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Architecture of hyperbranched polymers consisting of a stearyl methacrylate sequence via a living radical copolymerization

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ABSTRACT

The living radical photocopolymerization of 2-(*N*,*N*-diethyldithiocarbamyl)ethyl methacrylate (DCEM) as inimer and stearyl methacrylate (STM) as comonomer was carried out under UV irradiation. According to this method, we synthesized hyperbranched polymers (HP) consisting of a STM sequence having a long alkyl side chain. The gel permeation chromatography distribution of hyperbranched polymers had a unimodal pattern. The reactivity ratios ($r_1 = 0.79$ and $r_2 = 0.81$) were estimated by the Kelen–Tüdös method (DCEM: $[\mathrm{M}]_1$ and STM: $[\mathrm{M}]_2$). These values indicated that the two monomers showed almost equal reactivity toward propagating radical species. The radius of gyration (R_g) and the hydrodynamic radius (R_h) of copolymers were determined by static and dynamic light scattering (SLS and DLS), and the values of $R_\mathrm{g}/R_\mathrm{h}$ changed from 0.79 to 1.59 with an increment of the feed amount of STM. These results indicated that the copolymer structures changed from hard spheres to loose branched molecules in solution.

1. Introduction

The properties of hyperbranched polymers and dendrimers have been shown to be very different from those of linear polymers. For example, the lack of entanglements results in a lower viscosity. The large extent of end functional groups causes higher solubility in various solvents for hyperbranched polymers and dendrimers compared with linear structure at a given molecular weight [1–3]. Unlike dendrimers prepared by stepwise synthesis, hyperbranched polymers have diverse molecular weights and geometrical shapes. Recent advances in living polymerization have allowed easy preparation of hyperbranched polymers [4–6]. More recently, we presented novel routes of hyperbranched polymer preparation from 4-vinylbenzyl *N*,*N*-diethyldithiocarbamate [7] (VBDC) and 2-(*N*,*N*-diethyldithiocarbamyl)ethyl methacrylate [8] (DCEM; **1**) as inimers by a one-pot photopolymerization. VBDC or DCEM monomers played an important role in these homopolymerization systems as an inimer capable of initiating living radical polymerization of the vinyl group. These radical mechanisms were very similar to the alkoxyamine-initiated living radical polymerization system established by Moad and Rizzardo [9]. In a previous paper [10], we reported the kinetics of hyperbranched poly(ethyl methacrylate) (PEMA) by free-radical polymerization of the photofunctional inimer DCEM. We concluded that free-radical polymerization of the inimer DCEM proceeded by a controlled/living radical mechanism. Moreover, hyperbranched PEMA was prepared by living radical copolymerization of DCEM with ethyl methacrylate (EMA) under UV irradiation [11]. Two monomers (DCEM and EMA) showed almost equal reactivity toward both propagating species, and the composition was the same as for the comonomer feed. This result means that both the branching and the chain length (i.e., compact nature) of the hyperbranched molecules can be controlled statistically by the feed monomer ratios. In a previous work [12], we reported the architecture of polymer nanoparticles shell-cross-linked via a living radical mechanism. In this work, we constructed core nanoparticles with hyperbranched polymers formed by homopolymerization of inimers such as DCEM. The hyperbranched molecules formed from a controlled radical process of inimer DCEM were an almost perfect dendritic structure [degree of branching (DB) = ca. 0.5] [10]. On the other hand, we have also established a method of preparation of polymer brushes by *grafting from* photoinduced atom transfer radical polymerization (ATRP) of multifunctional polystyrene (PS) having *N*,*N*-diethyldithiocarbamate (DC) pendant groups with stearyl methacrylate (STM) [13]. Such polymer brushes with large aspect ratio took a geometrical anisotropic conformation such as a rod cylinder due to crowding of long alkyl (stearyl) side chains. In general, the compact nature of the hyperbranched polymers composed of coil chains such as methacrylate sequences depended strongly on the DB values. Hyperbranched polymers having higher DB values behaved as hard spheres in solution. Therefore, we can speculate from these results that the compact nature of hyper-

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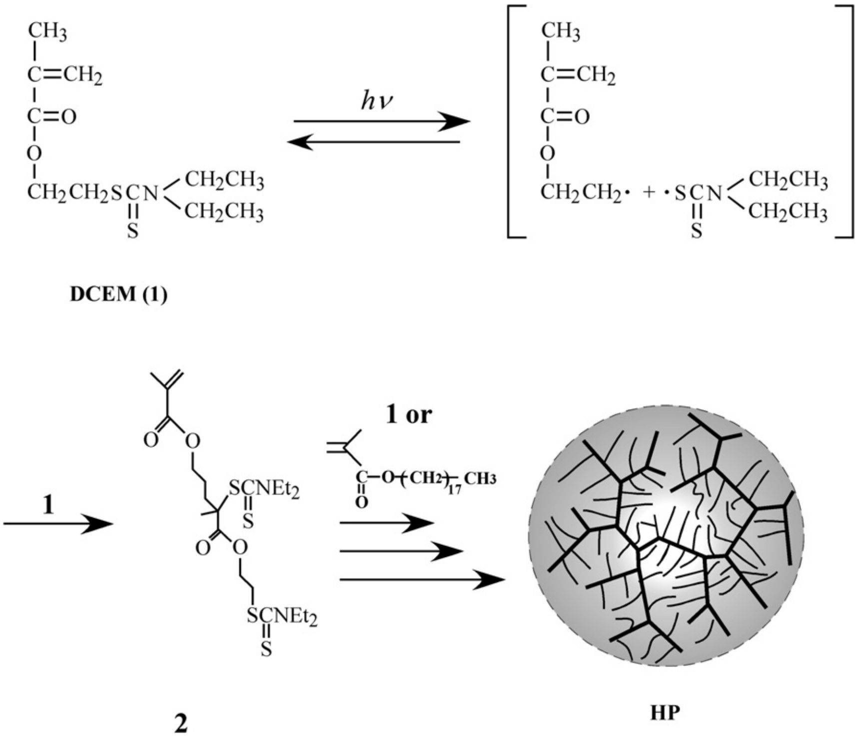

Scheme 1. Reaction scheme for synthesis hyperbranched polymer HP.

branched polymers may be controlled by the content of STM as comonomer, because poly(stearyl methacrylate) (PSTM) plays a role as the brush-like backbone due to their long alkyl chains.

In this article, we report synthesis of novel hyperbranched polymers (HP) having an STM backbone by living radical copolymerization of DCEM **1** with STM. Scheme 1 shows the initiation and propagation steps of living radical copolymerization of **1** with STM. The monomer reactivity ratio was calculated from proton nuclear magnetic resonance (^{1}H NMR) spectrometry of the copolymer produced. The compact nature of the hyperbranched polymers was demonstrated by their solution properties.

2. Materials and methods

2.1. Materials

DCEM, **1**, was synthesized by the reaction of 2-chloroethyl methacrylate with *N*,*N*-diethyldithiocarbamate sodium salt in acetone. Details concerning the synthesis and purification of inimer **1** have been given elsewhere [8]. STM (Tokyo Kasei Organic Chemicals, Tokyo) was purified by a separating funnel using hexane and aqueous sodium hydroxide to remove the polymerization inhibitor. Tetrahydrofuran (THF) and methanol (Tokyo Kasei Organic Chemicals, Tokyo) were used as received.

2.2. Copolymerization

Photocopolymerizations of DCEM (**1**) with STM (feed mole fraction of STM = 0.25–0.91; monomer concentration = 50 wt%) were carried out in THF by irradiation with UV light in a sealed glass ampoule under high vacuum at 40 °C for 1.5 h (250-W high-pressure mercury lamp, Ushio Denki SX-UI 250 HAMQ; UV intensity 42 mW/cm^2; irradiation distance 15 cm). After polymerization, the polymer was recovered by precipitation in methanol. The conversion of hyperbranched polymers (HP) was in the range 10–15% to determine the reactivity ratio (DCEM: $[M]_1$ and STM: $[M]_2$).

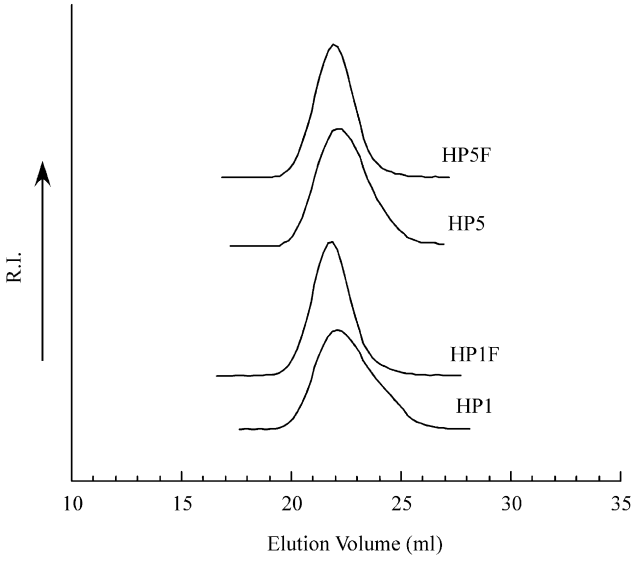

Fig. 1. GPC profiles of HP1, HP5, and their fractionated polymers (HP1F and HP5F).

2.3. Measurements

The composition of the hyperbranched polymers (HP) was determined by ^{1}H NMR spectrometry (300 MHz, Bruker GPX300 NMR spectrometer) in $CDCl_3$. The reactivity ratios were estimated by the Kelen–Tüdös method [14].

The weight-average molecular weight (M_w) and the radius of gyration (R_g) of HP were determined by static light scattering (SLS; Photal DLS 8000PNA, Otsuka Electronics, Tokyo; He–Ne laser $\lambda_0 = 632.8$ nm) in the Zimm mode in THF ($n_D = 1.40$; $[n] = 0.456$ cp) at 25 °C. The refractive index increment dn/dc of each HP was determined by a differential refractometer (Photal DRM-1021, Otsuka Electronics, Tokyo; $\lambda_0 = 632.8$ nm). Sample solutions were filtered