Degree of Branching of Hyperbranched Polystyrenes via a Controlled Radical Mechanism of an Inimer: Determination by a Kinetic Approach

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ABSTRACT: We studied, with a kinetic approach, the living nature and degree of branching (DB) of the formation of hyperbranched polystyrene by the free-radical photopolymerization of 2-(*N,N*-diethyldithiocarbamyl)methylstyrene in benzene. The free-radical polymerization proceeded with a living radical mechanism. Subsequently, we treated the kinetics of the initiation and propagation steps of the active A* and B* (side-group) sites with model compounds. The degradation rates of two types of dithiocarbamate groups at the A and B sites agreed well with theoretical trends for C—S bond dissociation energies predicted by the density functional theory for model compounds. The reactivity of the initiating B* groups was greater than that of the propagating A* groups. DB of the hyperbranched polymers was estimated to be 0.31 with both reaction rates in terms of Müller's equation. This result supported the DB value (0.39) estimated from NMR data. The hyperbranched molecules obtained in this work were not perfectly dendritic but had somewhat defective structures. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1810–1815, 2005

Key words: hyperbranched; density; radical polymerization; theory

INTRODUCTION

The properties of hyperbranched polymers and dendrimers are very different from those of linear polymers. For example, a lack of entanglements results in a lower viscosity. The large number of end-functional groups causes higher solubility in various solvents for hyperbranched polymers and dendrimers in comparison with linear structures at a given molecular weight.[1–3] Unlike dendrimers prepared by stepwise synthesis, hyperbranched polymers have diverse molecular weights and geometrical shapes. To understand the inner density profile, we must determine the degree of branching (DB) of hyperbranched polymers. For example, a fully branched polymer of AB_2 would have a branching factor of 0.5, but an AB_3 monomer would have a branching factor of 0.33. Recent advances in living polymerization have allowed the facile preparation of hyperbranched polymers. Recently, we presented novel routes for hyperbranched polymers from 2-(*N,N*-diethyldithiocarbamyl)methylstyrene (DTCS or **1**)[4] and 2-(*N,N*-diethyldithiocarbamyl)ethyl methacrylate (DTEM)[5] as inimers by a one-pot photopolymerization. DTCS and DTEM played an important role in these homopolymerization systems as inimers capable of initiating the living radical polymerization of the vinyl group. These radical mechanisms were very similar to those of the alkoxyamine-initiated living radical polymerization system established by Moad and Rizzardo.[6] To understand the reaction process of such self-addition vinyl polymerization, we must analyze the kinetics of these reactions.

Müller et al.[7] calculated the molecular parameters of hyperbranched polystyrene (PS) formed by the self-condensing vinyl polymerization of the *p*-chloromethylstyrene (CMS) inimer with the general structure AB*, where A is a vinyl group and B* is an initiating group. Our radical photopolymerization systems proceeded with a self-condensing mechanism similar to that described previously. More recently, we established a new determination method for DB of hyperbranched poly(ethyl methacrylate) by a kinetic approach.[8] We analyzed the initiation and propagation steps with model compounds and determined each rate constant. DB was calculated with Müller's theoretical equation for reactivity ratios. In a previous article,[9] we reported the kinetics of hyperbranched PS by the free-radical polymerization of the photofunctional inimer DTCS. We concluded that the free-radical polymerization of DTCS proceeded with a controlled radical mechanism. DB was determined from the NMR data of the polymerization products. It is
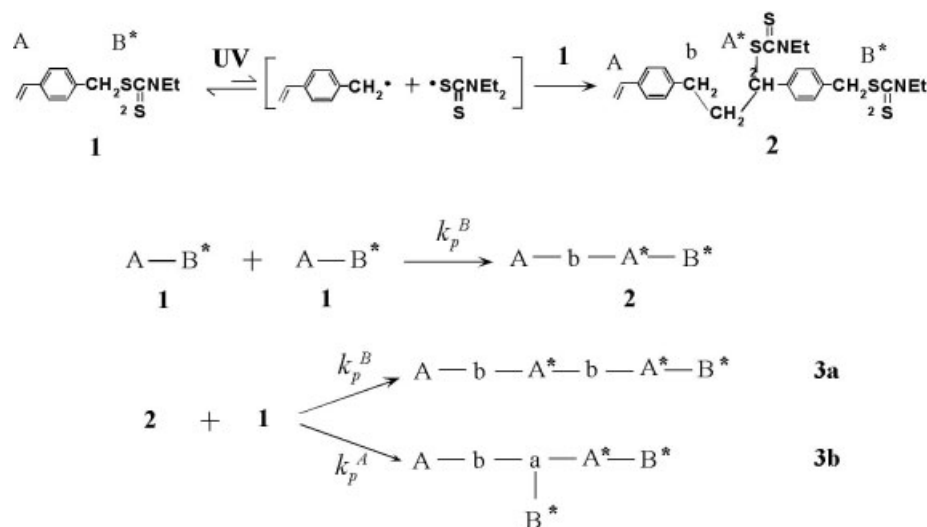
Scheme 1 Reaction of hyperbranched PS.

important to compare this result with the DB value estimated with the kinetic approach.

The photolysis of **1** produces an initiating benzyl radical with a less reactive dithiocarbamate (DC) radical[10–12] (see Scheme 1). Dimer **2** has two DC active sites and one double bond. Both the initiating B* group and the newly created propagating center A* can react with the vinyl group of any other molecule (monomer or polymer) in the same way with the propagation rate constants k_p^A and k_p^B, respectively. The initial steps up to the formation of trimer **3** are shown in Scheme 1. The addition of a vinyl group to a terminal A* or B* center leads to a linear linkage, whereas the addition of a double bond to a B* side group (**3b**) or an A* center within the polymer (the center of **3a**) leads to a branch point.

In this article, we present the kinetics of the initiation and propagation steps of the active A* and B* sites for the formation of hyperbranched PS with model compounds. DB is discussed with both propagation rates.

EXPERIMENTAL

Materials

CMS (Seimi Chemical Industry, Kanagawa-Ken, Japan) and styrene (Tokyo Kasei Organic Chemicals, Tokyo, Japan) were distilled in a high vacuum. N,N-Diethyldithiocarbamate sodium, benzyl chloride, 1-phenyl-1-chloroethane, benzene, acetone (Tokyo Kasei Organic Chemicals), and free radical 2,2,6,6-tetramethylpiperidinyloxy (TEMPO; Aldrich, Milwaukee, WI) were used as received.

Synthesis of the inimer and model compounds

Inimer DTCS was synthesized through the reaction of CMS with N,N-diethyldithiocarbamate sodium salt in

acetone. Details concerning the synthesis and purification of DTCS are reported elsewhere.[9] Two model compounds, benzyl N,N-diethyldithiocarbamate (BDC) and 1-(N,N-diethyldithiocarbamyl)ethylbenzene (DEB), were also synthesized by a similar reaction with benzyl chloride and 1-phenyl-1-chloroethane, respectively (see the chemical structures in Fig. 1) to assign the chemical shifts of the proton signals in NMR.

^{1}H-NMR (CDCl$_3$, δ, ppm) for BDC: 7.30–7.51 (aromatic protons), 4.61 (—CH$_2$—), 3.73, 4.02 (—CH$_2$— of DC group), 1.30 (—CH$_3$ of DC group). ^{1}H-NMR (CDCl$_3$, δ, ppm) for DEB: 7.30–7.51 (aromatic protons), 5.23 (—CH—), 3.73, 4.02 (—CH$_2$— of DC group), 1.30 (—CH$_3$ of DC group), 1.83 (—CH$_3$).

Photopolymerization

Photopolymerizations of **1** (50 wt % benzene solution) were carried out with various irradiation times at 25°C in a sealed glass ampule under a high vacuum (SXUI 250 HAMQ 250-W high-pressure mercury lamp, Ushio Denki, Tokyo, Japan; UV intensity = 42 mW/cm^2, irradiation distance = 15 cm). After the polymerizations, the polymer was recovered by precipitation with methanol. The conversion was estimated by gravimetric measurements. We also carried out the
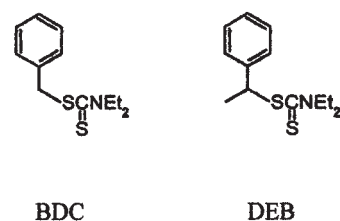

Figure 1 Chemical structures of model compounds BDC and DEB.

photopolymerizations of styrene with model compound DEB as the initiator under the same polymerization conditions (50 wt % benzene solution).

Kinetics of the initiation and propagation steps

The values of the initiation rate (R_i) were measured with the TEMPO free radical as follows. The free-radical polymerization of styrene was carried out in benzene at 25°C and was initiated by model compound DEB or BDC under UV irradiation with the addition of TEMPO. The initial time of consumption of the vinyl groups of styrene was measured by dilatometry. That is, the amount of volume shrinkage of the polymer produced was measured by the height change of the solution through a capillary (diameter [ϕ] = 2 mm). The densities of styrene and PS were 0.909 and 1.04 g/cm^3, respectively, at 20°C.[13]

k_p^A was estimated as follows. We made a first-order time–conversion plot for the photopolymerization of styrene initiated by model compound DEB. This plot (a straight line in the semilogarithmic coordinates) indicated that the polymerization proceeded by a living radical mechanism. Then, when the concentration of the propagating PS radical ([P_A^*]) was known, we could estimate the value of k_p^A from the slope of the first-order plot.

Characterization

The number-average molecular weight (M_n) and molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] of PS samples were determined by gel permeation chromatography (GPC). GPC measurements were car-
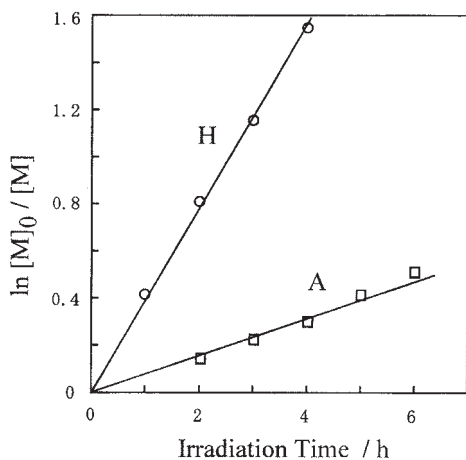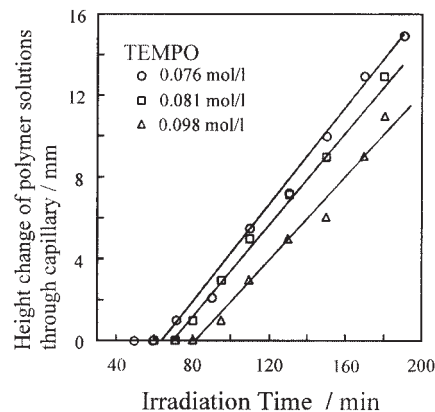
Figure 3 Relationship between the volume shrinkage of polymer solutions and the induction period. Styrene (5.88 mol/L) was polymerized in benzene at 25°C, and the polymerization was initiated by BDC (0.105 mol/L) under UV irradiation with a capillary (ϕ = 2 mm); the amounts of TEMPO were varied (0.076, 0.081, and 0.098 mol/L).

ried out with a Tosoh HLC-8120 high-speed liquid chromatograph (Tokyo, Japan) equipped with a refractive-index detector (RI), which was operated with two TSK gel columns, GMH$_{XL}$ [excluded-limit molecular weight (M_{EL}) = 4 × 10^8] and G2000H$_{XL}$ (M_{EL} = 1 × 10^4), in series with tetrahydrofuran as the eluent (flow rate = 1.0 mL/min) at 38°C. ^{1}H-NMR spectra were recorded on a JEOL GSX-500 500-MHz NMR spectrometer (Tokyo, Japan) in CDCl$_3$.

RESULTS AND DISCUSSION

Photopolymerizations of **1** were carried out with various irradiation times. As mentioned in a previous article,[9] no crosslinked or insoluble materials were observed. The GPC profiles for this system showed a unimodal distribution. We quoted from ref. 9 the first-order time–conversion plots of the photopolymerizations (see line H in Fig. 2; [M]$_0$ is the initial concentration of inimer **1**). The straight lines in the semilogarithmic coordinates indicated a constant concentration of the active species, and this indicated that the polymerization of inimer **1** was first-order in the monomer. The slope of the semilogarithmic plot, $S_H = R_p^H/[M]$ (where R_p^H, the propagation rate, is equal to $-d[M]/dt$; [M], the monomer concentration), was set equal to 1.07 × 10^{-4} s^{-1}. We discuss R_p^H later.

To understand the formation mechanism of the hyperbranched polymer, we analyzed the reaction steps of initiation and propagation with model compounds. First, the values of R_i were measured with model compounds BDC and DEB as initiators under the following conditions. Styrene (5.88 mol/L) was polymerized in benzene initiated by BDC (0.105 mol/L) under UV irradiation, with the additional amounts of TEMPO varied (0.076, 0.081, and 0.098 mol/L). Figure

Figure 2 First-order time–conversion plots. Line H is the polymerization system of inimer DTCS (50% benzene solution) at 25°C under UV irradiation; line A is the polymerization system of styrene (5.88 mol/L) in benzene initiated by DEB (0.105 mol/L) at 25°C under UV irradiation.
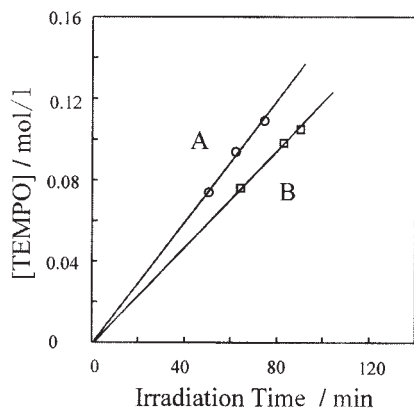
Figure 4 Relationship between the feed amount of TEMPO and the induction period. Line A is the polymerization system initiated by DEB in benzene at 25°C; line B is the polymerization system initiated by BDC in benzene at 25°C.

3 shows the relationship between the induction period and height changes of the solution through a capillary. The relationship of these induction periods and the feed of TEMPO is shown in Figure 4 (see line B). R_i is given by eq. (1):

$$R_i = -d[\text{TEMPO}]/dt = [\text{TEMPO}]_0/\text{Induction period} \tag{1}$$

R_i^B was 1.0×10^{-5} mol/(L s) from the slope for the initiator BDC system. Similar experiments were also carried out with model compound DEB as the initiator. The relationship of the induction periods and feed of TEMPO for the initiator DEB system is also shown in Figure 4 (line A; the feed conditions were [styrene] = 5.88 mol/L, [DEB] = 0.105 mol/L, and [TEMPO] = 0.074, 0.085, or 0.094 mol/L). R_i^A was determined to be 1.3×10^{-5} mol/(L s) from the slope for the initiator DEB system.

On the other hand, R_i was obtained as follows from the initiation kinetics:

$$R_i = k_d f[\text{I}] \tag{2}$$

where k_d, f, and [I] are the degradation rate constant, initiator efficiency, and initiator concentration, respectively. The values of $k_d^A f_A$ and $k_d^B f_B$ were determined to be 1.19×10^{-4} and 0.95×10^{-4} s^{-1}, respectively. f_A and f_B were the initiator efficiencies of DEB and BDC, respectively. Therefore, the reciprocals of these first-order rate constants meant the lifetimes of the model DEB and BDC radicals induced by UV irradiation.

The observed trends for $k_d^A f_A$ and $k_d^B f_B$ can be discussed with the C—S bond dissociation energies for the model compounds predicted from density functional theory calculations.[14] Figure 5 shows the results of the C—S bond dissociation energies and bond

lengths for several model compounds: BDC, DEB, and inimer **1** (these data are also taken from ref. 9). The steric factors are important in determining bond dissociation energies. This should be reflected in longer lengths for the breaking C—S bond in the ground state, for which steric factors are greater. The calculations predict that the C—S bond lengths will increase in the order DEB > BDC = **1**; that is, the formation of the secondary phenethyl radical should predominate over that of the primary benzyl radical. Moad and Rizzardo[6] and Kazmaier et al.[15] reported the molecular orbital calculations of alkoxyamine homolysis rates for alkoxyamine-initiated living radical polymerization. The prediction showed a marked dependence on the structures of both the nitroxide and radical compounds. For the secondary and tertiary alkoxyamines, steric factors appeared to be the dominant influence. The bond dissociation tendency obtained in our work is very similar to their results.

Subsequently, we estimated propagation rate R_p^A with model compound DEB. The photopolymerizations of styrene ([styrene]$_0$ = 5.88 mol/L) were carried out in benzene at 25°C and were initiated by DEB ([DEB]$_0$ = 0.105 mol/L), with the irradiation time varied. A first-order time–conversion plot of the photopolymerizations is shown in Figure 2 (see line A). The straight line in the semilogarithmic coordinates indicates a constant concentration of the active polymer radical P_A^*. The slope of the semilogarithmic plot, $S_A = k_p^A[P_A^*]$, was set equal to 2.0×10^{-5} s^{-1}. This value corresponds to a pseudo-first-order rate constant. Then, the lifetime of the model DEB radical ($k_d^A f_A = 1.19 \times 10^{-4}$ s^{-1}) was shorter (ca. sixfold) than that of P_A^*; that is, the primary radical was more active than polystyryl radical P_A^*. These results agreed well with the general information for the radical reactivities. Figure 6 shows plots of M_n and M_w/M_n versus the conversion; the dotted line indicates the theoretical M_n values. The observed M_n values increased with increasing conversion. However, the experimental points that did not fit included conversions up to 28%.
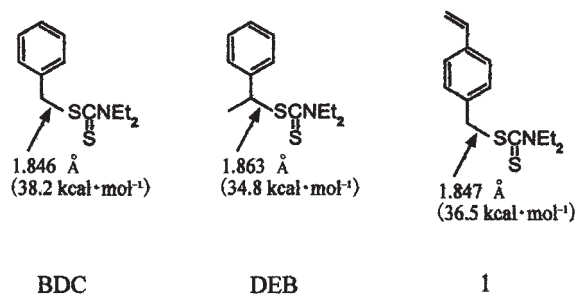

Figure 5 Results for the C—S bond dissociation energies and bond lengths for several model compounds calculated under the assumption of hemolytic bond cleavage at B3LYP/6-31G(d) corrected with zero-point energy.

This deviation indicated that f_A was not higher than 0.8. The M_w/M_n values were 1.9–2.1.

We could obtain the absolute rate constant (k_p^A) when the radical concentration ($[P_A^*]$) was known. We could not accurately determine $[P_A^*]$ by electron spin resonance (ESR) under UV irradiation because of weak ESR signals. In this work, the propagation rate constant (k_p) for styrene was calculated as follows:[16]

$$k_p[\text{L}/(\text{mol s})] = 10^{7.63} \exp[-32.51(\text{kJ}/\text{mol})/RT] \tag{3}$$

where R and T are the gas constant and absolute temperature, respectively. k_p was calculated to be 86 L/(mol s) at 25°C. As a result, $[P_A^*]$ was estimated to be about 2×10^{-7} mol/L.

As mentioned earlier, the photopolymerization of inimer **1** proceeded with competitive living radical mechanisms between the active A* and B* groups. Therefore, k_p^B could be estimated logically from the slope of line H (Fig. 2) when $[P_A^*]$ and $[P_B^*]$ were known values for the formation system of hyperbranched polymers. However, the assignment of active species P_A^* and P_B^* could not be distinguished even with ESR spectra. In the reaction elements shown in Scheme 1, we can see that k_p^B corresponds to the rate constant of the initiating B* groups reacting with the vinyl group of any other molecule. This rate can be regarded as R_i^B.

Next, we discuss DB of hyperbranched molecules with the reaction rates (the first-order rate constants $k_d^A f_A$, $k_d^B f_B$, and $k_p^A[P_A^*]$) obtained in this work. Müller et al.[7] calculated the DB of hyperbranched polymers made by self-condensing vinyl polymerization with kinetic considerations. They obtained the relationship
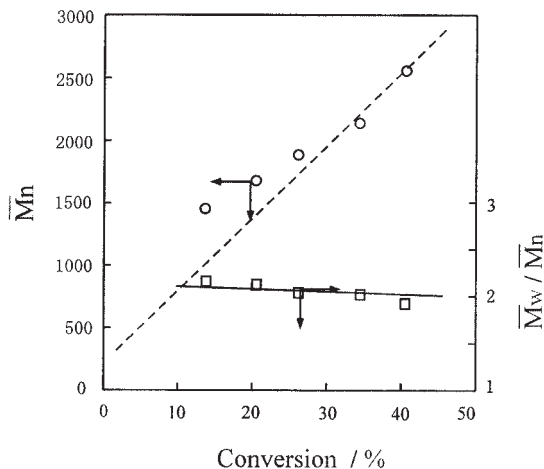

Figure 6 M_n and M_w/M_n versus the conversion for the polymerization of styrene (5.88 mol/L) initiated by DEB (0.105 mol/L) in benzene at 25°C. The dotted line indicates the theoretical values of M_n.

TABLE I
Calculated DB_∞ as Parameter of r[a]

	$r = S_A/k_d^B f_B$	$r = k_d^A f_A/k_d^B f_B$
r	0.21	1.25
DB_∞	0.31	0.50

[a] With the relation of $f_A = f_B = 1$ assumed.

between the degree of branching for full conversion (DB_∞) and the reactivity ratio ($r = k_p^A f_A/k_p^B f_B$). Such calculations assume that the rate constants for the propagation of both the inimer and monomer do not change with conversion, and no additional reactions occur. In this case, the polydispersity index of the polymer was very high and sharply increased with conversion. We estimated DB_∞ as a parameter of r with the first-order rate constants (see Table I). In this calculation, we assumed $f_A = f_B = 1$. The value of DB_∞ (0.31) estimated with $r = S_A/k_d^B f_B$ was overestimated because f was not higher than 0.8, as mentioned earlier. DB can be regarded as the ratio of branched units in the polymer to those in a perfect dendrimer. The limiting values are DB = 0 for linear polymers and DB = 1 for a perfect dendrimer. The statistical process of forming hyperbranched polymers gives DB $\leq$ 0.5.[17,18]

^{1}H-NMR data also provide some information about DB. A typical ^{1}H-NMR spectrum of hyperbranched PS (after 4 h of irradiation time, conversion = 0.78) is shown in ref. 9; this spectrum has the expected resonances for aromatic protons of PS (d and e, δ 6.3–7.3 ppm), for methyl (h, 1.2 ppm) and methylene protons (g, 3.7 and 4.0 ppm) of the DC groups, and for methylene protons adjacent to DC groups (f, 4.5 ppm) and confirms the presence of the hyperbranched structure. The ratio of the integration of the signals attributed to the —CH_2—DC protons (f) to that of the methylene protons of DC groups (g) provided information on DB. This ratio should be 2:4 for linear poly[2-(N,N-diethyldithiocarbamyl)methylstyrene] prepared by conventional radical polymerization and 1.5:4 for a perfect dendritic structure. The observed ratio of g to f was 1.44:4. Müller et al.[17] also calculated r with the NMR method as follows:

$$r = (1 - x - B^*)/(1 + \ln B^* - B^*) \tag{4}$$

where B^* is the fraction of the active center B* and x is the conversion. Because the values of x and B^* were 0.78 and 0.44, respectively, r could be estimated to be 0.85. Then, DB_∞ was estimated to be 0.39 from the NMR data. However, because of the various possible structures in the macromolecules, the precise determination of DB has not yet been successful and requires detailed NMR studies. It was concluded that the hyperbranched molecules that formed from the controlled radical process of inimer **1** were not perfectly

dendritic but were somewhat defective structures. Kinetic analysis may be one of the best methods for determining DB of hyperbranched molecules.

CONCLUSIONS

We studied the living nature of the formation of hyperbranched PS by the free-radical photopolymerization of inimer DTCS. According to first-order time–conversion plots, this polymerization system proceeded with competitive living radical mechanisms between initiator radical B* and monomer vinyl radical A*. We analyzed the initiation step with model compounds BDC and DEB with the aid of TEMPO as a radical scavenger. As a result, degradation rates $k_d^A f_A$ and $k_d^B f_B$ were estimated to be 1.19×10^{-4} and $0.95 \times 10^{-4} \text{ s}^{-1}$, respectively. We also analyzed the propagation step from the photopolymerization of styrene initiated by model compound DEB. The polymerization of styrene also proceeded with a controlled radical mechanism. The pseudo-first-order rate constant $k_p^A[\text{P}_A^*]$ was calculated to be $2.0 \times 10^{-5} \text{ s}^{-1}$. The lifetime of the primary DEB radical became shorter than that of active polymer radical P_A^*. DB_∞ was calculated to be 0.31 with Müller's theoretical equation for r. The hyperbranched molecules formed by the controlled radical process of inimer DTCS were not perfectly dendritic but were somewhat defective structures.

References

1. Hult, A.; Johansson, M.; Malmstrom, E. Adv Polym Sci 1999, 143, 2.
2. Kim, Y. H. J Polym Sci Part A: Polym Chem 1998, 36, 1685.
3. Davis, N.; Rannard, S. Mater Sci Eng 1997, 77, 158.
4. Ishizu, K.; Mori, A. Macromol Chem Rapid Commun 2000, 21, 665.
5. Ishizu, K.; Shibuya, T.; Mori, A. Polym Int 2002, 51, 424.
6. Moad, G.; Rizzardo, E. Macromolecules 1995, 28, 8722.
7. Müller, A. H. E.; Yan, D.; Wulkov, M. Macromolecules 1997, 30, 7015.
8. Ishizu, K.; Shibuya, T.; Kawauchi, S. Macromolecules 2003, 36, 3505.
9. Ishizu, K.; Ohta, Y.; Kawauchi, S. Macromolecules 2002, 35, 3781.
10. Otsu, T.; Yoshida, M. Makromol Chem Rapid Commun 1982, 3, 127.
11. Otsu, T.; Kuriyama, A. J Macromol Sci Chem 1984, 21, 961.
12. Otsu, T.; Yamashita, K.; Tsuda, K. Macromolecules 1986, 19, 287.
13. Polymer Handbook, 4th ed.; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; Wiley: New York, 1999.
14. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kodin, K. N.; Strain, M. C.; Farkas, O.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foreman, J. B.; Cioslowski, J.; Ortize, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.7; Gaussian: Pittsburgh, PA, 1998.
15. Kazmaier, P. M.; Moffat, K. A.; Georges, M. K.; Veregin, R. P. N.; Hamer, G. K. Macromolecules 1995, 28, 1841.
16. Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F. D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schwer, J. Macromol Chem Phys 1995, 196, 3267.
17. Yan, D.; Müller, A. H. E.; Matyjaszewski, K. Macromolecules 1997, 30, 7024.
18. Hölter, D.; Burgath, A.; Frey, H. Acta Polym 1997, 48, 30.