Photochemical Isomerization of Norbornadiene-Containing Polytriazoles Obtained by Click Chemistry Polyaddition

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ABSTRACT: Polyesters and polyethers containing norbornadiene (NBD) and 1,2,3-triazole units in the main chain are prepared by step growth polymerization of diester or diether NBD-based dialkynes with different aromatic diazides using coppercatalyzed azide–alkyne cycloaddition. The solubility and the physical properties of the resulting polytriazoles are investigated by differential scanning calorimetry, thermogravimetric analysis, size exclusion chromatography, and ¹H NMR spectroscopy, and are discussed taking into account of the chemical structures of the monomers. All of them are amorphous with glass transition temperatures ranging from 51 to 117 °C, number average molecular weight (M_n) values from 16 to 43 kDa

INTRODUCTION The increasing demand for resources and the rapid depletion of fossil deposits are the driving forces to develop new technologies to harvest the solar energy.^{1–5} A promising method for the conversion, storage and release of solar energy is to rely on the photochemical valence isomerization (PVI) of norbornadiene (NBD) into quadricyclane (QC) (Scheme 1).^{6,7} However, as NDB-containing materials absorb at low wavelengths in the visible region, it restricts the PVI performance of such systems functioning in sunlight. Therefore, the addition of sensitizers or chromophores,^{8–11} along with metal complex catalysts,^{12–14} have enhanced the PVI performances of NBD-containing polymer materials. This reversible photochemical process has also been employed in innovative switching operations of optical data storage systems.¹⁵

The synthesis and the photochemical properties of a broad range of polymers containing NBD pendant groups have been explored extensively. For instance, such materials can be and thermal degradation (T_{d10}) values from 175 to 292 °C. The photochemical valence isomerization (PVI) of the NBD units into quadricyclanes (QC) is investigated using UV–vis spectroscopy of polymer films spin-coated onto quartz substrates. For the first time the PVI of NBD into QC is demonstrated by ¹H NMR spectroscopy. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 223–231

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obtained by postpolymerization chemical modifications,^{16,17} cationic or radical polymerizations of NBD-containing vinyl monomers,^{18,19} and ring-opening copolymerization of NBD-containing glycidyl esters with carboxylic anhydrides.²⁰ Nishikubo and coworkers have developed the synthesis of poly(ester-amide)s,²¹ and polyesters,²² introducing the NBD in the main chain of the polymer by polyaddition of NBD-dicarboxylic acid with secondary diamines and diepoxides, respectively. More recently Ben Romdhane and coworkers have detailed the synthesis and photochemical properties of imide–amide organic models based on pentamethylated-NBD units,²³ as well as polyimides,²⁴ and polyamides,²⁵ obtained by polyaddition of dianhydride and dicarboxylic acid NBD derivatives with different aromatic diamines.

Since the advent of the click chemistry philosophy in 2001 by Sharpless and coworkers,²⁶ it has been an immense source of inspiration for the design of advanced multifunctional materials. The most studied and reliable click reaction

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to date is the copper-catalyzed azide–alkyne cycloaddition (CuAAC). The attractive features of this robust, orthogonal and efficient reaction have allowed the development of a broad range of macromolecular materials containing 1,2,3-triazole groups.^{27–32} The field of step growth polymerization has been particularly benefited from the application of CuAAC. A broad range of linear, branched or crosslinked poly(1,2,3-triazole)s,^{33–41} as well as poly(1,2,3-triazolium)s,⁴² have been synthesized from the polyaddition of difunctional or multifunctional azide and alkyne monomers.

Herein, we present the CuAAC polyaddition of dialkynes **2** and **5** with different aromatic diazides **6–10** to build a series of NBD-containing polytriazoles suitable for PVI. The obtained polymers are characterized by techniques such as ¹H NMR, size exclusion chromatography (SEC), Thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC). The PVI of the NBD residues into QC units is investigated by UV-vis spectroscopy from polymer films and is demonstrated for the first time by ¹H NMR from polymer solutions. An imminent question is the ability of the 1,2,3-triazole units to act as sensitizing agents to enhance the PVI of the NBD residues.

EXPERIMENTAL

Materials

Dicylopentadiene (95%), sodium hydride (60 wt % in paraffin oil), propargyl bromide (80% in toluene), 18-crown-6 (99%), potassium carbonate (99%), sodium azide (99.5%), *N*,*N*-diisopropylethylamine (DIPEA, 99%), 4,4'-dihydroxybenzophenone (99%), iodo (triethylphosphite) copper(I) (97%), anhydrous tetrahydrofuran (THF, 99.9%), potassium hydroxide (85%), propargyl alcohol (99%), acetylene dicarboxylic acid (95%), but-2-yne-1,4-diol diacetate (95%), *N*,*N'*-dicyclohexylcarbodiimide (99%), 4-dimethylaminopyridine (DMAP, 99%), and 1,2-dibromoethane (98%) were purchased from Aldrich and used as received. 2,5-Norbornadiene-2,3-dicarboxylic acid 1,²³ 2,5-norbornadiene-2,3-dimethylacetate 3,⁴³ 2,5-norbornadiene-2,3-diol 4,⁴⁴ and aromatic diazides **6–9**,^{45,46} were prepared according to previously reported methods.

Instrumentation

Monomers were purified by column chromatography using a Reveleris[®] X_2 Flash System from GRACE. NMR spectra were recorded at room temperature on a Bruker Advance II Spectrometer (250–400 MHz) using CDCl₃ or DMSO- d_6 as solvents with tetramethylsilane as the internal standard. The assignments of proton and carbon atoms are reported in

Supporting Information Scheme S1. SEC analyses were conducted with three columns Styragel HR 4E and using dimethylformamide containing LiBr as eluent. Number average molar masses (M_n), weight average molar masses (M_w), and chain dispersities ($\mathcal{D} = M_w/M_n$) were calculated based on polystyrene standards. DSC was performed on a DSC Q100 (TA Instruments) at a heating rate of 10 °C/min under nitrogen atmosphere. TGAs were performed on a TGA Q500 (TA Instruments) at 20 °C/min under nitrogen atmosphere. UV-vis spectra were recorded on a Lambda 35 UV-vis spectrophotometer (Perkin Elmer). Polymer films were irradiated in an UVACUBE 400 UV curing chamber (Honle) equipped with a 400-W bulb with an irradiation intensity of 1000 W/m².

Synthesis of Dipropargyl 2,5-Norbornadiene-2,3dicarboxylate (2)

A solution of dicyclohexylcarbodiimide (5.73 g, 27.8 mmol) in dichloromethane (12 mL) was added dropwise to a solution of propargyl alcohol (935 mg, 16.7 mmol), diacid **1** (1.00 g, 5.55 mmol), and DMAP (271 mg, 2.22 mmol) in dichloromethane (15 mL) maintained at 0 °C. After stirring at room temperature for 15 h, the reaction mixture was filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel, with a 9:1 mixture of petroleum ether and ethyl acetate, eluting **2** as a yellow liquid (1.14 g, 80.3%) after evaporation of the eluents.

¹H NMR (400 MHz, DMSO- d_6 , δ): 6.98 (m, H_a, 2H), 4.78 (d, J = 2.4 Hz, CH₂C≡CH, 4H), 3.92 (m, H_b, 2H), 3.56 (t, J = 2.4Hz, C≡CH, 2H), 2.12 (m, H_c, 2H); ¹³C NMR (100 MHz, DMSO d_6 , δ): 163.34 (C=O), 151.86 (C_d), 142.31 (C_a), 77.91 (C≡CH), 77.81 (C≡CH), 73.04 (C_c), 52.89 (C_b), 52.27 (CH₂C≡CH). HRMS: (ESI, m/z): [M + H]⁺ calcd for C₁₅H₁₃O₄, 257.0735; found, 257.0628.

Synthesis of 2,3-Dipropargyl-2,5-norbornadiene (5)

Sodium hydride (2.35 g, 58.8 mmol) was added in portions to a solution of **4** (1.80 g, 11.8 mmol) in 40 mL of anhydrous tetrahydrofuran maintained at 0 °C under argon. Propargyl bromide (5.3 mL, 47 mmol) and 18-crown-6 (3 mg, 0.01 mmol) were then added, and the mixture was stirred for 24 h at room temperature. After quenching the residual sodium hydride by methanol (10 mL) and water (10 mL), the solvents were evaporated under reduced pressure and the residue was extracted with dichloromethane (3×100 mL). The organic layers were combined and dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, with a 9:1 mixture of cyclohexane and ethyl acetate eluting **5** as a yellow liquid (1.74 g, 64.7%) after evaporation of the eluents.

¹H NMR (250 MHz, CDCl₃, δ): 6.79 (m, H_a, 2H), 4.23 (dd, $J_1 = 12$ Hz, $J_2 = 36$ Hz, CH₂OCH₂C≡CH, 4H), 4.03 (dd, $J_1 = 35$ Hz, $J_2 = 4$ Hz, CH₂OCH₂C≡CH, 4H), 3.57 (m, H_b, 2H), 2.42 (t, J = 2.5 Hz, C≡CH, 2H), 1.99 (m, H_c, 2H); ¹³C NMR (100 MHz, CDCl₃, δ): δ 149.49 (C_d), 142.47 (C_a), 79.79 (C≡CH), 74.43

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(C=CH), 71.79 (C_c), 64.80 (CH₂OCH₂C=CH), 56.61 (CH₂OCH₂C=CH), 52.59 (C_b). HRMS: (ESI, m/z): $[M + H]^+$ calcd for C₁₅H₁₇O₂, 229.1150; found, 229.1043.

Synthesis of 4,4'-Di(2-azidoethoxy)benzophenone (10)

Potassium carbonate (9.70 g, 70.2 mmol), 1,2-dibromoethane (61.0 mL, 708 mmol), and 18-crown-6 (6 mg, 0.02 mmol) were added to a solution of 4,4'-dihydroxybenzophenone (5.00 g, 23.3 mmol) in acetone (125 mL). The reaction mixture was refluxed under argon for 96 h, filtered, and evaporated to dryness. The residue was extracted with dichloromethane (3 imes100 mL). The combined organic phases were dried over MgSO₄, filtered, and concentrated under vacuum. The obtained solid (9.72 g, 98.0%) was used in the azidation step without any further purification. 4,4'-Di(2-bromoethoxy)benzophenone (9.72 g, 22.8 mmol) and sodium azide (8.90 g, 137 mmol) were added to a round-bottom flask containing 80 mL of dimethylformamide. The mixture was stirred in the dark for 20 h at 60 °C. The solvents were evaporated under reduced pressure and the residue was extracted with ethyl acetate (3 \times 100 mL). The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, with a 1:1 mixture of petroleum ether and ethyl acetate eluting 10 as a white solid (6.04 g, 75.1%) after evaporation of the eluents.

¹H NMR (400 MHz, DMSO- d_6 , δ): 7.71 (d, J = 8.8 Hz, H_3 , 4H), 7.01 (d, J = 8.8 Hz, H_2 , 4H), 4.27 (t, J = 4.8 Hz, $CH_2CH_2N_3$, 4H), 3.69 (t, J = 4.8 Hz, $CH_2CH_2N_3$, 4H); ¹³C NMR (100 MHz, DMSO- d_6 , δ): 193.10 (C₅), 161.22 (C₄), 131.84 (C₃), 130.30 (C₁), 114.22 (C₂), 67.06 (CH₂CH₂N₃), 49.41 (CH₂CH₂N₃). HRMS: (ESI, m/z): $[M + H]^+$ calcd for C₁₇H₁₇O₃N₆, 353.1283; found, 353.1357.

General Procedure for the Synthesis of NBD-Containing Polytriazoles by CuAAC Polyaddition in DMSO Synthesis of 11

Diazide **6** (156 mg, 0.59 mmol) was added to a solution of dialkyne **2** (251 mg, 0.98 mmol), $CuP(OEt)_3I$ (46 mg, 0.05 mmol), and DIPEA (127 mg, 0.98 mmol) in 6 mL of DMSO. After stirring at 60 °C for 24 h, the crude product was precipitated twice in methanol, centrifuged, and dried under vacuum at 60 °C for 8 h resulting in pure polytriazole **11** as a light brown powder (405 mg, 60.0%).

¹H NMR (250 MHz, DMSO- d_6 , δ): 8.17 (s, C=CH, 2H), 7.28 (s, H₁, 4H), 6.89 (s, H_a, 2H), 5.56 (s, CH₂N, 4H), 5.09 (s, COOCH₂, 4H), 3.83 (s, H_b, 2H), 2.02 (bs, H_c, 2H).

Synthesis of 12

The general procedure for CuAAC polyaddition was applied to dialkyne **2** (151 mg, 0.59 mmol), CuP(OEt)₃I (28 mg, 0.03 mmol), DIPEA (76 mg, 0.59 mmol), and diazide **7** (156 mg, 0.59 mmol) to obtain **12** as a light yellow powder (290 mg, 66.6%).

¹H NMR (250 MHz, DMSO- d_6 , δ): 8.21 (s, C=CH, 2H), 7.57 (d, J = 8.0 Hz, H_2 , 4H), 7.36 (d, J = 8 Hz, H_1 , 4H), 6.89 (s, H_{av}



Synthesis of 13

The general procedure for CuAAC polyaddition was applied to dialkyne **2** (151 mg, 0.59 mmol), diazide **8** (177 mg, 0.59 mmol), CuP(OEt)₃I (28 mg, 0.03 mmol), and DIPEA (76 mg, 0.59 mmol) to obtain **13** as a light brown solid (240 mg, 73.1%).

¹H NMR (250 MHz, DMSO- d_6 , δ): 8.96 (s, C=CH, 2H), 8.49 (s, H₄, 2H), 8.12 (bs, H₁, H₂, 4H), 7.78 (bs, H₃, 2H), 6.90 (s, H_a, 2H), 5.26 (s, COOCH₂C, 4H), 3.88 (s, H_b, 2H), 2.06 (bs, H_c, 2H).

Synthesis of 14

The general procedure for CuAAC polyaddition was applied to dialkyne **2** (151 mg, 0.59 mmol), diazide **9** (177 mg, 0.59 mmol), CuP(OEt)₃I (28 mg, 0.03 mmol), and DIPEA (76 mg, 0.59 mmol) to obtain **14** as a brown solid (323 mg, 98.4%).

¹H NMR (250 MHz, DMSO- d_6 , δ): 8.91 (s, C=CH, 2H), 8.14 (d, J = 7.5 Hz, H_1 , H_2 , 8H), 6.93 (s, H_a , 2H), 5.26 (s, COOCH₂, 4H), 3.89 (s, H_b , 2H), 2.06 (bs, H_c , 2H).

Synthesis of 15

The general procedure for CuAAC polyaddition was applied to dialkyne **2** (151 mg, 0.59 mmol), diazide **10** (208 mg, 0.59 mmol), CuP(OEt)₃I (28 mg, 0.03 mmol), and DIPEA (76 mg, 0.59 mmol) to obtain **15** as a brown solid (320 mg, 89.1%).

¹H NMR (250 MHz, DMSO- d_6 , δ): 8.23 (s, C=CH, 2H), 7.61 (d, J = 8.5 Hz, H₃, 4H), 7.01 (d, J = 8.5 Hz, H₂, 4H), 6.88 (s, H_a, 2H), 5.13 (s, COOCH₂, 4H), 4.81 (s, CH₂CH₂N, 4H), 4.49 (s, CH₂CH₂N, 4H), 3.83 (s, H_b, 2H), 2.08 (bs, H_c, 2H).

Synthesis of 16

The general procedure for CuAAC polyaddition was applied to dialkyne **5** (256 mg, 1.12 mmol), diazide **6** (210 mg, 1.12 mmol), CuP(OEt)₃I (52 mg, 0.056 mmol), and DIPEA (145 mg, 1.12 mmol) to obtain **16** as a brown solid (280 mg, 60.0%).

¹H NMR (250 MHz, DMSO- d_6 , δ): 8.10 (s, C==CH, 2H), 7.28 (s, H₁, 4H), 6.71 (s, H_a, 2H), 5.54 (s, CH₂N, 4H), 4.33 (s, CH₂OCH₂CN, 4H), 4.05 (dd, $J_1 = 12$ Hz, $J_2 = 39$ Hz, CH₂OCH₂CN, 4H), 3.42 (s, H_b, 2H), 1.77 (bs, H_c, 2H).

Synthesis of 17

The general procedure for CuAAC polyaddition was applied to dialkyne **5** (150 mg, 0.66 mmol), diazide **7** (174 mg, 0.66 mmol), CuP(OEt)₃I (28 mg, 0.03 mmol), and DIPEA (85 mg, 0.66 mmol) to obtain **17** as a brown solid (260 mg, 80.2%).

¹H NMR (250 MHz, DMSO- d_6 , δ): 8.14 (s, C==CH, 2H), 7.58 (bs, H₂, 4H), 7.35 (bs, H₁, 4H), 6.73 (s, H_a, 2H), 5.59 (s, CH₂N, 4H), 4.36 (s, CH₂OCH₂CN, 4H), 4.08 (dd, J_1 = 12 Hz, J_2 = 39 Hz, CH₂OCH₂CN, 4H), 3.43 (s, H_b, 2H), 1.77 (bs, H_c, 2H).



Synthesis of 18

The general procedure for CuAAC polyaddition was applied to dialkyne **5** (150 mg, 0.66 mmol), diazide **8** (198 mg, 0.66 mmol), CuP(OEt)₃I (28 mg, 0.03 mmol), and DIPEA (85 mg, 0.66 mmol) to obtain **18** as a brown solid (270 mg, 77.5%).

¹H NMR (250 MHz, DMSO- d_6 , δ): 8.92 (s, C==CH, 2H), 8.52 (s, H₄, 2H), 8.16 (bs, H₁, H₂, 4H), 7.82 (bs, H₃, 2H), 6.76 (s, H_a, 2H), 4.46 (s, CH₂OCH₂CN, 4H), 4.13 (dd, J_1 = 12 Hz, J_2 = 38 Hz, CH₂OCH₂CN, 4H), 3.50 (s, H_b, 2H), 1.85 (bs, H_c, 2H).

Synthesis of 19

The general procedure for CuAAC polyaddition was applied to dialkyne **5** (150 mg, 0.66 mmol), diazide **9** (198 mg, 0.66 mmol), CuP(OEt)₃I (28 mg, 0.03 mmol), and DIPEA (85 mg, 0.66 mmol) to obtain **19** as a brown solid (245 mg, 70.4%). This latter was insoluble in all organic solvents and thus could not be characterized by ¹H NMR.

Synthesis of 20

The general procedure for CuAAC polyaddition was applied to dialkyne **5** (150 mg, 0.66 mmol), diazide **10** (232 mg, 0.66 mmol), CuP(OEt)₃I (28 mg, 0.03 mmol), and DIPEA (85 mg, 0.66 mmol) to obtain **20** as a brown solid (325 mg, 85.0%).

¹H NMR (300 MHz, DMSO- d_6 , δ): 8.30 (s, C==CH, 2H), 7.61 (d, J = 8.0 Hz, H_2 , 4H), 7.01 (d, J = 8.0 Hz, H_3 , 4H), 6.72 (s, H_a , 2H), 4.77 (s, CH₂CH₂N, 4H), 4.48 (s, CH₂OCH₂CN, 4H), 4.35 (s, CH₂CH₂N, 4H), 4.07 (dd, $J_1 = 13$ Hz, $J_2 = 45$ Hz, CH₂OCH₂CN, 4H), 3.58 (s, H_b , 2H), 1.80 (bs, H_c , 2H).

Typical Procedure for Photochemical Valence Isomerization of the NBD Residues in the Film State

Thin films were prepared by spin coating onto quartz wafers 0.25 wt % solutions of polytriazoles **11–20** in *N*-methylpyrrolidone. An initial scan by UV-vis spectrophotometer between 200 and 500 nm was performed in order to determine the maximum absorption wavelengths. The polymer films were then irradiated at times ranging from 2 to 300 min and were immediately characterized by UV-vis spectros-copy after each period of irradiation.

RESULTS AND DISCUSSION

Synthesis of Dialkyne and Diazide Monomers

NBD-based dialkyne monomers **2** and **5** were obtained using two-step and three-step chemical pathways (Scheme 2),

respectively. Dialkyne **2** was prepared from the Diels-Alder reaction between freshly distilled cyclopentadiene and acetylene dicarboxylic acid followed by esterification of the resulting NBD dicarboxylic acid **1** with propargyl alcohol in 80% yield.²³ Dialkyne **5** was prepared by the Diels-Alder reaction between dicyclopentadiene and but-2-yne-1,4-diol diacetate followed by the saponification of the resulting NBD diacetate **3** by potassium hydroxide in methanol.^{43,44} The resultant diol **4** was then alkylated with propargyl bromide using sodium hydride yielding monomer **5** in 65% yield.

Aromatic diazides **6** and **7** were obtained from the straightforward nucleophilic substitution of the corresponding dichlorides by sodium azide.⁴⁵ Sulfonated diazides **8** and **9** were prepared by diazotation of the corresponding aromatic primary amines followed by reaction of the resulting diazonium salts with sodium azide.⁴⁶ Finally, diazide **10** was prepared by alkylation of 4,4'-dihydroxybenzophenone with 1,2-dibromoethane followed by azidation of the resulting dibromide using sodium azide. Purification of the monomers and their isolated intermediates was achieved by column chromatography. Characterization of newly prepared monomers **2**, **5**, and **10** was carried out by ¹H, ¹³C NMR, and ESI-HRMS techniques.

Synthesis and Characterization of Polytriazoles 11-20

NBD-containing polytriazoles having ester (11-15) and ether (16-20) linkages in their repeating unit were synthesized from the CuAAC polyaddition of stoichiometric mixtures of dialkynes 2 and 5 and aromatic diazides 6-10. Polymerizations were carried out during 24 h at 60 °C in dimethylsulfoxide using CuP(OEt)₃I as a catalyst and DIPEA as a base (Scheme 3). The combination of rather rigid, noncovalently interacting 1,2,3-triazole (hydrogen bonding) and presence of aromatic rings (π -stacking) within the polymer backbones resulted in polymers being insoluble in methanol (MeOH), acetone, tetrahydrofuran (THF), ethyl acetate (EtOAc), and acetonitrile (ACN). However, all polytriazoles but 19 are soluble in N-methylpyrrolidone (NMP), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Therefore, polymers 11–18 and 20 could be characterized by ¹H NMR, SEC, and UV-vis spectroscopy.

¹H NMR of polytriazoles **11–18** and **20** clearly corroborated the efficiency of the CuAAC polyaddition. For instance, Figure 1 exhibits the typical chemical shift changes for polytriazole



SCHEME 2 Synthesis of NBD-based dialkyne monomers 2 and 5.



SCHEME 3 Synthesis of NBD-containing polytriazoles **11–20** by CuAAC polyaddition of dialkynes **2** and **5** with aromatic diazides **6–10**.

12, which is obtained from the polyaddition of dialkyne **2** and diazide **7**. Indeed, the appearance of the 1,2,3-triazole signal at 8.12 ppm, the quantitative shifts of the azidomethyl signal from 4.39 to 5.11 ppm and the methylene signal adjacent to the alkyne group from 4.78 to 5.61 ppm confirm the effective occurrence of the CuAAC polyaddition. Moreover, the absence of signals arising from chain-ends further corroborates the polymeric nature of polytriazole **12**. All of these features were observed in the ¹H NMR spectra of all the synthesized polytriazoles.

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Thermal Properties

Thermal properties of polytriazoles **11–20** were investigated by DSC and TGA experiments (Table 1). DSC results clearly demonstrated the amorphous nature of all polytriazoles. assessed by measuring the temperature for 10% weight loss (T_{d10}) under inert atmosphere obtained by TGA (Table 1 and Supporting Information Fig. S2). T_{d10} values are significantly influenced by the chemical nature of both monomer units and range from 175 to 292 °C, the highest value being obtained for the combination of ether-based dialkyne **5** and benzophenone diazide **10**. These values are considerably

Indeed, the presence of a single glass transition temperature

 (T_g) is revealed ranging from 78 to 117 °C for polyesters

11-15 and from 51 to 93 $^\circ\text{C}$ for polyethers 16-20. The

lower $T_{\rm g}$ values of the former groups are most probably due

to the enhanced flexibility of the ether unit compared to the



FIGURE 1 ¹H NMR (25 °C, DMSO-*d*₆) of dialkyne 2, diazide 7, and the resulting polytriazole 12.

TABLE 1 Solubility,	Physical, and	Photochemical	Properties	of NBD-	Containing	Polytriazoles	11-20
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Polymer	MeOH, EtOAc, ACN Acetone	CH ₂ CI ₂ , CHCI ₃	NMP	DMF, DMSO	<i>M</i> _n (kDa) ^a	Ð	T _g (°C) ^b	<i>T</i> d10 (°C) ^c	$\lambda_{\max} \ (nm)^d$	$k_{ m app}~(imes~10^{-4}/ m s)^{ m d}$
11(2+6)	-	\sim	+	+	19.6	1.77	97	241	225	-
12(2+7)	_	+	++	++	43.0	2.20	117	232	260	0.26
13(2+8)	-	\sim	++	++	19.6	1.69	96	229	240	-
14(2+9)	_	\sim	++	++	19.6	1.69	84	246	275	0.40
15(2+10)	-	\sim	+	++	27.4	1.68	78	222	290	4.34
16(5+6)	_	\sim	+	+	16.3	1.59	63	284	225	-
17(5+7)	-	\sim	+	+	18.3	1.95	93	285	260	0.71
18(5+8)	_	\sim	+	+	18.3	1.76	82	175	240	-
19(5+9)	-	\sim	\sim	\sim	-	-	51	206	240	-
20(5+10)	_	\sim	+	+	23.5	1.75	67	292	290	8.00

++) soluble at 10 mg/mL. (+) soluble at 1 mg/mL. (~) partially soluble at 1 mg/mL. (-) totally insoluble even at 1 mg/mL.

^a Estimated by GPC according to the polystyrene standards in DMF.

lower than previously reported ester- or ether-containing polytriazoles ($T_{d10} \sim 330-380 \,^{\circ}\text{C}$),⁴⁷ and aromatic polytriazole resins ($T_{d10} \sim 400-570 \,^{\circ}\text{C}$).⁴⁸ The relatively moderate thermal stability of polytriazoles **11–20** most probably results from the thermally driven cleavage of NBD units as previously observed for NBD-containing polyimides ($T_{d10} \sim 267-337 \,^{\circ}\text{C}$),²⁴ and polyamides ($T_{d10} \sim 175-276 \,^{\circ}\text{C}$).²⁵ Hash residual values ranging from 33 to 41% were obtained in accordance with previously reported polytriazoles.^{38,47,48}

Photochemical Properties

Polytriazoles **11–20** were characterized by UV-vis spectroscopy to determine their maximum absorption wavelengths (λ_{max}) . λ_{max} values are mainly guided by the chemical nature of the diazide monomer (Supporting Information Fig. S3). Chemical nature of the dialkyne monomer has no influence on λ_{max} except for *p*-diphenylsulfone-based polytriazoles **14** $^{\rm b}$ Obtained from the second trace of DSC measurements conducted at a heating rate of 10 $^\circ\text{C}/\text{min}.$

^c Temperature at 10% weight loss in TGA at 20 °C/min heating rate.

^d Obtained by UV-vis spectroscopy.

and **19**. Indeed, a 40 nm difference in their λ_{max} values is observed, most probably due to the poor solubility of **19** in NMP and thus resulting in the analysis of mainly low molar mass species. For both series of ester- and ether-based polytriazoles, λ_{max} increases in the following order with respect to the diazide monomer: phenyl **(6)** < *m*-diphenylsulfone **(8)** < diphenyl **(7)** < *p*-diphenylsulfone **(9)** < benzophenone **(10)**. This increase in λ_{max} is essential for the PVI and highlights the ability of the polytriazoles to harvest light in a broader range of wavelength.

Thin films were prepared by spin coating onto quartz substrates solutions of polytriazoles **12**, **14**, **15**, **17** and **20** in NMP. PVI experiments were then carried out by UV irradiation of the thin films for times ranging from 1 to 300 min. For all PVI experiments, the changes in UV spectra are comparable with a gradual decrease of the absorption intensity. A typical example is shown in Figure 2 for polytriazole **20**. The intensity



FIGURE 2 Change in the UV spectra of polytriazole **20** in the film state during UV irradiation.



FIGURE 3 Evolution of the absorbance at 250 nm with UV irradiation time for polytriazole 20.



Polymer

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FIGURE 4 (a) Conversion of NBD units versus irradiation time and (b) first-order plots of the PVI of polytriazoles () 20; (\blacksquare **15**; (△) **17**; (●) **14**, and (□) **12** in the film state.

of the absorption at 290 nm gradually decreases with the increase in irradiation time indicating that NBD residues are converted to QC groups. As previously observed for NBDcontaining polyesters,²² evolution of the UV-vis spectra during UV irradiation showed isosbestic points (e.g., at 250 nm for polymer 20) meaning that the conversion of NBD units into QC groups occurred selectively without side reaction in the film state. The conversion of the NBD units into QCs (τ) was calculated from the changes in absorbance at λ_{max} during UV irradiation experiment. The residual absorbance (A_{residual}) was calculated from an exponential fit $(A_t = A_0 \exp(-t/\alpha) + A_{residual})$ of the experimental results (Fig. 3).⁴⁹ A_{residual} was then used in the determination of the conversion of NBD units into QCs $(\tau = (A_0 - A_t)/(A_0 - A_{residual})$ with A_t the absorbance at time t and A_0 the initial absorbance.

As shown in Figure 4(a), the PVI of the polytriazoles exhibit significantly different rates of NBD conversion. The PVI experiments obey first-order kinetics in the initial reaction stage as reported earlier in literature for NBD-containing polymers [Fig. 4(b)].²¹⁻²⁵ The rate constants of NBD conversion (k_{app}) were calculated from the slope of the linear fit of the first-order plots (Table 1). Obtained k_{app} values suggest a strong influence of the chemical structure of both the dialkyne and the diazide monomers on the rates of NBD conversion. For instance, $k_{\rm app}$ of the diester series (12 and 15) are significantly lower than for the diether-based polytriazoles (17 and 20). Besides, as observed earlier for NBD-containing polyesters,¹⁰ the benzophenone moiety is a better photosensitizer over the other studied aromatic groups which explains the highest rate of NBD conversion and k_{app} values for polytriazoles **15** and **20**.

Finally, for the first time the PVI of NBD-containing polymers have been demonstrated by ¹H NMR spectroscopy. Figure 5 displays the ¹H NMR spectra of polytriazole **15** in DMSO-*d*₆



FIGURE 5 ¹H NMR (at 25 °C in DMSO- d_6) of polytriazole **15** (a) before and (b) after UV irradiation.

before and after 300 min of UV irradiation. It can be clearly observed that the NBD conversion into QCs is almost quantitative, as confirmed by the quasi-total disappearance of the characteristic signals of the NBD unit at 6.88 and 3.81 ppm as well as the concomitant appearance of the two new signals at 2.26 and 2.08 ppm corresponding to the resulting QC unit. This is an unprecedented observation and a quantitative proof of the efficient PVI of the NBD/QC system.

CONCLUSIONS

Two novel dialkyne monomers having NBD unit were synthesized, characterized, and were combined with various aromatic diazides for the preparation of NBD containing polytriazoles by CuAAC step growth polymerization with high molecular weights. UV-vis and ¹H NMR studies of the PVI showed the complete conversion of NBD residues into QC molecules. This study shows the relationship between the monomer's structure, solubility, thermal behavior, UV absorption, and photochemical reactivity of the resulting polytriazoles. Whereas fastest PVI was obtained for benzophenone-containing polytriazoles, no significant influence of the 1,2,3-triazole groups could be highlighted.

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