

Synthesis and Characterization of Methyl Methacrylate/Styrene Hyperbranched Copolymers via Living Radical Mechanism

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ABSTRACT: Free-radical copolymerizations of *N,N*-diethylaminodithiocarbamoylmethylstyrene (inimer: DTCS) with a methyl methacrylate (MMA)/zinc chloride (ZnCl_2) complex 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. The reactivity ratios ($r_1 = 0.56$ and $r_2 = 0.52$: DTCS [M_1]; MMA [M_2]) obtained for this copolymerization system were different from a corresponding model system (alternating copolymer) of a styrene

and MMA/ ZnCl_2 complex ($r_1 = 0.25$ and $r_2 = 0.056$). It was found that the hyperbranched copolymers produced exhibited a random branching structure. It was found that the Lewis acid ZnCl_2 formed the complex not only with MMA but also with the carbamate group of inimer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2490–2495, 2003

Key words: hyperbranched; living polymerization; nanotechnology

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)/styrene or maleimide (MI)/styrene. The polymerization can be initiated by radical initiators such as 2,2'-azobisisobutyronitrile (AIBN) or by UV light irradiation, but the polymerization process is uncontrollable.^{1,2} More recently, Chen et al.³ reported a synthetic method for alternating *N*-substituted maleimide/styrene copolymers possessing a designed molecular weight with a narrow molecular weight distribution via atom transfer radical polymerization (ATRP). A 2,2,6,6-tetramethylpiperidinyloxy (TEMPO)-mediated living radical polymerization process also provided an alternating structure of the MA/styrene copolymers.^{4,5}

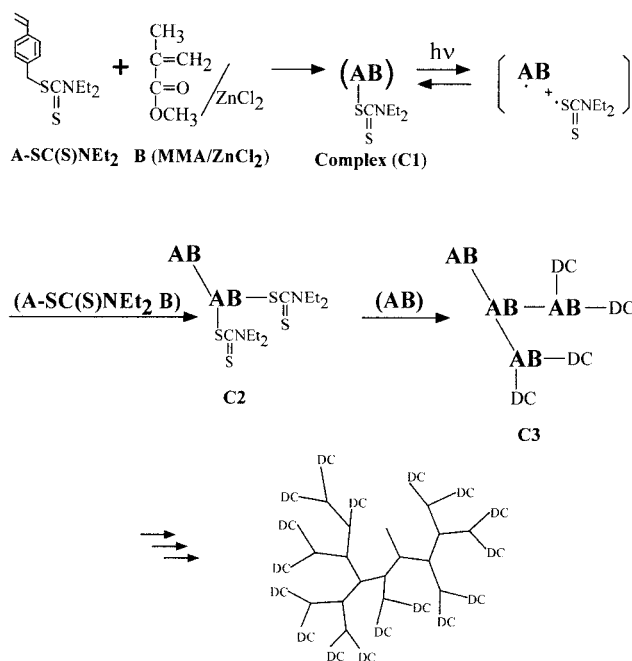
On the other hand, recent advances in living radical polymerization have allowed facile preparation of hyperbranched polymers. The self-condensing vinyl polymerization process first demonstrated using a living

cationic polymerization⁶ was later expanded to TEMPO-mediated living radical⁷ and group-transfer polymerization processes.^{8,9} ATRP of *p*-chloromethylstyrene (CMS) similarly provided hyperbranched polymers.^{10,11} There are some basic references to both living radical and hyperbranched macromolecules.^{12–14} More recently, we presented a novel route to hyperbranched polymers from *N,N*-diethylaminodithiocarbamoylmethylstyrene [DTCS: $\text{A}-\text{SC}(\text{S})\text{NEt}_2$] (Scheme 1) as an inimer by one-pot photopolymerization.¹⁵ There is also a basic reference to such an iniferter concept and living radical polymerization.¹⁶ We proved from the kinetic studies that free-radical polymerization of the inimer DTCS proceeded with a living radical mechanism such as stepwise polymerization, although the propagating sites had two different reactivities (benzyl and phenylethyl-like radicals).¹⁷

Moreover, we also presented a novel synthesis of alternating hyperbranched copolymers by living radical copolymerization of the inimer DTCS with MA under UV light irradiation.¹⁸ The reactivity ratios $r_{\text{DTCS}} = 0$ and $r_{\text{MA}} = 0.15$ were estimated by a curve-fitting procedure. These reactivities showed strong alternation and the propagating radicals proceeded always with a homopolymerization of 1:1 complexes formed between the donor and acceptor monomers. However, the dilute-solution properties of such alternating hyperbranched copolymers could not be studied due to the easy ring opening of MA. On the other hand, hyperbranched copolymers were obtained by

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ATRP of CMS with *N*-cyclohexylmaleimide (NCMI) catalyzed by $\text{CuCl}/2,2'$ -bipyridine.¹⁹ The monomer reactivity ratios were evaluated to be $r_{\text{NCMI}} = 0.107$ and $r_{\text{CMS}} = 0.136$. So, this system showed poor alternation. Subsequently, we synthesized alternating MI/styrene hyperbranched copolymers by free-radical copolymerization of DTCS with MI.²⁰ These alternating hyperbranched copolymers behaved as hard spheres in the dilute solution. It is well known that highly alternating copolymers are also prepared by copolymerizing strongly electron-accepting monomers such as an MMA/Lewis acid complex with electron-donating monomers such as styrene.^{21–23}

In this article, we studied the free-radical copolymerization behavior of the inimer DTCS with an MMA/ ZnCl_2 complex under UV light irradiation. The composition of the hyperbranched copolymers was determined by FTIR spectroscopy using the characteristic absorbance of DTCS and carbonyl moieties. The copolymerization behavior was discussed from the viewpoint of the reactivity ratios (r_1 and r_2) compared to the linear analogs of the alternating model system of styrene with an MMA/ ZnCl_2 .

EXPERIMENTAL

Copolymerization

DTCS was synthesized by the reaction of CMS (Seimi Chemical Industry) with *N,N*-diethyldithiocarbamate sodium salt in acetone. Details concerning the synthesis and purification of the inimer DTCS were given elsewhere.^{15,24}

Photocopolymerizations in tetrahydrofuran (THF) of DTCS with the MMA/ ZnCl_2 complex (ZnCl_2 , 0.4 mol equivalent to MMA; total amounts of DTCS and MMA, 0.6–0.7 g; the feed mol fractions of DTCS: $F_1 = 0.20$ – 0.80 ; HC11: $F_1 = 0.20$; HC12: $F_1 = 0.25$; HC13: $F_1 = 0.33$; HC14: $F_1 = 0.67$; HC15: $F_1 = 0.75$; HC16: $F_1 = 0.80$; monomer concentration = 50 wt%) were carried out by irradiation with UV light for 30 min in a sealed glass ampule under a vacuum at 25°C (250 W high-pressure mercury lamp, Ushio Denki SX-UI 250 HAMQ; irradiation distance 15 cm). After polymerization, the polymer was recovered by precipitation in a mixture of methanol (30 mL) and a small aqueous solution (2 mL) of NaOH (10 mg). The polymer was purified from the reprecipitation using the THF–methanol system. The conversion was estimated from measuring the yield of the polymers. We also carried out a similar copolymerization in the absence of ZnCl_2 in THF ($F_1 = 0.14$ – 0.83 ; irradiation time = 30 min).

Characterization

To evaluate the reactivity ratios (r_1 and r_2), the composition of the hyperbranched copolymers was determined by FTIR spectroscopy (Shimadzu FTIR-8500). A calibration curve was constructed using a mixture of the hyperbranched homopolymer of DTCS and poly(methyl methacrylate) (PMMA) (characteristic absorbance of DTCS: 1516 cm^{-1} , and carbonyl moiety: 1732 cm^{-1}). Two monomers, M_1 and M_2 , are defined as the inimer DTCS and MMA, respectively. The reactivity ratios, r_1 and r_2 , were estimated by Fineman–Ross²⁵ or Kelen–Tudos plots.²⁶ To discuss the branched structure, $^1\text{H-NMR}$ spectra (500 MHz, JEOL GSX-500 NMR spectrometer) of the hyperbranched copolymers were measured in dimethyl sulfoxide- d_6 ($\text{DMSO-}d_6$).

The apparent weight-average molecular weights (M_w) and polydispersity (M_w/M_n) of the hyperbranched copolymers were determined by gel permeation chromatography (GPC; Tosoh high-speed liquid chromatograph HLC-8020) using polystyrene standard samples as a calibration with THF as the eluent at 38°C, two TSK gel columns, GMH_{XL} and G2000H_{XL} in series, and a flow rate of 1.0 mL/min).

Differential scanning calorimetry (DSC) measurements were recorded on a Siko Instruments DSC 220C to determine the glass transition temperature (T_g). Indium and zinc were used as calibration standards. The heating rate was $10^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

Alternating linear copolymers were prepared by copolymerizing strongly electron-accepting monomers such as the MMA/ ZnCl_2 complex with electron-donating monomers such as styrene ($r_1 = 0.25$ and $r_2 = 0.056$).²³ It has been suggested that alternation re-

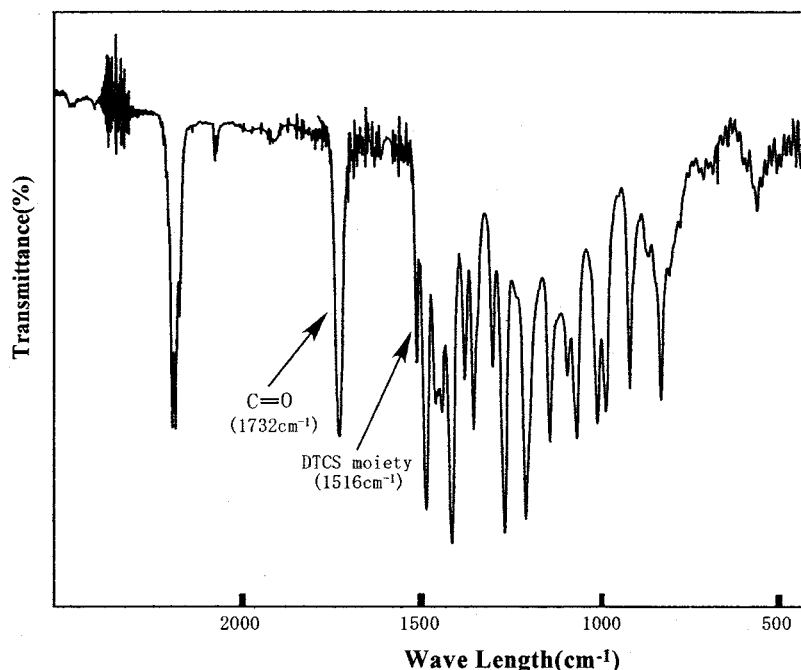


Figure 1 FTIR spectrum of copolymer HC14 ($F_1 = 0.67$): (a) carbonyl moiety at 1732 cm^{-1} ; DTCS absorbance at 1516 cm^{-1} .

sults from the homopolymerization of 1:1 complexes formed between the donor and acceptor monomers. So, it can also be expected that DTCS [A—SC(S)NEt₂] and MMA/ZnCl₂ (B) form a 1:1 complex (C1) (see Scheme 1). Photolysis of C1 leads to the initiating benzyl radical with a less reactive DC radical. This benzyl radical can add to a vinyl group of a second molecule C1 to produce dimer C2. Dimer C2 corresponds to an AB₂ monomer with two initiating/propagating sites. By repeating these elementary reactions, this polymerization system proceeds to form alternating hyperbranched copolymers.

To demonstrate whether this concept is valid, photocopolymerizations (system A) of DTCS with the MMA/ZnCl₂ complex were carried out by varying the feed comonomer concentration ($F_1 = 0.20$ – 0.80). It was found in a previous work²³ that the optimum addition amount of ZnCl₂ was 0.4 mol equivalent to the MMA monomer unit. To estimate the reactivity ratios (r_1 and r_2), the yield of the copolymers was in the range of 10–20% under a short irradiation time (30 min) with UV light. In no case were crosslinked or insoluble materials observed.

A typical FTIR spectrum of the copolymer-produced HC14 ($F_1 = 0.67$) is shown in Figure 1. The spectrum shows the expected absorbance for the carbonyl group (1732 cm^{-1}) and aromatic ring (1600 and 840 cm^{-1}) and the characteristic absorbance for DTCS (1516 cm^{-1}). To determine the composition of the copolymers, a calibration curve was constructed using a mixture of a hyperbranched homopolymer of DTCS (HPS) and PMMA (DTCS absorbance at 1516 cm^{-1} ,

and carbonyl groups, at 1732 cm^{-1}). Figure 2 shows the calibration curve, where OD indicates the optical density. Each copolymer composition f_1 could be calculated using this calibration. Plots of the dependence of the instantaneous copolymer composition f_1 (DTCS [M_1]; MMA [M_2]) on the comonomer feed composition, F_1 , for experimental A systems in the presence of ZnCl₂ are shown in Figure 3 (curve A). If this copolymerization proceeds with an alternating mechanism,

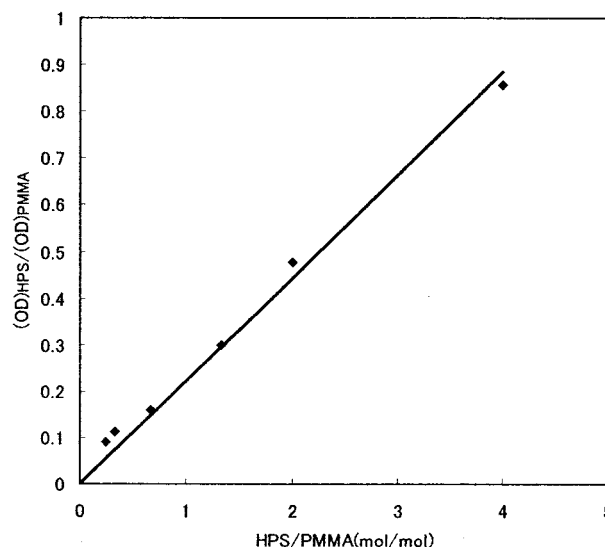


Figure 2 Calibration curve constructed using a mixture of the hyperbranched homopolymer of DTCS (HPS) and PMMA (DTCS absorbance at 1516 cm^{-1} and carbonyl group at 1732 cm^{-1}).

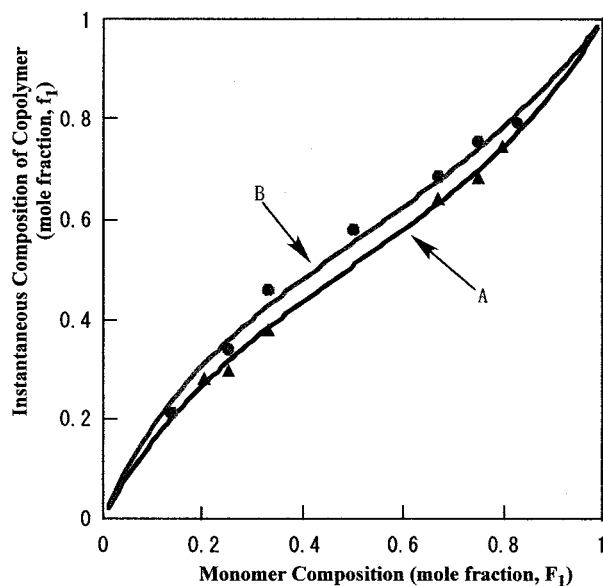


Figure 3 Plots of the dependence of instantaneous copolymer composition f_1 on the comonomer feed composition F_1 : (A) A system in the presence of ZnCl_2 ; (B) B system in the absence of ZnCl_2 .

the observed values f_1 should be about 0.5, regardless of the variation of the comonomer feed composition. However, it seems from curve A that free-radical copolymerization of this system leads to a more random nature. The reactivity ratios ($r_1 = 0.56$ and $r_2 = 0.52$) were estimated by the Fineman–Ross plot (see Fig. 4), where F and f indicate the feed comonomer composition $[M_1]/[M_2]$ and the copolymer composition $d[M_1]/d[M_2]$, respectively.

Subsequently, photocopolymerizations (system B) of DTCS with MMA were also carried out in the absence of ZnCl_2 by varying the feed comonomer

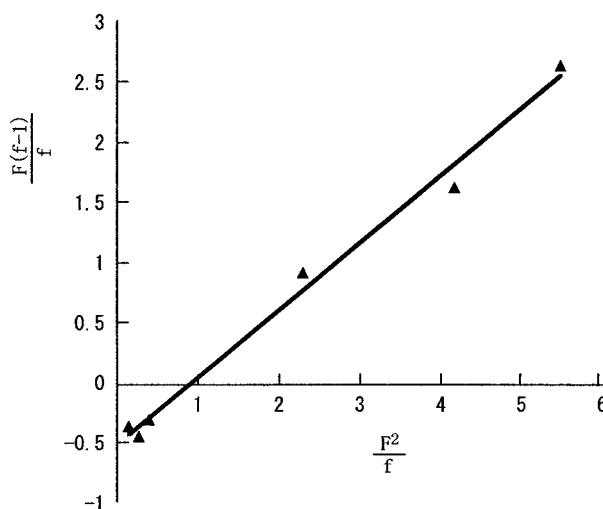


Figure 4 Fineman–Ross plot for the A system: F and f indicate the feed comonomer composition $[M_1]/[M_2]$ and the copolymer composition $d[M_1]/d[M_2]$, respectively.

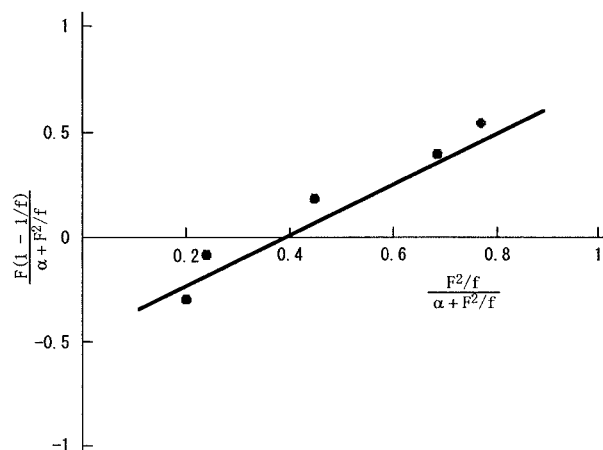


Figure 5 Kelen–Tudos plot for the B system: $\alpha = 0.87$.

concentration ($F_1 = 0.14$ – 0.83) in THF for 30 min. In this system also, crosslinked or insoluble materials were not observed. Plots of the dependence of the instantaneous copolymer composition f_1 on the comonomer feed composition F_1 are shown in Figure 3 (curve B). Reactivity ratios ($r_1 = 0.74$ and $r_2 = 0.41$) were estimated by a Kelen–Tudos plot. Constant α was 0.87 (see Fig. 5). These values are very similar to those observed in system A. On the other hand, the reactivity ratios for styrene and MMA as a model system were $r_1 = 0.52$ and $r_2 = 0.46$.²⁷ In the formation of hyperbranched copolymers, MMA seems to somewhat interpenetrate into the propagating copolymer chains compared to the model compounds. The $>\text{C}=\text{S}$ bond of the DC group has a similar chemical nature to that of the $>\text{C}=\text{O}$ bond of MMA. It seems, therefore, that Lewis acid ZnCl_2 forms the complex not only with MMA but also with the DC group of DTCS. It is concluded that copolymerizations (A system) do not proceed with the homopolymerization of a 1:1 complex between the donor and acceptor monomers.

GPC profiles of hyperbranched copolymers for the A and B systems showed a broad unimodal pattern. The molecular weight distributions (M_w/M_n) for the A and B systems were in the range of 1.29–1.74 and 1.42–1.61, respectively. The apparent M_w 's for the A and B systems were in the range of 3400–6700 and 4200–8100, respectively. In a solid film, it is important to make clear whether the PMMA chains are miscible or immiscible to the polystyrene backbones. DSC measurement of the solid films is one of the best methods to resolve such a problem. Only T_g (57°C) one was clearly visible in the trace of the specimen HC14 ($M_w = 3600$, $f_1 = 0.62$). The observed T_g of the hyperbranched copolymer is somewhat lower than those of the PMMA and polystyrene linear homopolymers. On the other hand, the T_g of the hyperbranched homopolymer ($M_w = 9.0 \times 10^4$) of the inimer DTCS was

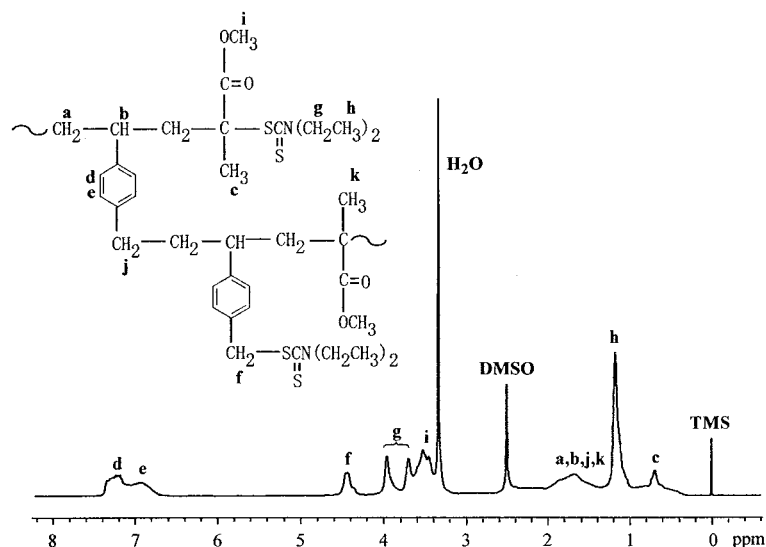


Figure 6 $^1\text{H-NMR}$ spectrum of copolymer HC12 ($F_1 = 0.25$) in $\text{DMSO-}d_6$.

66°C. The existence of one T_g is indicative of phase mixing because the copolymerization of DTCS with MMA proceeded with a random mechanism.

A typical $^1\text{H-NMR}$ spectrum of the hyperbranched copolymer HC12 ($F_1 = 0.25$) is shown in Figure 6. The spectrum shows the expected resonance for the aromatic protons of polystyrenes (d and e, δ 6.7–7.4 ppm), the methylene protons (g, 3.7 and 4.0 ppm), and methyl protons (h, 1.2 ppm) of the DC groups, the methylene protons adjacent to the DC groups (f, 4.5 ppm), and the methoxy protons (i, 3.5 ppm) and methyl protons (c, 0.7 ppm) of PMMA. Other methyl protons (k) of PMMA were overlapped with the signals of methylene and the methyne protons (a, b, and j) of the main chains. Then, the spectrum confirms the presence of a copolymer. The composition of hyperbranched copolymers can be calculated from the integration ratio of aromatic protons (d and e) of DTCS and methoxy protons (i) of PMMA. The observed DTCS fraction of HC12 was almost the same value as that of the composition ($f_1 = 0.30$) obtained from the FTIR spectrum. In all the $^1\text{H-NMR}$ spectra of the hyperbranched copolymers for the A and B systems, the number of DC groups was more than 0.91–0.98 per DTCS unit. So, free-radical copolymerization of the A and B systems seemed to proceed with the living radical mechanism, regardless of the random nature.

An asymmetric monomer such as DTCS may lead to a lower degree of branching (DB) due to differences in the reactivity of the primary benzyl and secondary phenethyl-like radicals. The growth of hyperbranched macromolecules is governed by the relative rate reaction at benzyl, phenethyl-like, or MMA radicals. In our system, the methylene moieties in which benzyl radicals attack MMA correspond to branch points. This signal should appear around 1.5 ppm. However, we

cannot calculate the DB from the $^1\text{H-NMR}$ spectra because this signal overlaps with polystyrene and PMMA backbone signals (1.4–1.9 ppm; see Fig. 6). It is necessary to clarify the DB in the next investigation strategy. The solution properties of such hyperbranched copolymers are also interesting. This matter will be discussed elsewhere.

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