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Synthesis of alternating hyperbranched copolymers using photofunctional inimer via living radical mechanism

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Abstract

Copolymerizations of *N*,*N*-diethylaminodithiocarbamoylmethylstyrene (inimer: DTCS) with maleic anhydride (MA) were carried out under UV light irradiation. DTCS monomers play an important role in this copolymerization system as an inimer that is capable of initiating living radical polymerization of the vinyl group. Reactivity ratios ($r_1 = 0$ and $r_2 = 0.15$) were estimated by the curve-fitting procedure (DTCS [M_1]; MA [M_2]). These reactivities showed strong alternation and the propagating copolymer radicals proceeded always with homopolymerization of 1:1 complexes formed between the donor and acceptor monomers. Examination of the ^{1}H nuclear magnetic resonance (NMR) of copolymerization products confirmed the presence of hyperbranched structure.

Keywords: Alternating hyperbranched copolymer; Inimer; Living radical polymerization

1. Introduction

It is well known that an alternating copolymer can be easily obtained by the copolymerization of an electron-rich monomer and an electron-deficient monomer through the formation of charge transfer complexes. One of the extensively studied systems is maleic anhydride (MA) and styrene. The polymerization can be initiated by radical initiators such as AIBN or by UV light irradiation, but the polymerization process is uncontrollable [1,2]. More recently, Chen et al. [3] reported the synthetic method for alternating *N*-substituted maleimide/styrene copolymers possessing a designed molecular weight with narrow molecular weight distribution via atom transfer radical polymerization (ATRP). 2,2,6,6-Tetramethylpiperidinyloxy (TEMPO)-mediated living radical polymerization process also provided alternating structure of MA/styrene copolymers [4,5].

On the other hand, recent advances in living polymerization have allowed facile preparation of hyperbranched polymers. The self-condensing vinyl polymerization process first demonstrated using a living cationic polymerization [6], was later expanded to TEMPO-mediated living radical [7] and group-transfer polymerization process [8,9]. ATRP of *p*-chloromethylstyrene (CMS) similarly provided hyperbranched polymers [10,11]. Moreover, we presented a novel route to hyperbranched polymers from *N*,*N*-diethylaminodithiocarbamoylmethylstyrene (DTCS: **B**) as an inimer by one-pot photopolymerization [12]. Controlled synthesis of hyperbranched polymers has been reported in a recent work by Frey et al. [13] on the basis of cyclic inimers. In their works, hyperbranched polyglycerols with relatively narrow polydispersity ($\bar{M}_w/\bar{M}_n = 1.13$–$1.47$) were obtained. More recently, Knauss et al. [14] reported the studies on the controlled synthesis of hyperbranched polystyrenes (PS : $\bar{M}_w/\bar{M}_n < 1.2$) based on a method that combines living anionic polymerization with a convergent process in a one-pot reaction. On the other hand, the hyperbranched copolymers were obtained by ATRP of CMS with *N*-cyclohexylmaleimide (NCMI) catalyzed by CuCl/2,2′-bipyridine [15]. The monomer reactivity ratios were evaluated to be $r_{NCMI} = 0.107$ and $r_{CMS} = 0.136$. But, this system showed poor alternation.

In this article, we present a novel synthesis of alternating hyperbranched copolymers by living radical copolymerization of inimer DTCS with MA under UV light irradiation. Reactivity ratio was calculated from the copolymer compositions by means of FT-IR spectra (carbonyl moiety and characteristic absorbance of DTCS). Hyperbranched structure was recognized by ^{1}H nuclear magnetic resonance (NMR). New synthetic strategy mentioned in this work allows one-step formation of alternating hyperbranched copolymers and technological uses for nanostructured materials.

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2. Experimental

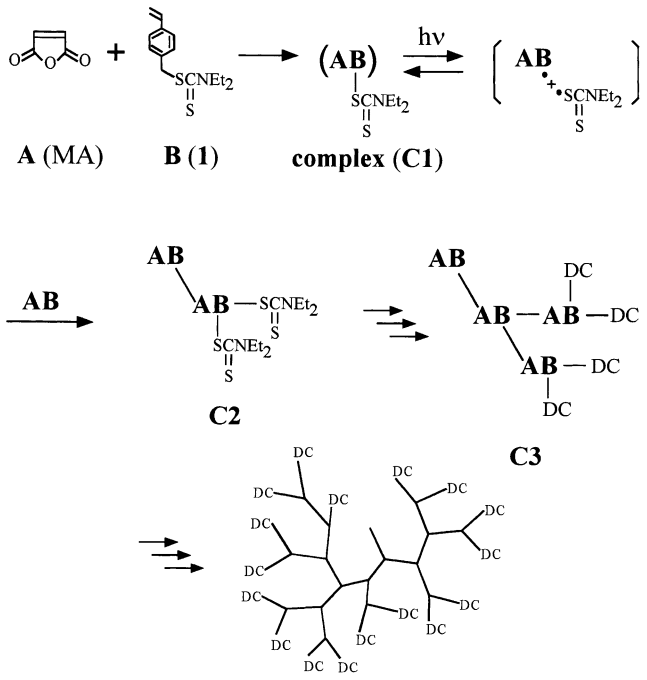
2.1. Copolymerization

DTCS was synthesized by the reaction of CMS with *N*,*N*-diethyldithiocarbamate sodium salt in acetone. Details concerning the synthesis and purification of inimer DTCS have been given elsewhere [16,17].

Photo-copolymerizations in acetone solution of DTCS with MA (the feed mole fractions of DTCS = 0.15–0.85; monomer concentration = 45 wt%) were carried out by irradiation with UV light for 0.75–1.5 h in a sealed glass ampoule under high vacuum at 20°C (250 W high-pressure mercury lamp, Ushio Denki UI 250D; irradiation distance 15 cm). After polymerization, the polymer was recovered by precipitation in acetone/*n*-hexane mixture (acetone 25 vol.%). The solvents used in these copolymerizations (acetone and *n*-hexane) were distilled over calcium hydride.

2.2. Characterization of hyperbranched copolymers

In order to evaluate the reactivity ratios (r_1 and r_2), the composition of hyperbranched copolymers was determined by FT-IR spectroscopy (Shimadzu FTIR-8500). Calibration curve was constructed using the mixture of hyperbranched homopolymer of DTCS and MA (characteristic absorbance of DTCS; 1500 cm^{-1} and carbonyl moiety; 1760 cm^{-1}). Two monomers, M_1 and M_2, are defined as the inimer DTCS and MA, respectively. The reactivity ratios, r_1 and r_2 were estimated by the curve-fitting procedure. ^1H NMR spectra of hyperbranched copolymers were taken in $CDCl_3$ (500 MHz, JEOL GSX-500 NMR spectrometer).



Scheme 1.

3. Results and discussion

Compound DTCS has an interesting structure because it contains a polymerizable styrene group and an initiating/propagating moiety consisting of a carbamate (DC) group. It is well known that highly alternating copolymers are prepared by copolymerizing strongly electron-accepting monomers such as MA or maleimide with electron-donating monomers such as styrene [18]. It has been suggested that alternation results from the homopolymerization of 1:1 complexes formed between the donor and acceptor monomers. So, it can also be expected that MA (**A**) and compound DTCS (**B**) form 1:1 complex (**C1**) (see Scheme 1). Photolysis of **C1** leads to the initiating benzyl radical with a less reactive DC radical that undergoes primary radical termination [19,20]. This benzyl radical can add to vinyl groups of a second molecule of **C1** to produce dimer **C2**. Dimer **C2** corresponds to an AB_2 monomer with two initiating/propagating sites. By repeating these elementary reactions, this polymerization system proceeds to form alternating hyperbranched copolymers.

To demonstrate this concept, photo-copolymerizations of DTCS with MA were carried out varying the feed comonomer concentration (feed mole fractions of DTCS = 0.15–0.85, monomer concentration = 45 wt% acetone solution). In order to estimate the reactivity ratios, the yield of copolymers was in the range of 10–14% under short irradiation time with UV light (0.75–1.5 h). The reaction rate of these copolymerizations was more rapid than that of homopolymerization of DTCS.

Typical FT-IR spectrum of the copolymer produced (feed mole fraction of DTCS = 0.75) is shown in Fig. 1. Spectrum showed the expected absorbance for carbonyl group (1860 and 1760 cm^{-1}), aromatic ring (1600 and 840 cm^{-1}), and characteristic absorbance for DTCS (1720 and 1500 cm^{-1}). Extremely small quantities of MA absorbance were observed around 3500 cm^{-1}, due to ring opening of MA.

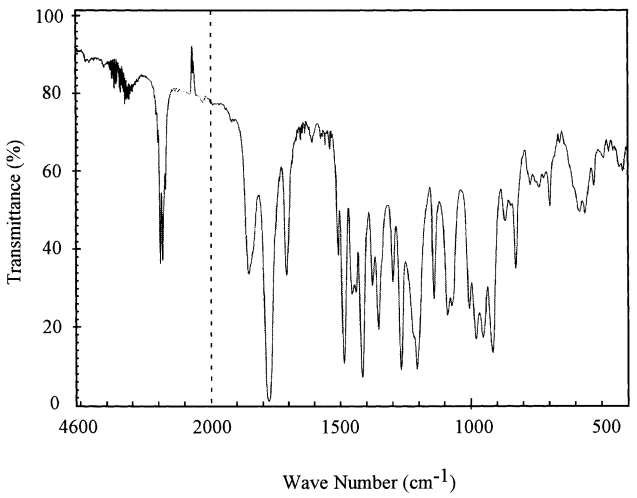


Fig. 1. FT-IR spectrum of the copolymer produced (feed mole fraction of DTCS = 0.75).

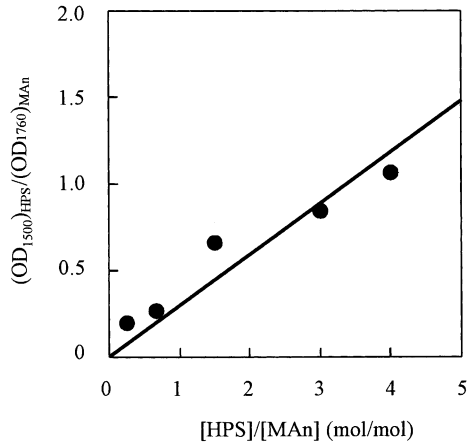


Fig. 2. Calibration curve constructed using the mixture of hyperbranched homopolymer of DTCS and MA.

In order to determine the composition of the copolymers, the calibration curve was constructed using the mixture of hyperbranched homopolymer of DTCS (HPS) and MA (DTCS absorbance at 1500 cm^{-1} and carbonyl groups at 1760 cm^{-1}). Fig. 2 shows the calibration curve, where OD and HPS indicate the optical density and hyperbranched homopolymer of DTCS, respectively. Each copolymer composition F_1 could be calculated using this calibration. Plots of the dependence of instantaneous copolymer composition F_1 (DTCS [M_1]; MA [M_2]) on the comonomer feed composition, f_1 for experimental series are shown in Fig. 3. It is found that the observed values are fitted on the solid line (F_1 = ca. 0.5) regardless of the variation of comonomer feed composition. The dotted line indicates the curve for model compounds of styrene and MA ($r_1 = 0.04$ and $r_2 = 0$ [18]).

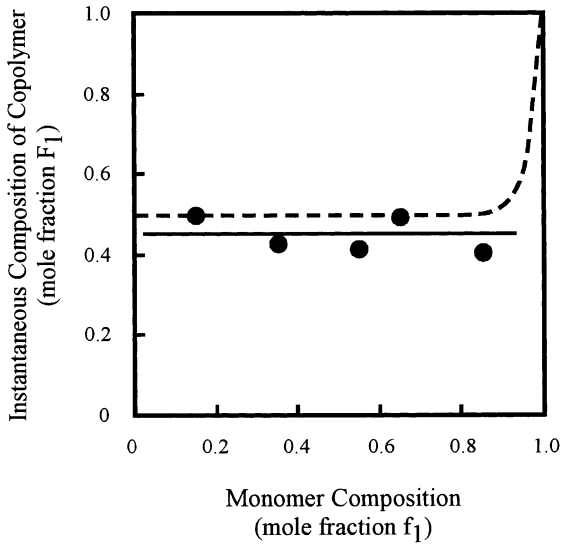


Fig. 3. Plot of the dependence of instantaneous copolymer composition F_1 (DTCS [M_1]; MA [M_2]) on the comonomer feed composition f_1, solid line; observed data, dotted line; curve for model compounds of styrene and MA ($r_1 = 0.04$ and $r_2 = 0$).

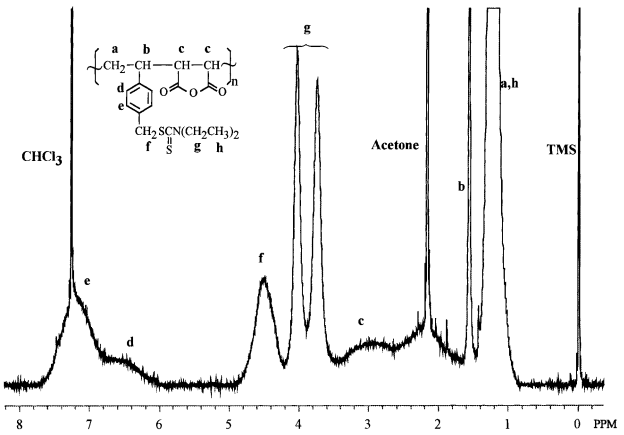


Fig. 4. ^{1}H NMR spectrum of hyperbranched alternating copolymer (feed mole fraction of DTCS = 0.75) in $CDCl_3$.

Reactivity ratios r_1 and r_2 were estimated by the curve-fitting procedure. Reactivity ratios: $r_1 = 0$ and $r_2 = 0.15$ were well fitted on the solid line in Fig. 3. It is found that photo-copolymerization reactivity of DTCS with MA shows strong alternation. In this copolymerization system, the propagating copolymer radicals proceed always with homopolymerization of 1:1 complexes formed between the donor and acceptor monomers.

Typical ^{1}H NMR spectrum of hyperbranched alternating copolymer (feed mole fraction of DTCS = 0.75) is shown in Fig. 4. Spectrum shows the expected resonance for the aromatic protons of polystyrenes (d and e; δ 6.7–7.7 ppm), the methylene protons (g; 3.7 and 4.0 ppm) of the DC groups, and the methylene protons adjacent to DC groups (f; 4.5 ppm). The broad signals from 1.4 to 3.5 ppm are assignable to CH (b and c) and CH_2 (a) protons of the main chain. The methyl protons (h; 1.2 ppm) of the DC groups are overlapped with signal a. Sharp spikes at 2.2 ppm reflect signal from acetone used for precipitation. Therefore, spectrum confirms the presence of the hyperbranched structure. The asymmetric monomer such as DTCS may lead to lower degrees of branching due to differences in the reactivity of the primary benzyl and the secondary phenethyl-like radicals. Matyjaszewski et al. [21,22] reported that the resulting microstructure that a hyperbranched polyacrylate is formed by ATRP. Assuming that there are no side reactions, such as termination by coupling or intramolecular cyclization, alternating hyperbranched copolymer should have one double bond per macromolecule. However, such signals assignable to double bond were not observed in ^{1}H NMR (see Fig. 4) due to high molecular weight of hyperbranched copolymer produced. The growth of the hyperbranched macromolecule is governed by the relative rate of reaction at either benzyl or phenethyl-like radical. When considering the ideal statistics of chain growth of DTCS/MA complex, assuming equal reactivity constants for benzyl and phenethyl-like radicals, the integration ratio of signal f to g should equal to 1:4. The observed ratios f:g were in the range of 1:2.5–1:2.9. This

result means that the structures of the macromolecules were not perfectly dendritic but contained a respectable amount of linear units. In order to make clearer the degree of branching, it is necessary to study the inner density profile of alternating hyperbranched copolymers from their solution properties. The results obtained will be reported in the near future.

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