Controlled/"Living" Click Polymerization with Possible Bi-Directional Chain-Growth Propagation during Polyaddition

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Abstract: In this work, we found a new class of controlled/"living" polymerization system, which proceeds bidirectional fashion using click reaction of AB monomer bearing azide and alkyne functionalities in a single molecule. The click polymerization of the AB monomer proceeded well using both azide and alkyne initiators in a well-controlled manner in either growth direction to afford polymers with predetermined molecular weights and narrow molecular weight distributions as well as the terminal structures inherited from the initiator. Especially, the polymerizations with the difunctional initiators provided well-defined linear polymers with azide or alkyne groups at both termini. This approach also allows for polymerization control over the second monomer to give a block copolymer.

Introduction

Owing to its high efficiency under mild conditions, the copper-catalyzed cycloaddition reaction between azides and alkynes, referred to as a "click reaction", is now widely utilized in various fields.[1-17] In polymer chemistry, the high efficiency of bond formation led to step-growth polymerizations for AB-type or AA-/BB-type monomers containing both azide and alkyne groups within a single molecule, in which the polyaddition proceeds through intermolecular click reactions to afford polymers with triazole rings as the main chain.[18-30]

There was a hypothesis that polymerization utilizing click reactions could proceed in a chain-growth manner by prioritizing the reaction only at polymer chain terminal. Typically, polyaddition reaction is categorized into step-growth polymerizations, in which it is difficult to control primary structures, unlike vinyl monomer polymerization via chain-growth mechanisms, with only a few exceptions.[31-33] In the click reactions of small molecules without the active use of ligands, it has been reported that neighboring bifunctional azide compounds predominantly yield products containing two triazole rings.[34] This is attributed to the triazole acting as a ligand for the copper catalyst, facilitating intramolecular click reactions. If triazoles formed within polymer chains act similarly, selective reactions at the polymer chain terminal may enable chain-growth polymerization. In fact, Gao et al. reported the formation of hyperbranched polymers with narrow molecular weight distributions through the click polymerization of alkyne-azide AB_2 monomers using trifunctional cores.[35-38] Furthermore, the potential possibility for controlling the AB-type monomer polymerization has also been reported, although its details and applicability remain unclear.[39-41]

In this polymerization, the triazole ring formed during the initiation and propagation reactions could be employed as a ligand for the copper catalyst. This results in the catalyst being captured on the produced polymer, enabling the selective reaction of the azide group at the polymer chain terminal. Based on this mechanism, the present study aims to develop novel effective initiators for the click polymerization. In addition, by designing an alkyne-type initiator, it is anticipated that the alkyne at the chain end can selectively undergo reactions to enable the progression of controlled polymerization, in which the AB monomer behaves as a BA monomer and the insertion direction of the monomer progresses from the azide group toward the alkyne group (Figure 1). This presents a novel system of bidirectional precision polymerization, as it allows for control on either direction, which is unprecedented in traditional polymerization concepts.[42-45] This approach holds promise for the development of new functionalized polymers.

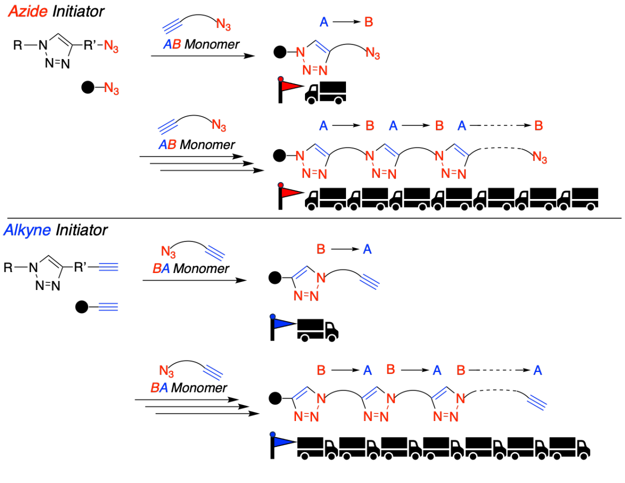
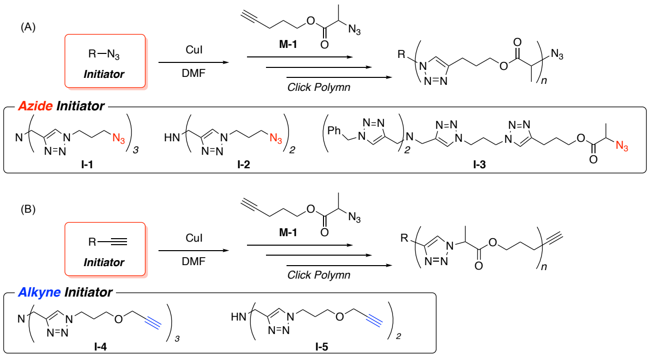


Figure 1. Illustrated scheme of bi-directional controlled/"living" click polymerization.

To address these challenges, we also aimed to develop a chain-growth controlled/"living" polyaddition system through selective reactions of azide or alkyne group at polymer chain terminal. This could be achieved by designing initiators bearing triazole ligands, which effectively capture copper catalysts. Herein, an ester-linked AB monomer with azide and alkyne groups at their termini was designed as a simple monomer for click polyaddition, which is similar to the monomer we had employed for radical polyaddition between allyl and halide groups.[46,47] We have thus far investigated the controlled/"living" click polymerization of the alkyne-azide AB-type monomer using initiators with different functionalities (e.g., mono-, di-, and tri-functional azide and alkyne initiators), as shown Scheme 1.



Scheme 1. Bi-Directional Controlled/"Living" Click Polymerization of Alkyne-Azide AB-type Monomer Using Different Functional Initiators.

Results and Discussion

The design of initiator structures for controlled/"living" click polymerization was investigated for both azide and alkyne terminus. To achieve more efficient coordination with the copper catalyst and rapid initiation reactions, the initiators **I-1** to **I-3** were designed, which are terminal azide compounds with triazole rings linking to amino groups. Also, the terminal alkyne compounds with two or three triazole rings were also designed and synthesized (**I-4** and **I-5**).

Using these initiators, the polymerization of an ester-type AB monomer (**M-1**) possessing both alkyne and azide groups within a single molecule was carried out in DMF at 20 °C, employing copper iodide (CuI) as the catalyst. Table 1 summarizes the number-average molecular weight (M_n) and molecular weight distributions (MWDs) of the polymers thus obtained. The polymerization proceeded smoothly to afford polymers with multimodal peaks in the size-exclusion chromatography (SEC) curves either in the presence or absent of the initiators (Figure S8). However, it is notable that fairly narrow MWDs of the main peak of the polymers were observed (M_w/M_n ~ 1.1), when appropriate initiators were employed. In particular, the trifunctional initiators **I-1** and **I-4** resulted in polymers with precisely controlled molecular weight and MWDs as it has been seen in the conventional living polymerizations.

Figure 2 shows typical examples of the polymerization of AB monomer (**M-1**), which was conducted using a trifunctional azide-(**I-1**) and alkyne-type (**I-4**) initiator in the presence of copper iodide as the catalyst in DMF at 20 °C. Compared with the results using the reported **I-1** as the initiator (Figure 2A), Figure 2B presents the conversions of alkyne and azide groups in the monomer when the alkyne-type initiator was employed. In both cases, quantitative polymerization proceeded. The polymerization using the alkyne-type initiator **I-4** proceeded at a slightly faster than that with **I-1** and almost completed within several tens of hours, that initiated by the azide-type initiator. Furthermore, in the polymerization with the azide-type initiator, the alkyne group of the monomer was nearly completely consumed along with some residual azide groups retaining. In contrast, when the alkyne-type initiator was used, the alkyne groups retained while the azide groups were entirely consumed. These results suggest that the unreacted terminal functional group corresponding to each initiator remains at the polymer growing terminal. The molecular weights and MWDs of the obtained polymers are shown in Figures 2C–E. Although small peaks of the oligomers were also observed at low molecular weight regions in all cases, both of the azide- and alkyne-type initiator resulted in SEC curves with narrow distributions as the main peaks in the higher molecular weight region, which shifted towards higher molecular weights as the reaction proceeded. The M_n of the main peak increased in direct proportion to the conversion, maintaining close to the calculated values. This indicates that the propagation reactions occurred dominantly at the polymer chain ends, realizing a chain-growth controlled/"living" click polymerization process effectively with both azide- and alkyne-type initiators.

Table 1. Controlled/"Living" Click Polymerization with Various Initiators.[a]

entry	Initiator	Terminal	[Initiator]$_0$/[CuI]$_0$ (mM)	time (h)	N_3 Conv.[b] (%)	M_n[c] (SEC)	M_n (calcd)[d]	M_w/M_n[c]
1	None	–	–/5.0	75	97	2,000	–	7.49
2	**I-1**	azide	5.0/5.0	50	91	9,300[e]	8,750	1.08
3	**I-1**	azide	5.0/15	94	>99	11,700[e]	9,480	1.08
4	**I-2**	azide	5.0/5.0	2	92	9,300[e]	8,680	1.12
5	**I-2**	azide	5.0/10	8	96	10,600[e]	9,040	1.16
6	**I-3**	azide	5.0/5.0	70	98	5,500[e]	9,580	1.64
7	**I-4**	alkyne	5.0/15	46	>99	11,900[e]	9,520	1.08
8	**I-5**	alkyne	5.0/10	5	99	9,700[e]	9,340	1.14

[a] Polymerization conditions: [monomer]$_0$/[initiator]$_0$ = 250/5.0 mM in DMF at 20 °C. [b] Determined by ^{1}H NMR analysis of the reaction mixture. [c] Determined by SEC analysis against PMMA standards. [d] M_n (calcd) = FW(monomer) x ([monomer]$_0$/[initiator]$_0$) x conversion/100 + FW(initiator). [e] M_n of the main peak at higher molecular weight region.

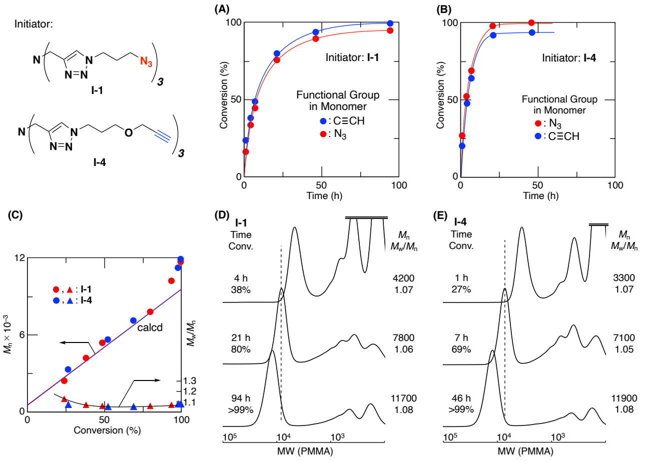


Figure 2. Click polymerization of ester-type AB monomer (**M-1**) with trifunctional initiator (**I-1** and **I-4**) in DMF at 20 ºC: $[\mathrm{M}]_0/[\text{initiator}]_0/[\mathrm{CuI}]_0 = 250/5/15$ mM.

The polymers with narrow MWDs in the higher molecular region thus obtained with **I-1** and **I-4** were further analyzed by the ^{1}H NMR spectroscopy after purification using a preparative SEC (Figure 3). In all spectra, the peaks attributed to the repeating structure of the polymers connected with triazole rings were observed (*a*–*f*). In addition to the repeating units, the peaks derived from the initiators were also detected as *g*–*k* with **I-1** and as *g*–*m* with **I-4**, respectively. In the case of the azide-type **I-1**, the methine peak (*e′*) was detected, which should be adjacent to the azide group at the polymer terminus. Meanwhile, the peak (*e′*) was not observed for the alkyne-type **I-4**, but other peaks (*a′* and *b′*) corresponding to those of terminal alkyne and its adjacent methylene group were observed due to the opposite direction of monomer addition. For both types of the polymers, the molecular weights calculated by the integral ratios between the peaks of initiator and repeating units were close to the theoretical values assuming that one polymer chain was formed per one initiator molecule.

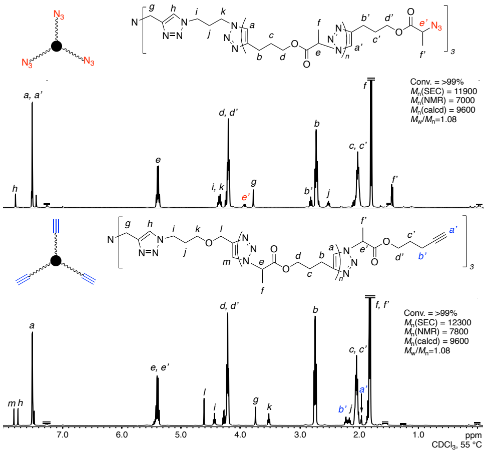


Figure 3. ^{1}H NMR analysis of the poly(**M-1**) obtained from trifunctional azide (top) or alkyne (bottom) initiators (**I-1** and **I-4**, respectively) in $CDCl_3$ at 55 °C.

The polymers were further analyzed using MALDI-TOF MS (Figure 4). In both mass spectra, predominantly a single series of the peaks was observed and they were separated at 181 interval each, which is corresponding to the molecular weight of the monomer (**M-1**; FW: 181.2). The absolute molecular weights of each peak were consistent with the theoretical values on the assumption that polymerization proceeded from an initiator molecule (**I-1** or **I-4**), resulting in polymers with azide or alkyne terminal groups, respectively. The existence of terminal functional groups in these polymers were also confirmed by FT-IR spectroscopy (Figure S9). In the spectra of the polymer form **I-1**, the peak was observed at around 2,000 cm^{-1} corresponding to the stretching vibration of the azide group as in the monomer. In contrast, with the alkyne-type initiator (**I-4**), the peak for the azide group disappeared and the peak corresponding to the CH stretching vibration of the alkyne group was remained at around 3,200 cm^{-1}. These demonstrate that the polymerization proceeded via a chain growth mechanism to afford polymers with terminal azide or alkyne functional groups depending on the initiators, irrespective of the direction of propagation reaction.

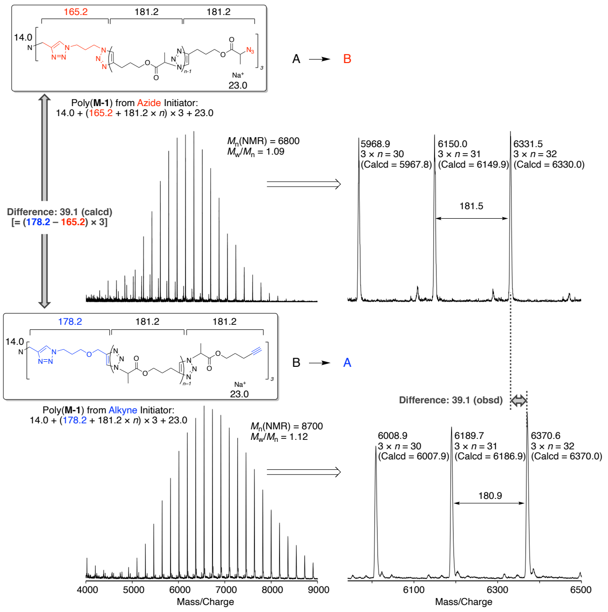


Figure 4. MALDI-TOF MS spectra of the poly(**M-1**) obtained from trifunctional azide (top) and alkyne (bottom) initiators (**I-1** and **I-4**, respectively).

As already shown in the SEC curves in Figure 2, the oligomer peaks were contained in the product other than the main peak. After the polymerization with **I-1** was completed, the low-molecular-weight region of the polymer was also fractionated by the preparative SEC (Figure S10-S12). In the ^{1}H NMR spectrum of the oligomer, peaks corresponding neither to the initiator nor terminal functional groups, i.e., azide and alkyne, were not observed. Furthermore, MALDI-TOF MS analysis also revealed that the units derived from the initiator were absent and the molecular weights agreed with only the sum of several monomer units, indicating that the low-molecular-weight polymers were identified as cyclic oligomers.

Thus, we hypothesize that the polymerization proceeded via the following plausible mechanism: the copper catalyst first coordinates with the initiator, and thus the azide group in the initiator selectively reacts with the monomer to initiate the polymerization (Scheme S1). The newly-generated triazole ring may function as the ligand for copper capturing the catalyst around polymer chain, and consequently to induce selective reactions of the functional groups at the polymer termini. Thus, since the catalyst exists near the polymer chains, the polymer termini react preferentially to result in chain-growth polymerization even with different amounts of the catalyst loading (also see; entries 2 and 3 or 4 and 5 in Table 1). As the minor reaction, the catalyst occasionally facilitates reactions between free monomers, leading to the formation of oligomers. These oligomers, possessing both alkyne and azide groups, can either integrate into the chain-growth polymerization or undergo an intramolecular reaction to form the cyclic oligomers as byproducts. Also, the number of the growing terminal in the polymer chain might be the factor for controlled growth and the monofunctional initiator **I-3** resulted in broader MWDs even with extended triazole rings (also see; entry 6 in Table 1 and Figure S8).

Note that the difunctional initiator can produce linear polymers, with which the control of click polymerization has been believed to be difficult so far. The polymerizations with the difunctional initiators (**I-2** and **I-5**) were performed under the similar conditions using CuI as the catalyst (Figure 5). Even in the cases with difunctional initiators, the M_n of the main peaks linearly increased with the azide group, maintaining values close to the theoretical values similarly to those with trifunctional initiators. Though the contents of the oligomer with difunctional initiators were slightly larger than those with trifunctional initiators, the SEC profiles showed slightly broader but fairly narrow MWDs, which remained narrow while the peak shifted toward higher molecular weight regions as the reaction progressed. The obtained polymers were also further purified and analyzed by ^{1}H NMR (Figure S13). As in the case with trifunctional initiators, the polymer exhibited well-defined structure from the initiator residue. Thus, it was demonstrated that the polymerization proceeded well in a controlled/"living" fashion even with bifunctional alkyne-type initiators to yield well-defined linear polymers with azide or alkyne groups at both termini.

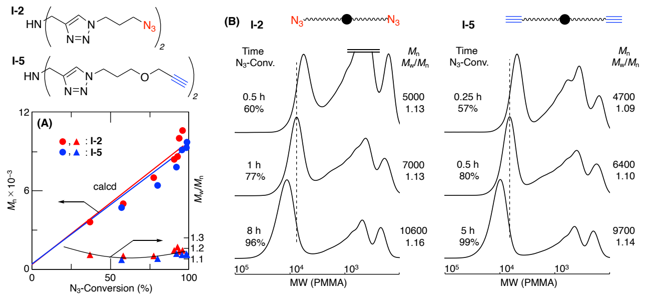


Figure 5. Conversion-M_n (A) and SEC curves (B) for the polymers from difunctional azide (**I-2**) or alkyne initiator (**I-5**). Polymerization condition: [**M-1**]$_0$ = 250 mM; [initiator]$_0$ = 5.0 mM; [CuI]$_0$ = 10 mM in DMF at 20 °C.

The molecular weight control over the initiator concentration was confirmed by changing the initial feed ratio of monomer to initiator from 25 to 100 with the tri- and di-functional initiators (**I-1** and **I-2**). Figure 6 illustrates the M_ns and MWDs of the obtained polymers at various loadings of the initiator. The M_n of the resulting polymers increased as the initiator feed ratio decreased, which agreed with the theoretical values calculated from the monomer-initiator feed ratio and monomer conversion. In the SEC profiles, although the intensity of the oligomer peaks increased as the M_n became higher, the main peaks exhibited relatively narrow MWDs in all cases (M_w/M_n = 1.1–1.2). Thus, the controllability of the M_n was demonstrated as in the case of conventional living polymerizations.

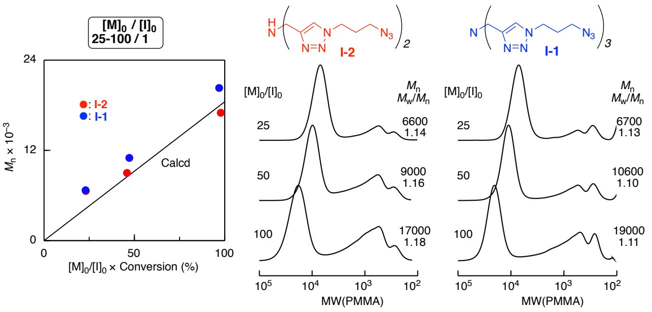


Figure 6. Click polymerization of **M-1** with di or trifunctional initiator (**I-1** and **I-2**) in DMF at 20 ºC at varying feed ratios: [M]$_0$ = 250 mM; [initiator]$_0$/[CuI]$_0$ = 1/3 (for **I-1**) or 1/2 (for **I-2**).

Finally, the controlled/"living" polymerization was applied for the synthesis of block copolymer (Figure 7). Using the difunctional initiator **I-2**, **M-1** was first polymerized to obtain poly(**M-1**) with narrow MWDs and azide termini at both ends. After purification by precipitation, the polymer was employed as the macroinitiator for the polymerization of another type of monomer, amide monomer **M-2** as the second monomer. The second stage of the polymerization also proceeded smoothly, and the SEC curve of the product exhibited a unimodal main peak that shifted toward the higher molecular weight region after precipitation, indicating the formation of the block copolymer. The resulting block copolymer was further analyzed by ^{1}H NMR spectroscopy (Figure S14). The spectrum showed the broad peaks corresponding to the repeating units derived from **M-2** in addition to the peaks derived from the original macroinitiator. The composition ratio calculated by using these peaks matched with the theoretical values. Thus, it was demonstrated that an ABA-type triblock copolymer, consisting of polyamide and polyester segments, was successfully synthesized through this polymerization.

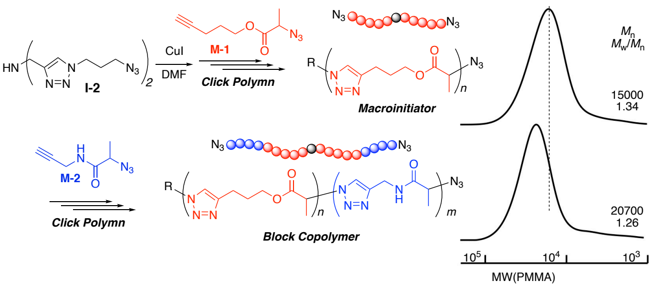


Figure 7. Block copolymerization of **M-1** and amide-type monomer (**M-2**) using poly(**M-1**) as the macroinitiator in DMF at 0 °C: [**M-1**]$_0$ = 250 mM, [**I-2**]$_0$ = 2.5 mM, [CuI]$_0$ = 5 mM for 1st block, and [**M-2**]$_0$ = 125 mM, [poly(**M-1**)]$_0$ = 2.5 mM, [CuI]$_0$ = 5 mM for 2nd block.

Conclusion

Various alkyne- and azide-type initiators were applied for the controlled/"living" click polymerization. Regardless of the terminal structures and unlike conventional living polymerizations, a unique bidirectional chain-growth propagation of AB monomers occurred either from azide or alkyne terminal, establishing a new paradigm in precision polymerization. Furthermore, this may hold significant potential for the synthesis of not only novel linear polymers but also new types of block copolymers. Notably, as long as the monomers possess both alkyne and azide groups, the intervening structure appears to have minimal constraints expanding the scope of applicable monomers, which is now under investigations in our laboratory.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords: Living Polymerization • Click Reaction • Chain Growth Polymerization • Bi-Directional • Block Copolymerization

[1] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004-2021.

[2] C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem*. **2002**, *67*, 3057-3064.

[3] V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem., Int. Ed*. **2002**, *14*, 2596-2599.

[4] N. J. Agard, J. A. Prescher, C. R. Bertozzi, *J. Am. Chem. Soc.* **2004**, *126*, 15046-15047.

[5] P. Wu, A. K. Feldman, A. K. Nugent, C. J. Hawker, A. Scheel, B. Voit, J. Pyun, J. M. J. Fréchet, K. B. Sharpless, V. V. Fokin, *Angew. Chem., Int. Ed.* **2004**, *43*, 3928-3932.

[6] A. Krasiński, Z. Radić, R. Manetsch, J. Raushel, P. Taylor, K. B. Sharpless, H. C. Kolb, *J. Am. Chem. Soc.* **2005**, *127*, 6686-6692.

[7] J. A. Opsteen, J. C. M. van Hest, *Chem. Commun.* **2005**, 57-59.

[8] B. A. Laurent, S. M. Grayson, *J. Am. Chem. Soc.* **2006**, *128*, 4238-4239.

[9] J.-F. Lutz, *Angew. Chem., Int. Ed.* **2007**, *46*, 1018–1025.

[10] W. H. Binder, R. Sachsenhofer, *Macromol. Rapid Commun.* **2007**, *28*, 15-54.

[11] C. D. Hein, X.-M. Liu, D. Wang. *Pharm. Res.* **2008**, *25*, 2216-2230.

[12] R. K. Iha, K. L. Wooley, A. M. Nyström, D. J. Burke, M. J. Kade, C. J. Hawker, *Chem. Rev.* **2009**, *109*, 5620-5686.

[13] S. I. Presolski, V. P. Hong, M. G. Finn, *Curr. Protoc. Chem. Biol.* **2011**, *3*, 153-162.

[14] K. Satoh, J. E. Poelma, L. M. Campos, B. Stahl, C. J. Hawker *Polym. Chem.* **2012**, *3*, 1890-1898.

[15] B. T. Worrell, J. A. Malik, V. V. Forkin, *Science* **2013**, *340*, 457-460.

[16] V, Castro, H. Rodríguez, F. Albericio, *ACS, Comb, Sci.* **2016**, *18*, 10-14.

[17] Z. Geng, J. J. Shin, Y. Xi, C. J. Hawker, *J, Polym, Sci.* **2021**, *59*, 963-1042.

[18] D. D. Díaz, S. Punna, P. Holzer, A. K. McPherson, K. B. Sharpless, V. V. Fokin, M.G. Finn, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 4392.

[19] D. J. V. C. van Steenis, O. R. P. David, G. P. F. van Strijdonck, J. H. van Maarseveen, J. N. H. Reek, *Chem.Commun.* **2005**, *34*, 4333-4335.

[20] N. G. Angelo, P. S. Arora, *J. Am. Chem. Soc.***2005**, *127*, 17134-17135.

[21] N. V. Tsarevsky, B. S. Sumerlin, K. Matyjaszewski, *Macromolecules* **2005**, *38*, 3558-3561.

[22] M. van Dijk, K. Mustafa, A. C. Dechesne, C. F. van Nostrum, W. E. Hennink, D. T. S. Rijkers, R. M. J. Liskamp, *Biomacromolecules* **2007**, *8*, 327–330.

[23] M. van Dijk, M. L. Nollet, P. Weijers, A. C. Dechesne, C. F. van Nostrum, W. E. Hennink, D. T. S. Rijkers, R. M. J. Liskamp, *Biomacromolecules* **2008**, *9*, 2834–2843.

[24] S. Binauld, D. Damiron, T. Hamaide, J. P. Pascault, E. Fleury, E. Drockenmuller, *Chem. Commun*. **2008**, 4138-4140.

[25] C. Besset, S. Binauld, M. Ibert, P. Fuertes, J.-P. Pascault, E. Fleury, J. Bernard, E. Drockenmuller, *Macromolecules* **2010**, 43, 17–19.

[26] M.-A.Berthet, Z. Zarafshani, S. Pfeifer, J.-F. Lutz, *Macromolecules* **2010**, *43*, 44–50.

[27] S. Binauld, E. Fleury, E. Drockenmuller, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 2470-2476.

[28] A. Touris, N. Hadjichristidis, *Macromolecules* **2011**, *44*, 1969–1976.

[29] A. Hashidzume, T, Nakamura, T. Sato. *Polymer* **2013**, *54*, 3448-3451.

[30] J. Yang, L. Chen, M. Zhu, M. W. Ishaq, S. Chen, L. Li, *Macromolecules* **2022**, *55*, 6830–6840.

[31] A. Yokoyama, R. Miyakoshi, T. Yokozawa, *Macromolecules* **2004**, *37*, 1169-1171.

[32] E. E. Sheina, J. Liu, M. C. Iovu, D. W. Laird, R. D. McCullough, *Macromolecules* **2004**, *37*, 3526-3528.

[33] T. Yokozawa, A. Yokoyama, *Chem. Rev.* **2009**, *109*, 5595-5619.

[34] V. O. Rodionov, V. V. Fokin, M. G. Finn, *Angew. Chem., Int. Ed.* **2005**, *117*, 2250-2255.

[35] X. Cao, Y. Shi, X. Wang, R. W. Graff, H. Gao, *Macromolecules* **2016**, *49*, 760-766.

[36] X. Cao, Y, Shi, H, Gao, *Synlett* **2017**, *28*, 391-396.

[37] X. Cao, Y. Shi, W. Gan, H. Gao, *Chem. Eur. J.* **2018**, *24*, 5974-5981 .

[38] H. Naguib, X. Cao, H. Gao, *Macromol. Chem. Phys.* **2019**, *220*, 1900221.

[39] A preliminary part of this work was presented at the 67th SPSJ Annual Meeting, the Society of Polymer Science, Japan; Nakamura, T.; Uchiyama, M.; Satoh, K.; Kamigaito, M. *Polym. Prepr., Jpn*. **2018**, 67(1), 3E03.

[40] W. Gan, X. Cao, Y. Shi, H. Gao, *J. Polym. Sci.* **2020**, *58*, 84-90.

[41] K. Ma, X. Jin, W. Gan, C. Fan, H. Gao, *Polym. Chem.* **2022**, *13*, 891–897.

[42] Handbook of Radical Polymerization; K. Matyjaszewski, T. P. Davis, Eds.; Wiley-Interscience: New York, 2002.

[43] *Cationic Polymerizations*, ed. K. Matyjaszewski, Marcel Dekker, New York, 1996.

[44] M. Morton, *Anionic Polymerization, Principles and Practice*, Academic Press, Inc., New York, 1983.

[45] H. L. Hsieh and R. P. Quirk, *Anionic Polymerization: Principles and Practical Applications (Plastics Engineering Series)*, M. Dekker, Inc., New York, 1996.

[46] K. Satoh, M. Mizutani, M. Kamigaito, *Chem. Commun.* **2007**, *12*, 1260-1262.

[47] M. Kamigaito, *Bull. Chem. Soc. Jpn* **2024**, *97*, uoae069..

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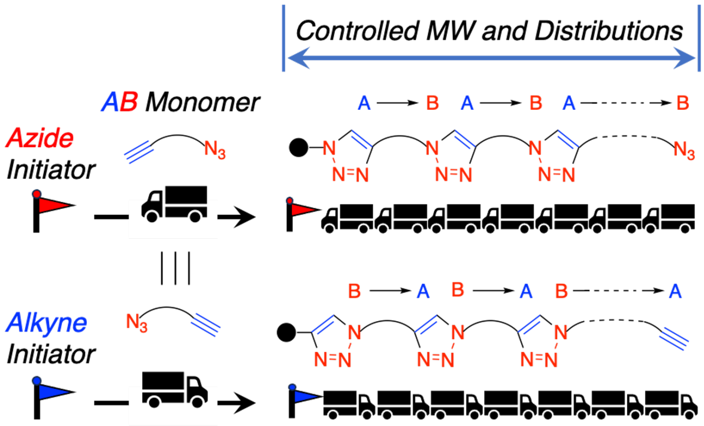

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