# Click chemistry step growth polymerization of novel α-azide-ω-alkyne monomers†

**Sandra Binauld,[ab] Denis Damiron,[b] Thierry Hamaide,[b] Jean-Pierre Pascault,[a] Etienne Fleury[a] and Eric Drockenmuller*[b]**

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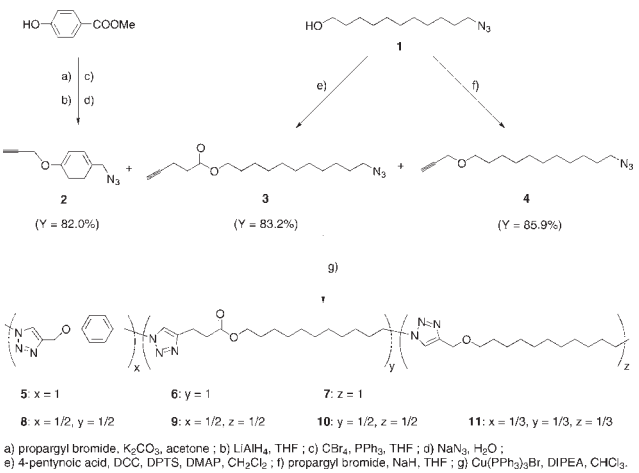
**A novel step growth polymerization A–B strategy based on the click chemistry polyaddition of tailor-made α-azide-ω-alkyne low molar mass monomers was developed, leading to polytriazole (co)polymers with tunable structures and properties.**

Since its introduction in 2001 by Sharpless and co-workers,[1] the concept of click chemistry has been a wide source of inspiration for the design of advanced multifunctional polymer materials.[2] One of the most studied and reliable click reaction so far has been the copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of an azide ($R–N_3$) and an alkyne ($R–C\equiv CH$). This enhanced regioselective chemical pathway is tolerant to humidity, oxygen, a wide range of functionalities, and proceeds with almost quantitative yields under mild conditions in different reaction media. All these advantages have been extensively applied to the different fields of materials science and polymer chemistry, allowing the synthesis and functionalization of a wide range of macromolecular architectures, *e.g.*, 2D and 3D organic and inorganic substrates, linear, block and star-like copolymers, dendrimers and dendritic architectures, hyperbranched materials as well as hydrogels and polymer networks.[3]

The elaboration of linear polytriazoles by catalyzed or uncatalyzed click chemistry step growth polymerization of dialkyne and diazide monomers, oligomers or polymers, has been thoroughly investigated.[4] However, the main drawback of these A–A/B–B strategies resides on the difficulty to achieve stoichiometry between antagonist click functionalities, broad distributions of linear and cyclic chains with limited degree of polymerization being generally obtained. To a smaller extent A–B polyaddition strategies have also been investigated. Matyjaszewski and co-workers reported the click coupling of α-azide-ω-alkyne polystyrenes, yielding mixtures of linear and cyclic macromolecules.[5] Similar architectures were also obtained by Liskamp and co-workers using microwave-assisted cycloaddition of peptide-based A–B monomers in dilute conditions ([monomer] $<$ 100 mg $mL^{-1}$).[6] This approach was more recently used to design well-defined polystyrene and poly(*N*-isopropyl acrylamide) macrocycles.[7]

Herein, we develop a novel A–B polyaddition strategy based on the click chemistry step growth polymerization of tailor-made low molar mass heterofunctional monomers (Scheme 1). First, three stable α-azide-ω-alkyne monomers were synthesized using straightforward synthetic procedures. Then, the step growth (co)polymerization of these monomers yielded (co)polymers with tunable structures and properties.

In order to adjust the thermal properties, the distance between two triazole linkages, as well as the controlled degradation of the resulting polymers, different α-azide-ω-alkyne monomers were prepared and characterized by $^1H$ and $^{13}C$ NMR. Monomer **2** was synthesized from methyl 4-hydroxybenzoate using sequential alkylation, reduction, bromination and azidation procedures.[8] Monomer **3** was prepared by DCC/DPTS esterification of 4-pentynoic acid and 11-azidoundecanol, **1**.[9] Monomer **4** was obtained from nucleophilic substitution of propargyl bromide by sodium 11-azidoundecanolate in anhydrous THF. This reaction proceeded with high yield and fidelity without being affected by the surrounding azide functionality. It therefore represents a versatile and efficient single-step pathway for the alkylation of azide derivatives. Monomers **2–4** are stable in the absence of copper(I) catalyst, as no traces of addition products were observed even after prolonged storage at *ca.* −4 °C. One advantage of the chosen structures is that all synthesized monomers have a $(n_C + n_O)/n_N$ ratio higher than 3, and could therefore be manipulated without any significant risk of explosion.[8]




**Scheme 1** Synthesis and click chemistry step growth (co)polymerization of α-azide-ω-alkyne monomers **2–4**.

[a] *Université de Lyon, CNRS UMR5223, Ingénierie des Matériaux Polymères, INSA de Lyon, Laboratoire des Matériaux Macromoléculaires, Villeurbanne, F-69621, France*
[b] *Université de Lyon, CNRS UMR5223, Ingénierie des Matériaux Polymères, Université de Lyon 1, Laboratoire des Matériaux Polymères et Biomatériaux, Villeurbanne, F-69622, France. E-mail: eric.drockenmuller@univ-lyon1.fr*

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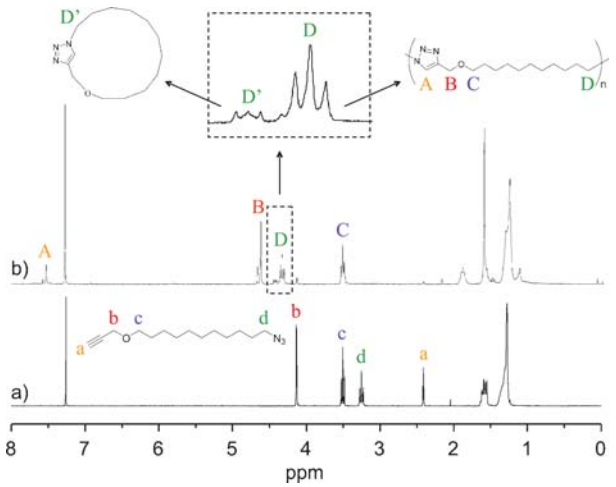


**Fig. 1** $^1$H NMR spectra of (a) monomer **4** and (b) polytriazole **7**.

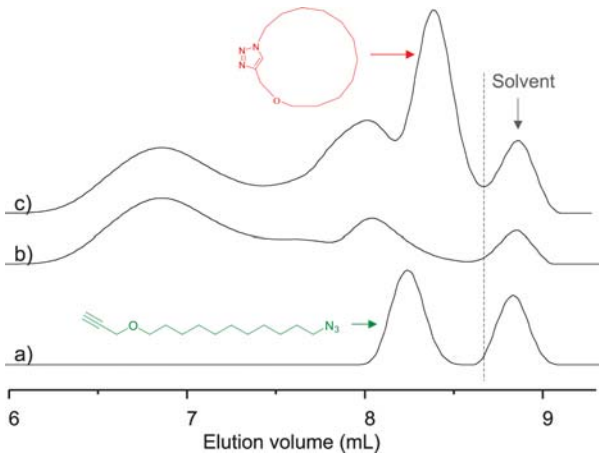


**Fig. 2** SEC analysis of monomer **4** and resulting polytriazole **7** in $CHCl_3$ ((a) monomer, (b) precipitated polymer, (c) crude polymer).

First, monomers **2–4** were polymerized in chloroform (0.2 M of monomers) using $Cu(PPh_3)_3Br$ and DIPEA as catalytic system (respectively 0.01 and 3 equivalents according to the monomer). Resulting homopolymers were characterized by $^1$H and $^{13}$C NMR as well as SEC analyses.

As an example, $^1$H NMR spectra of monomer **4** and corresponding polytriazole **7** are presented in Fig. 1. The click chemistry polyaddition of the monomer is confirmed by the appearance of the characteristic signal of the triazole rings at 7.51 ppm, as well as the disappearance of the alkyne signal at 2.41 ppm. Also, during the polyaddition process the signals of methylene groups adjacent to alkyne and azide functionalities at 3.25 and 4.12 ppm were progressively shifted to 4.32 and 4.61 ppm, respectively. The splitting of the signals at 7.51, 4.61 and 4.32 ppm (towards 7.56, 4.66 and 4.42 ppm, respectively) must be pointed out as they highlight the presence of 13 mol% of a cyclic derivative arising from monomer **4** intramolecular click reaction. This low molar mass cycle could be easily isolated after precipitation of the polymer in diethyl ether, as confirmed by $^1$H NMR analysis of the filtrate and the precipitate. The ratio of cyclic *vs.* linear species could be easily tuned by varying the monomer weight fraction in the reaction media (0.1–50 wt% of monomer). Further work regarding the elaboration of cycles through cyclization of well-defined heterofunctional oligomers is currently under progress.

SEC experiments performed in $CHCl_3$ on monomer **4**, crude polymerization mixture and precipitated polymer **7** are plotted on Fig. 2. It first appears that no monomer **4** remains in the polymerization mixture, pointing out the complete conversion characteristic of the click chemistry process. Corroborating $^1$H NMR data, a significant amount of a lower molar mass compound corresponding to the intramolecular click reaction of monomer **4** appears at an elution volume of 8.4 mL. Also, as discussed above, this compound could be isolated and was absent from the SEC traces of precipitated polytriazole **7**. Other cyclic structures obtained from the intramolecular reaction of heterofunctional dimers and oligomers are overlaid with the smallest linear species at elution volumes of 7.5–8.2 mL. The weight average molar mass of the linear polytriazoles were estimated by deconvolution of the peak at *ca.* 6.8 mL yielding $M_n$ values of *ca.* 13 000 g mol$^{-1}$ according to polystyrene standards. The same dilution-mediated distribution of cyclic and linear species was observed for polytriazole **6** and **10**.

Then, in order to adjust the solubility and the thermal properties of the resulting materials, different copolymers were prepared using every stoichiometric combination of monomers **2–4**, yielding copolymers **8–11**. In addition to NMR and SEC (when soluble in $CHCl_3$), all polytriazoles were characterized by DSC and ATG in order to investigate their thermal properties in relation with the monomer(s) structure(s). The solubility and thermal properties of (co)polymers **5–11** are summarized in Table 1. Concerning polytriazole **5**, the combination of the backbone rigidity, the hydrogen bonding capacity of triazole rings and the π-stacking of the phenyl groups results in a material only partially soluble in DMSO. DSC analysis of this polymer shows an amorphous behaviour for temperatures ranging from 0 to 200 °C. However, its melting temperature might be higher than its degradation temperature, as generally observed for highly crystalline aromatic polymers such as aramides.

Polytriazoles **6** and **7** are semi-crystalline powders ($T_m$ = 115 and 107 °C, respectively) soluble in halogenated and polar aprotic solvents. Compared to **5**, this solubility difference results from the longer size, the lower inter-chain cohesion and the lower rigidity of the $C_{11}$ segments separating two consecutive triazole linkages. Both polymers have a glass transition temperature ($T_g$) of *ca.* −10 °C, higher than polyester and polyether analogues (−44 °C and −80 °C for PTMO and $C_{11}$ polyester, respectively).[9] Thus, triazole groups participate to the increase of $T_g$, most probably toward interchain

**Table 1** Characteristics of polytriazoles **5–11**

| Sample | **2** : **3** : **4**[a] | $T_g$/°C | $T_m$/°C | Solubility[b] | $M_n$[c]/g mol$^{-1}$ |
|---|---|---|---|---|---|
| **5** | 1 : 0 : 0 | 125 | — | — | — |
| **6** | 0 : 1 : 0 | −12 | 115 | C, D, S | 13 300 |
| **7** | 0 : 0 : 1 | −9 | 107 | C, D, S | 13 300 |
| **8** | 1 : 1 : 0 | 5 | — | S | — |
| **9** | 1 : 0 : 1 | 20 | — | S | — |
| **10** | 0 : 1 : 1 | −17 | 81 | T, C, D, S | 12 100 |
| **11** | 1 : 1 : 1 | 0 | — | S | — |

[a] Mol%. [b] T = THF, C = $CHCl_3$, D = $CH_2Cl_2$, S = DMSO. [c] Obtained by SEC in $CHCl_3$ according to polystyrene standards.

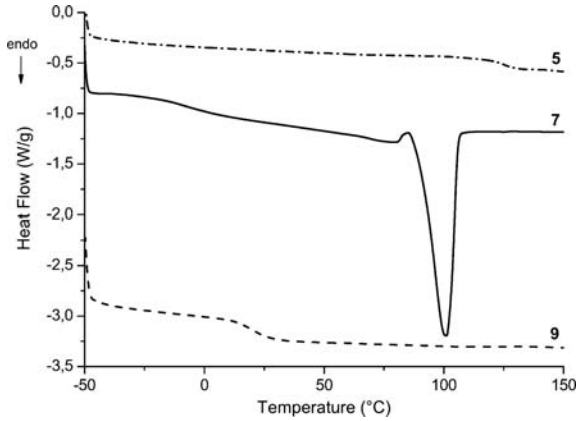


**Fig. 3** DSC Thermograms of polytriazole homopolymers **5**, **7** and corresponding copolymer **9** obtained from monomers **2** and **4**.

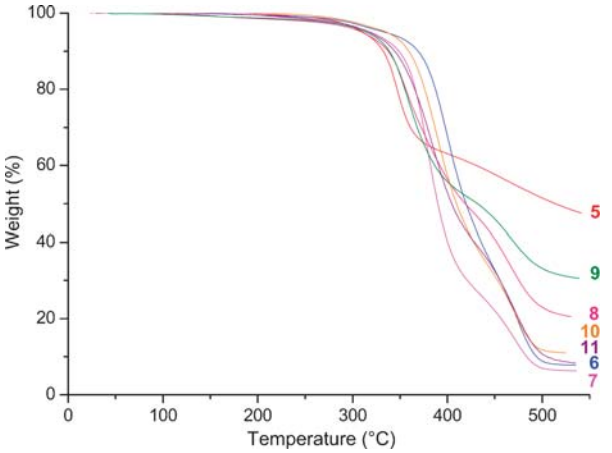


**Fig. 4** TGA analyses of polymers **5–11**.

hydrogen bonding interactions. However, $T_g$ remains lower than for corresponding polyamide derivatives ($T_g$ = 50 °C for $C_{12}$ polyamide).

The replacement of the ester linkage by an ether only slightly changes the melting temperature ($T_m$) of **6** and **7**, indicating that thermal properties are mainly ruled by the triazole ring units. Such high $T_m$ values cannot be attributed to crystallization of the $C_{11}$ methylene segments only. Therefore the whole repeating unit involving hydrogen bonding triazole rings participates to the crystal structure.

Copolymers **8**, **9** and **11** based on monomer **2** are amorphous with $T_g$ values of *ca.* 5, 20 and 0 °C, respectively. Similarly to the corresponding homopolymers **6** and **7**, copolymer **10** is semi-crystalline ($T_m$ = 81 °C). However, crystallisable segments are shorter in this random copolymer, leading to a reduction of the crystal size, that lowers the melting temperature of **10** compared to the corresponding homopolymers **6** and **7**.

The click chemistry step growth polymerization of A–B monomers allows to easily combine different heterofunctional monomers, leading to a range of polytriazoles with tunable properties. Besides the solubility properties, Fig. 3 shows an example of the influence of the monomer structures on the thermal properties of the resulting materials. Indeed, DSC thermograms of homopolymers **5**, **7** and the corresponding copolymer **9** highlight the change in the thermal and therefore mechanical properties (shift of $T_g$ and loss of crystallinity) resulting from the combination of monomers with distinct structures.

Finally, ATG analyses (Fig. 4) show that all synthesized polytriazoles are relatively stable, resulting in degradation temperatures (at 10 wt% loss under nitrogen) from 330 to 380 °C. Here again, the influence of the monomer combinations on the final material properties is illustrated, since the loss of weight varies significantly with the initial monomer structure. For instance, polytriazoles containing benzyl monomer **2** in a ratio of at least 50 mol% (*e.g.* polytriazoles **5**, **8** and **9**) present a high amount of ash (47, 30 and 20 wt%, respectively) compared to polytriazoles based on aliphatic monomers.

In conclusion, we developed a versatile strategy for the elaboration of polytriazole (co)polymers by click chemistry step growth polymerization of low molar mass α-azide-ω-alkyne monomers. This robust synthetic approach can be extended to a wide range of linear polytriazoles and well-defined cyclic architectures with targeted properties. Moreover, the use of click chemistry enables further post-functionalization of the resulting macromolecular architectures since it allows to carry functionalities through their synthesis.

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