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Chain-Growth Cycloaddition Polymerization via a Catalytic Alkyne [2 + 2 + 2] Cyclotrimerization Reaction and Its Application to One-Shot Spontaneous Block Copolymerization

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ABSTRACT: A cobalt-catalyzed alkyne [2 + 2 + 2] cycloaddition reaction has been applied to polymerizations yielding linear polymers via selective cross-cyclotrimerization of yne−diyne monomers, which occurs in a chain-growth manner. Additionally, through control of the alkyne reactivity of the two monomers, this method was efficiently applied to the spontaneous block copolymerization of their mixture. Here we present the proposed mechanism of the catalyst transfer process of this cycloaddition polymerization.

Cycloaddition polymerization reactions are a versatile means for synthesizing unique polymers, as exemplified particularly in recent utilizations of [4 + 2] cycloadditions between alkynes and dicyclopentadienones and [3 + 2] cycloadditions of alkynes and azides (Hüisgen reaction).[1] These processes proceed using a variety of monomer systems such as AB and A_2/B_2, generating various macromolecules. Their propagation occurs in a step-growth manner to yield polymers with relatively high polydispersity having uncontrolled molecular weights.

The alkyne [2 + 2 + 2] cycloaddition reaction occurring in the presence of an appropriate transition-metal catalyst has attracted interest as a straightforward means of synthesizing substituted benzenes.[2] In macromolecule synthesis, it has been reported that homocycloaddition (cyclotrimerization) can polymerize diyne compounds such as 1,8-nonadiyne in a step-growth manner. This process with polymerization of AB_2-type monomers yields highly branched macromolecules.[3a,b] (Homo)-cyclotrimerization of alkynes has also been utilized for construction of benzene-core dendrimers.[3c] However, more controlled polymerizations that produce linear polymers via the reaction of AB-type monomers **I** comprising monoalkyne and diyne moieties (Scheme 1) have not been reported to date. This is largely because of the difficulty in directing alkyne reactivities toward selective cross-coupling. The selective cross-coupling between the monoalkyne and diyne parts (path a) yields linear polymers. Alternatively, polymerization involving a self-coupling reaction (path b and/or c) forms linear and branched structures in a noncontrolled manner. Herein we report the first realization of the selective formation of linear polymers from yne−diyne monomer **I** via a catalytic alkyne cycloaddition reaction. In addition, polymerization proceeded in a chain-growth manner, achieving control over the molecular weights and polydispersity of the resultant polymers. The method was applied to one-shot spontaneous block copolymerization using two monomers having different reactivities.

As an effective catalyst for alkyne cycloaddition reactions, we developed dipimp/$CoCl_2 \cdot 6H_2O$/Zn [dipimp = 2-(2,6-diisopropylphenyl)iminomethylpyridine], which catalyzes the cycloaddition of a variety of alkynes to the corresponding substituted benzenes under mild reaction conditions.[4] To apply this catalysis to the synthesis of linear polymers, we had to control the reactivity of the alkynes to promote selective cross-coupling (path a in Scheme 1). The reaction of simple terminal alkynes such as phenylacetylene and 1-hexyne yielded the corresponding trisubstituted benzenes quantitatively: the reaction of 1,6-diynes containing terminal alkynes proceeded along a self-cycloaddition pathway to yield dimers and trimers [see the Supporting Information (SI) for more details].[4] In contrast, the reaction of a 1:1 mixture of 1,6-diyne **1** and propargyl alcohol **2a** or ether **2b** containing an internal alkyne proceeded smoothly to furnish the cross-coupled product **3** quantitatively without homocoupling of **1** (Scheme 2). The internal alkyne structure prevented self-addition, and the fact that 4-octyne (**2c**) failed to react indicated the importance of the participation of the propargylic oxygen with **2a** and **2b**.

On the basis of these results, we designed yne−diyne **4a** as a type-**I** prototype monomer, expecting it to undergo selective cross-cycloaddition (Scheme 3). Table 1 and Figure 1 summarize the results of cobalt-catalyzed cycloaddition reactions of yne−diyne **4a**. For this reaction, a mixture of **4a**, dipimp/$CoCl_2 \cdot 6H_2O$ (5 mol %), and Zn powder (15 mol %) in *N*-methyl-2-pyrrolidone (NMP) was stirred at 50 °C in either the presence and absence of the alkyne additive as an activator. Samples of the reaction mixture extracted using a syringe at the indicated times were analyzed by gel-permeation chromatography (GPC) [eluent, THF; calibration, polystyrene (PS) standards]. Figure 1a depicts the results of the reaction in run 4 of Table 1.

In all cases, the catalysis produced polymers with M_n in the range $(4.0-8.2) \times 10^3$ and having a unimodal profile on GPC charts. The presence of an alkyne additive made the polydispersity (PDI = M_w/M_n) narrower than when the reaction was performed in its absence. Thus, the addition of a catalytic amount of $MeO_2CC{\equiv}CCO_2Me$ (DMAD) or triyne **5** (5−15 mol %) as an activator led to a PDI as narrow as 1.22−1.28 (runs 2−5). As shown in Figure 1b, plots of M_n versus conversion in the absence of an alkyne additive were nonlinear over 50% of the conversion (run 1; also see SI-Figures 1 and 2). In contrast, the addition of an

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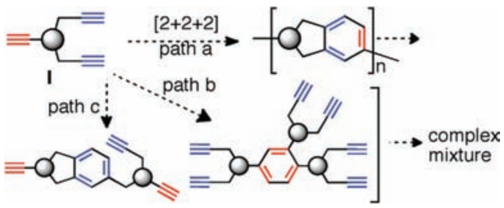
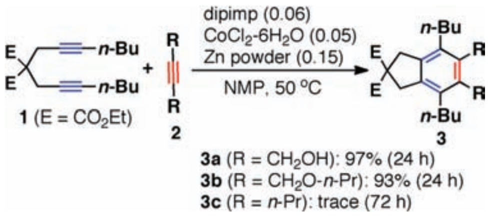
Scheme 1. [2 + 2 + 2] Cycloaddition Reactions of Yne−Diyne I



Scheme 2. Model Reactions for Designing Monomers



Scheme 3. Polymerization of Triyne Monomer 4a

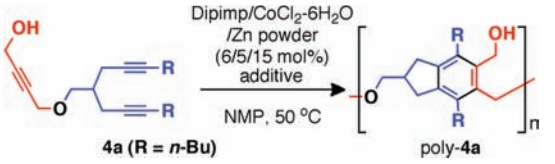
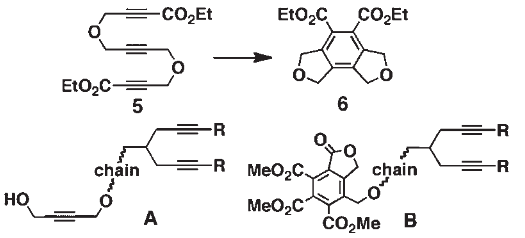


Table 1. Cobalt-Catalyzed Cycloaddition Polymerization of 4a

run	additive (mol %)	time (h)	conv. (%)[a]	$10^{-3}M_n$[b]	PDI[b]
1	none	2	75	8.19	1.43
2	DMAD (15)[c]	2	95	6.76	1.28
3	DMAD (5)[c]	4	90	4.00	1.22
4	**5** (15)	3	92	6.28	1.26
5	**5** (10)	1	96	6.46	1.35

[a] Determined by ^{1}H NMR analysis of samples taken from the reaction mixture. [b] PDI = M_w/M_n, as determined by GPC analyses in THF using PS standards. [c] Terminal structures of the polymers:



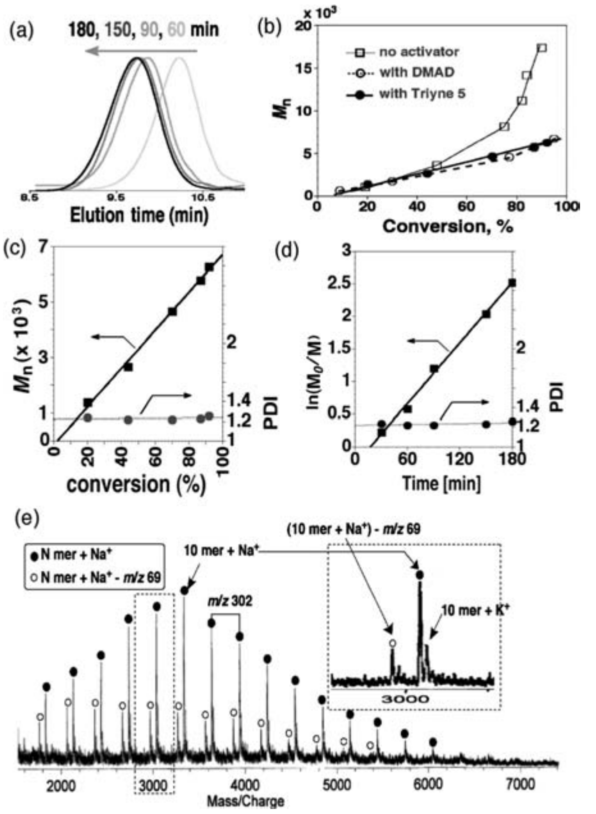
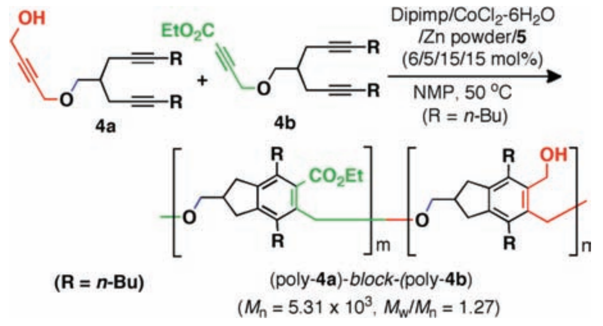


Figure 1. (a) GPC charts of poly-**4a** obtained from the reaction of run 4 in Table 1. (b) Plots of M_n vs conversion for runs 1, 2 and 4. (c) Plots of M_n (■) and PDI (●) vs conversion for run 4. (d) Plots of ln $[M]_0/[M]$ (■) and PDI (●) vs time for run 4. (e) MALDI−TOF mass spectra of poly-**4** obtained by sampling from the reaction of run 4.

electron-deficient alkyne [DMAD or triyne **5**, each of which is a very active alkyne in the (homo)cyclotrimerization] activated the catalysis to start the polymerization quickly, and the increase in M_n was proportional to the monomer conversion (also see SI-Figures 3−6). The mass spectrometry and NMR analyses of the polymers obtained from the DMAD-activated reactions (runs 2 and 3; SI-Figure 11) indicated that the product comprised a mixture of polymers having two types of terminal structures, **A** and **B**. Meanwhile, the reactions activated by triyne **5** (runs 4 and 5) proceeded smoothly without participation of **5** in the polymerization and yielded polymers of type **A** having a narrow PDI when **5** was converted to **6**. As revealed by the MALDI−TOF mass spectra shown in Figure 1e (also see SI-Figure 12), the two series of major peaks were in agreement with values calculated using the formulas 302.2*n* + 23.0 (●) and 302.2*n* + 23.0 − 69.0 (○), where 302.2 is the mass of the monomer unit, 23.0 is the mass of Na^+, and 69.0 is the mass of a terminal propargyl moiety ($HOCH_2C{\equiv}CCH_2$) resulting from poly-**4a** fragmentation under the analytical conditions. Plots of M_n and PDI values for the polymers versus conversion over the entire polymerization process were linear, with PDI ≤ 1.26 (Figure 1a,c). Values of M_n determined by GPC were in good agreement with those determined by NMR analysis (SI-Figure 13). The semilogarithmic kinetic plot of the polymerization was linear up to 92% conversion (Figure 1d). These results clearly indicate that polymerization proceeded in a chain-growth manner.

Next, we applied the method to the polymerization of a mixture of two monomers with different reactivities. The model study revealed that electron-deficient alkynes such as alkynyl esters react with diynes much more rapidly than propargylic alcohols (Scheme 2; also see the SI). On the basis of these results, yne−diyne **4b** was designed as a second monomer, and the polymerization of a mixture of **4a** and **4b** in a 0.06/0.05/0.15/0.15 dipimp/$CoCl_2\cdot6H_2O$/Zn/**5** catalyst system was investigated

Scheme 4. Polymerization of a Mixture of Monomers 4a and 4b



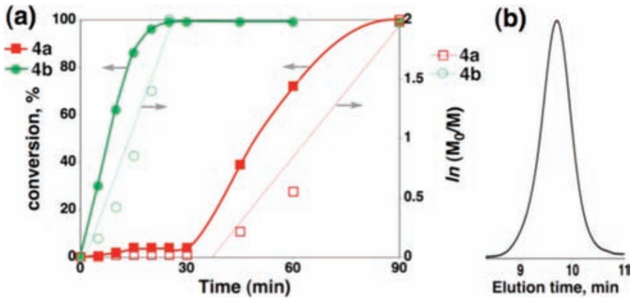
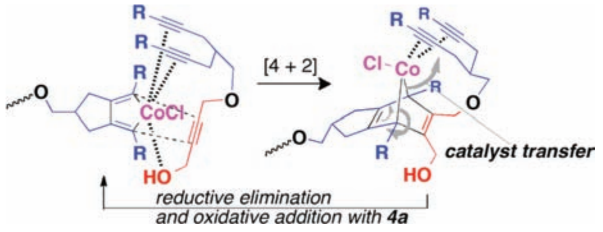


Figure 2. Polymerization behavior of a mixture of **4a** and **4b**. (a) Plots of conversion (●, **4a**; ■, **4b**) and ln $[M]_0/[M]$ (○, **4a**; □, **4b**) vs time. (b) GPC profile of the resulting polymer (after 90 min).

Scheme 5. Proposed Mechanism of the Propagation Steps



(Scheme 4). The polymerization behavior as shown by plots of conversion and ln $[M]_0/[M]$ versus time for each monomer is presented in Figure 2a (also see SI-Figures 8 and 9).

The resultant polymer showed a unimodal GPC profile (Figure 2b) with $M_n = 5.31 \times 10^3$ and a low PDI (1.27). As shown in Figure 2a, the more reactive monomer **4b** was completely consumed within 30 min of its transitioning into the reaction with the less reactive monomer **4a**. For each monomer, the semilogarithmic kinetic plot of polymerization (ln $[M]_0/[M]$) vs time) (Figure 2a) was almost linear. These results demonstrate that the polymerization reaction proceeded in a chain-growth manner accompanied with replacement of monomers from one to another as a result of the large reactivity difference of the two monomers. As a result, the reaction of a mixture of **4a** and **4b** spontaneously gave a copolymer structurally similar to the block copolymer produced by one-shot polymerization.[6]

Currently, we propose for this polymerization the catalyst transfer mechanism[5] depicted in Scheme 5, although the immortal polymerization mechanism cannot be ruled out. The cobalt catalyst may be intramolecularly transferred from the [4 + 2] cycloaddition intermediate to the diyne termini simultaneously with its reductive elimination when a ligand (dipimp) may not participate any longer in the propagation process (see SI-Figure 14 for a more detailed discussion). At the initiation stage, concurrent beginning of the reaction is essential to attain controlled polymerization. Thus, the addition of a highly reactive electron-deficient alkyne such as DMAD or triyne **5**, which undergoes cyclotrimerization much more rapidly than the monomer(s) employed, might enable a quick, simultaneous generation of an active catalyst in a short period.

In conclusion, we have demonstrated that the alkyne [2 + 2 + 2] cycloaddition reaction catalyzed by dipimp/$CoCl_2 \cdot 6H_2O$/Zn is applicable to polymerization, yielding linear polymers via a selective cross-cyclotrimerization reaction that occurs in a chain-growth manner. To the best of our knowledge, this is the first example of chain-growth cycloaddition polymerization. The utilization of this method for one-shot spontaneous block copolymerization of a mixture of two monomers has also been demonstrated. On the basis of the high functional group compatibility with the catalysis,[4] this method may be useful in preparing diverse functionalized polymers in a controlled manner. Further investigation of the reaction mechanism and applications is underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures and characterization of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Goodall, G. W.; Hayes, W. *Chem. Soc. Rev.* **2006**, *35*, 280–312. Meldal, M.; Tornøe, C. W. *Chem. Rev.* **2008**, *108*, 2952–3015. Liu, J.; Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2009**, *109*, 5799–5867. Iha, R. K.; Wooley, K. L.; Nyström, A. M.; Burke, D. J.; Kade, M. J. *Chem. Rev.* **2009**, *109*, 5620–5686. Qin, A.; Lam, J. W. Y.; Tang, B. Z. *Chem. Soc. Rev.* **2010**, *39*, 2522–2544.

(2) Yamamoto, Y. *Curr. Org. Chem.* **2005**, *9*, 503–519. Kotha, S.; Brahmachary, E.; Lahiri, K. *Eur. J. Org. Chem.* **2005**, 4741–4767. Gandon, V.; Aubert, C.; Malacria, M. *Curr. Org. Chem.* **2005**, *9*, 1699–1712. Gandon, V.; Aubert, C.; Malacria, M. *Chem. Commun.* **2006**, 2209–2217. Chopade, P. R.; Louie, J. *Adv. Synth. Catal.* **2006**, *348*, 2307–2327. Tanaka, K. *Chem.—Asian J.* **2009**, *4*, 508–518.

(3) (a) Li, Z.; Lam, J. W. Y.; Dong, Y.; Dong, Y.; Sung, H. H. Y.; Williams, I. D.; Tang, B. Z. *Macromolecules* **2006**, *39*, 6458–6466. (b) Häussler, M.; Liu, J.; Zheng, R.; Lam, J. W. Y.; Qin, A.; Tang, B. Z. *Macromolecules* **2007**, *40*, 1914–1925. (c) Hecht, S.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1999**, *121*, 4084.

(4) Saino, N.; Amemiya, F.; Tanabe, E.; Kase, K.; Okamoto, S. *Org. Lett.* **2006**, *8*, 1439–1442. Goswami, A.; Ito, T.; Okamoto, S. *Adv. Synth.*

Catal. **2007**, *349*, 2368–2374. Watanabe, J.; Sugiyama, Y.; Nomura, A.; Azumatei, S.; Goswami, A.; Saino, N.; Okamoto, S. *Macromolecules* **2010**, *43*, 2213–2218.

(5) Yokozawa, T.; Yokoyama, A. *Chem. Rev.* **2009**, *109*, 5595–5619.

(6) For instance, see: Wu, R.; Al-Azemi, T. F.; Bisht, K. S. *Macromolecules* **2009**, *42*, 2401–2410. Aoi, K.; Miyamoto, M.; Chujo, Y.; Saegusa, T. *Macromol. Symp.* **2002**, *183*, 53–64. Shibasaki, Y.; Sanada, H.; Yokoi, M.; Sanda, F.; Endo, T. *Macromolecules* **2000**, *33*, 4316–4320. Haucourt, N. H.; Peng, L.; Goethals, E. J. *Macromolecules* **1994**, *27*, 1329–1333. Ariga, T.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 7106–7107.