected by filtration, washed with water and dried in oven at 120 °C for 4 h. Yield: 84%; Mp: 263 °C.

¹H NMR (DMSO-*d*₆): δ (ppm) 6.22 (s, 2H), 6.69 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 8.20 (d, *J* = 5.8 Hz, 2H), 8.78 (d, *J* = 5.8 Hz, 2H).



Scheme 3.

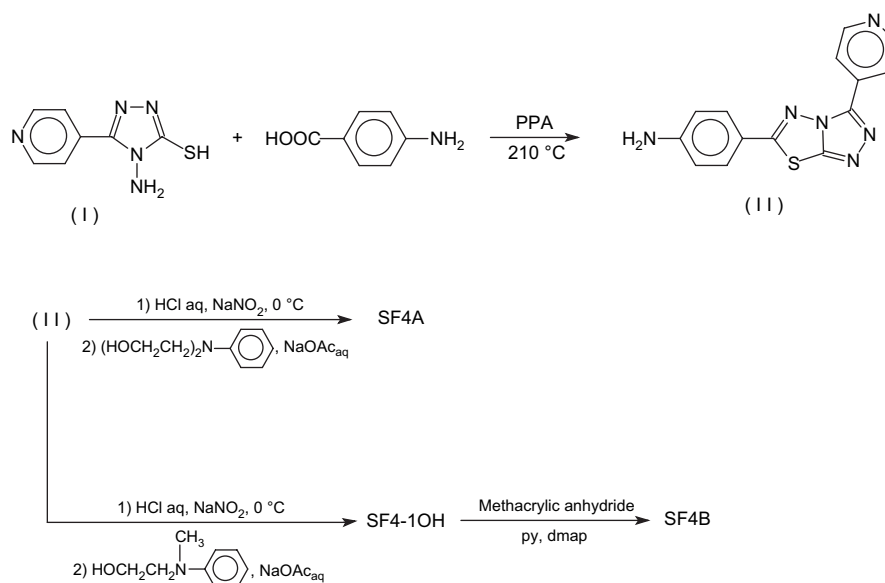


Chart 1.

2.2. 2-[4-[4-(*N,N*-Di-2-hydroxyethylamino)phenylazo]-phenyl]-5-(4-pyridyl)-1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazole (SF4A)

Compound **II** (1.500 g, 5.096 mmol) was suspended in 20 mL of water. The suspension was cooled at 0–4 °C in an ice-bath. Hydrochloric acid (1.3 mL, 37%) was added and the suspension became a brown solution. Then, sodium nitrite aqueous solution (0.385 g; 5.555 mmol) was added dropwise. After 40 min of reaction, the diazonium salt solution was poured under stirring into a solution containing sodium acetate (1.43 g), *N,N*-dihydroxyethylaniline (0.923 g, 5.096 mmol) water (50 mL) and ethanol (150 mL). Immediately the formation of a red solid was observed. This was recovered by filtration and recrystallized from DMF/H₂O. Yield: 53%; Mp: 297 °C.

¹H NMR (DMSO-*d*₆): δ (ppm) 3.58 (m, 8H), 4.83 (s, 2H), 6.87 (d, *J* = 9.2 Hz, 2H), 7.79 (d, *J* = 9.4 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 2H), 8.18–8.26 (m, 4H), 8.84 (d, *J* = 6.4 Hz, 2H).

2.3. 2-[4-[4-(*N*-2-Hydroxyethyl-*N*-methylamino)-phenylazo]phenyl]-5-(4-pyridyl)-1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazole (SF4-1OH)

The same procedure of synthesis and recrystallization of SF4A was adopted. The coupling agent was *N*-methyl-*N*-(2-dihydroxyethyl) aniline instead of *N,N*-dihydroxyethylaniline. Yield: 58%. Mp: 287 °C.

¹H NMR (DMSO-*d*₆): δ (ppm) 3.07 (s, 3H), 3.55 (m, 4H), 4.80 (s broad, 1H), 6.84 (d, *J* = 9.2 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 8.18–8.26 ppm (m, 4H), 8.83 (d, *J* = 5.0 Hz, 2H).

2.4. 2-[4-[4-(*N*-Methacryloyloxyethyl-*N*-methylamino)-phenylazo]phenyl]-5-(4-pyridyl)-1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazole (SF4B)

SF4-1OH (4.000 g, 8.762 mmol) was dissolved in pyridine (16 mL) containing catalytic amount of *N,N*-dimethylamino-pyridine (0.0630 g, 0.5143 mmol). After cooling the solution (~10 °C) with an ice-bath, methacrylic anhydride (1.70 mL, 11.39 mmol) was added slowly. The reaction was continued for one night. The reaction mixture was poured in 100 mL of water and the solid was recovered by filtration, washed with plenty of water and dried. Purification of the raw product was performed by chromatographic column. The product was dissolved in chloroform. The stationary phase was silica gel and the mobile phase was a mixture of chloroform/methanol at 2% in volume in methanol. TLC confirmed the efficiency of purification. Finally the chromophore solution was poured into hexane so as to obtain a crystalline product. Yield: 20%; Mp: 203 °C.

¹H NMR: (CDCl₃): δ (ppm) 1.80 (s, 3H), 3.01 (s, 3H), 3.65 (t, *J* = 5.8 Hz, 2H), 4.26 (t, *J* = 5.4 Hz, 2H), 5.46 (s, 1H), 5.96 (s, 1H), 6.67 (d, *J* = 9.0 Hz, 2H), 7.77 (d, *J* = 9.3 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 8.19 (d, *J* = 4.2 Hz, 2H), 8.74 (d, *J* = 4.2 Hz, 2H).

2.5. Polymer synthesis

PUSF4 was prepared by solution polycondensation. PMA10 and PMA20 were prepared by radical polyaddition in solution. The synthesis of PUSF4 and PMA10 is described in detail.

2.5.1. PUSF4

SF4A (0.413 g, 2.371 mmol) and tolylen-2,4-diisocyanate (0.951 mL, 2.371 mmol), were solved in 4 mL *N*-methyl-2-pyrrolidone under flowing nitrogen in a round bottomed flask equipped with magnetic stirrer and condenser; the temperature was raised to 120 °C and held constant for 4 h. After this period, the mixture was more viscous. Then it was poured under stirring into 100 mL methanol. A red solid formed which was recovered by filtration, dissolved in DMF and again reprecipitated by pouring into 100 mL of methanol. After filtration, washing with methanol and drying in oven at 100 °C for 2 nights, the yield was 85%.

Anal. Calcd for (C₃₃H₂₈N₁₀O₄S)_{*n*} C 59.99%, H 4.27%, N 21.20%. Found C 59.08%, H 4.35%, N 21.11%.

2.5.2. PMA10

0.500 g of SF4B (0.500 g, 1.013 mmol) and 0.97 mL of freshly distilled methylmethacrylate (9.117 mmol) were dissolved in a glass vial in 5 mL of anhydrous pyridine. α,α'-Azobutyronitrile (AIBN) (0.016 g, 0.1013 mmol) was added as radical initiator. After three freeze-thaw cycles the vial was sealed under vacuum and held at 80 °C for 3 days. The reacted viscous mixture was then poured dropwise into 100 mL of methanol under stirring. The resulting orange solid product was filtered, redissolved in 20 mL DMF and again poured in methanol. The final product, after filtration, was dried in oven at 100 °C for 2 nights.

Yield: 82%. ¹H NMR spectra of the polymers are consistent with the expected structures and allowed to determine the actual molar composition of the copolymers, which is 8% for PMA10 and 18% for PMA20.

3. Physical measurements

The thermal behaviour of monomers and polymers was studied by DSC technique (Perkin Elmer Pyris, scanning rate 10 °C/min, nitrogen flow), optical observations (Zeiss Axioscop polarizing microscope, Mettler FP90 heating stage), thermogravimetric analysis (Mettler TG50, air atmosphere). ¹H NMR spectra were recorded on Varian and Gemini Spectrometers operating at 200 MHz or at 300 MHz. X-ray diffraction patterns were recorded on a flat film camera (Ni-filtered Cu Kα radiation). Inherent viscosities of polymers (0.5 g/dL solution, 25.0 °C, NMP solvent for PUSF4; 0.154 g/dL solutions CHCl₃ solvent for PMA10 and PMA20) were measured using an Ubbelohde viscometer. Density of polymers was measured, at 25 °C, by the floatation technique in CCl₄/heptane suspensions.

Dipole moments of the ground μ_g and excited states μ_e of (**II**) and SF4A have been determined by means of the Electro-Optical Absorption (EOA) spectroscopy by which the

difference of absorption of a solution with ($\epsilon^E(\varphi, \tilde{\nu})$) and without ($\epsilon(\tilde{\nu})$) an externally applied electric field E is measured with light parallelly ($\varphi = 0^\circ$) and perpendicularly ($\varphi = 90^\circ$) polarized to the direction of E [6]. For uniaxial phases, induced in a solution by both an alternating and a constant electric field of about $3 \times 10^6 \text{ V m}^{-1}$, the dichroism $\epsilon^E(\varphi, \tilde{\nu}) - \epsilon(\tilde{\nu})$ depends on the orientational order of the molecules due to their ground-state dipole moment μ_g , the shift of the absorption band proportional to the dipole difference $\Delta\mu = \mu_e - \mu_g$, and on the electric field dependence of the electric transition dipole moment $\mu_{eg}(E)$. UV/vis spectra, required for the evaluation of the integral absorption (μ_{eg}^2), were recorded with a Perkin–Elmer Lambda 900 spectrophotometer at 298 K.

The corona-poling set-up for polymers used a 25 μm diameter gold wire placed at about 1 cm from the film surface. The HV generator was grounded to heating stage and the whole apparatus was held in a controlled atmosphere (dry-nitrogen) box. The poling voltage and time was optimized for each polymer in order to fully preserve chemical integrity of the materials. The final applied voltages (times) were 4.5 kV (10 min) for PUSF4, 6 kV (30 min) for PMA10 and 6 kV (60 min) for PMA20.

A Quantel Brilliant Q-switched Nd:YAG laser (frequency up to 10 Hz, 5 ns pulse duration, 400 mJ per pulse) provided the fundamental beam output at 1064 nm for SHG measurements. This source fed a Solid State Raman Shifter (MolTech CRS-14, Barium Nitrate as the active substance) which shifted the beam output to 1368 nm in order to avoid resonance enhancement of the nonlinear signal. The NLO characterization was carried out by performing in situ SHG measurements during the poling. The typical procedure used for the samples consisted in measuring the SHG growth while the samples were heated for the above reported times at temperature 10°C below the T_g , with the electric field on. The films were then cooled down to room temperature at $1^\circ\text{C}/\text{min}$ and the electric field was finally switched off. Absorption spectra measurements of the films were performed before and immediately after the poling, to estimate independently the polar order of the dipoles through the decrease of the absorption coefficient [7] (see Fig. 1 below). The nonlinear coefficient d_{33} of the samples was obtained by measuring the intensity of SHG pulse, carefully calibrated with a Maker fringes reference experiment [8] of a quartz crystal slab (110) ($d_{11} = 0.335 \text{ pm/V}$ [9]). SH signal was corrected taking into account samples thickness and refractive index, measured by spectroscopic ellipsometer. The angle between the film surface normal and the laser beam was 20° . The laser beam was p -polarized and the d_{33} was calculated within the assumption $d_{31} = d_{15} = d_{33}/3$. The uncertainty of the d_{33} coefficients can be estimated to 20%.

4. Results and discussion

NLO activity of SF4A chromophore was investigated by the EOAM technique [6]. The relevant data for the aniline precursor **II** and for SF4A (Table 1) have been evaluated under the assumption that μ_{eg} is parallel to the orientation of both μ_g and μ_e and that the small polarizability terms in the

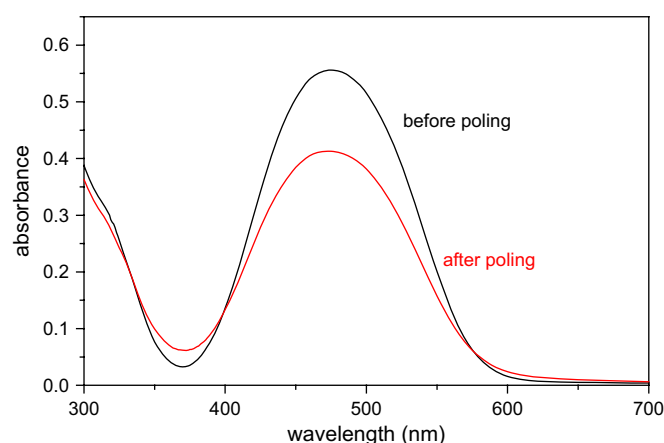


Fig. 1. UV/vis absorption spectrum of PUSF4 film.

description of $\epsilon^E(\varphi, \tilde{\nu}) - \epsilon(\tilde{\nu})$ can be neglected. In Table 1 all μ 's and β 's are corrected to the gas phase except for $\bar{\mu}_g$ which is given as an example for how molecular properties can be drastically enhanced by the interaction with the surrounding matrix [10].

The $\mu_g\beta_0$ value of SF4 is fairly good being comparable with DR1 and DANS chromophores which are reference standards in the field [12]. The increase of β_0 and $\mu_g\beta_0$ of SF4A in comparison with precursor (**II**) is due to its higher transition dipole moment of the long-wavelength CT absorption band, their different spectral positions, as well as on the change of the dipole difference $\Delta\mu$ by approximately a factor of 1.4, 1.4, and 1.5, respectively. The structure of the absorption spectra allow interpreting the long-wavelength band of SF4A as a new band originated by the introduction of a new chromophoric system, the diazo chromophore, with a long-wavelength CT absorption band of high intensity (Fig. 2).

The second band of SF4A possesses approximately the same intensity as the first band of (**II**) but is shifted about 30 nm to shorter wavelength due to the interaction of the diazo chromophore with the transition localized in the compound (**II**) residue of SF4A (about 250–350 nm). Thus, the increase of β_0 for SF4A can not be traced back to the intensifying and shifting of the CT band of the precursor (**II**), it is rather due to the introduction of the new transition of the diazo group. The ground-state dipole moments are in both cases, SF4A and (**II**), differently oriented within the molecular framework and the differently polarized absorption bands do not contribute to

Table 1
UV/vis and EOAM data^a of the precursor **II** and the chromophore SF4A

	λ_{eg}	μ_{eg}	$\mu_g\beta_0$	β_0^d	μ_g^b	$\bar{\mu}_g^c$	$\Delta\mu$
II	336.0	6.4	133	17	7.8 ± 0.1	9.7	9.7 ± 0.4
SF4A	468.3	8.9	778	94	8.2 ± 0.2	10.2	14.2 ± 0.7

^a λ_{eg} (nm); μ_{eg} (D); μ_g (D); $\Delta\mu$ (D); β_0 (10^{-30} esu); $\mu_g\beta_0$ (10^{-48} esu).

^b Gas phase values.

^c Measurements have been performed in 1,4-dioxane at a molar concentration of about 10^{-5} M at 298 K. The solvent effect has been corrected by the Onsager continuums model.

^d Data have been calculated according to the phenomenological convention (Ref. [11]).

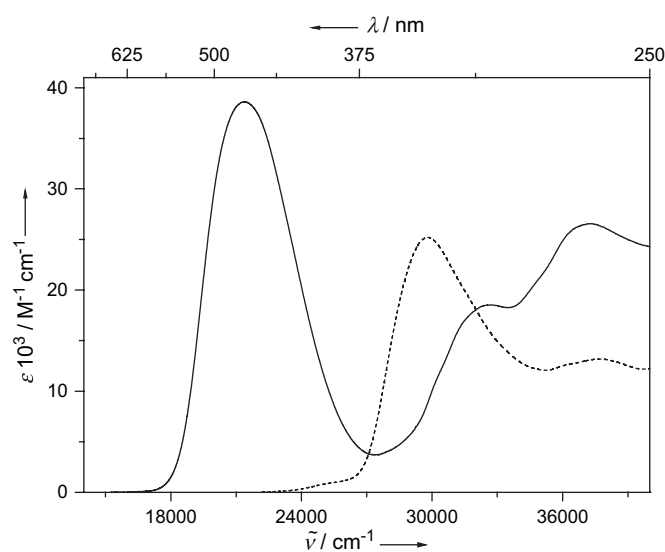


Fig. 2. UV/vis absorption spectra of chromophores (II) (---) and SF4A (—) in 1,4-dioxane ($T = 298$ K, ca. 10^{-5} M).

tensor coordinates of the hyperpolarizability tensor belonging to the same direction within the molecule. Therefore, for the estimation of β_0 of SF4A the contribution of the second absorption band of SF4A is not taken into account.

Basic properties of the polymers are reported in Table 2.

The highest glass transition is observed for the polyurethane, and this is expected, being probably related the formation of H-bonding between the urethane N–H groups and several acceptors atoms, including nitrogen atoms of the 4-pyridyl groups. The higher T_g of PMA20 as compared with PMA10 is consistent with the higher content of chromophore. All polymers, analyzed by optical microscopy and X-ray diffraction, are amorphous. The amorphous nature has been proved also for thin films of the polymers obtained by spin-coating and used in the NLO measurements. The decomposition temperatures are well higher than T_g , this allowing safe poling procedures.

Some optical and NLO data of the polymers are given in Table 3.

The refractive indices of the polymers are relatively high and their behaviour seems to reflect the density of π -electron conjugated systems present in the polymers [1f]. Nonlinear coefficients of the polymers are fairly good, if we consider that they are substantially free from resonance enhancement.

This point is proved, as an example, by the UV/vis spectrum of a PUSF4 film reported in Fig. 1, which clearly shows that at the second harmonic wavelength (684 nm) the absorbance of the polymer film is almost null. Moreover, by comparison between Tables 2 and 3, it is seen that d_{33} coefficients scale well with the chromophore number density and order parameter, as expected [12]. The lowest Φ is observed for PUSF4.

Table 2
Some properties of the polymers

	T_g (°C)	T_d (°C)	η_{inh} (dL/g)	d (g/cm ³)	N (10^{20} mol/cm ³)
PUSF4	170	303	0.10	1.335	12
PMA10	136	263	0.10	1.231	4
PMA20	150	262	0.13	1.264	8

Table 3
NLO characterization of polymers

	T_{poling} (°C)	n (1368 nm)	n (684 nm)	Φ^a	d_{33} (pm/V)
PUSF4	150	1.75	1.84	0.26	11
PMA10	125	1.57	1.61	0.29	7.4
PMA20	140	1.64	1.70	0.33	11.5

^a Order parameter.

This could be related (a) to the fact that for PUSF4 the chromophore concentration is maximum and (b) to the fact that, due to the urethane groups, strong hydrogen bonds are present in the polymer that could hamper the orientation of chromophores under the poling field. In the case of PMA10, as compared with PUSF4, the order parameter is slightly higher, so that the lower d_{33} is probably due to the lower chromophore concentration. The best results are obtained for PMA20. In this polymer, the chromophore concentration is two times higher than PMA10, but not as high as PUSF4, this allowing an higher order parameter to be reached, perhaps also aided by the higher poling temperature with respect to PMA10. All these qualitative evaluations have some interest, if we consider, for instance, that for PUSF4 and PMA20 the chemical connection of the chromophore to the chain is different and so they are the conformational degrees of freedom involved in the orientation process.

For all the polymers the time stability of the NLO activity was studied by recording the SHG signal from a sample stored at 80 °C as a function of time and by comparing it with the SHG reference signal of a Y-cut quartz crystal in order to correct for long term fluctuations of the incident laser power. The results of the test are given in Fig. 3.

After the initial fast loss [13], NLO signals show a small slope as a function of the time in such a way that after 27 days the amount of initial d_{33} retained is between 75% and 85% for all the polymers; the uncertainty of the measurements does not allow significant differences to be drawn among the three polymers. In any case, the time stability can be considered quite good for all, given also the moderately high baking

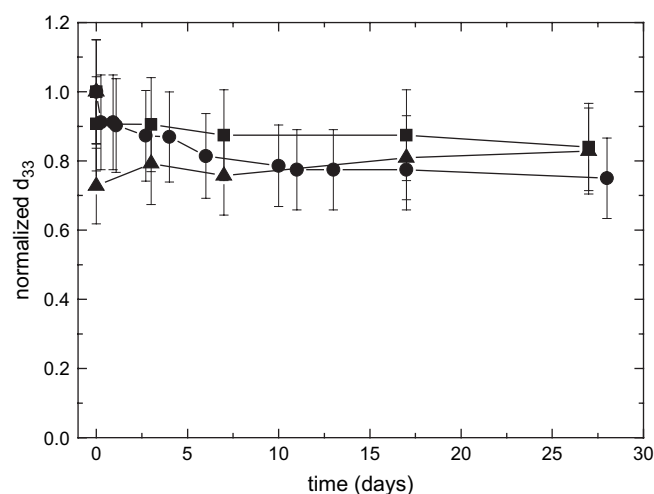


Fig. 3. Normalized d_{33} (i.e. $d_{33}(t)/d_{33}(t=0)$) as a function of the baking time for the studied polymers. Baking temperature 80 °C. PMA10 triangles, PMA20 squares, PUSF4 circles.

temperature, and this result is particularly unexpected for the methacrylate copolymers for which poor time behaviours were generally reported [14].

Acknowledgements

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