Living Polymerization of Aryl Isocyanides by Multifunctional Initiators Containing Pd–Pt μ-Ethynediyl Units

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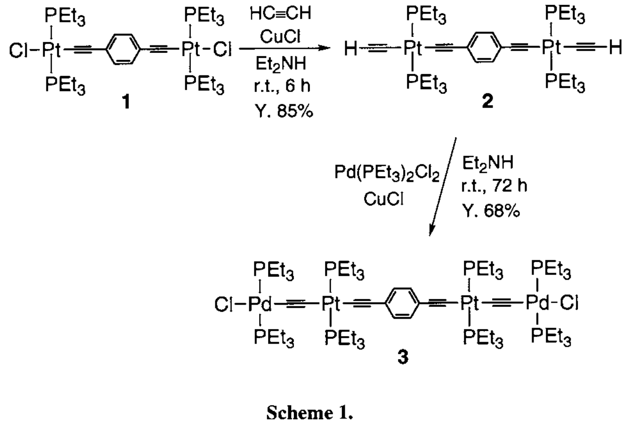
Multinuclear acetylide complexes containing two or three Pd–Pt μ-ethynediyl units have been prepared and successfully applied to a multifunctional initiator for the living polymerization of aryl isocyanides, which gives two- or three-armed poly(isocyanide)s with a narrow polydispersity index in good yields.

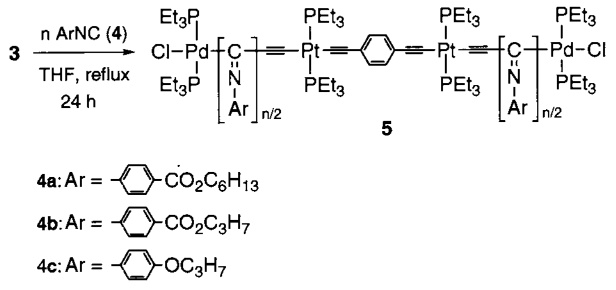
Polymerization using transition metal complexes has attracted much attention in the fields of polymer science and organometallic chemistry in terms of novel polymer syntheses and mechanistic interest.[1] The development of molecular architecture in polymer science has produced polymers with well-controlled three-dimensional shapes such as star-shaped, hyper-branched and dendritic polymers.[2] These polymers have unique properties and functions that are clearly different from those of linear polymers. Although multinuclear complexes possessing plural active sites for polymerization have a potential as an effective initiator for the synthesis of star polymers, the most important subject is whether all metal sites really work for polymerization.[3] Recently we have reported the polymerization of aryl isocyanides by Pd–Pt μ-ethynediyl complexes, in which aryl isocyanides insert into the Pd–C bond successively.[4,5] Since this polymerization system has a real living nature and proceeds with a quantitative initiator efficiency, we have examined the application to a multifunctional system. Herein we wish to present the living polymerization of aryl isocyanides by a multifunctional initiator to give star-shaped poly(aryl isocyanide)s with well-controlled arms.

The synthesis of tetranuclear acetylide complex **3** containing two Pd–Pt μ-ethynediyl units was performed as shown in Scheme 1. Treatment of *p*-diethynylbenzene-bridged diplatinum complex (**1**)[6] with acetylene in diethylamine at room temperature in the presence of a CuCl catalyst gave a diethynyl analog (**2**) in 85% yield.[7] Palladium moieties were introduced by the reaction of **2** with $Pd(PEt_3)_2Cl_2$ under similar conditions to give complex **3** in 68% yield[8] (Scheme 1). Complex **3** was fully characterized by means of spectral measurements and elemental analysis.



Scheme 1.

Polymerization of *p*-hexyloxycarbonylphenyl isocyanide (**4a**) in the presence of complex **3** smoothly proceeded under reflux in THF resulting in brown-yellow polymers (**5a**)–(**5c**) in quantitative yields.[4,5] According to the gel permeation chromatography (GPC) analysis using polystyrene standards, the average molecular weight (M_n) of **5a** was 32000, and the polydispersity index (M_w/M_n) was 1.11. The small polydispersity index suggests the present reaction to be a living polymerization. Other aryl isocyanides such as *p*-propoxycarbonylphenyl (**4b**) and *p*-propoxyphenyl isocyanides (**4c**) also polymerized by **3** to give polymers **5d** and **5e**, respectively, with a narrow distribution of molecular weight (Scheme 2 and Table 1).



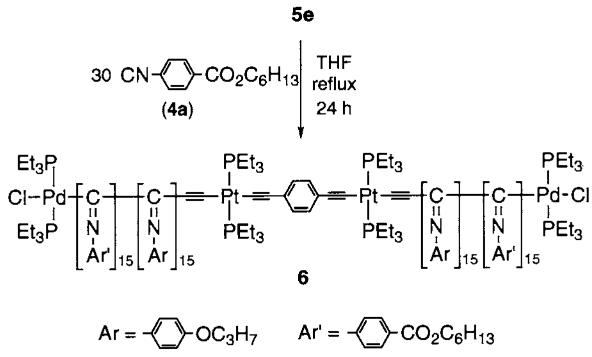
Scheme 2.

Table 1. Polymerization of Aryl Isocyanides **4** by Mutifunctional Initiators **3** and **7**[a,b]

Run	Initiator	Monomer	n[c]	Polymer	M_n[d]	M_w/M_n[d]
1	**3**	**4a**	200	**5a**	32000	1.11
2	**3**	**4a**	120	**5b**	19000	1.09
3	**3**	**4a**	60	**5c**	9000	1.11
4	**3**	**4b**	60	**5d**	6900	1.14
5	**3**	**4c**	30	**5e**	4500	1.09
6	**7**	**4a**	300	**8a**	41000	1.17
7	**7**	**4a**	120	**8b**	18000	1.08
8	**7**	**4b**	30	**8c**	5200	1.07
9	**7**	**4c**	30	**8d**	4300	1.07

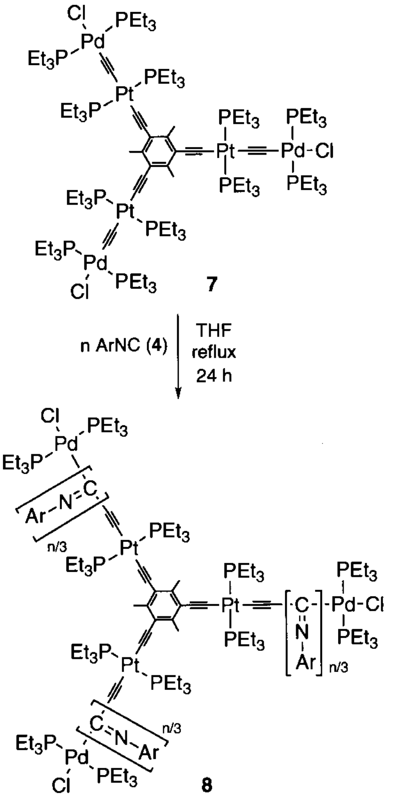
[a] Standard conditions: initiator 5 μmol, THF 10 mL, reflux, 12h. [b] In all reactions isocyanide monomers were completely consumed to produce polymers in quantitative yields. [c] Molar ratio of monomer/initiator. [d] M_n and M_w/M_n were determined by a GPC analysis using polystyrene standards.

Direct evidence that both palladium end groups of complex **3** actually initiate the polymerization with a living nature in the present polymerization was obtained by trace experiments of the synthesis of block-copolymer **6** using GPC and ^{31}P NMR. Thus, the ^{31}P NMR spectrum of initiator **3** exhibited two singlets at δ 16.2 and 10.4. The former was assignable to the phosphine on palladium and the latter to that on platinum, since the latter signal was accompanied by satellite signals due to the coupling with a ^{195}Pt nucleus (J = 2467 Hz). In contrast, ^{31}P NMR spectrum of **5e** (M_n = 4500 and M_w/M_n = 1.09), which was prepared by the reaction of **3** with 30 equiv of **4c**, did not show a signal at δ 16.2 but new signals assigned to the phosphorous atom bound to the palladium around δ 12. Successive addition of 30 equiv of **4a** to a solution of **5e** led to the second polymerization to give a block-copolymer (**6**) with M_n = 8100 and M_w/M_n = 1.24 in a quantitative yield (Scheme 3). In the ^{31}P NMR spectrum of **6**, signals attributable to the phosphorus atom on the palladium were observed at about δ 14, which was consistent with the chemical shift of the phosphorus atom on the palladium of **5c**. The clean shift of ^{31}P NMR signals as well as the GPC peak to a higher molecular-weight region unequivocally showed that complex **3** acts as a bifunctional initiator for the polymerization of aryl isocyanides.



Scheme 3.

Then we investigated the polymerization by multinuclear complex **7**, which contains three Pd–Pt μ-ethynediyl units and has been successfully prepared from a trinuclear platinum acetylide complex[9] by the similar reactions used for the synthesis of **3**, to develop a trifunctional initiator. Complex **7** acted as an effective initiator for the polymerization of aryl isocyanides to give polymers (**8**) with a narrow distribution of molecular weight in quantitative yields (Table 1, Scheme 4). Since this system also exhibited a living nature, successive reactions with two kinds of isocyanides **4c** and **4a** gave block copolymer **9** having an analogous structure to complex **6**. ^{31}P NMR study of **8** and **9** suggested that the reaction with isocyanides occurs at all of the three Pd–Pt μ-ethynediyl units in **7** and the resulting polymers **8** and copolymer **9** have a star-shaped structure.



Scheme 4.

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References and Notes

1 For recent reviews, see: H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, **34**, 1143 (1995); E. Drent and P. H. M. Budzelaar, *Chem. Rev.*, **96**, 663 (1996); W. Kaminsky, *J. Chem. Soc., Dalton Trans.*, **1998**, 1413; M. Sawamoto and M. Kamigaito, *CHEMTECH*, **37**, 30 (1999).

2 For recent reviews, see: D. A. Tomalia, A. M. Naylor, and W. A. Goddard III, *Angew. Chem., Int. Ed. Engl.*, **29**, 138 (1990); J. Issberner, R. Moors, and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, **33**, 2413 (1994).

3 W. Risse and R. H. Grubbs, *Macromolecules*, **22**, 4462 (1989); H. H. Fox, J.-K. Lee, L. Y. Park, and R. R. Schrock, *Organometallics*, **12**, 759 (1993); S. M. Hoff and B. M. Novak, *Macromolecules*, **26**, 4067 (1993); T. J. Deming, B. M. Novak, and J. W. Ziller, *J. Am. Chem. Soc.*, **115**, 2366 (1994); L. S. Boffa and B. M. Novak, *Macromolecules*, **30**, 3494 (1997).

4 K. Onitsuka, T. Joh, and S. Takahashi, *Angew. Chem., Int. Ed. Engl.*, **31**, 851 (1992); K. Onitsuka, K. Yanai, F. Takei, T. Joh, and S. Takahashi, *Organometallics*, **13**, 3862 (1994).

5 F. Takei, K. Yanai, K. Onitsuka, and S. Takahashi, *Angew. Chem., Int. Ed. Engl.*, **35**, 1554 (1996); F. Takei, K. Yanai, K. Onitsuka, and S. Takahashi, *Chem. Eur. J.*, **6**, 983 (2000).

6 S. Takahashi, Y. Ohyama, E. Murata, K. Sonogashira, and N. Hagihara, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 349 (1980).

7 K. Sonogashira, T. Yatake, Y. Tohda, S. Takahashi, and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, **1977**, 291; K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi, and N. Hagihara, *J. Organomet. Chem.*, **145**, 101 (1978).

8 H. Ogawa, K. Onitsuka, T. Joh, S. Takahashi, Y. Yamamoto, and H. Yamazaki, *Organometallics*, **7**, 2257 (1988); K. Onitsuka, T. Joh, and S. Takahashi, *Bull. Chem. Soc. Jpn.*, **65**, 1179 (1992).

9 N. Ohshiro, F. Takei, K. Onitsuka, and S. Takahashi, *Chem. Lett.*, **1996**, 871; N. Ohshiro, F. Takei, K. Onitsuka, and S. Takahashi, *J. Organomet. Chem.*, **569**, 195 (1998).