

Synthesis and Nonlinear Optical Properties of a Peripherally Functionalized Hyperbranched Polymer by DR1 Chromophores

Annabelle Scarpaci,[†] Errol Blart,[†] Véronique Montembault,[‡] Laurent Fontaine,^{*,‡} Vincent Rodriguez,^{*,§} and Fabrice Odobel^{*,†}

CNRS, Chimie et Interdisciplinarité: Synthèse, Analyse, Modélisation (CEISAM), UMR CNRS 6230, Université de Nantes, 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France, LCOM-Chimie des Polymères, UCO2M, UMR CNRS 6011, Université du Maine, Avenue O. Messiaen, 72085 Le Mans Cedex 9, France, and Institut des Sciences Moleculaires, UMR 5255 CNRS, University of Bordeaux, 351 cours de la Libération, 33405 Talence Cedex, France

ABSTRACT The first peripheral postfunctionalization of a hyperbranched polyimide by nonlinear optic chromophores (DR1 derivative) was achieved using two different routes. The first one consists in the esterification of the terminal carboxylic acid groups, whereas the second is based on copper-catalyzed Huisgen reaction of the terminal propargylic ester groups. The resulting polymers display good solubility in classical organic solvents and good filmability because thick films can be prepared (up to 2.7 μm). The second-order nonlinear optical properties were measured by SHG at 1064 nm and we show that these hyperbranched polymers exhibit good poling efficiency and good thermal stability since the electro-optic activity remains stable up to 130 °C. These results illustrate the potential of hyperbranched polymers to host second-order nonlinear optical chromophores to replace dendrimers or classical linear polymers generally used in this area.

KEYWORDS: hyperbranched polymer • nonlinear optic • click chemistry • peripheral functionalization • disperse red one • second harmonic generation

INTRODUCTION

Second-order nonlinear optical (NLO) polymers have received significant attention because of their high potential for electro-optic (EO) applications. The EO polymers are generally composed of push–pull organic chromophores, hosted in a polymer matrix (1–3). However, the polymer host must fulfill several key requirements to ensure the high quality of the device. The desired properties of the polymer matrix are thermal and photochemical stability, filmability, transparency at the laser wavelength (generally 1.55 μm), and easy and scalable synthesis with relatively inexpensive starting materials. Besides, and equally important, the host structure should allow an efficient poling of the chromophores while stabilizing for a long time the asymmetric order generated in the material upon electric field exposure. The vast majority of the EO organic materials is composed of chromophores attached as side-chain pendant groups in a linear polymer (3, 4). It is well-accepted that chromophores tend to aggregate by dipole–dipole electro-

static interactions, a factor that is detrimental for the poling efficiency (1, 4, 5). This problem becomes even more crucial with high-performance NLO chromophores, because they exhibit very large dipolar moments (1, 6). Recently, Dalton and co-workers have highlighted the importance of the shape of the chromophore and the role of the macromolecular architecture to weaken the intermolecular electrostatic interactions (4, 7–9). Indeed, when NLO chromophores are organized into branched or dendritic architectures, the intermolecular electrostatic interactions are significantly reduced, thus allowing a higher poling efficiency and leading to a larger electro-optic (EO) coefficient (7, 9–11). Besides, the thermal and temporal stabilities of the chromophores alignment are often significantly improved in these dendritic structures (9, 10). Accordingly, because of these unique properties, along with their high solubility and low solution viscosity (12), dendritic materials are appealing matrices to host NLO chromophores. This prompted us to exploit this class of materials because they could display novel and unique properties compared to the well-investigated linear EO polymers. Knowing, however, that the preparation of dendrimers is usually time-consuming, because it requires multistep synthetic schemes and tedious purification steps to isolate each generation (13), we decided rather to turn our attention to hyperbranched polymers. Hyperbranched polymers can be prepared in one pot and are often alternative materials with spherical shapes and properties similar to dendrimers (14). Although hyperbranched polymers have

* Corresponding author. Fabrice Odobel: Tel: 33 (0)2 51 12 54 29 (F.O.); 33 (0)2 43 83 33 25 (L.F.); 33 (0)-5 40 00 69 71 (V.R.). Fax: 33 (0)2 51 12 54 02 (F.O.); 33 (0)2 43 83 37 54 (L.F.); 33 (0)-5 40 00 84 02 (V.R.). E-mail: Fabrice.Odobel@univ-nantes.fr (F.O.); laurent.fontaine@univ-lemans.fr (L.F.); v.rodriguez@ism.u-bordeaux1.fr (V.R.).

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[†] Université de Nantes.

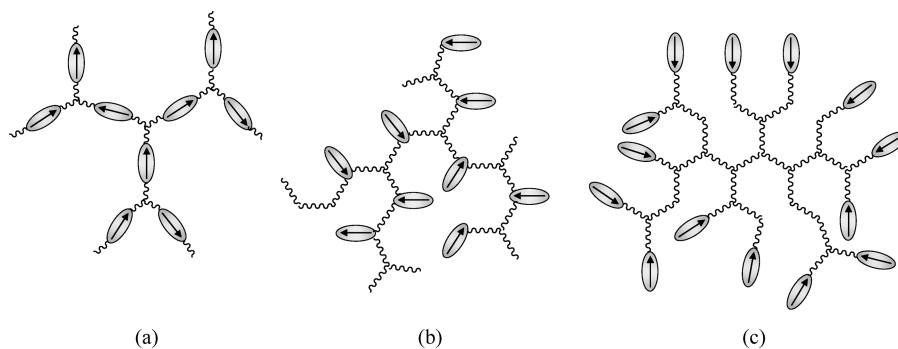
[‡] Université du Maine.

[§] University of Bordeaux.

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Scheme 1. Illustration of the Three Possible Organizations of the NLO Chromophores (arrows) in a Dendritic Architecture: (a) Main-Chain, (b) Side-Chain, and (c) Peripheral



been known since 1950s (15), their use for EO applications has been reported only recently (16–19). Three types of organization of the chromophores can be imagined in a branched material (Scheme 1).

The main-chain structure (Scheme 1a) results from the polymerization of an A_2 (difunctional) monomer with a B_3 (trifunctional) monomer bearing the chromophore. The main-chain structure has only been successfully used by Qin et al. (18) employing Disperse Red one (DR1) inspired chromophores. The main-chain organization of the chromophores in a hyperbranched polymer has been reported (18, 19) but the chromophores must be linked via very flexible chains in order to have sufficient mobility to rearrange during the poling process. With the side-chain organization (Scheme 1b), the chromophore mobility is larger and these materials are obtained by polymerization of an A_2 monomer bearing the chromophore and a B_3 monomer. The rare examples of side-chain NLO hyperbranched polymers reported so far in the literature are mainly based on DR1 chromophores (16, 17). To the best of our knowledge, the preparation of peripherally functionalized hyperbranched

NLO polymers (Scheme 1c) has never been reported, although it was presented with dendrimers (20). Toward this goal, we first investigated the introduction of NLO chromophores in the periphery of a hyperbranched polymer by postfunctionalization. The latter strategy is very attractive because the chromophores will not be exposed to the polymerization conditions, which are sometimes very harsh, especially for polyimides. Besides, a large variety of different materials could be produced effortlessly from only one polymer precursor. Among the possible hyperbranched polymers, we selected the polyimide-based one reported by Xu and Economy because it displays a high T_g and good solubility, stability, and filmability (21). In addition, the fluorinated groups of the anhydride monomer could limit the optical loss (22), and the large number of carboxylic acid terminal groups offers an easy access to postfunctionalization (Figure 1).

The postfunctionalization of **HP-COOH** has been performed according to two different pathways (Scheme 2). The most direct approach consists in the esterification of the carboxylic acid terminal groups of the hyperbranched poly-

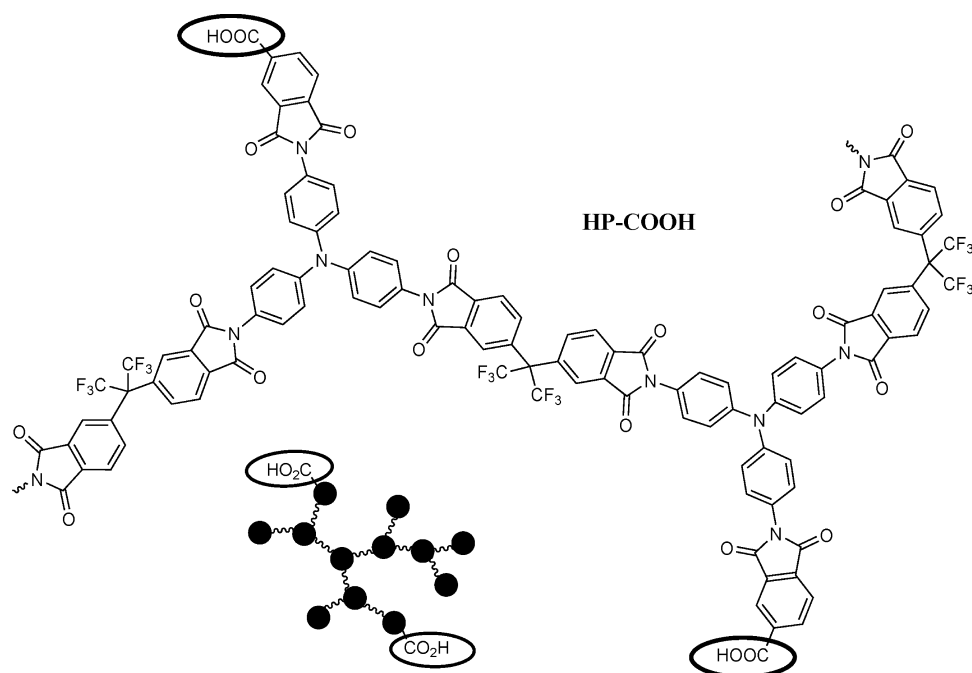
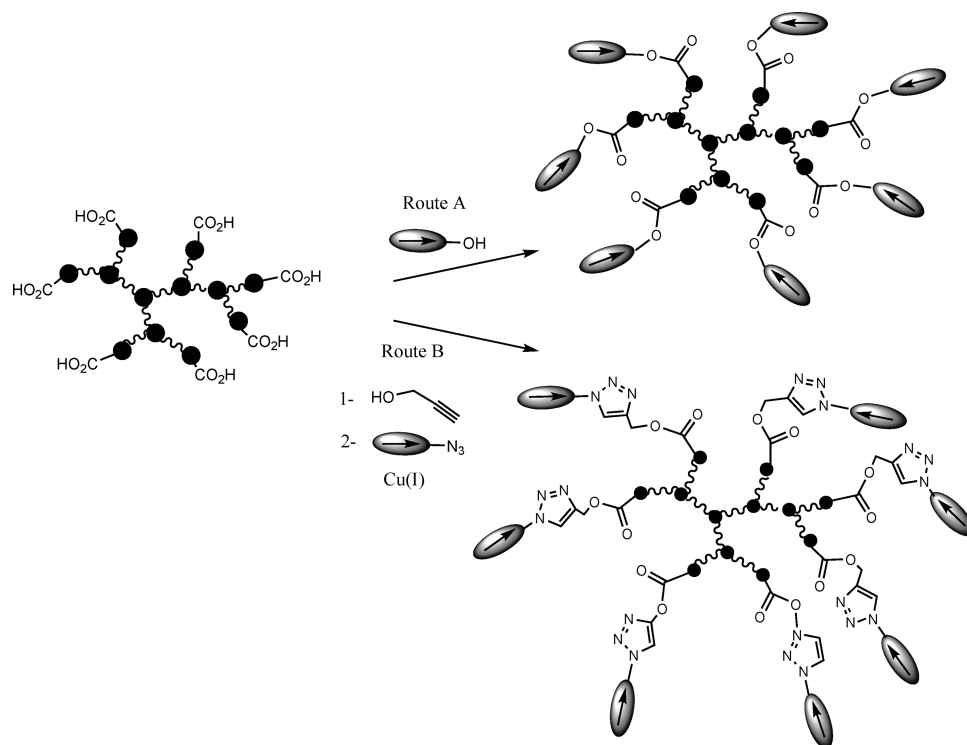


FIGURE 1. Structure of the hyperbranched polyimide HP-COOH and its schematic representation.

Scheme 2. Illustration of the Two Routes Investigated in This Work to Functionalize the Hyperbranched Polymer HP-COOH^a



^a Route A: chromophore-OH, DMTMM, NMM, THF, R.T. Route B: (1) propargylic alcohol, DMTMM, NMM, THF, R.T.; (2) chromophore-N₃, CuBr(PPh₃)₃, *i*Pr₂EtN, THF, R.T.

Table 1. Specific Properties of the Polymers^a

entry	polymer	M_n (g/mol)	M_w (g/mol)	PDI	T_g (°C)	T_d (°C)	d (μm)	d_{33} (pm/V)
1	HP-COOH	1800	2200	1.2	n. o. ^c	460		
2	HP-COO-≡-H	^b	^b	^b	137	274		
3	HP-COO-DR1	13800	24800	1.8	n. o. ^c	352	2.7	65
4	HP-COO-Trz-DR1	11100	25300	2.3	n. o. ^c	290	2.1	42

^a T_g = glass transition temperature. T_d = decomposition temperature (T_d measured at 5% weight loss). d = thickness of the film. d_{33} was measured at 1064 nm. ^b SEC analysis was not performed because of the insufficient solubility of this material in THF. ^c n. o. = not observable.

mer by alcohol functionalized chromophores (Scheme 2, route A). The second one is based on the copper-catalyzed 1,3-dipolar Huisgen cycloaddition (23) involving an azide functionalized chromophore and a propargyl ester group on the polymer (Scheme 2, route B).

In this work, the well-known DR1 chromophore was used as the active NLO unit, because of its simple synthetic accessibility and the impressive catalogue of available NLO data for this compound (24). We report herein the successful preparation of new EO materials based on hyperbranched polymers and the investigation of their electro-optic properties.

RESULTS AND DISCUSSION

Synthesis of the Materials. The synthesis of the hyperbranched polyimide **HP-COOH** was carried out according to the procedure reported by Xu et al. (21). In our case however, size exclusion chromatography (SEC) indicated relatively lower molecular weights and a narrower polydispersity index (Table 1) compared to those reported by Xu et al. ($M_n = 7300$; $M_w = 14\,200$; PDI = 1.95) (21).

These differences are likely due to the nature of the solvent used to make the SEC analysis. Indeed, we performed the latter in THF, whereas Xu et al. used *N*-methyl-2-pyrrolidone (NMP). We believe that NMP is capable of H-bonding the relevant sites within the polyimide matrix, unfolding the latter to a certain extent and leading therefore to a larger hydrodynamic volume than in THF, where the macromolecular architecture would be denser. Furthermore, thermogravimetry analysis (TGA) afforded a decomposition temperature (T_d) of 460 °C, which is slightly higher than the value reported in the literature (T_d around 400 °C) (21).

Once the polymer **HP-COOH** was in hand, we first undertook the postfunctionalization of the carboxylic acid terminal groups by esterification of the latter with the hydroxyl derivatized chromophore **1** (Route A, Scheme 2). The reaction was carried out in *N*-methylmorpholine (NMM) with stoichiometric dimethoxytriazine-*N*-methylmorpholinium chloride (DMTMM) as condensing agent, efficiently yielding the expected NLO material **HP-COO-DR1**. The covalent attachment of the DR1 chromophore is unambig-

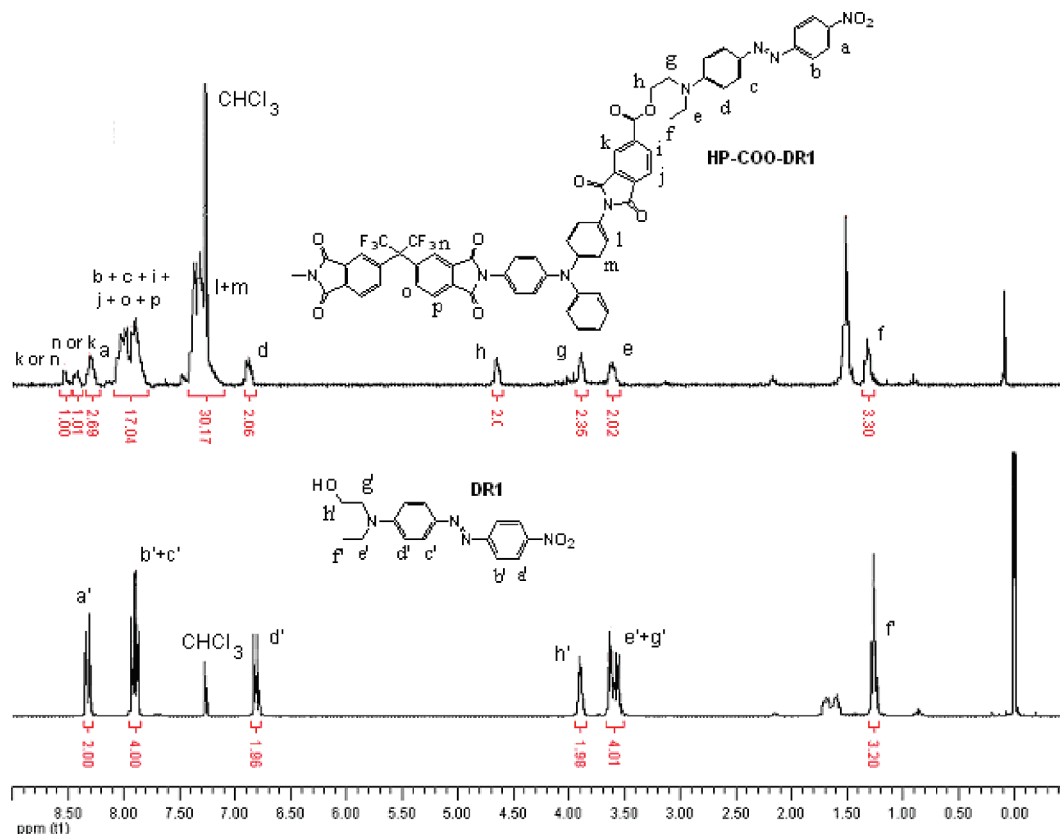
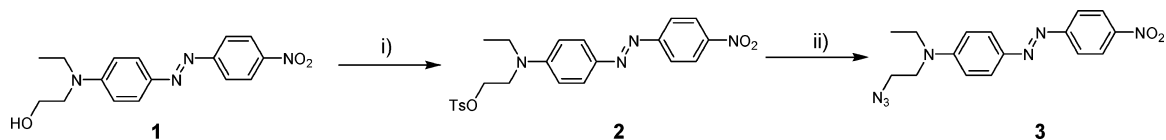


FIGURE 2. Overlay of the ^1H NMR spectra of HP-COO-DR1 polymer (up) and of the chromophore DR1 (down).

Scheme 3. Synthesis of the Azido Functionalized Chromophore **3**^a



^a Reagents and conditions: (i) TsCl, pyridine, CH_2Cl_2 , R.T., 12 h, 84%; (ii) NaN_3 , DMF, 60°C , 12 h, 92%.

ously evidenced at first glance by the color change from pale yellow to deep red. In addition, the corresponding ^1H NMR spectrum clearly displays the signals pattern of the chromophore along with that of the polyimide starting polymer (Figure 2). Moreover, the downfield shift of the signal of the CH_2 protons of the ethanolamine chain (from 3.89 ppm to 4.64 ppm) confirmed the esterification of the chromophore (h' to h , Figure 2).

To postfunctionalize HP-COOH, we explored a second strategy, based on click chemistry. Impressive efficiency, high selectivity, and mild conditions are among the main reasons that the copper-catalyzed Huisgen 1,3 dipolar addition was successful (23). The latter relies on the regioselective copper-assisted addition of an alkyne on an azide derivative, leading to a triazole ring. In our case, it was therefore mandatory to functionalize HP-COOH and the chromophore DR1 with alkyne and azide pendant groups, respectively.

First of all, we prepared the azido functionalized chromophore **3** (25) in two steps from chromophore **1** (Scheme 3): the hydroxyl group of compound **1** was activated in the first place by tosylation with tosyl chloride in pyridine to afford compound **2** in 84% yield. Nucleophilic substitution

of the tosyl group by azide could then take place, affording chromophore **3** in 92% yield. Meanwhile, the free alkyne pendant groups were introduced by esterification of the carboxylic acid terminal groups of HP-COOH with propargylic alcohol. This reaction proceeded smoothly using the above-mentioned activation conditions with DMTMM.

In a second step, the copper-catalyzed Huisgen reaction involving chromophore **3** and HP-COO-alkyne was carried out at room temperature in a mixture of $i\text{Pr}_2\text{EtN}/\text{THF}$ and with $\text{CuBr}(\text{PPh}_3)_3$ as catalyst, leading to HP-COO-Trz-DR1 in a good yield. As can be observed in Figure 3, the corresponding ^1H NMR spectrum nicely evidenced the successful end-capping of the hyperbranched polymer because the acetylenic proton ($\equiv\text{H}$) signal of the parent polymer disappeared, whereas the characteristic signals of the DR1 appeared. Interestingly, the signal of the $\text{O}-\text{CH}_2$ group of the propargylic units experienced a clear downfield shift from 5.05 ppm to 5.44 ppm after the formation of the triazole (Figure 3). In addition, the FT-IR spectrum of HP-COO-Trz-DR1 revealed the absence of the stretching band of the N_3 group (around 2100 cm^{-1}), attesting to the effective covalent binding of chromophore **3** to the polymer backbone.

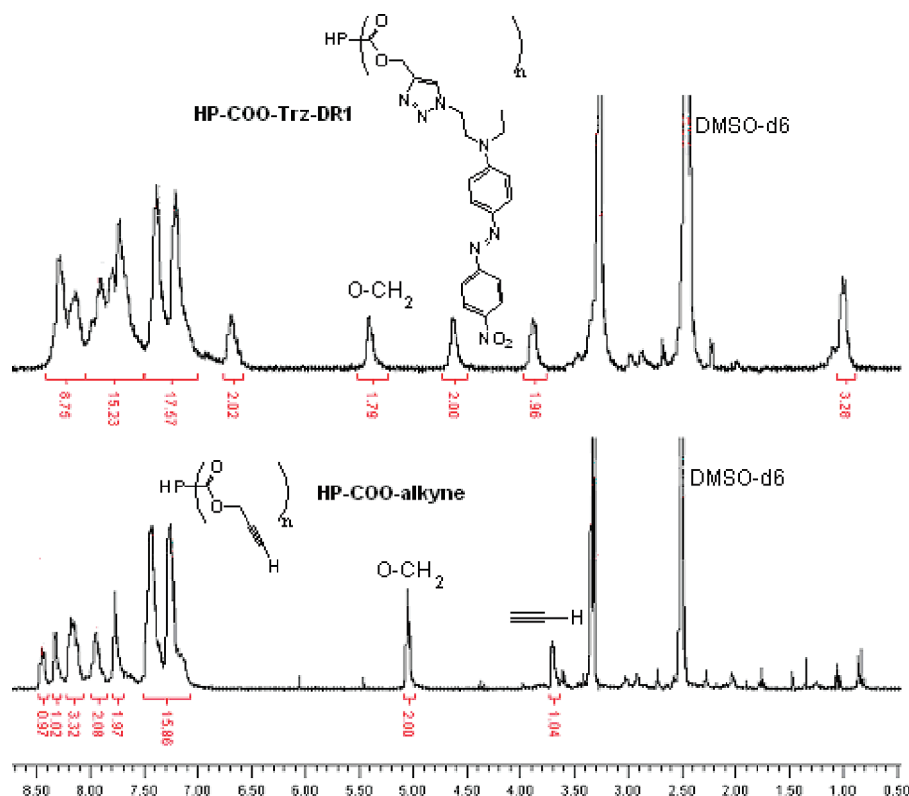


FIGURE 3. ^1H NMR spectra of HP-COO-Trz-DR1 (up) and of HP-COO- \equiv -H (down) polymers.

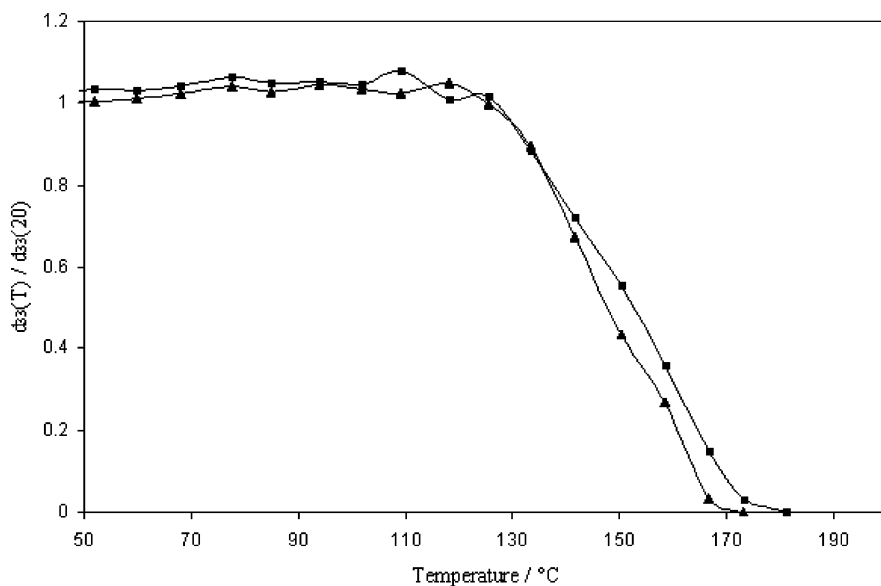


FIGURE 4. Thermal stability of the electro-optic activity of the studied polymers (HP-COO-DR1 (squares) and HP-COO-Trz-DR1 (triangles)) upon heating an initially poled film at a rate of $2\text{ }^\circ\text{C}/\text{min}$ in the air.

SEC analyses of these DR1 functionalized polymers showed an important increase in the molecular weight upon postfunctionalization (entry 1 vs 3 and 4, Table 1). This is consistent with an increase of the polymer size because of a swelling of the structure induced by the disappearance of the hydrogen bonds involved with the terminal carboxylic acid groups of the **HP-COOH** precursor. Besides, it is important to keep in mind that SEC analyses using linear polystyrene as calibration standard often underestimates the molecular weights of hyperbranched polymers, with difference as much as ~ 40 times lower being reported in the literature

(14). Interestingly, these NLO hyperbranched materials present relatively narrow polydispersity index since they are 1.8 and 2.3 for **HP-COO-DR1** and **HP-Trz-DR1**, respectively (Table 1 and Figure 4). The chromophore concentration in **HP-COO-DR1** and **HP-COO-Trz-DR1** has been determined by UV-vis spectroscopy titration, assuming that the absorption coefficient of the chromophore has not changed upon its immobilization. This assumption seems reasonable because there is no electronic coupling between the chromophore and the polymer core because of the saturated $\text{CH}_2\text{-CH}_2$ linker. The chromophore concentrations in **HP-**

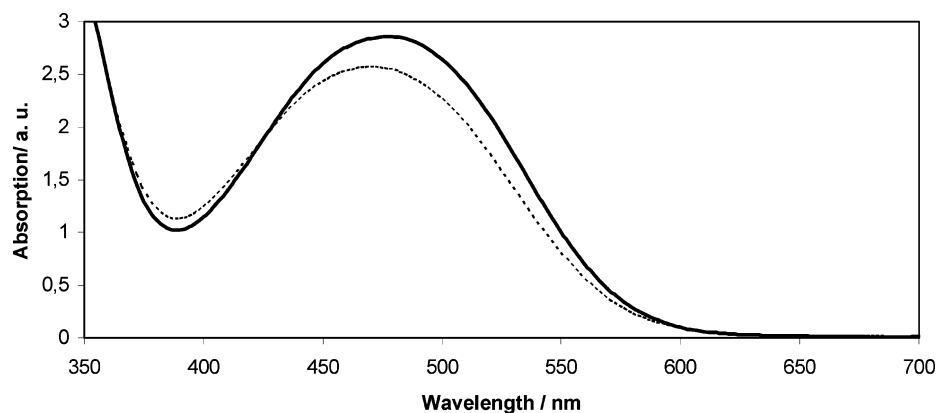


FIGURE 5. Overlay of the absorption spectrum of a film of the polymer HP-COO-Trz-DR1 before (straight line) and after poling (dashed line).

COO-DR1 and HP-COO-Trz-DR1 were estimated at 23 and 20 wt %, respectively. These are relatively high values if one envisions to use this hyperbranched material with chromophores with high $\mu\beta$ values, but these concentrations are lower than those found in methacrylate DR1-based linear polymers (about 50 wt %) (24, 26).

The glass transition temperature of these new materials was investigated by DSC analysis, but HP-COO-≡-H was the only polymer for which the T_g was detectable ($T_g = 137$ °C). This value is significantly lower than that measured in the parent structure (HP-COOH, $T_g = 460$ °C) and it can be explained by the disappearance of the hydrogen bonds between terminal carboxylic groups and by the plastifying effect of the propargylic groups. ATG analyses showed a significant decrease of the T_d upon postfunctionalization because of the introduction of the less thermally stable organic units grafted on HP-COOH (Table 1). Interestingly, triazole linkage seems to decrease the overall thermal stability of the polymer.

Electro-optic Properties of the Hyperbranched Polymers. These new hyperbranched materials were first spin-casted from NMP solution to afford good optical quality and thick films (up to 2.7 μm), confirming thus the good filmability of these polymers. Wire poling under high electric field (3.9 kV) was subsequently carried out at 150 °C for 1 h for each polymer, followed by a rapid cooling to room temperature to freeze the orientation of the chromophores. The orientation of the chromophores is clearly manifested by the decrease in the intensity and the shift (about 8 nm) of the 478 nm absorption band of the chromophore upon poling (Figure 5). The d_{33} coefficients were measured by second harmonic generation (SHG) at 1064 nm (27). In spite of the relatively low chromophore concentration in comparison with those of classical linear DR1 methacrylate polymers (26, 28), similar d_{33} coefficients up to 65 pm/V have been measured. These values are in agreement with those measured for side-chain hyperbranched polymers containing DR1 derivatized chromophores with similar loading levels (16). Interestingly, the d_{33} measured in the hyperbranched polymers HP-COO-DR1 and HP-COO-Trz-DR1 are higher than those measured in linear polymethacrylate polymers functionalized with a similar DR1 chromophore

at the same weight concentration (28, 29). Although the host matrix is different, this could point to a higher poling efficiency because of the dendritic architecture of this polymer. However, a decrease in the d_{33} coefficient (from 65 to 42 pm/V) is observed when a triazole unit is placed between the chromophore and the polymer backbone. For the present moment, we have no rational explanation to this phenomenon, but it indicates that the connectivity between the hyperbranched matrix and the chromophores influences the poling efficiency.

The thermal stabilities of the NLO activities of the polymers were finally investigated by depoling experiments, in which the real time decays of their SHG signals were monitored as a function of the temperature (Figure 4). Both polymers (HP-COO-DR1 and HP-COO-Trz-DR1) exhibit satisfying stability of the chromophore orientation, because there is no real decrease of the SHG signal up to 130 °C (Figure 4). Contrary to the poling efficiency, the linkage between the chromophore and the polymer has little effect on the thermal stability of the alignment.

CONCLUSION

In this work the polymer of Xu and Economy, to host DR1 chromophores, was used with the objective to explore the construction and the properties of EO materials based on hyperbranched polymers. We have succeeded in functionalizing this polymer according to two different approaches. The first route is based on the esterification of the carboxylic terminal residues of the polymer, whereas the second relies on the copper-catalyzed Huisgen 1,3-cycloaddition of propargylic esters with azide functionalized chromophores. Both approaches proved to be suitable to attach NLO chromophores to the polymer, because very soluble materials were obtained in high yields and these routes enable us to prepare, in large scale, EO polymers that present good film-forming properties (thickness up to 2.7 μm). Besides, these strategies certainly offer the synthetic versatility, a feature that is needed to rapidly tune the properties of the materials (structure of the linker between the chromophore and the polymer, concentration and nature of the chromophore). Moreover, the d_{33} coefficients remain stable up to 130 °C in these materials. The classical DR1 chromophore was used

to valid the potential of the hyperbranched polymers for electro-optics. In the literature, there are many push–pull chromophores (1, 4) with much higher quadratic hyperpolarizability values than DR1, which can be potentially used in order to develop hyperbranched materials with stable and very large electro-optic coefficients. Although some of these very active chromophores are sensitive to nucleophiles, the synthetic procedures developed herein rely on particularly mild reaction conditions (reactions carried out at room temperature) and could certainly be compatible with their chemical stabilities. Works are under way in our team to explore this possibility.

EXPERIMENTAL SECTION

Materials. 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium DMTEM (30), and copper of bromo-*tris*-triphenylphosphine ($\text{CuBr}(\text{PPh}_3)_3$) (31) were prepared according to the methods described in the literature. (4,4'-(Hexafluoro-isopropylidene)diphtalic anhydride 6-FDA and 1,2,4-benzene-tricarboxylic anhydride BTCA were purchased from Aldrich and purified by sublimation before use. *N,N*-Dimethylacetamide (DMAc) and *m*-xylene were purchased from Aldrich and distilled under reduced pressure before use. All other chemicals were purchased from Acros and used as received.

Methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 300 MHz Bruker spectrometer. Chemical shifts for ^1H NMR spectra are referenced relative to residual protium in the deuterated solvent (CDCl_3 , $\delta = 7.26$ ppm).

High resolution electro-spray mass spectra (HR-ESMS) were collected in positive mode on a MS/MS ZABSpec TOF of Micro-mass equipped with geometry EBE TOF. The samples were injected in DCM. Elementary analyses were carried out by combustion using a CHN 2400 analyzer for carbone, hydrogen and nitrogen and by pyrolysis using a O Vario EL III analyzer for oxygen. UV–visible absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer.

FTIR spectra were recorded using a FTIR spectrometer (Clark-MXR CPA).

Molecular weights and molecular weight distributions were measured using 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. THF was used as the eluent at a flow rate of 1 mL min^{-1} at 35 °C. Polystyrene standards ($580\text{--}483 \times 10^3 \text{ g mol}^{-1}$) were used to calibrate the SEC. Thermal analyses were performed using a TA Instruments Q500 in a nitrogen atmosphere at a heating rate of 10 °C/min.

Second harmonic generation (SHG) measurements were performed using the optical setup described in a previous study (32). 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 $<20 \mu\text{J}$; 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 d_{ij} , as well as the linear absorption coefficients of the harmonic wave (532 nm) in the parallel (α_{\parallel}) 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 (33).

4-*N*-Ethyl-*N*-(2-tosyloxyethyl)amino-4'-nitroazobenzene (2).

To a solution of compound **1** (1.14 g, 3.61 mmol, 1 equiv) in dichloromethane (6.5 mL) and pyridine (1.58 mL) was added *p*-toluenesulfonyl chloride (894 mg, 4.69 mmol 1.3 equiv). After being stirred for 12 h at R.T., the reaction was quenched by the addition of a 1 N solution of hydrochloric acid (13.5 mL) and aqueous NH_4Cl (20 mL). The aqueous phase was extracted twice with dichloromethane. The combined organic solutions were dried on MgSO_4 , filtered, and evaporated to give the crude product, which was purified by silica gel column chromatography using dichloromethane as eluent. Compound **2** was obtained as a red solid (1.42 g, 84%). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 8.34 (d, 2H, $J = 8.7$ Hz); 7.93 (d, 2H, $J = 8.7$ Hz); 7.84 (d, 2H, $J = 8.7$ Hz); 7.73 (d, 2H, $J = 8.7$ Hz); 7.27 (d, 2H, $J = 8.7$ Hz); 6.62 (d, 2H, $J = 8.7$ Hz); 4.22 (t, 2H, $J = 6.0$ Hz); 3.71 (t, 2H, $J = 6.0$ Hz); 3.44 (q, 2H, $J = 7.5$ Hz); 2.40 (s, 3H); 1.20 (t, 3H, $J = 7.5$ Hz). ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 156.64; 150.53; 145.12; 143.99; 138.75; 129.88; 127.85; 126.10; 124.69; 122.68; 119.98; 111.38; 66.41; 49.08; 46.04; 21.64; 12.22. HRMS-Cl: m/z calcd for $\text{C}_{25}\text{H}_{24}\text{N}_4\text{O}_5\text{S}$, 469.1546 (MH^+); found, 469.1546. Anal. Calcd for $\text{C}_{25}\text{H}_{24}\text{N}_4\text{O}_5\text{S}$: C, 58.9; H, 5.16; N, 11.9; O, 17.0; S, 6.84. Found: C, 58.6; H, 5.32; N, 11.8; O, 16.6; S, 6.49. FT-IR (KBr, cm^{-1}): 2972, 2931 ($\nu_{\text{st}(\text{CH}_2)}$); 1600, 1588 ($\nu_{\text{st}(\text{C}=\text{O})}$). UV–vis (CH_2Cl_2): λ_{max} (ϵ ($\text{mol}^{-1} \text{ L cm}^{-1}$)) = 471 nm (34 400).

4-*N*-Ethyl-*N*-(2-azidoethyl)amino-4'-nitroazobenzene (3).

To a solution of compound **2** (1.42 g, 3.02 mmol, 1 equiv) in DMF (10 mL) was added sodium azide (982 mg, 15.11 mmol, 5 equiv). After being stirred for 20 h at 60 °C, the solution mixture was diluted with diethyl ether and washed several times with a saturated aqueous solution of sodium chloride. The combined organic solutions were dried on Na_2SO_4 , filtered, and evaporated to give a crude product, which was purified by silica gel column chromatography using dichloromethane as eluent. Compound **3** was obtained as a red solid (946 mg, 92%). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 8.33 (d, 2H, $J = 9.3$ Hz); 7.93 (d, 2H, $J = 9.3$ Hz); 7.92 (d, 2H, $J = 9.3$ Hz); 6.78 (d, 2H, $J = 9.3$ Hz); 3.52–3.62 (m, 6H); 1.27 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 156.71; 150.80; 147.55; 144.03; 126.24; 124.67; 122.68; 111.53; 49.57; 48.98; 45.90; 12.28. HRMS-Cl: m/z calcd for $\text{C}_{16}\text{H}_{17}\text{N}_7\text{O}_2$, 340.1522 (MH^+); found, 340.1523. Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{N}_7\text{O}_2$: C, 56.6; H, 5.05; N, 28.9; O, 9.43. Found: C, 56.7; H, 5.01; N, 28.9; O, 9.34. UV–vis (CH_2Cl_2): λ_{max} (ϵ ($\text{mol}^{-1} \text{ L cm}^{-1}$)) = 471 nm (36 700). FT-IR (KBr, cm^{-1}): 2991, 2978, 2937 ($\nu_{\text{st}(\text{CH}_2)}$); 2103 ($\nu_{\text{st}(\text{N}_3)}$); 1602, 1586 ($\nu_{\text{st}(\text{C}=\text{O})}$).

Polymer HP-COO-DR1. To a solution of carboxylic acid hyperbranched polymer **HP-COOH** (700 mg, 0.76 mmol, 1 equiv) and alcoholic chromophore **1** (0.91 mmol, 1.2 equiv) in THF (12 mL) was added *N*-methylmorpholine (0.18 mL, 1.52 mmol, 2 equiv) and then dimethoxytriazine-*N*-methylmorpholine chloride (254 mg, 0.91 mmol, 1.2 equiv). The solution was stirred in the dark one night at R. T. The reaction mixture was then poured in 120 mL of Et_2O , and a powder precipitated. The crude product was collected by filtration. The raw product was dissolved in 8 mL of NMP and poured in 80 mL of MeOH. The product was collected by filtration, washed with 100 mL of methanol, and dried under a vacuum at 30 °C overnight to lead to a red powder in 81% yield. ^1H NMR (300 MHz, CDCl_3), δ (ppm): 8.52 (bs, $\text{H}_{(\text{k} \text{ or } \text{n})}$); 8.41 (bs, $\text{H}_{(\text{k} \text{ or } \text{n})}$); 8.28 (bs, H_a); 8.01–7.88 (bm, H_{Ar}); 7.34–7.30 (bm, H_{Ar}); 4.64 (bm, H_b); 3.88 (bm, H_g); 3.59 (bm, H_e); 1.30 (bm, H_f). UV–vis: (CH_2Cl_2). λ_{max} : 469 nm. SEC (polystyrene): $M_n = 13\,800$; $I_p = 1.8$. FT-IR (KBr, cm^{-1}): 2971, 2929, 2870 ($\nu_{\text{st}(\text{CH}_2)}$); 1782, 1724, 723 ($\nu_{\text{st}(\text{C}=\text{O})}$); 1377 ($\nu_{\text{st}(\text{C}=\text{N})}$); 1254 ($\nu_{\text{st}(\text{C}=\text{F})}$). ATG/DSC (10 °C/min, N_2): Tg: no observed; Td = 352 °C.

Polymer HP-COO-≡-H. To a solution of carboxylic acid hyperbranched polymer **HP-COOH** (1 g, 1.09 mmol, 1 equiv) and propargylic alcohol (0.7 mL, 10.9 mmol, 10 equiv) in THF (17 mL) was added *N*-methyl morpholine (0.26 mL, 2.18 mmol,

2 equiv) and then dimethoxytriazine-*N*-methylmorpholine chloride (362 mg, 1.31 mmol, 1.2 equiv). The solution was stirred in the dark one night at R.T. The reaction mixture was then poured in 170 mL of methanol, and a yellow powder precipitated. The product was collected by filtration, washed with 100 mL of methanol, and dried under a vacuum at 30 °C overnight. The product (880 mg) was obtained in 83% yield. ¹H NMR (300 MHz, DMSO-*d*₆), δ (ppm): 8.44 (bd, 1H); 8.32 (m, 1H); 8.14 (m, 3H); 7.94 (m, 2H); 7.76 (m, 2H); 7.00–7.50 (m, 14H); 5.04 (bs, 2H); 3.70 (bs, 1H). FT-IR (KBr, cm⁻¹): 2952, 2879 ($\nu_{\text{st}(\text{CH}_2)}$); 2124 ($\nu_{\text{st}(\text{C}\equiv\text{C})}$); 1782, 1722, 1669, 722 ($\nu_{\text{st}(\text{C}=\text{O})}$); 1383 ($\nu_{\text{st}(\text{C}-\text{N})}$); 1261 ($\nu_{\text{st}(\text{C}-\text{F})}$). ATG/DSC (10 °C/min, N₂): $T_g = 137$ °C; $T_d = 274$ °C.

Polymer HP-COO-Trz-DR1. A solution of the acetylene-terminated hyperbranched polymer **HP-COO-≡-H** (600 mg, 0.62 mmol, 1 equiv), chromophore **3** (300 mg, 0.88 mmol, 1.4 equiv), *N,N*-diisopropylethylamine (0.16 mL, 0.62 mmol, 1 equiv) and CuBr(PPh₃)₃ (54 mg, 0.12 mmol, 0.2 equiv) in 15 mL of THF was stirred in the dark at R. T. for 24 h. The reaction mixture was poured in 150 mL of Et₂O and a red powder precipitated. The product was collected by filtration, washed with 100 mL of Et₂O, and dried under a vacuum at 30 °C overnight. **HP-COO-Trz-DR1** (704 mg) was obtained in 88% yield. ¹H NMR (300 MHz, DMSO-*d*₆), δ (ppm): 7.50–8.24 (m, 16H); 7.00–7.50 (m, 14H); 6.72 (bs, 2H); 5.44 (bs, 2H); 4.66 (bs, 2H); 3.92 (bs, 2H); 1.05 (m, 3H). UV-vis: (CH₂Cl₂): $\lambda_{\text{max}} = 465$ nm. SEC (polystyrene): $M_n = 11\ 100$; $I_p = 2.3$. FT-IR (KBr, cm⁻¹): 3071, 2971 ($\nu_{\text{st}(\text{CH}_2)}$); 1782, 1724, 722 ($\nu_{\text{st}(\text{C}=\text{O})}$); 1376 ($\nu_{\text{st}(\text{C}-\text{N})}$); 1254 ($\nu_{\text{st}(\text{C}-\text{F})}$). ATG/DSC (10 °C/min, N₂): $T_g =$ not detectable; $T_d = 290$ °C.

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