A new crosslinkable system based on thermal Huisgen reaction to enhance the stability of electro-optic polymers[†]

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The thermal Huisgen cycloaddition reaction is a new and efficient process to crosslink electro-optic polymers, since it leads to an effective increase of the thermal alignment stability of the NLO chromophores.

One of the major obstacles limiting the practical applications of polymer-based nonlinear optical (NLO) materials for optical telecommunications is the relatively low temporal and thermal stability of the non-centrosymmetric alignment of the chromophores. This limitation has been somewhat solved by the advent of high glass transition temperature (T_{a}) polymers such as polyimides, especially when the NLO chromophores are chemically bonded to the polymer backbones.¹ However, the chromophores can be prone to decomposition or sublimation when the materials are subjected to the high temperatures endured by the polymer during the preparation or the poling. An alternative strategy to enhance the stability of NLO activity is to focus on retarding the mobility of the polymer segments via crosslinking. Crosslinking reactions have been performed either thermally or photochemically, and stabilization of dipole alignment has been achieved in both approaches.² In this context, the group of Jen and coworkers has reported the use of Diels-Alder reaction to thermally crosslink several electro-optic organic materials, and a marked improvement of the stability of the chromophore orientation after poling was observed.^{3,4} However, only a relatively small number of thermal crosslinking reactions have been reported in the field of organic second order nonlinear materials,³⁻⁶ because the suitable system should fulfil three distinct properties which are difficult to bring together. First of all, the crosslinkable groups must remain inert during the polymerization step and the storage in order to avoid the premature crosslinking of the material. Second, the crosslinking temperature (T_c) has to be above or close to the glass transition temperature (T_g) to ensure an efficient poling of the chromophores before the crosslinking reaction starts; and finally the crosslinking reaction has to be relatively fast at $T_{\rm c}$ in order

to limit the impact of side reactions, such as chromophore degradation. $\!\!\!\!^4$

In previous work,⁷ we have extensively studied a methacrylatebased crosslinkable polymer named PIII reported by Boutevin *et al.*,⁶ composed of a Disperse Red 1 (DR1) derivative functionalized with a carboxylic acid function, which crosslinked with a pendant epoxy group as side chain (Fig. 1). Although this polymer displays significantly appealing features such as easy, large-scale synthesis and relatively satisfying temporal stability (up to 100 °C), several deficiencies such as a limited storage period at room temperature, because of premature crosslinking, hampered the use of this material. Besides, the largest achievable thickness of a monolayer film with PIII was only 1.3 µm by spin coating. Moreover, the appearance of hydroxyl groups upon crosslinking raises the absorbance at 1.5 µm, since the second harmonic stretching of the latter is located at this wavelength.⁸

In this contribution, we report a new crosslinking system based on the implementation of the thermal Huisgen reaction, which proved particularly efficient to lock the chromophore orientation after the poling step. Copper-catalyzed Huisgen 1,3-dipolar cycloaddition is a very popular reaction, referred to as a click reaction, and has been used extensively to graft molecular units on polymers, on surfaces or simply to synthesize new compounds.⁹ Recently, it has been successfully used to attach site isolation groups on NLO chromophores to limit their propensity to form intermolecular ferroelectric associations,¹⁰ but to the best of our knowledge the simple thermal version of the Huisgen reaction has never been used as a crosslinking system, particularly with organic electro-optic materials. The absence of any metalbased compound to catalyse the crosslinking process was a requirement for such an application, since it would first decrease the crosslinking temperature much below $T_{\rm g}$, second it would enhance the electric conductivity when the film is submitted to the



Fig. 1 Structures of the NLO polymers described in this study.

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high poling voltage and finally it could induce phase segregation. Copper-free crosslinking of difluorinated cyclooctyne derivatives with azides was reported for *in vivo* imaging or photodegradable polymers, but this activated alkyne cannot be used to crosslink NLO materials because it would react far below the T_g of the polymer thus preventing the chromophore orientation.¹¹

To investigate the potential utility of the thermal Huisgen reaction as a crosslinking process for electro-optic polymers, we prepared two new crosslinkable materials (PAS1 and PAS2), analogous to the known PIII polymer (Fig. 1).6 These polymers were synthesized by radical copolymerization of three methacrylate monomers: a monomer bearing an alkyne group (TMSMA), the monomer 5 incorporating the DR1-type chromophore at the same concentration as that in PIII (30 mol%), but functionalized by an azido group, and methyl methacrylate (MMA) (Scheme 1). The alkyne monomer was protected by a trimethylsilyl (TMS) group to avoid the anticipated side reactions of terminal alkynes with the free radicals formed during the polymerization reaction.¹² To minimize the production cost, we also studied how the presence of MMA as co-monomer impacts the properties of the final polymer. Therefore, PAS1 and PAS2 were prepared in the presence and in the absence of MMA, respectively (Scheme 1).

The synthesis of the new polymers is relatively straightforward and can be performed on a 10 g scale or even more in a few days owing to its high efficiency and its technical simplicity. Firstly, chromophore 3 was prepared by a diazocoupling reaction of 4-amino-3-nitrobenzoic acid 1 with compound **2** under acidic conditions in 67% yield.¹³ Then the amidification of the carboxylic acid function borne by compound 3 was carried out in the presence of 4-azidoaniline hydrochloride 4. N-methylmorpholine (NMM) and dimethoxytriazine-N-methylmorpholine (DMTMM)¹⁴ as condensing agent to lead to the NLO chromophore 5 in quantitative yield. Finally, the PAS1 and PAS2 polymers were synthesized in about 75% yield by free-radical copolymerization of the above monomers using AIBN as an initiator (Scheme 1). The polymers PAS1 and PAS2 exhibit high solubility in common polar organic solvents, such as CH₂Cl₂, CHCl₃, THF, DMF and DMSO, and non saturating concentration of 250 g L^{-1} could be obtained in o-dichlorobenzene. The number average molecular weight (M_n) and the polydispersity index (PDI) were



Scheme 1 Synthetic route for the polymers PAS1 and PAS2.

measured by size exclusion chromatography calibrated with polystyrene standards and the data are collected in Table 1. The chromophore loading levels are, respectively, 47 and 42 wt% in PAS1 and PAS2. From differential scanning calorimetry (DSC) analysis, the glass transition temperatures (T_{o}) of PAS1 and PAS2 were measured at 88 and 89 °C. respectively (see Fig. 1 SI[†]). Moreover, the DSC trace exhibits a first broad exothermic peak assigned to Huisgen crosslinking reaction at a temperature around 160 °C, followed by a second higher exothermic peak around 290 °C attributed to the classical decomposition of triazoles into nitrenes (Table 1).¹⁵ Besides, thermal gravimetric analyses showed that PAS1 and PAS2 polymers display a good thermal stability since the decomposition temperatures (T_d) are 295 and 285 °C, respectively. These observations indicate that the presence of MMA monomer does not influence to a great extent the thermal properties of these new materials and therefore MMA can be used as a co-monomer to decrease the amount of TMSMA.

A second advantage of this crosslinking reaction is the possibility to follow and to quantify the extent of crosslinking by monitoring the decrease in intensity of the azide absorption band around 2100 cm⁻¹ by FTIR spectroscopy. As shown in Fig. 2, the crosslinking of a PAS1 film is complete in less than one hour at 150 °C. Finally, films with good optical quality and satisfying thicknesses (up to 1.8 μ m) were prepared by spin coating solutions of the polymers PAS1 and PAS2 in *o*-dichlorobenzene, evidencing the good filmability of these new polymers. Wire poling under high electric field (3.9 kV) was carried out at 90 °C for one hour for each material. Then, the films were heated at 150 °C for an additional hour to perform the Huisgen crosslinking reaction and were rapidly cooled to room temperature in order to freeze the orientation of the chromophores.

The obtained poled/cured polymer films were very tough and gained good solvent resistance after crosslinking. The quantitative crosslinking of the films was confirmed by the disappearance of azide absorption bands (around 2100 cm⁻¹) in FTIR spectra (Fig. 2).

The d_{33} coefficients of these films were measured at 1064 nm by second harmonic generation (SHG). Values of 56 and 50 pm V⁻¹ were determined for PAS1 and PAS2, respectively. Unsurprisingly, these values are similar to the d_{33} value of PIII polymer (60 pm V⁻¹) since a similar chromophore was used at the same concentration (30 mol%). Thermal stability of the electro-optic activity of the polymers was investigated by depoling experiments, in which the real time decay of the SHG signal was monitored for non crosslinked PAS1, crosslinked PAS1 and PAS2 and the reference polymer PIII as a function of the temperature (Fig. 3).

Table 1 Specific properties of the polymers: glass transition temperature (T_g) , crosslinking temperature (T_c) , decomposition temperature (T_d) , film thickness (d), and d_{33} measured at 1064 nm

	${M_{ m n}}^a/{ m g\ mol^{-1}}$	${M_{ m w}}^a/{ m g\ mol^{-1}}$	PDI ^a	$T_{\rm g}/^{\circ}{\rm C}$	$T_{\rm c}/^{\circ}{\rm C}$	$T_d^{\ b}/^\circ C$	d/µm	$\overset{d_{33}/\mathrm{pm}}{\mathrm{V}^{-1}}$
PAS1	7500	13 500	1.8	88	160	295	1.8	56
PAS2	7100	13 500	1.9	89	160	285	1.6	50
PIII	5700	9600	1.69	65	150	270	1.3	60

^{*a*} Determined by size exclusion chromatography (SEC) calibrated with polystyrene standards. ^{*b*} Measured at 5 wt.% decomposition.



Fig. 2 Evolution of the intensity of the stretching band of azide in PAS1 film as a function of the heating time at 150 °C.



Fig. 3 Thermal stability of electro-optic activity of polymers PAS1 and PAS2 upon heating a film, initially poled at a rate of $2 \,^{\circ}C \min^{-1}$ in the air.

These results clearly show that this new crosslinking process increases the stability of the electro-optic activity of the polymers. When the polymer is simply poled but not crosslinked, the chromophores start to relax at 80 °C (circles), while NLO properties are maintained up to 137 °C after crosslinking (squares and triangles). In other words, the present crosslinking system leads to a gain of EO stability of ca. 60 °C for the PAS1 and PAS2 materials and represents a real improvement compared to the previously known polymer PIII (diamonds), in which the NLO stability was kept only until 105 °C. The temporal stability of PIII was studied and proved to be satisfactory for several days at 85 °C, therefore it is reasonable to anticipate that PAS1 and PAS2 will be as stable and probably even more so.¹⁶ Finally, it should be pointed out that no significant stability difference is noted for the polymer incorporating MMA monomer (PAS1 vs. PAS2). The production cost of these new materials can thus be substantially lowered, without impairing their NLO properties.

In conclusion, we present the first example of crosslinkable EO polymers based on the thermal Huisgen reaction. The polymers can be prepared on a large scale (>10 g) due to a facile synthetic procedure and they exhibit good film-forming properties. After the poling process, a smart control of the absorption band of azide groups, monitored by FTIR, can be used to follow the crosslinking process. The resulting materials exhibit very satisfying thermal alignment stability, the d_{33} coefficient remaining constant up to about 140 °C. These results demonstrate that the thermal Huisgen 1,3-dipolar azide–alkyne "click" reaction can be used successfully to ensure the efficient crosslinking of NLO polymers. In this work, a derivative of the well-known DR1 chromophore, for which there

exists a large body of information, was used to give a proof of concept for this new crosslinking process, but certainly without any claim to compete with the best known electro-optic materials in term of d_{33} . The extension of this concept to a chromophore exhibiting a larger quadratic hyperpolarizability than DR1 could lead to polymers which combine high r_{33} coefficients along with good electro-optic stability. Furthermore, this version of the Huisgen reaction will certainly also be useful for other applications where crosslinking is required, for example light emitting diode technology or organic field effect transistors.¹⁷

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