Multibranching Polymerization: Palladium-Catalyzed Ring-Opening Polymerization of Cyclic Carbamate To Produce Hyperbranched Dendritic Polyamine†

Masato Suzuki,* Atsuhiko Ii, and Takeo Saegusa‡

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

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Recently, hyperbranched dendritic macromolecules are attracting much attention due to their specific structures and characteristics. These molecules with regular branching have been prepared by a stepwise method, i.e., repetition of reactions and subsequent purification.[1,2] Another synthetic method recently developed is polycondensation or polyaddition of a AB_n type monomer although the product polymer has imperfect branching.[3] The present paper presents a new concept for chain polymerization, adequately termed "multibranching polymerization (MBP)", which provides a dendritic polymer involving the initiator as the core (Scheme I). The most characteristic aspect of MBP is *multiplication* of the propagating ends at every step of propagation.

Our previous exploration of Pd-catalyzed ring-opening polymerization[4] suggested to us an idea of MBP as well as a monomer structure for it, i.e., 5,5-dimethyl-6-ethenylperhydro-1,3-oxazin-2-one (1). The key point of the monomer design is that 1 has an amidic proton which is a dormant propagating end (vide infra).[5] In agreement with our plan, 1 was polymerized at room temperature in THF with the aid of $Pd_2(dba)_3{\cdot}CHCl_3$–2dppe, as catalyst, to produce dendritic polyamine **2** together with evolution of CO_2 (Scheme II).

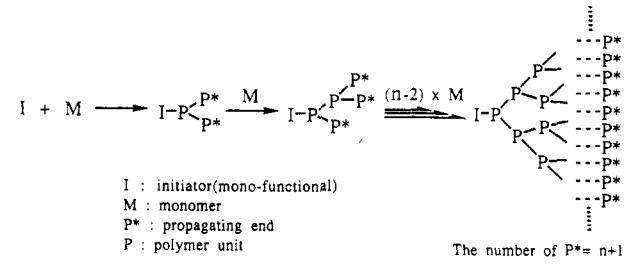
As expected, primary or secondary amines worked as the initiators for the polymerization to manipulate molecular weights of the product polymers. Table I shows representative results employing benzylamine, as initiator. ^1H NMR spectra of reaction mixtures revealed that the monomer was almost quantitatively converted to the polymer. Purification to exclude ligands from the polymer allowed the low molecular weight part to escape. Therefore, as lower molecular weight polymer were produced, the isolate yields were reduced and the $\overline{DP}$ values became higher than those calculated on the feed ratio of the initiator to monomer. The control reaction without any initiators proceeded slowly, but insoluble product was obtained[6] (run 4); however, its IR spectrum was completely identical with that of the soluble polymer produced with the initiator.

The polymer structure was identified by ^{13}C and ^1H NMR spectra, as compared with models such as neopentylamine, *N*-allylneopentylamine, and *N,N*-diallylneopentylamine. These spectra indicated that the polymer has incomplete branching consisting of not only primary and tertiary but also secondary amino moieties; the former are a polymer end and a branching junction, respectively, and the latter is a nonbranching junction. Figure 1 shows the representative ^1H NMR spectrum together with chemical shift values of methylene protons of three models; these values suggested peak assignments of the polyamine **2**. The ^1H NMR spectra offered clues to calculate $\overline{DB}$ (degree of branching) values as well as $\overline{DP}$ values of the product polymers. The $\overline{DB}$ value is a unit ratio of the tertiary amino moiety to the total of the secondary and tertiary ones; it was calculated on the basis of relative intensity between peaks a-2 and a-3 as well as e-2 and e-3 (Table I). Since peak f was assignable to benzylic protons from the initiator of benzylamine, the integral ratio of peak f to others afforded the $\overline{DP}$ value, which was in good agreement with that given by VPO measurement of the molecular weight (Table I). Accordingly, it was concluded that all of the polymer molecules originated exclusively in the initiator of benzylamine.

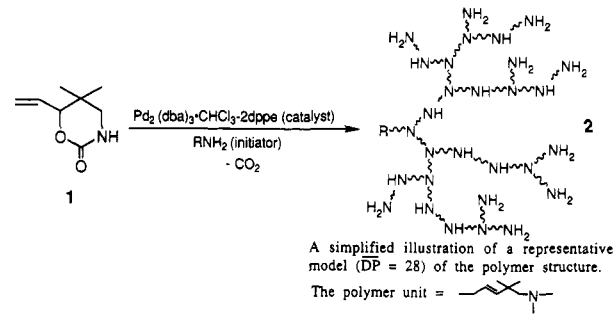
As for the molecular weight distribution of the product polymer, measurement of a M_w/M_n value by GPC was impossible for polyamine **2** because long tailing of a peak was observed due to interaction of **2** with a polystyrene bed in a column. Therefore, primary and secondary amino groups of **2** were transformed to carbamate groups by treatment with *n*-butyl isocyanate, and the resultant polymer was subjected to GPC measurement (eluent, $CHCl_3$; PSt standard); the obtained M_w/M_n value was 1.35 (run 2 in Table I).

Scheme III proposes a most reasonable mechanism for polymerization; the π-allylpalladium complex **3** is the key intermediate.[7] The initiator of a primary amine[8] attacks

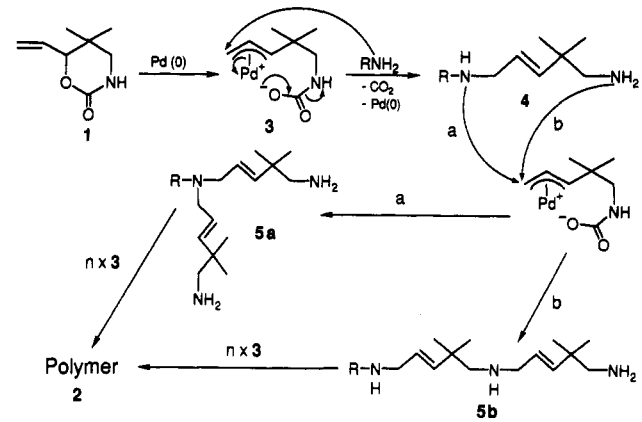
Scheme I
Conceptional Scheme of Multibranching Polymerization (Multiple Coefficient = 2)



Scheme II



Scheme III



† New Ring-Opening Polymerization via π-Allyl Complex. 3.
‡ Present address: Kansai Research Institute, Kyoto Research Park, 17, Chudoji Minami-Machi, Shimogyo-ku, Kyoto 600, Japan.

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Table I
Pd-Catalyzed Ring-Opening Polymerization of 5,5-Dimethyl-6-ethenylperhydro-1,3-oxazin-2-one (1)[a]

run	catalyst[b] (mol %)	initiator[c] (mol %)	time (day)	yield[d] (%)	$\bar{M}_n$[e]	$\overline{DP}$ VPO[f]	$\overline{DP}$ NMR[g]	$\overline{DB}$[h] (%)
1	0.5	10.1	2	60	1860	15.8	17.8	44
2	0.5	5.0	2	85	3190	27.8	28.6	44
3	0.5	2.5	2	quant	5330	47.0	46.6	52
4	1.5	0	3	quant	insoluble			

[a] In THF at room temperatures. [b] $Pd_2(dba)_3{\cdot}CHCl_3$–2dppe. [c] $PhCH_2NH_2$. [d] Isolate yield of the polymer after purification (except for run 4, see supplementary material). [e] Measured by VPO in $CHCl_3$ at 40 °C. [f] ($\bar{M}_n$ – MW of benzylamine)/(MW of 1 – 44). [g] See text. [h] Degree of branching (see text).

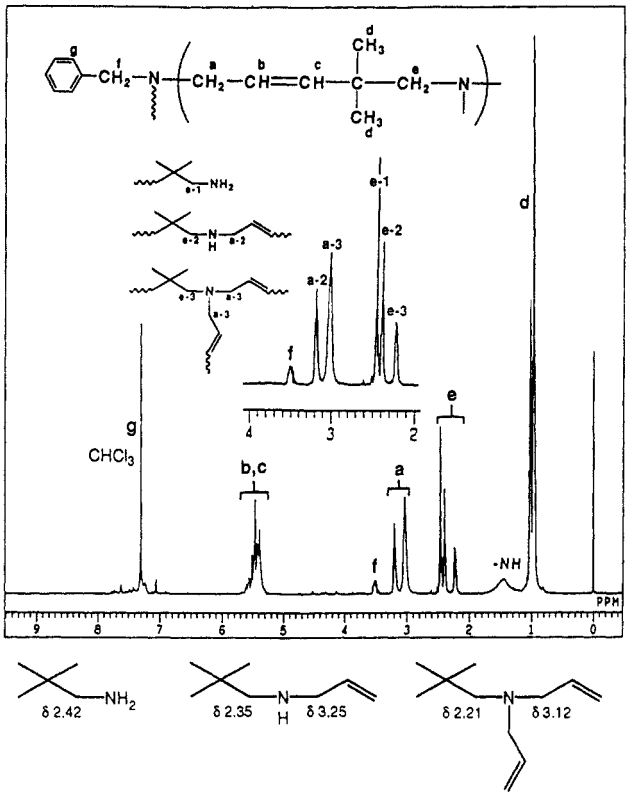

Figure 1. ^1H NMR spectrum (400 MHz, $CDCl_3$) of the polyamine **2** (run 1 in Table I) and chemical shift values of methylene protons of the models.

the electrophilic site of **3** to produce diamine **4**, releasing CO_2 and regenerating a Pd(0) complex.[9] Since both of the two amino groups of **4** have the ability to react with **3**, two kinds of triamines, **5a** and **5b**, are possible. Repetition of this reaction of **3** with primary and secondary amino groups,[10] whose relative reactivity reflects the degree of branching, gives rise to production of hyperbranched dendritic polyamine incorporating the initiator, as core. Accordingly, primary and secondary amino groups are propagating ends, whose numbers increase with the progress of the polymerization; this is MBP.

Though having highly branched structures, poly(ethylenimine) prepared from ethylenimine involves no apparent core; this is an essential difference from a dendritic polymer. Further studies about MBP are under investigation including block and graft polymer synthesis, kinetics, and other monomers for MBP.

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Supplementary Material Available: The recipe for monomer synthesis and a typical experimental procedure for polymerization and a figure of the ^{13}C NMR spectrum of polyamine **2** (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This field has been pioneered by Tomalia and Newkome whose groups synthesized "dendrimer" and "arborol", respectively. For a recent review, see: Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.

(2) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4252 and references cited therein.

(3) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592. Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043. Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.

(4) Suzuki, M.; Sawada, S.; Saegusa, T. *Macromolecules* **1989**, *22*, 1505. Suzuki, M.; Sawada, S.; Yoshida, S.; Saegusa, T. *Polym. Prepr., Jpn.* **1988**, *37*, 259 (*Engl. Ed.* E-107). Ii, A.; Haruyama, T.; Suzuki, M.; Saegusa, T. *Prepr.(II) Annu. Meeting (Autumn) Chem. Soc. Jpn.* **1988**, 814.

(5) Two methyl groups of **1** are introduced to avoid a side reaction, i.e., β-hydrogen elimination in the π-allylpalladium intermediate **3** (Scheme III).

(6) There is no reasonable speculation for a cross-linking reaction. Alternatively, the insolubility is ascribed to a physical character of this polymer. Generally, polyamine sometimes becomes insoluble during storage; the soluble polymers produced with the initiator also became insoluble after they were stored in a dry state even under a nitrogen atmosphere.

(7) π-Allylpalladium intermediates have been proposed in Pd-catalyzed reactions of allyl carbamates with active methylene compounds: Minami, I.; Ohashi, Y.; Shimizu, I.; Tsuji, J. *Tetrahedron Lett.* **1985**, *26*, 2449.

(8) As for initiation in the control reaction without an initiator, the following two systems are speculated. (1) The monomer itself acts as the initiator; the amidic proton of **1** is abstracted by a nucleophilic site of **3** to start polymerizartion. (2) Decarboxylation and subsequent ring closure of **1** via **3** produce four- and/or six-membered cyclic amine(s) having a N–H group which initiates polymerization. The N-tosylated derivative of **1** produces the corresponding azetidine *N*-tosylate in the presence of a Pd catalyst: Tamaru, Y.; Hojo, M.; Yoshida, Z. *J. Org. Chem.* **1988**, *53*, 5731.

(9) In order to support this mechanism, **1** was reacted with 10 equiv of diethylamine; the 1:1 adduct, i.e., *N,N*-diethyl-(5-amino-4,4-dimethyl-2-pentenyl)amine was isolated in 11% yield.

(10) It should be commented on why unimolecular cyclization of intermediate **3** to produce stable six-membered amine hardly occurred. For this cyclization isomerization of **3** to a thermodynamically unfavorable π-allyl complex **3b** is required. This process is much slower than intermolecular attack by amine, i.e., polymerization. The paper cited in ref 8 also reported no production of the six-membered derivative.