

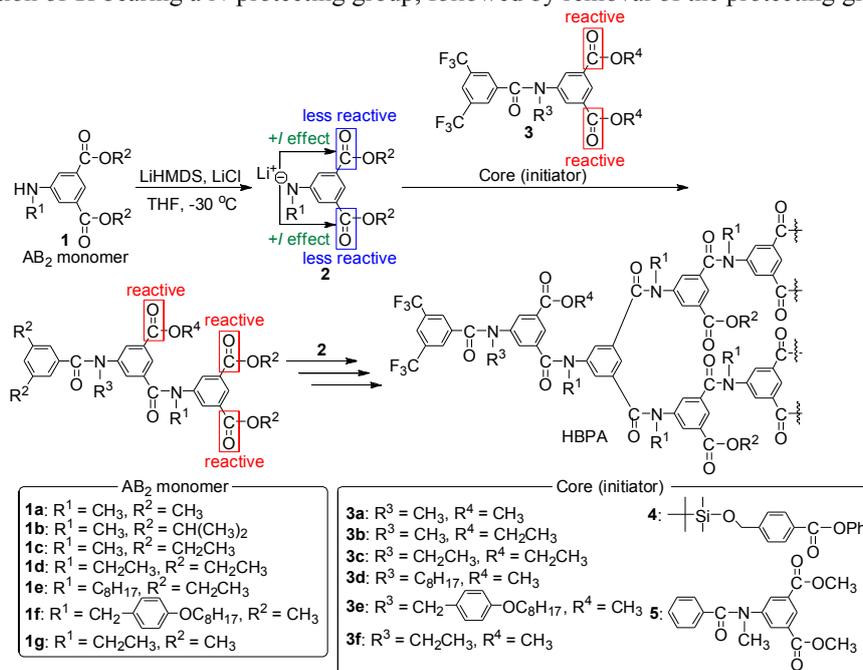
Synthesis and Properties of Well-Defined Hyperbranched Polyamides by Chain-Growth Condensation Polymerization of AB₂ Monomers

Yoshihiro Ohta, Yusuke Kamijyo, Tsutomu Yokozawa
Department of Material and Life Chemistry, Kanagawa University
Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan
E-mail: yokozt01@kanagawa-u.ac.jp

Introduction

Hyperbranched polymers have received considerable attention in recent years due to their unusual properties arising from their unique molecular architecture. In contrast to the multistep syntheses of dendrimers, hyperbranched polymers can be prepared by one-step polymerization of AB_m ($m \geq 2$) type monomers, but their physical properties depend on polymer topology, molecular weight, and molecular weight distribution, which are not well controlled. Several approaches have been investigated to achieve control of the molecular weight and molecular weight distribution of hyperbranched polymers. Suzuki and coworkers carried out ring-opening isomerization polymerization of cyclic latent AB₂ monomers from a core molecule in a chain-growth polymerization manner. The M_w/M_n of the obtained polymer was 1.3-1.5 with M_n in the range from 2000 to 3000, but when attempts were made to synthesize polymer with higher molecular weight by decreasing the amount of the initiator, the polymer precipitated.¹ Another approach is the slow monomer addition (SMA) method,² using core molecules on an insoluble solid support³ or highly reactive core molecules.⁴ This method provided polymers with controlled molecular weight and low polydispersity ($M_w/M_n < 1.3$) when the monomer/core ratio was less than about 100. Above that ratio, however, the molecular weight distribution became broad or the deviation of the observed molecular weight from the calculated value increased even when polymers with low polydispersity were obtained. These results probably arose from self-polymerization of AB₂ monomers at high feed ratio.

Herein, we report a new approach to obtain hyperbranched polymers with controlled molecular weight and low polydispersity by living polymerization of AB₂ monomers: chain-growth condensation polymerization. We focused on the change of substituent effects between monomer and polymer. In the condensation polymerization of 5-(alkylamino)isophthalic acid ester (**1**) as an AB₂ monomer with a base, both ester moieties in the amide anion of **2** would be deactivated owing to the inductive effect (+I effect), thereby suppressing self-polymerization, and **2** would selectively react with the core molecule (initiator) **3** and the terminal ester moieties of the polymer to afford a well-defined hyperbranched polymer (Scheme 1), in a similar manner to that in which AB-type monomers undergo chain-growth condensation polymerization.⁵ This polymerization method allowed us to synthesize a variety of hyperbranched polyamides (HBPA) with different solubility and thermal properties, such as glass transition temperature (T_g) and 10% weight-loss temperature (T_d^{10}), simply by changing the *N*-alkyl group of AB₂ monomers **1**. The effects of the *N*-alkyl group and the terminal ester alkyl group on the solubility, T_g , and T_d^{10} of HBPA were investigated. Furthermore, we synthesized unsubstituted *N*-H HBPA by the polymerization of **1f** bearing a *N*-protecting group, followed by removal of the protecting group with acid.



Scheme 1

Results and Discussion

Polymerization of 5-(methylamino)isophthalic acid ethyl ester **1c** as an AB₂ monomer with core **3b** was carried out in the presence of lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS) and LiCl in THF at -30 °C to yield HBPA with low polydispersity ($M_w/M_n \leq 1.13$) and well-defined molecular weight ($M_n = 2370$ -39300) depending on the feed ratio of the monomer to the core (from 7 to 200) (Figure 1). The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra showed that the obtained HBPA included the core unit, indicating that the polymerization proceeds by selective reaction of the monomer with the core and the polymer ends, without side reactions (Figure 2). Polymerization of other AB₂ monomers with *N*-ethyl, octyl, and 4-octyloxybenzyl (OOB) groups afforded the corresponding well-defined HBPA. HBPA with the *N*-OOB group was converted to unsubstituted *N*-H HBPA with low polydispersity by treatment with trifluoroacetic acid (TFA). The solubility of HBPA depended upon the nature of the *N*-alkyl groups and the terminal ester moieties. The glass transition temperature (T_g) (Figure 3) and 10% weight-loss temperature (T_d^{10}) of HBPA depended upon the molecular weight, as well as the nature of the *N*-alkyl groups and terminal ester moieties.

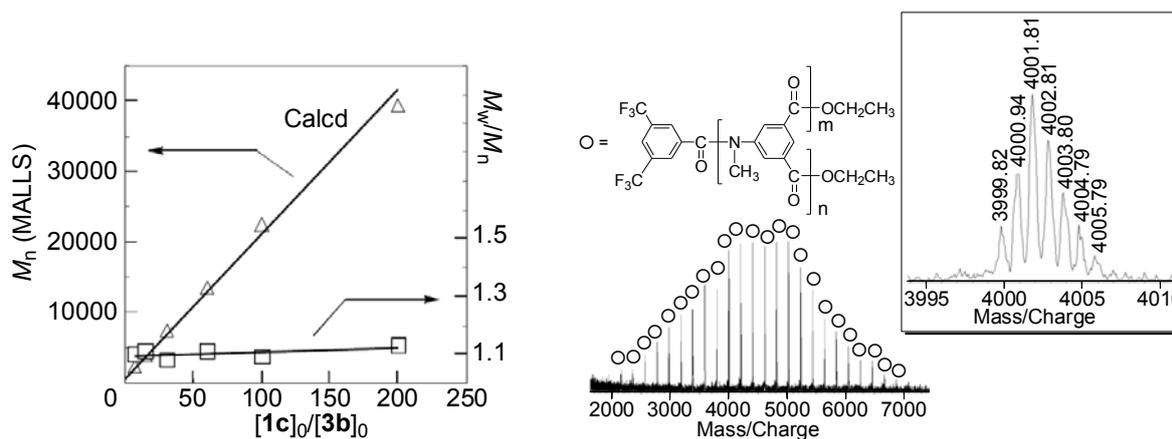


Figure 1. M_n and M_w/M_n values of Poly1c as a function of the feed ratio of **1c** to **3b**.

Figure 2. MALDI-TOF mass spectra of Poly1c obtained by the polymerization of **1c** onto **3b** ($[1c]_0/[3b]_0 = 15$).

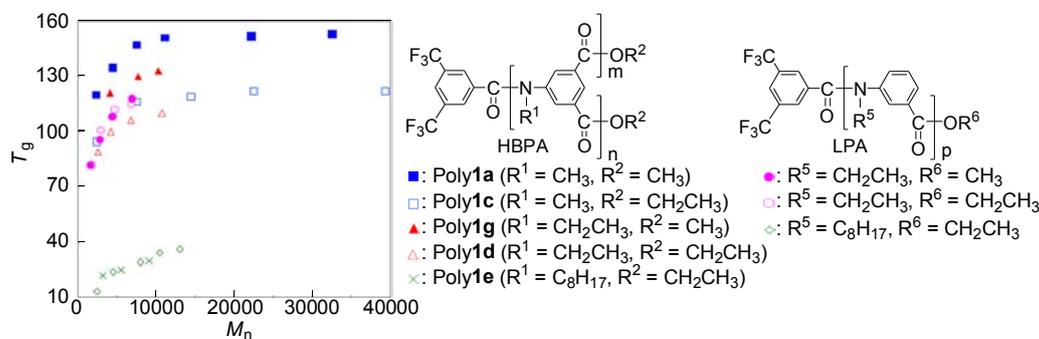


Figure 3. T_g of HBPA and LPA as a function of M_n of HBPA and LPA.

Reference

- (a) M. Suzuki, A. Ii, T. Saegusa, *Macromolecules*, **25**, 7071(1992). (b) M. Suzuki, S. Yoshida, K. Shiraga, T. Saegusa, *Macromolecules* **31**, 1716(1998).
- (a) A. Sunder, R. Hanselmann, H. Frey, R. Mulhaupt, *Macromolecules*, **32**, 4240(1999). (b) P. Bharathi, J. S. Moore, *Macromolecules*, **33**, 3212(2000). (c) A. Möck, A. Burgath, R. Hanselmann, H. Frey, *Macromolecules* **34**, 7692(2001). (d) R. K. Kainthan, E. B. Muliawan, S. G. Hatzikiriakos, D. E. Brooks, *Macromolecules* **39**, 7708(2006).
- P. Bharathi, J. S. Moore, *J. Am. Chem. Soc.* **119**, 3391(1997).
- D. P. Bernal, L. Bedrossian, K. Collins, E. Fossum, *Macromolecules* **36**, 333(2003).
- T. Yokozawa, A. Yokoyama, *Chem. Rev.* **109**, 5595(2009).