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Effect of feed rate of monofunctional monomers on structure of hyperbranched copolymers formed by self-condensing vinyl copolymerization in semibatch reactor

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ABSTRACT

Hyperbranched polymers (HBPs) formed by a self-condensing vinyl copolymerization, SCVCP, of monofunctional monomers M gradually fed into a reactor containing inimers AB^*, which had been charged initially, were investigated using a kinetic model. Under the assumption that no cyclization occurred during polymerization, changes in the average degree of polymerization (DP), the degree-of-polymerization dispersity, the degree of branching (DB), and the number of structural units in the hyperbranched copolymers at different feed rates of monomers M were calculated by a generating function method. The distribution of the degree of polymerization could be narrowed with the addition of monomers M, and the degree-of-polymerization dispersity was increased slightly at a slower feed rate parameter of M, ϕ. A higher DB of the HBPs could be obtained at a slower feed rate and a specific stopping ratio of M, θ. For instance, a final DB of approximately 0.62 was attained at $\phi = 0.2$ and $\theta = 1.2$, which was higher than the maximum DB of 0.5 attained in a batch system with monomers M at $\theta = 0.6$.

1. Introduction

Dendrimers and hyperbranched polymers have been studied with numerous structures and synthetic strategies due to their unique molecular structure, which consists of a large number of branching points and functional end groups. These materials exhibit characteristic features that are very different from those of linear polymers. For example, a lack of entanglements results in lower viscosity, and the large number of peripheral or side functional groups results in higher solubility [1–9]. Hyperbranched polymers, HBPs, can be prepared by simple one-pot polymerizations, such as step-wise polymerizations of AB_x-type monomers (x is greater than or equal to two), for which a large variety of monomers with different functional groups are available [10–12].

Furthermore, HBPs can be prepared by self-condensing vinyl polymerization, SCVP [13–18], which involves an AB^* inimer, such as p-(chloromethyl) styrene, consisting of a vinyl group A and an initiating group B^*. The chain reaction is the active B^* reacting with the double bond A of another monomer. Thus, a dimer is formed comprising one A group and two active groups: B^* and A^*. The new active center A^*, produced from the reaction of group A with B^*, can also react with the double bond of another molecule and form a branch point on the resulting larger molecule. Self-condensing vinyl polymerizations have been applied to various types of living/controlled polymerizations, such as ring-opening, nitroxide-mediated radical, atom transfer radical, and group transfer polymerizations [19–23].

Hyperbranched copolymers can also be prepared via copolymerization with the addition of conventional monomers, M, to incorporate different functional groups into HBPs. For example, degradable hyperbranched copolymers

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could be prepared by the copolymerization of inimers containing ester or disulfide groups with styrene or methyl methacrylate [24]. The dependence of the molecular structures of hyperbranched copolymers formed via a self-condensing vinyl copolymerization, SCVCP, in a batch system on the ratio of M to AB* and the effects of differences in relative reactivity have been well discussed. It was previously shown that the molecular weight distribution (MWD) became narrower with the addition of M monomers in a batch reactor, but the degree of branching decreased at a high ratio of M to AB* under an equal rate coefficient (ERC). It was also found that the hyperbranched copolymers with various molecular weight could be synthesized via the self-condensing group transfer copolymerization of the inimer 2-(2-methyl-1-triethylsiloxy-1-propenyloxy) ethyl methacrylate with different ratio of monomer: methyl methacrylate [25,26]. If the reactivity between the A and B* or A and A* groups in the inimer are higher than those of the monomer M, then DB could increase to a level higher than that in an ERC system. However, the reactivity of the inimer or monomer is dependent on the chemical nature, catalyst, and temperature. It would limit the choice of specific reactivity to control the polymer architecture of the hyperbranched copolymers.

The slow addition of monomers into a reactor in the semi-batch process is an alternative method for changing the molecular weight and structure of HBPs. Hyperbranched polymers generated from the copolymerization of AB_2-type monomers slowly added to trifunctional C_3 cores, as well as monomers AB* gradually added to trifunctional C_3^* cores, using various feed rates in the semi-batch process were investigated by a kinetic model in our previous work [27,28]. A lower degree-of-polymerization dispersity and higher DB of HBPs could be obtained by a slower addition procedure. The feed rate of the conventional monomers M, with one vinyl group, into a reactor containing inimer AB* initially could alter the competition reaction rates among the reactive groups. It may also result in different molecular structures of HBPs during a self-condensing vinyl copolymerization. In this study, the generating function method was further applied to a self-condensing vinyl copolymerization of inimers AB* with monofunctional monomers M in semibatch mode. The effects of the feed rate and stopping ratio of monomers M on structural parameters, such as molecular weight, dispersity, and the degree of branching of the hyperbranched copolymers, will be well discussed.

2. Kinetic model of self-condensing vinyl copolymerization of inimers AB* with monofunctional monomers M

Self-condensing vinyl copolymerizations involve inimers AB* and monofunctional monomers M. For example, inimer: p-(chloromethyl)styrene containing a vinyl group (A) and a active group $-CH_2Cl$ (B*) could be copolymerization with another monomer styrene (M) containing one vinyl group [14–16]. The active group B* can initiate the polymerization of the vinyl groups of either A or M. This reaction generates a new active group, A* or M*, and B* is converted into the product group "b" [25–28]:

$$A + B^* \xrightarrow{k_{AB^*}} A^* + b \quad (1)$$

$$M + B^* \xrightarrow{k_{MB^*}} M^* + b \quad (2)$$

For example, AB* can react with another AB* or M to form a dimer, either Ab-A*B or Ab-M*.

Furthermore, the new active center A* or M* can also react with an A group of any other molecule or with monomer M to form a larger molecule. Here, "a" and "m" denote the product groups of A* and M*, respectively:

$$A + A^* \xrightarrow{k_{AA^*}} A^* + a \quad (3)$$

$$M + A^* \xrightarrow{k_{MA^*}} M^* + a \quad (4)$$

$$A + M^* \xrightarrow{k_{AM^*}} A^* + m \quad (5)$$

$$M + M^* \xrightarrow{k_{MM^*}} M^* + m \quad (6)$$

where k_{IJ} are the reaction rate coefficients between groups I and J, which are assumed to be equal in this study. There are 18 possible reactions between the various structural units (not functional groups or molecules), as described in Appendix A. These reactions can also be expressed in the following kinetic scheme:

$$G(u_{i1}) + G(u_{i2}) \xrightarrow{k_i} G(u_{i3}) + G(u_{i4}) \quad i = 1, 2, \ldots, \text{ or } 18 \quad (7)$$

Table 1 presents the corresponding parameters u_{ij} and k_i, where

$G(1) = AB^*$ (inimer)
$G(2) = Ab^{\sim}$
$G(3) = {}^{\sim}A^*B^*$
$G(4) = {}^{\sim}A^*b^{\sim}$
$G(5) = \succ aB^*$
$G(6) = \succ ab^{\sim}$
$G(7) = M$ (monomer)
$G(8) = {}^{\sim}M^*$
$G(9) = {}^{\sim}m^{\sim}$

Although the effects of intramolecular cyclization on the structures of hyperbranched polymers are important for non-linear polymerization systems, in this study, we

Table 1
The parameters of u_{ij} and k_i.

u_{11}	u_{12}	u_{13}	u_{14}	k_1	=	1	1	2	3	k_{AB^*}
u_{21}	u_{22}	u_{23}	u_{24}	k_2		1	2	2	4	k_{AB^*}
u_{31}	u_{32}	u_{33}	u_{34}	k_3		3	1	4	3	k_{AB^*}
u_{41}	u_{42}	u_{43}	u_{44}	k_4		3	2	4	4	k_{AB^*}
u_{51}	u_{52}	u_{53}	u_{54}	k_5		5	1	6	3	k_{AB^*}
u_{61}	u_{62}	u_{63}	u_{64}	k_6		5	2	6	4	k_{AB^*}
u_{71}	u_{72}	u_{73}	u_{74}	k_7		1	3	3	5	k_{AA^*}
u_{81}	u_{82}	u_{83}	u_{84}	k_8		1	4	3	6	k_{AA^*}
u_{91}	u_{92}	u_{93}	u_{94}	k_9		2	3	4	5	k_{AA^*}
$u_{10\,1}$	$u_{10\,2}$	$u_{10\,3}$	$u_{10\,4}$	k_{10}		2	4	4	6	k_{AA^*}
$u_{11\,1}$	$u_{11\,2}$	$u_{11\,3}$	$u_{11\,4}$	k_{11}		1	7	2	8	k_{MB^*}
$u_{12\,1}$	$u_{12\,2}$	$u_{12\,3}$	$u_{12\,4}$	k_{12}		3	7	4	8	k_{MB^*}
$u_{13\,1}$	$u_{13\,2}$	$u_{13\,3}$	$u_{13\,4}$	k_{13}		5	7	6	8	k_{MB^*}
$u_{14\,1}$	$u_{14\,2}$	$u_{14\,3}$	$u_{14\,4}$	k_{14}		3	7	5	8	k_{MA^*}
$u_{15\,1}$	$u_{15\,2}$	$u_{15\,3}$	$u_{15\,4}$	k_{15}		4	7	6	8	k_{MA^*}
$u_{16\,1}$	$u_{16\,2}$	$u_{16\,3}$	$u_{16\,4}$	k_{16}		8	1	9	3	k_{AM^*}
$u_{17\,1}$	$u_{17\,2}$	$u_{17\,3}$	$u_{17\,4}$	k_{17}		8	2	9	4	k_{AM^*}
$u_{18\,1}$	$u_{18\,2}$	$u_{18\,3}$	$u_{18\,4}$	k_{18}		8	7	9	8	k_{MM^*}