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RESEARCH ARTICLE

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Preparation of a New Electro-optic Polymer Cross-Linkable via Copper-Free Thermal Huisgen Cyclo-Addition and Fabrication of Optical Waveguides by Reactive Ion Etching

Clément Cabanetos,[†] Hind Mahé,[‡] Errol Blart,[†] Yann Pellegrin,[†] Véronique Montembault,[§] Laurent Fontaine,[*,§] Frédéric Adamietz,[⊥] Vincent Rodriguez,[*,⊥] Dominique Bosc,[*,‡] and Fabrice Odobel[*,†]

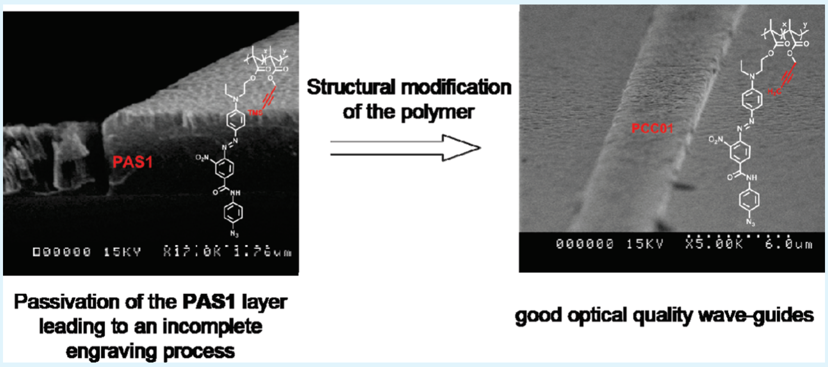
[†]Université de Nantes, CNRS, Chimie et Interdisciplinarité: Synthèse, Analyse, Modélisation (CEISAM), UMR CNRS n° 6230, 2, rue de la Houssinière – BP 92208 – 44322 Nantes Cedex 3, France.

[‡]Laboratoire Foton, UMR CNRS 6082, CCLO, ENSSAT, BP 80518, 22305 Lannion cedex, France.

[§]LCOM-Chimie des Polymères, UCO2M, UMR CNRS 6011, Université du Maine, Avenue O. Messiaen, 72085 Le Mans Cedex 9, France.

[⊥]Université de Bordeaux, Institut des Sciences Moléculaires, UMR CNRS 5255, 351 cours de la Libération, 33405 Talence Cedex, France.

ABSTRACT:



High-quality trails of ridge waveguides were successfully fabricated using a new cross-linkable polymer (**PCC01**) by UV photolithography followed by Reactive-Ion Etching (RIE) process. The cross-linking reaction of **PCC01** is based on the copper-free Huisgen cyclo-addition between an azide and an acetylene group. The new cross-linkable polymer (**PCC01**) consists of a structural modification of the previously described materials (Scarpaci *et al. Polym. Chem.* **2011**, *2*, 157), because the ethynyl group is functionalized by a methyl group instead of the TMS protecting group. This feature prevents the formation of silica (SiO_2) generated by trimethylsilyl groups and which was stopping the engraving process before completion. Herein, we describe the synthesis, the NLO characterizations, and the fabrication of a high-quality ridge waveguide with **PCC01**. The new cross-linkable polymer **PCC01** not only solves the problems encountered with our previously described polymers, but also presents an enhancement of the electro-optic stability, because d_{33} coefficients up to 30 pm/V stable at 150 °C were recorded.

KEYWORDS: nonlinear optic, cross-linking, Huisgen reaction, electro-optic, polymer, optical waveguide

INTRODUCTION

Organic nonlinear optical (NLO) materials have continuously drawn great interest because of their numerous advantages over conventional inorganic NLO crystals ($LiNbO_3$), such as shorter response times, larger bandwidths, higher electro-optic (EO) coefficients, and high processability. Accordingly, polymeric materials are attractive candidates as active components for the fabrication of electro-optic devices.[1,2] An organic NLO material is generally composed of push–pull organic chromophores, in which a π-conjugated bridge is end-capped by a donor and an acceptor moieties, hosted in the polymeric matrix.[1,3,4] Moreover, chromophores need to be oriented (poled) by applying an external electric field in order to generate a macroscopically noncentrosymmetric material.[1,5] However, thermal and temporal relaxation of the chromophores in the polymer, due to their high ground-state dipole moment, is the major obstacle for practical applications because it leads to a decay of the bulk NLO activity.[3,6] Polymeric matrixes with high glass-transition temperature (T_g) were mainly selected in guest–host systems to prevent the chromophores relaxation.[7] Unfortunately, the

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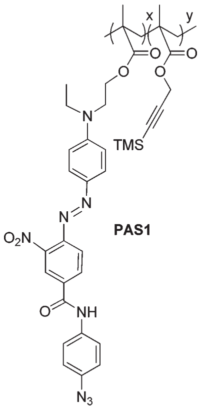


Figure 1. Structure of a previously reported cross-linkable polymer (**PAS1**).[15]

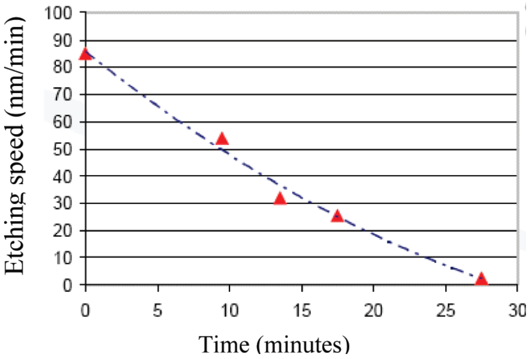


Figure 2. RIE rate on the **PAS1** layer as a function of time.

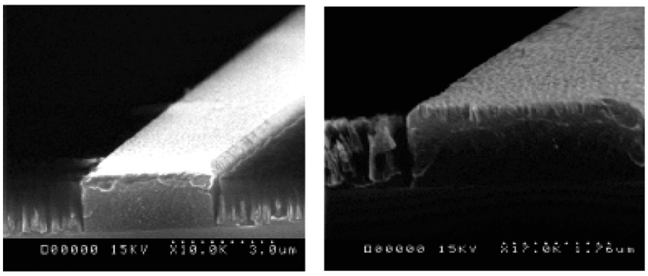


Figure 3. Scanning electron microscope (SEM) pictures of a **PAS1** ridge waveguide.

efficiency of the poling process depends on the T_g of the polymeric medium and it decreases as the temperature is raised because of the thermal randomization of the chromophores.[8] Moreover, the necessary high T_g for stability requires that all the waveguide constituent layers withstand the poling temperature. Unfortunately, because the latter is high, several defaults usually occur. Another very efficient strategy to maintain the long term chromophore orientation is to develop cross-linkable polymers, which consist in freezing the chromophores organization after the poling, by forming new covalent bonds between the polymer chains or between the chromophore and the polymer chains. 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 transition glass temperature (T_g), but they must react quickly just above the Tg. Second, they must be compatible with the polymerization reaction so that 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 cyclo-addition,[9,10] the cyclodimerization of trifluorovinylether,[11] the thermal decomposition of cyclobutanone[12] and the epoxide opening with a carboxylic acid.[13] However, some of them are not fully satisfying. For example, the Diels—Alder cyclo-addition is a reversible reaction and the dienophile tends to react with the double bonds of the chromophore.[3,10] The shelf lifetime 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 temperatures, 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.[14] Although these materials exhibit exceptional stabilities they are expensive to fabricate and/or these strategies are not fully compatible with industrial developments.

In recent years, we have designed a number of cross-linkable systems based on the use of the copper-free thermal Huisgen 1,3-dipolar cyclo-addition, occurring between azide and acetylenic groups and yielding a mixture of 1,4 and 1,5 triazole isomers.[15,16] In our previous systems, polymers derivatized with NLO chromophores were bearing complementary cross-linkable functions on both the latter and the polymer backbone. The structure of a typical electro-optic polymer that is cross-linkable upon copper-free thermal Huisgen 1,3-dipolar cyclo-addition is depicted in Figure 1 (**PAS1**).[15]

First of all, the **PAS1** displays high solubility in the most commonly used solvents allowing to produce films with high optical quality (no light scattering) and with thicknesses up to 2.7 μm. Moreover, the synthesis of **PAS1** allows to scale up quantities to hundreds of grams within a week of benchwork. These features represent practical advantages for a practical application. Besides, second-order nonlinear optical coefficients (d_{33}) were measured at 1064 nm by second harmonic generation (SHG), giving promising result for that kind of chromophore, because 44 pm/V have been reached. Finally, the dynamic thermal stabilities of poled thin films were investigated by depoling experiments and clearly revealed that the cross-linking reaction enhances the stability of the electro-optic activity (135 °C). In consideration of these results, the **PAS1** represented a promising material for the fabrication of wave-guides in view of its incorporation into EO devices such as the Mach—Zehnder electro-optic modulator. Therefore, ridge optical waveguides were prepared with polymer **PAS1** using UV photolithography followed by Reactive-Ion Etching (RIE) process.[17,18] Unfortunately, two major problems were encountered. The etch rate during the RIE is relatively slow because of the formation of silica (SiO_2) generated by trimethylsilyl groups present in the polymer (Figure 2).[19] Second, the silica film stops the engraving process before completion (Figure 3). The consequences on the ridge waveguide quality are shown in Figure 3. These pictures clearly reveal an etching resistance of the **PAS1** layer leading to an incomplete engraving process.

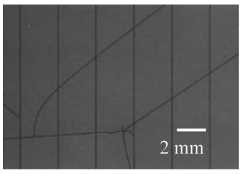


Figure 4. Picture of a **PAS1** film after several days of storage showing the appearance of cracks after the RIE process.

Moreover, after several days of storage, we can observe the appearance of cracks all over the PAS1 film (Figure 4). The TMS group probably induces cracking of the film and thereby affects the optical quality of the waveguide.

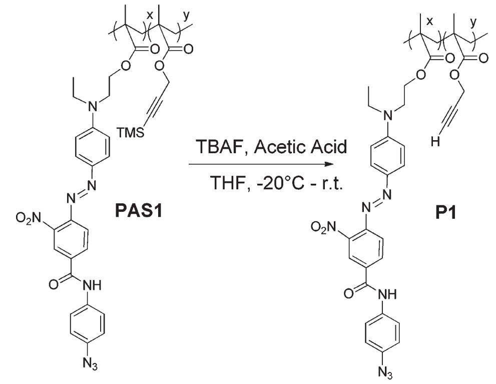
A previously reported kinetic study indicated that it was not necessary to cleave the TMS protecting group on the polymer prior its utilization, according to the fast cross-linking rate measured with TMS functionalized alkyne which was very similar to terminal free alkyne.[16] Solutions must be found to avoid the above-mentioned problems. In this paper, we report a satisfying solution which consists in the replacement of the TMS protecting group by a methyl group. We describe herein the synthesis, the characterizations and first fabrication of a high-quality ridge waveguide with this new class of cross-linkable polymers that are based on copper-free Huisgen cyclo-addition. We also show that the new polymer **PCC01** not only solves the above-mentioned problems for practical application, but also presents an enhancement of the electro-optic stability.

■ EXPERIMENTAL SECTION

Materials. Compounds **2**[16] and **CH$_3$MA**[20] were prepared according to the methods described in the literature.

Methods. NMR spectra were recorded using a Bruker 300 MHz instrument (ARX-300, Bruker) with tetramethylsilane (TMS) as the internal standard and CDCl$_3$ as the solvent. The IR spectra were recorded using a FTIR 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 μm guard column) followed by two columns (Polymer Laboratories (PL), 2 PL gel 5 μm MIXED-D columns), with a SpectraSYSTEM RI-150 detector. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1 mL/min at 35 °C. Polystyrene standards (580—483 × 10^3 g mol^{-1}) were used to calibrate the SEC. High-resolution electro-spray mass spectra (HR-ESMS) were collected in positive mode on a 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.[21] 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 μJ; repetition rate 50 Hz; pulse width 15 ns). The laser beam initially polarized out of the plane of incidence (s) was passed through a combination of a rotating half waveplate and a fixed quarter waveplate (vertical fast axis) to address all possible polarizations, from linear, over elliptical to circular polarization. The second-harmonic intensity was then recorded vs the rotation angle of the half waveplate (called hereafter ψ), and the resulting continuous polarization scans ψ-p and ψ-s together with the usual p-p and s-p Maker fringes patterns can be used to obtain more accurately the magnitude of nonlinear susceptibilities.[22] 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 ($\alpha_{\perp}$) 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 pm/V at 1064 nm. Further details about the general procedure to determine the linear and nonlinear optical constants can be found elsewhere.[23]

Scheme 1. Synthesis of polymer P1



Preparation of Polymer PCC01. Compound **2** (3 equiv., generally 300 mg), compound **CH$_3$MA** (7 equiv.) and AIBN (10% molar) were dissolved in THF (10 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 rt under reduced pressure. A red powder was obtained with 84% yield.

^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 7.92 (m, 20 H); 6.83 (m, 12H); 4.52 (b s, 13 H); 4.10 (b s, 3H); 3.54 (m, 11H); 1.82 (m, 55H); 1.03 (m, 35H). SEC (polystyrene): Mn (g/mol): 6700; PDI = 2.12. FT-IR (KBr, cm^{-1}): 2958 ($\nu_{st(CH2)}$); 2260 ($\nu_{st(C\equiv C)}$); 2114 ($\nu_{st(N3)}$); 1728 (Ester $\nu_{st(C=O)}$); 1599, 1507 (Amide $\nu_{st(C=O)}$). 1555 ($\nu_{st(C=C)}$) UV — Vis (CH$_2$Cl$_2$): λ_{max} (%w) = 480 nm (62). TGA-DSC (10 °C/min): Tg = 100 °C; Tc= 173 °C; Td = 266 °C.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. The fastest and most convenient route to obtain a TMS free polymer consists in the cleavage of the latter from a freshly synthesized batch of **PAS1**. The deprotection of the trimethylsilyl group was performed with tetrabutylammonium fluoride (TBAF) following the conditions described by Haddleton and co-workers (Scheme 1).[24]

Unfortunately, the obtained dark red powder was insoluble in common polar organic solvents, preventing thus any use and characterizations of the new polymer **P1**. This result clearly shows that the steric hindrance, generated by the TMS protecting group, is a crucial parameter for the solubility, because the Fourier-Transform Infra-Red spectrum of **P1** revealed that the azido band, around 2110 cm^{-1}, was still present and very intense

Scheme 2. Synthesis of PCC01

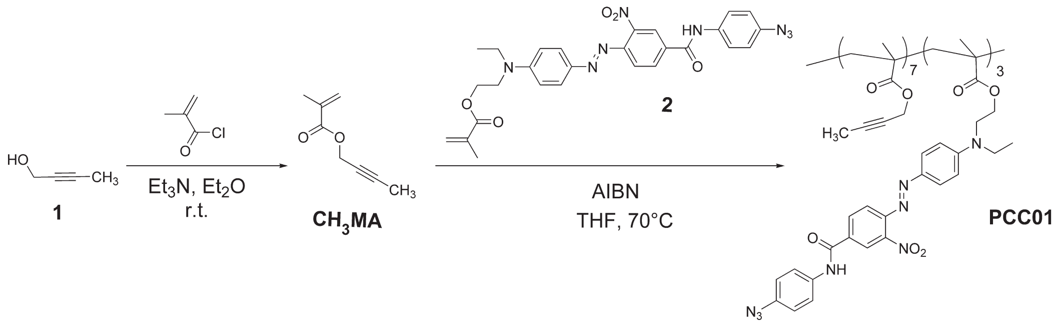


Table 1. Molar Fractions of Each Monomer in the Copolymer PCC01 as a Function of the Feed Ratio

feeding molar ratio of the monomers		molar fraction in the copolymer[a]					
2	**CH_3MA**	**2**	**CH_3MA**	conversion[b] (%)	reaction time (min)	ξ[c]	η[c]
0.2	0.8	0.16	0.84	3.5	10	0.89	0.95
0.3	0.7	0.24	0.76	4	10	0.82	0.77
0.4	0.6	0.29	0.71	5.5	10	0.72	0.69
0.5	0.5	0.34	0.66	8.1	10	0.59	0.55
0.6	0.4	0.38	0.62	10	10	0.43	0.40
0.7	0.3	0.39	0.61	5	5	0.24	0.32
0.8	0.2	0.41	0.59	7	5	0.11	0.19

[a] Average value of that determined by UV−visible spectrophotometry and by ^{1}H NMR. [b] On the basis of the yield determined with the mass of polymer obtained after precipitation in methanol. [c] η, ξ: Kelen-Tüdos parameters [26]

accounting thus that the cross-linking reaction has not occurred during the deprotection reaction. It certainly reduces the aggregation of the chromophores by preventing their close contact. The challenge was to synthesize a new acetylenic monomer functionalized with a new protecting group in few steps using the cheapest starting material for potential industrial applications. The presence of a substituent on the propargylic methacrylate derivative is a prerequisite because the radical polymerization is not compatible with terminal alkyne.[25] Therefore, the desired methyl propargylic methacrylate (**CH_3MA**) monomer was prepared in 78% yield by esterification of methacryloyl chloride by the commercially available but-2-yn-1-ol **1** (Scheme 2).[20]

The polymer **PCC01** was synthesized in 84% yield by free-radical copolymerization initiated by azobisisobutyronitrile (**AIBN**) with a 3/7 molar mixture of the chromophoric monomer **2** and the previously prepared **CH_3MA** monomer (Scheme 2). 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 integrating the surface of the signals in the ^{1}H NMR spectra. The results of these two analyses are consistent with one another and gave a percentage of chromophore around 62% in weight. The FTIR spectra clearly revealed the presence of a weak C≡C stretching band at 2260 cm^{-1} and the intense azide stretching band at 2114 cm^{-1}. The number-average molecular weight (M_n) and the polydispersity index (PDI) estimated around 6700 g/mol and 2.12 respectively referenced versus polystyrene standards were determined by size exclusion chromatography and are in the same range as those measured for the **PAS1**.[15]

The placement of the chromophores relative to the propargylic motifs (statistic or block copolymers) was previously reported for the **PAS1** by the determination of the monomer reactivity ratios.[16] A similar study was performed with **PCC01**. Hence, different ratios of the monomers **2** (r_2) and **CH_3MA** (r_{CH3MA}) were polymerized in the same conditions as for the preparation of the polymer, but the reaction was stopped at low conversion (below 10%). The composition of the resulting polymers was determined by UV−visible spectrophotometry (Table 1).

The experimental results were analyzed with the methods of Fineman−Ross[27] and Kelen −Tüdos[26] to calculate the monomer reactivity ratios. Both methods give the same reactivity ratio values, which are: $r_{CH3MA} = 1.030 \pm 0{,}001$ and $r_2 = 0.021 \pm 0.001$.

$r_{CH3MA} > r_2$ indicates that the radical of **CH_3MA** reacts faster with a **CH_3MA** monomer than with **2**. These results are the opposite of those obtained for the **PAS1** ($r_2 = 1.041 \pm 0.001$ and $r_{TMSMA} = 0.009 \pm 0.001$). Introduction of silyl group into various methacrylate monomers was previously found to dramatically modify the reactivity ratios of methacrylates.[28] This can be related to electronegativity of silicon and to steric effect of the trimethylsilyl group according to Durand and co-workers. Taking into account these values of the reactivity indexes and the ratio of the two monomers, the monomer distribution can be simulated.[29] Because the concentration of the chromophores in both polymers is much lower than that of propargyl methacrylate (3/7), the simulation indicates that about 1.4 chromophores are neighbored with 1 propargyl unit for the **PAS1**, whereas 1 chromophore is statistically surrounded by 6 propargyl units for the **PCC01** at similar loadings. Therefore, in the new polymer

Table 2. Specific Properties of the Polymers[a]

entry	polymer	T_g (°C)	T_c (°C)	T_d (°C)	d (μm)	d_{33} (pm/V)	stability (°C)[b]
1	**PCC01**	100	173	266	0.9	42 ± 5	150
2	**PAS1**	89	160	263	1.2	50 ± 5	135

[a] T_g = glass transition temperature; T_c = cross-linking temperature; T_d = decomposition temperature (T_d measured at 5 wt % decomposition); d = thickness of the film; d_{33} coefficients measured at 1064 nm. [b] Temperature at which the SHG signal dropped by 5% of its initial value.

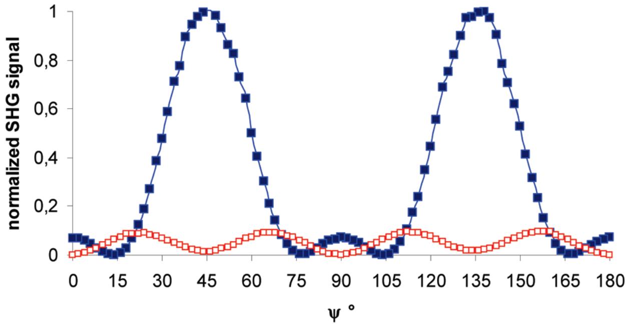


Figure 5. Experimental normalized transmitted Maker fringe patterns of polymer **PCC01** using continuous polarization scan ψ−p (blue) and ψ−s (red) obtained at an incident angle of 60°.

PCC01, the chromophores are more isolated from themselves, limiting their propensity to aggregation.

The polymer **PCC01** was studied by thermogravimetric analysis (TGA) to determine the decomposition temperature (T_d) and by differential scanning calorimetry (DSC) to ascertain the glass transition temperature (T_g) and the cross-linking temperature (T_c) (Table 2).

Interestingly, we observed that the cross-linking temperature (Tc) depends on the nature of the substituent on the alkyne. The inductive effect provided by the electron donor methyl group decreases the reactivity of functionalized terminal alkynes with azide more than the steric hindrance generated by the TMS, yielding a higher Tc for **PCC01** than that of **PAS1**. This is in line with a previous study.[16]

Before measuring its second-order NLO response, the polymer **PCC01** was spun cast over glass substrates from non saturated filtered solutions of 250 g/L in *o*-dichlorobenzene, through 0.2 μm PTFE membranes. Films were then heated at 60 °C on a heating plate for 1 h to ensure removal of all residual solvent. Homogenous films with very good optical quality (no light scattering) were prepared and thicknesses up to 3.2 μm were reached. In order to evaluate the EO activity of the polymer **PCC01**, the same conditions as those for **PAS1** were used, first wire poling under high electric field (3.8 kV) was performed under air atmosphere at 90 °C, close to its T_g and very below T_c, for 1 h. Second, the temperature was then increased up to 150 °C for one supplementary hour to induce the cross-linking of the system, while still applying the electric field. The d_{33} second-order coefficient were measured with a YAG Laser at 1064 nm by second harmonic generation (SHG) using Maker's fringe techniques (Figure 5), and results are gathered in Table 2. The SHG coefficient of the polymer **PCC01** (42 pm/V) is equivalent to that measured in previously studied on **PAS1** (50 pm/V). The dynamic thermal stability of poled **PCC01** sample was, then, investigated by monitoring the decay of the SHG signal as a function of the temperature (Figure 5).

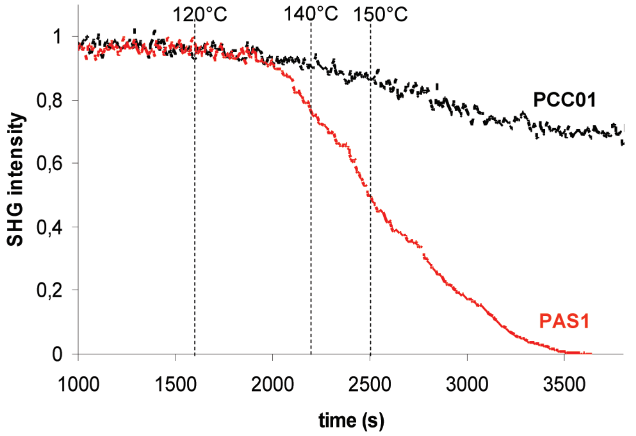


Figure 6. Thermal stability of **PCC01** and PAS1 films upon heating an initially poled and cross-linked film at a rate of 2 °C/min.

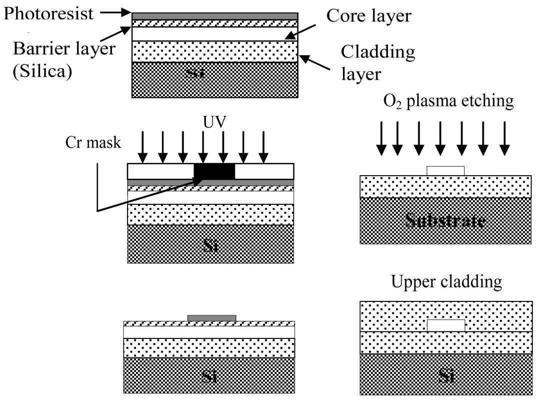


Figure 7. General scheme of the process steps of fabrication of an optical waveguide.

The depoling study clearly shows that the overall macroscopic SHG stability of **PCC01** was increased, when compared to **PAS1** (Figure 6). Besides, it is important to note that 70% of the initial SHG signal, corresponding to a value of 30 pm/V, was maintained at 150 °C (Figure 6). The enhanced stability can be explained by the isolation of chromophoric units leading to a higher cross-linking efficiency since higher local concentration of alkyne around azido derivatized DR1. In conclusion, the **PCC01** preserves all of the advantages of the **PAS1** and exhibits even higher thermal stability of the NLO activity.

Taking into account these encouraging results, we started the preparation of ridge wave-guides with **PCC01** using the previously mentioned techniques over silicon substrate (Figure 7).[18] Gratifyingly, the etch rate remained constant and equal to 140 nm/min, corresponding to an average rate classically reported for organic polymers.[30] This demonstrates that the engraving problem met with **PAS1** was due to the presence of TMS groups and that its replacement by a methyl group is an effective strategy (Figure 8).[19]

Furthermore, no cracks were observed upon storage for several months in sharp contrast with **PAS1**. Besides, waveguides of high optical quality were obtained, a sine-qua-non issue for its utilization for the fabrication of a Mach−Zehnder modulator.

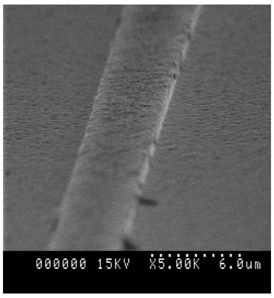


Figure 8. Picture of a ridge waveguide made with **PCC01**.

CONCLUSIONS

In this work, a new electro-optic cross-linkable polymer **PCC01** was prepared and fully characterized in order to solve inherent problems of the **PAS1** during the fabrication of organic waveguides. Therefore, a new polymer incorporating methyl protecting alkynes was prepared and it kept a high solubility in most commonly used solvents allowing thus to produce homogeneous and thick films with good optical quality. The measurements of the SHG coefficient indicate that the value of **PCC01** is in the same range of that obtained with previously reported DR1 based polymers. Moreover, an enhancement of the SHG thermal stability close to 10 °C was monitored. Finally, the elaboration of good optical quality waveguides was successfully achieved with this new cross-linkable polymer **PCC01**. The fabrication of a stable electro-optic modulator with new materials is under way and will be reported in due course.

AUTHOR INFORMATION

Corresponding Author

*Tel: +33 (0)2 51 12 54 29 (F.O.); +33 (0)-5 40 00 69 71 (V. R.); +33 (0)2 96 46 91 23 (D.B.); +33 (0)2 43 83 33 25 (L.F.). Fax: +33 (0)2 51 12 54 02 (F.O.); +33 (0)5 40 00 84 02 (V.R.); +33 (0)2 96 46 90 76 (D.B.); +33 (0)2 43 83 37 54 (L.F.). E-mail: Fabrice.Odobel@univ-nantes.fr (F.O.); v.rodriguez@ism.u-bordeaux1.fr (V.R.); dominique.bosc@enssat.fr (D.B.); laurent.fontaine@univ-lemans.fr (L.F.).

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