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Simpler and more efficient strategy to stabilize the chromophore orientation in electro-optic polymers with copper-free thermal Huisgen reaction

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ABSTRACT

A new strategy is proposed to stabilize the electro-optic (EO) activity of second-order materials using copper-free thermal Huisgen 1,3-dipolar cross-linking reaction. It consists in freezing the chromophores orientation after the poling process by a cross-linking reaction based on the 1,3-dipolar cycloaddition between an azide and an alkyne. To reach this goal, the synthesis of new methacrylate type polymers bearing a derivative of Disperse Red 1 chromophore was performed. The polymeric structure is bearing a cross-linkable function on its backbone and the complementary reactive function is brought by a small molecule called "doping agent" (**DA**), containing several complementary cross-linking groups, evenly distributed in the polymer film. Materials have been prepared and exhibit large second-order nonlinear optical coefficients (d_{33}) up to 60 pm/V at the fundamental wavelength of 1064 nm. Moreover, the thermal stability of the orientation of the chromophores could reach 150 °C upon cross-linking with such materials, which is higher than previously described cross-linkable EO polymers based on this reaction. Furthermore, this new strategy widens the possibilities offered by copper-free thermal Huisgen 1,3-dipolar cycloaddition as cross-linking reaction for EO polymers.

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1. Introduction

For the last past two decades, the development of organic nonlinear optical (NLO) materials has generated a huge interest owing to their potential applications in optical switching, information storage or signal processing [1–4]. Compared to NLO inorganic crystals, such as lithium niobate, organic NLO materials display faster response times, larger bandwidths, higher electro-optic coefficients and better processability [3,5,6]. Accordingly, polymeric materials represent attractive candidates for the fabrication of electro-optic devices, such as Mach Zendher interferometer [7–10]. Organic NLO materials are generally composed of push-pull organic chromophores, in which a π -conjugated bridge is end-capped by a donor and an acceptor moiety. For the practical processing of the chromophores

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into thick and good optical quality films, their incorporation in a polymer matrix is most often a prerequisite [8,9,11]. The chromophores are finally oriented by applying a high external electric field to generate their noncentrosymmetric organization inside the matrix, which is a key requirement to observe the bulk electro-optic activity. The polymeric electro-optic material must also fulfill other requirements such as a high chemical, thermal and photochemical stability and a high transparency at the laser wavelength, generally 1.55 µm for telecommunication. However, the temporal instability of the poled chromophores is certainly the most stringent limitation of the organic electro-optic materials for their industrial utilization [12,13]. Indeed, in most organic materials, the chromophores tend to relax and adopt a head-to-tail organization due to their high ground-state dipole moment. As a result, the development of strategies to permanently freeze the chromophores orientation after the poling process is of a paramount practical significance for the applications [13]. The development of new host matrices allowing a high stability of the poled chromophores is certainly equally important as the synthesis of new chromophores possessing large hyperpolarizability coefficients (β). The two most investigated strategies to prevent the chromophore relaxation are firstly to embed the chromophores into



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a high glass transition temperature (T_g) polymer and secondly to use cross-linkable matrices. High glass transition temperature polymer maintains the organization of the chromophores owing to the high viscosity of the medium even at significant temperature [14–17], while cross-linkable systems enable to freeze the chromophores orientation by the formation of new covalent bonds inside the material after the poling process. Cross-linkable NLO polymers can be classified into two categories. The first one is generally based on a condensation reaction conducted in two steps with monomers substituted by multiple polymerization groups [18-22] while the second is based on specific cross-linking groups which are distinct from the polymerization groups, which only react above T_g . This second strategy is much more convenient and more reproducible than the first one which demands a very difficult control of the course of the condensation reaction. However, there are few cross-linking reactions which fulfill the criteria to be used for such application. First, the reacting groups need to be dormant below the glass transition temperature (T_g) , but they must react quickly just above the T_g . Second, they must be compatible with the polymerization reaction so as the cross-linking reaction does not start during the preparation of the polymer. Third, the reacting groups should be quite selective to one another and should not react with the chromophores to prevent their degradation. The very few cross-linking reactions successfully implemented to electro-optic polymers are: the anthracene-maleimide Diels-Alder cycloaddition [7,23-25], the cyclodimerization of trifluorovinylether [26-28], the thermal decomposition of cyclobutanone [29] and the epoxide opening with a carboxylic acid [30–33]. However, some of them are not fully satisfying. For example, the Diels-Alder cycloaddition is a reversible reaction and the dienophile tends to react with the double bonds of the chromophore [12,23]. The shelf-storage of the systems employing an epoxide and a carboxylic acid is modest owing to a premature cross-linking occurring at room temperature and the cyclodimerization of trifluorovinylether requires high temperature, which may not be compatible with all polymer or chromophore thermal stabilities, besides at high temperature the poling efficiency is decreased. Stable thermal and temporal electro-optic materials were also designed by layer-by-layer self-assembly methods or by supramolecular interactions [22,34-43]. Although these materials exhibit exceptional stabilities they are expensive to fabricate and/or these strategies are not fully compatible with industrial developments. Recently, we reported a new cross-linkable strategy based on copper-free thermal Huisgen 1,3-dipolar reaction [44,45]. In the previous systems, one cross-linkable group (azide) was borne by the chromophore and the complementary group (acetylenic group) was placed on the polymer backbone as a pendant group (PAS1 Fig. 1, and system A Fig. 2).

Despite the relatively high thermal stability of the electro-optic activity of these new polymers, acquired thanks to the cross-linking process, they present two potential limitations. First, we observed a premature cross-linking process upon shelf-storage at room temperature for several months. This could be cumbersome, since even at a low percentage of cross-linking reaction, the initially high solubility of the polymer could significantly diminish and prevents the preparation of concentrated solution for spin-coating. Secondly, the above strategy requires the double functionalization of the chromophore, one for the attachment of the polymerization group (methacrylate in the present case) and the other for the cross-linking group (azido or alkyne, Figs. 1 and 2). The introduction of two functional groups could represent a tedious and costly synthetic task with powerful chromophores, whose synthesis is, itself, often challenging [12,23]. A modification of our initial strategy is proposed herein, which overcomes the above limitations. It is based on the utilization of a complementary small molecule containing several cross-linking groups, called doping agent (DA), which is mixed with the electro-optic polymer just before the preparation of the film (Fig. 2). Thus, the direct contact of the two complementary crosslinkable groups is avoided during storage, since it occurs only in the final step of the process during the preparation of the solution for the spin-casting of the two materials. Besides, with this new formulation, the introduction of a cross-linking group on the chromophore is not strictly necessary. However, a system bearing cross-linkable group both on the polymer and on the chromophore (system D) was prepared to test its relative electro-optic stability compared to the other materials (systems A, B and C; Fig. 2). The concept, based on the mixing of a complementary cross-linking agent, was already reported by Jen and coworkers, but using Diels—Alder cycloaddition as cross-linking reaction and proved to be successful [7,25,46,47].

In this paper, we describe the synthesis and the characterizations of three new polymeric matrices and doping agents (Schemes 1 and 2). The electro-optic stability of the mixtures corresponding to the systems C and D is at least as high as that obtained with initial system A, demonstrating the pertinence of this new strategy and enlarging the scope of the copper-free Huisgen cycloaddition as cross-linking reaction to stabilize the macroscopic electro-optic activity of organic materials.

2. Experimental part

2.1. Materials

4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride **DMTMM** [48], compounds **1** [44], **3** [45], **5** [49], **6** [50], **10** [51], **DA1** [52] and **DA2** [53] were prepared according to the procedures described in the literature.

2.2. Methods

NMR spectra were recorded using a Bruker 300 MHz instrument (ARX-300, Bruker) with tetramethylsilane (TMS) as the internal standard and CDCl₃ as the solvent. The IR spectra were recorded using an FT-IR spectrometer (Clark-MXR CPA). UV–Visible absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer. Thermal analyses were performed using a TA instruments Q100 in a nitrogen atmosphere at a heating rate of 10 °C/min. The number- and weight-average molecular weights and molecular weight distributions were determined using a size exclusion chromatography (SEC) on a system equipped with a SpectraSYSTEM AS 1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 μ m MIXED-D columns), with a SpectraSYSTEM RI-150 detector. Tetrahydrofuran (THF) was used as the



Fig. 1. Illustration of a previously studied cross-linkable EO polymer (PAS1).



Fig. 2. Illustration of the cross-linking strategies based on copper-free Huisgen cycloaddition.

mobile phase at a flow rate of 1 mL/min at 35 °C. Polystyrene standards $(580-483.10^3 \text{ g mol}^{-1})$ were used to calibrate the SEC. High resolution electro-spray mass spectra (HR-ESMS) were collected in positive mode on an MS/MS ZABSpec TOF of Micromass equipped with a geometry EBE TOF. The samples were injected in DCM. Column chromatography was carried out with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh). Air sensitive reactions were carried out under argon in dry solvents. Second harmonic generation (SHG) measurements were performed using the optical setup described in a previous study [54]. Polarized SHG Maker fringe patterns were recorded before and, from time to time, after the poling process, using a 1064 nm Nd:YAG laser operating at very low irradiance (pulse energy <20 μ]; repetition rate 50 Hz; pulse width 15 ns). A general SHG matrix method applicable to multilayered anisotropic absorbing linear/nonlinear media has been applied, allowing experimental determination of the resonance-enhanced NLO coefficients dij, as well as the linear absorption coefficients of the harmonic wave (532 nm) in the parallel ($\alpha_{||}$) and perpendicular (α_{\perp}) directions with respect to the poling field. Thus, absorption of the harmonic wave was explicitly taken into account and SHG coefficients were determined using the quartz reference with coefficient $d_{11} = 0.3 \text{ pm/V}$ at 1064 nm. Further details about the general procedure to determine the linear and nonlinear optical constants can be found elsewhere [54,55]. The indexes of refraction have been assumed isotropic in accordance to the weak thicknesses of all samples. Only anisotropic linear absorption coefficients (α_{ll} and α_{\perp}) of the harmonic wave (close to resonance) have been considered by measuring the absorbance maxima before (A_0) and after poling (A). Therefore, assuming no degradation of the chromophores during the poling process, we have $A_0 = \langle \alpha \rangle = (2\alpha \bot + \alpha_{II})/3$ before poling, and, after poling we obtain directly the in-plane absorption term $\alpha_{\wedge} = A$. Finally, it is easy to determine the last anisotropic absorption coefficient $\alpha_{II} = 3A_0 - 2A$.

2.3. Synthesis of the materials

2.3.1. Compound 2

To a solution of carboxylic acid compound **1** (100 mg, 0.235 mmol, 1 equiv.) and MeOH (V = 5 mL) in THF (V = 5 mL) was added *N*-methylmorpholine (V = 0.07 mL, 0.705 mmol, 3 equiv.) and then dimethoxytriazine-*N*-methylmorpholine chloride

(**DMTMM**), (0.78 mg, 0.281 mmol, 1.2 equiv.). The solution was stirred one night at room temperature. Solvents were then evaporated under reduced pressure to give the crude product, which was purified by silica gel column chromatography using dichloromethane as eluting system leading to 101 mg of compound **2** (96%).

¹H NMR (300 MHz, CDCl₃, MeOD), δ (ppm): 8.48 (d, 1H, J = 1.8 Hz); 8.25 (dd, 1H, J = 8.4 Hz, J = 2.1 Hz); 7.89 (d, 2H, J = 9 Hz); 7.77 (d, 1H, J = 8.4 Hz); 6.81 (d, 2H, J = 9 Hz); 6.10 (s, 1H); 5.59 (s, 1H); 4.38 (t, 2H, J = 6.6 Hz); 3.97 (s, 3H,); 3.75 (q, 2H, J = 6 Hz); 3.53 (q, 2H, J = 6.9 Hz); 1.94 (s, 3H); 1.25 (t, 3H, J = 7.2 Hz). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 173.49; 167.26; 164.90; 151.70; 148.37; 146.82; 144.09; 135.77; 133.41; 129.85; 126.91; 126.27; 125.26; 118.64; 111.46; 61.59; 55,32; 52.67; 48.72; 45.63; 18.29; 11.22. HRMS-ESI: m/z calcd for C₂₂H₂₄N₄O₆: 440.1696, found: 441.1774(MH⁺). FT-IR (KBr, cm⁻¹): 2954 (v_{st(CH2})); 1727 (v_{st(C=0})); 1602, 1563 (v_{st(C=C})). UV–Vis. (CH₂Cl₂): λ_{max} (ε (mol⁻¹ L cm⁻¹)) = 478 (32 600).

2.3.2. DA3

To a suspension of 2,4,6-trichloro-1,3,5-triazine (0.5 g, 2.74 mmol, 1 equiv.) in THF was added but-2-yn-1-ol (1.5 g, 27.4 mmol, 10 equiv.) and K_2CO_3 (1.2 g, 8.1 mmol, 3 equiv.). The reaction mixture was stirred at 60 °C overnight. Solvent was removed and the crude was dissolved in 80 mL of dichloromethane. Acetic acid and water were added and the two layers separated. The organic one was washed with brine, dried over MgSO₄ to give the desired compound after evaporation of the solvents (1.7 g, 60%).

¹H NMR (300 MHz, CDCl₃), δ (ppm): 5.01 (m, 6H); 1.82 (s, 9H). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 172.9; 73.05; 57.14; 4.12. EI-MS: *m*/*z* calcd for C₁₅H₁₅N₃O₃: 285.11 found: 286.11 (MH⁺). FT-IR (KBr, cm⁻¹): 2242 ($\nu_{st(C=C)}$); 1571 ($\nu_{st(C=C)}$); 1333 ($\nu_{st(C=N)}$). TGA-DSC (10 °C/min): $T_d = 242$ °C.

2.3.3. DA4

In a 10 mL round bottom flask, a solution of **10** (0.25 g, 0.86 mmol, 1 equiv.) in 2 mL of TFA was cooled down to 0 °C. A mixture of sodium nitrite (0.235 mg, 3.44 mmol, 4 equiv.) in 0.5 mL of water was added slowly. The solution was stirred at 0 °C for 15 min. Then, a solution of sodium azide (0.220 mg, 3.44 mmol, 4 equiv.) in 0.5 mL of water was added. The reaction mixture was stirred at 0 °C during 1 h and warmed up to room temperature. Iced water was added to dichloromethane, the two layers were



Scheme 1. Synthesis of EO polymers P1, P2 and P3.

separated and the organic one was washed with brine twice and dried over anhydrous MgSO₄. After filtration and evaporation of solvent, the corresponding compound was dissolved in Et_2O and passed through a short plug of silica. After evaporation the expected product was obtained (0.25 g, 78%).

¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.03 (d, 6H, J = 8.7 Hz); 6.92 (d, 6H, J = 8.7 Hz). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 144.44; 134.51; 125.12; 120.03. EI-MS: m/z calcd for C₁₈H₁₂N₁₀: 368.12 (M), found: 340.13 (M – N₂); 312.14 (M – 2N₂); 284.09 (M – 3N₂). FT-IR (KBr, cm⁻¹): 2101 (v_{st(N3})); 1618 (v_{st(C}=_C)). TGA-DSC (10 °C/min): $T_d = 173$ °C.

2.3.4. General procedure of polymerization

Compound **2** or **3** (3 equiv., generally 600 mg), compound N_3MA or **TMSMA** (7 equiv.) and **AIBN** (2%m equiv.) were dissolved in THF (8 mL) in a dry schlenk tube. The mixture was degassed by three freeze-pump-thaw cycles, and heated for 18 h at 70 °C in the dark. After getting back to room temperature, the mixture was precipitated when poured dropwise in methanol (80 mL). The solid was washed twice and isolated by centrifugation. The solid was dried

for 12 h at room temperature under reduced pressure. A red powder was obtained.

2.3.4.1. **P1** (yield: 60%). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.44 (s, 1H); 8.19 (s, 1H); 7.80 (m, 3H); 6.78 (s, 2H); 4.57 (br s, 4H); 3.73 (m, 10.4H); 1.77 (m, 13H); 0.20 (br s, 24H). SEC (polystyrene): Mn (g/mol): 10 700; PDI = 1.4. FT-IR (KBr, cm⁻¹): 2958 ($\nu_{st(CH2)}$); 2183 (ν_{st} ($c\equiv_{C}$)); 1728 ($\nu_{st(C=0)}$); 1598 ($\nu_{st(C=C)}$). UV–Vis (CH₂Cl₂): λ_{max} (% w) = 480 nm (48). TGA-DSC (10 °C/min): T_g = 93 °C; T_d = 250 °C.

2.3.4.2. **P2** (yield: 72%). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.46 (s, 1H); 8.18 (s, 1H); 7.70 (m, 3H); 6.76 (s, 2H); 4.00 (m, 5H); 3.35 (m, 8.4H); 1.20 (m, 8.5H); 0.99 (m, 14.4H). SEC (polystyrene): Mn (g/mol): 11500; PDI = 2.9. FT-IR (KBr, cm⁻¹): 2958 (v_{st(CH2})); 2108 (v_{st(N3})); 1725 (v_{st(C=0})); 1580 (v_{st(C=C})). UV–Vis (CH₂Cl₂): λ_{max} (% w) = 478 nm (51). TGA-DSC (10 °C/min): $T_g = 90$ °C; $T_d = 244$ °C.

2.3.4.3. **P3** (yield 65%). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.48 (s, 1H); 8.10 (s, 1H); 7.70 (m, 5H); 6.86 (s, 2H); 6.71 (s, 2H); 9.91 (m, 5H); 3.42 (m, 8H); 1.77 (m, 9H); 0.90 (m, 15H). SEC (polystyrene):



Scheme 2. Synthesis of doping agents DA1, DA2, DA3 and DA4.

Mn (g/mol): 5400; PDI = 3.3. FT-IR (KBr, cm⁻¹): 2932 ($v_{st(CH2)}$); 2109 ($v_{st(N3)}$); 1728 (Ester $v_{st(C=0)}$); 1599, 1507 (Amide $v_{st(C=0)}$); 1565 ($v_{st(C=C)}$). UV–Vis (CH₂Cl₂): λ_{max} (%w) = 480 nm (55). TGA-DSC (10 °C/min): $T_g = 110$ °C; $T_d = 254$ °C.

3. Results and discussion

3.1. Synthesis and characterizations

Polymers **P1**, **P2** and **P3** were synthesized following the general route laid out in Scheme 1. Disperse Red 1 (**DR1**) was used as NLO chromophore, for its ease of synthesis and functionalization and because there is a large body of informations about this compound, allowing comparisons with previously reported systems [44,45].

Starting with the previously described monomer **1** [44], esterification of the carboxylic acid group by methanol or amidification by azidoaniline was carried out *via* activation with the 4-(4,6dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (**DMTMM**) in presence of N-methylmorpholine (**NMM**) as a base and led to the desired monomers (**2** and **3**) in quasi quantitative yields (Scheme 1). The **DMTMM** presents several advantages such as a cheap and scalable synthesis, a good storage stability and high reactivity at room temperature and is fully compatible with methacrylate derivatives [48]. The polymers **P1**, **P2** and **P3** were synthesized in 60%, 72% and 65% yield respectively by free-radical copolymerization initiated by azobisisobutyronitrile (AIBN) with a 3/7 molar ratio of the chromophoric monomer and the suitable complementary monomer (5 or 6) (Scheme 1). The number- and weight average molecular weight (Mn) and the polydispersity index (PDI) referenced versus polystyrene standards were determined by size exclusion chromatography (Table 1). The percentage of chromophore incorporated in the polymer was determined by two different methods, namely UV-visible spectrophotometry at 480 nm, corresponding to the charge transfer absorption band of the chromophore and by integration of the surface of the signals in the ¹H NMR spectra. The results of these two analyses are consistent with one another and gave a percentage of chromophore around 48% in weight (29% in mole) for polymer P1, 51% (28% in mole) for P2 and finally 55% (27% in mole) for P3. Interestingly, the molar composition of the chromophores in the polymers is relatively similar to that of the feed (30%). The FT-IR spectra clearly

Table 1									
Specific	properties	of	the	polymers.	T_g	=	glass	transition	temperature;
T_d = decomposition temperature (T_d measured at 5% wt decomposition).									

Entry	Polymer	Mn (g mol ⁻¹)	Mw (g mol ⁻¹)	PDI	T_g (°C)	$T_d(^{\circ}C)$
1	P1	10,700	15,000	1.4	93	250
2	P2	11,500	33,000	2.9	90	244
3	P3	5400	17,800	3.3	110	254

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Table 2 Specific properties of the mixtures (polymer + **DA**). $T_{\rm cross}$ = cross-linking temperature measured at the maximum of the exothermic peak on the DSC trace. $T_{\rm g}$ = glass transition temperature. $T_{\rm d}$ = decomposition temperature determined at 5% weight loss.

Entry	Mixture	Polymer	DA	T_{g} (°C)	$T_{\rm cross}$ (°C)	$T_{\rm d}$ (°C)
1	M1	P1	DA1	93	150	250
2	M2	P2	DA2	90	143	244
3	M3	P2	DA3	90	174	252
4	M4	P1	DA4	93	157	251
5	M5	P3	DA3	110	182	238

revealed the presence of a weak $C \equiv C$ stretching band around 2260 cm⁻¹ for **P1** and the characteristic intense azide stretching band around 2180 cm⁻¹ for **P2** and **P3**.

The three polymers **P1-P3** exhibit high solubility in common polar organic solvents, such as CH₂Cl₂, CHCl₃, THF, DMF and DMSO, and non-saturating concentrations up to 250 g/L in *o*-dichlorobenzene have been reached. However, after cross-linking the solubility of the polymer has been drastically decreased since the polymer film cannot be dissolved upon soaking in a solvent.

In parallel to the polymer preparations, four doping agents were synthesized following the routes depicted in Scheme 2.

It was decided to select **DA** whose preparation could be accomplished with minimum synthetic efforts for scalable preparative process in view of practical applications. The syntheses of **DA1** and **DA2** were described earlier [52,56]. The doping agent **DA3** was prepared in a manner analogous to that for **DA2** in 60% yield by a nucleophilic addition of 2-butyn-1-ol on cyanuric chloride **8** in the presence of K₂CO₃. The synthesis of **DA4** starts with the reduction of commercial *N*,*N*,*N*-tris(4-nitrophenyl)amine **9** with

hydrazine monohydrate in presence of palladium on charcoal [51]. The freshly formed tri-aminophenylamine **10** was engaged in a diazotation reaction with nitrite acid, affording a non-isolated diazonium salt which was directly quenched by sodium azide to give **DA4** with 78% yield. This modified Sandmeyer reaction produced **DA4** in 50% yield over two steps.

To determine the glass transition (T_g), the decomposition (T_d) and the cross-linking temperatures (T_{cross}), polymers **P1**, **P2** and **P3** were first mixed in dichloromethane with the complementary **DA** used in equimolar amount (versus the number of cross-linking groups) and the homogenous solutions were vacuum-evaporated at low temperature. The decomposition temperature (T_d) of the mixture was recorded by thermogravimetric analysis (TGA), while the T_g and the T_{cross} were determined by differential scanning calorimetry (DSC). The results of the analyses are gathered in Table 2 and a typical DSC trace is showed in Fig. 3.

The DSC trace features a first endothermic breakdown around 90 °C attributed to the glass transition temperature (T_g) of the polymer. It should be noted that the **DA** does not significantly modify the T_g of the polymer, inferring that the former displays relatively insignificant plastifying effect. Then, a first exothermic peak at around 140 °C is assigned to the Huisgen cross-linking reaction. A very intense exothermic peak, around 240 °C, is attributed to the decomposition of triazole probably into nitrene [57]. A similar exothermic reaction was previously reported in triazole based polymers by Ergin and coworkers [53]. TGA analysis showed that all polymers exhibit high thermal stability since the decomposition temperatures (T_d), were never below 240 °C (Table 2). Interestingly, the cross-linking temperature of the different mixtures, incorporating polymers **P1** or **P2**, depends on the nature of the doping agent. It is well-accepted and



Fig. 3. Differential scanning calorimetry trace of the mixture M2 (P2+DA2) recorded under nitrogen flow with a scanning rate of 10 °C/min. Blue trace: first scan, red trace: return to RT, green trace second scan. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

experimentally verified that Huisgen cycloaddition reaction is generally faster with electron-withdrawing substituent on the alkyne group or with electron-releasing substituent on the azido function [58]. The fact that T_{cross} for **P1** mixed with **DA4** (157 °C) is a slightly higher than that measured with DA1 (150 °C) could be explained by a higher reactivity and mobility of DA1 relative to DA4. Indeed, large and rigid molecules, like DA4, certainly exhibit reduced mobility than floppy and small molecules. Furthermore, the higher cross-linking temperature measured in M3 (P2 + DA3)compared to that with M2 (P2 + DA2), clearly shows that the methyl group on the propargylic cross-linking group of the doping agent decreases its reactivity by electron-releasing effect and probably by steric hindrance (Table 2). These findings demonstrate that structural and functional modifications on the cross-linking groups can be used to tune the kinetics of this cross-linking reaction.

3.2. Nonlinear optical measurements

Before measuring the nonlinear optical properties, the mixtures were spun cast over glass sheets from filtered solutions of 200 g/L in o-dichlorobenzene, through 0.2 µm PTFE membranes. Films were then heated at 70 °C on a heating plate for 2 h to ensure removal of residual solvent. All the mixtures display high solubility in odichlorobenzene allowing producing homogeneous films with high optical quality (no light scattering) and with thickness up to 4.1 μ m. In order to evaluate the EO activity of the mixtures, the chromophores were poled with a 3.9 kV electric field for 1 h via corona poling at 90 °C. Temperature was then increased to 140 °C for one supplementary hour to induce the cross-linking process. The initial high optical quality of films was conserved in the majority of cases upon poling excepted for the mixture **M1** composed of the polymer P1 with the doping agent DA1. Whatever the different poling conditions used, the systematic degradation of the films of M1 was observed as illustrated in Scanning Electron Microscopy (SEM) images (Fig. 4).

The comparison between **M1** and **M4** poled films clearly reveals that the degradation is bound to the doping agent **DA1**. Although not proved, the surface deformation causing scattering losses, could be explained by a lack of resilience of the very sensitive benzylic groups to the charges in motion generated by the electric field [59,60].

The d_{33} 's harmonic generation (SHG) coefficient of the films **M2–M5** were then measured by second harmonic generation using Maker's fringe techniques with a YAG Laser at 1064 nm and the results are gathered in Table 3. The indexes of refraction at the fundamental wavelength (1064 nm) and the harmonic wavelength (532 nm) have been determined (during the SHG fitting procedure) *circa* 1.5 ± 0.1 and 1.9 ± 0.1 respectively, following the method

Table 3

Second harmonic generation coefficients determined by SHG technique; d: thickness of the film; d_{33} resonance-enhanced coefficients measured at 1064 nm and extrapolated (static value) following the two-states approximation [62,63]; stability: temperature at which 5% of the initial SHG signal is lost.

Entry	Material	d (nm)	d ₃₃ (pm/V) @1064 nm	$\lambda_{\max}(nm)$	d_{33} (pm/V) ∞ nm (static)	Stability (°C)
1	M2	750	45.5	480	6.7	115
2	M3	640	52.3	482	7.5	130
3	M4	1010	42.1	482	6.0	135
4	M5	735	60.0	484	8.2	150
5	PAS1	1220	44.5	476	7.1	137

described in references [54,55,61]. Note the strong dispersion of the optical index at 532 nm which is close to the absorption maximum for all materials.

The SHG coefficients (d_{33}) of the different materials are relatively similar to one another and within the same range than previously measured with **DR1**-grafted methacrylate polymers with similar chromophore loading such as **PAS1** [30,44,45]. Interestingly, mixture **M5**, which contains cross-linkable chromophores, displays a much higher electro-optic coefficient certainly testifying of a higher poling efficiency. The dynamic thermal stabilities of poled materials were investigated by depoling experiments, in which decay of the SHG signal was monitored as a function of the temperature (Fig. 5).

Several interesting conclusions can be drawn from these depoling experiments. First, the cross-linking reaction systematically enhances the stability of the NLO activity of all the mixtures relative to the uncross-linked polymer (P1 or P2). For a poled only polymer (P1 or P2), the chromophores start to relax at around 75 °C, which is close to T_g in agreement with what is generally observed with other polymers, while cross-linked mixtures are stable at least until 115 °C (Table 3). Second, the mixtures M3 and M4 display a similar NLO stability than that measured with PAS1 which corresponds to the most stable nonlinear optical polymer synthesized with our initial approach (system A, Fig. 2). This result indicates that the combination of simpler polymers, such as P1 or P2, with a doping agent can lead to satisfying nonlinear optical stability, which is in the same range as that obtained with a more complex polymer (such as PAS1) with potential shelf-life instability. Finally polymer P3, combined with DA3, exhibits the highest SHG stability among all the Huisgen-cross-linked based materials we have tested so far [45]. Although, P3 still requires the double functionalization of the chromophore, it most probably exhibits longer shelf-life stability since the two complementary cross-linking groups are not present in the polymer during storage and therefore represents a significant improvement over PAS1. Although the NLO stability of the above materials is not the highest



Fig. 4. Scanning Electron Microscopy (SEM) images of an M1 film before and after poling.



Fig. 5. Thermal stability of the studied matrices upon heating an initially poled film at a rate of 2 $^\circ\text{C}/\text{min}.$

ever reported in the field of electro-optic organic materials [10], the Huisgen cross-linking reaction presented herein represents a promising strategy since it enables to maintain the chromophore orientation at a higher temperature than many reported cross-linked NLO polymers [26,29,64,65] and as important the thermal stability of these polymers lies above 85 °C which is the lowest threshold temperature for practical applications [10].

4. Conclusions

A new implementation of copper-free thermal Huisgen cycloaddition, as cross-linkable reaction for quadratic nonlinear optical polymers, has been developed. It is based on the introduction of the two complementary cross-linkable groups (azide and alkyne) in two different materials, mixed just before the preparation of the film. The new system consists in a polymer containing the chromophore (**DR1**) and a single cross-linking group (azide or alkyne) as pendant groups and a second material, corresponding to the doping agent, containing several units of the complementary crosslinkable group. In this study we have shown that mixtures of the above mentioned polymer and a suitable doping agent are miscible in the most commonly used organic solvents and allow to produce homogeneous and thick films with good optical quality. Secondly, this new strategy probably overcomes the potentially short shelfstorage lifetime, since the cross-linkable groups are separated until the utilization of the polymers. Second-harmonic generation measurements demonstrate, first that the doping of such polymers with a suitable polyazide or polyalkyne reagent does not alter the orientation of the chromophores, since the SHG coefficients of the mixtures M1-M5 (d_{33} up to 60 pm/V) were in the same range as that reported for DR1-based polymers. Secondly, depoling experiments revealed that the stability of the chromophore orientation in these mixtures is not only enhanced compared to uncross-linked polymer, but is also comparable to that obtained with the best cross-linkable polymer PAS1 described in our previous studies. This latter result demonstrates that the derivatization of the chromophore with a cross-linking group is not an absolute requirement for this copper-free Huisgen cross-linking reaction to be used. This feature broadens the scope and versatility of this new cross-linking methodology and most probably widens the possibilities offered by copper-free Huisgen cross-linking reaction in the field of electrooptic materials. Finally, when a cross-linking group (azide) is positioned on both the chromophore and on the polymer backbone, the highest electro-optic stability was recorded (150 °C). This result tends to indicate that the mixture of two complementary materials is certainly more efficient to raise the glass transition temperature of a polymer by Huisgen reaction than when the two cross-linking groups are grafted on a single polymer. The next step is to apply this fully operational strategy to chromophores having higher second hyperpolarizability coefficient than **DR1**, in order to prepare stable polymers with high EO coefficients.

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