

Synthesis and Characterization of Soluble Hyperbranched Polymer via Initiator-Fragment Incorporation Radical Polymerization of Divinylbenzene with Dimethyl 2,2'-Azobisisobutyrate

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ABSTRACT: The homopolymerization of divinylbenzene (DVB) as an excellent crosslinker (0.20 mol/L) with dimethyl 2,2'-azobisisobutyrate (MAIB) proceeded homogeneously without any gelation at 80°C in benzene when the MAIB concentrations as high as 0.30–0.50 mol/L were used, yielding soluble polymers. In the polymerization at the concentrations of [DVB] = 0.20 mol/L and [MAIB] = 0.50 mol/L, the polymer yield increased with time and leveled off over 90 min. The molecular weight and molecular weight distribution increased with polymer yield. The vinyl groups of DVB were observed to be almost completely consumed in about 80 min, by FT near-IR spectroscopic analysis. The homogeneous polymerization system involved ESR-observable polymer radical, the concentration of which increased with time up to 3.4×10^{-5} mol/L. The polymer formed in

the polymerization for 2 h consisted of 46 mol % of DVB unit and 54 mol % of the methoxycarbonylpropyl group as MAIB fragment, indicating that an initiator-fragment incorporation radical polymerization proceeds in the present polymerization. The polymer was soluble in benzene, tetrahydrofuran, ethyl acetate, chloroform, acetone, and *N,N*-dimethylformamide, while it was insoluble in *n*-hexane, acetonitrile, dimethyl sulfoxide, methanol, and water. The results of the multiangle laser light scattering and viscometric measurements revealed that the individual polymer molecules were formed as hyperbranched polymer nanoparticles. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 664–670, 2006

Key words: radical polymerization; branched; ESR/EPR; crosslinking; polystyrene

INTRODUCTION

In recent years, much attention has been paid to the synthesis of dendritic polymers such as dendrimers and hyperbranched polymers because of their unique structures and properties, namely, globular and void-containing shape, a large number of terminal groups, no crystallization, high solubility, and low solution viscosity.^{1–6}

In a wide variety of approaches for the hyperbranched polymer synthesis, are also included some radical-mediated polymerizations, a typical approach of which is the selfcondensing radical vinyl polymerization using a vinyl monomer bearing an initiating group (inimer).^{1–3,5,6}

Radical polymerization involving a divinyl monomer is well known to give insoluble crosslinked polymer, the molecular weight of which is treated to be extremely high or infinite. On the other hand, in the conventional radical polymerization, the molecular

weight of the resultant polymer decreases with increasing initiator concentration because of accelerated termination owing to the increased radical concentration. Consequently, the use of much higher initiator concentration in the polymerization of a divinyl monomer leads to a great decrease in the molecular weight so that the resultant polymer eventually becomes soluble, and its structure is no longer linear but hyperbranched. The molecular weight decrease and hence the solubility increase are promoted by the presence of retarder or chain transfer reagent.^{7–9} Thus, a soluble hyperbranched polymer can be formed in the polymerization of a divinyl monomer with an initiator of high concentration, where many initiator-fragments are incorporated as terminal groups into the polymer molecule via initiation and primary radical termination [initiator-fragment incorporation radical polymerization (IFIRP)].^{7,10–12}

We have synthesized several hyperbranched polymers by IFIRP, including divinylbenzene (DVB), ethylene glycol dimethacrylate, and divinyl adipate.^{7,10–12} The hyperbranched polymers obtained were formed in the polymerizations of divinyl monomers in the presence of a monovinyl monomer or a retarder. Recently, we have found that soluble hyper-

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branched polymers were also obtained in the homopolymerization of DVB with dimethyl 2,2'-azobisisobutyrate (MAIB) at high concentrations.

The present article describes the results on the IFIRP of DVB with MAIB in benzene and characterization of the resultant polymers.

EXPERIMENTAL

Materials

Divinylbenzene (DVB) (supplied by Nippon Steel Chemical) was a mixture of *m*- and *p*-isomers (2:1), and used after distillation. Dimethyl 2,2'-azobisisobutyrate (MAIB) (supplied by Wako Pure Chemical Industries) was recrystallized from methanol. Benzene was treated by sulfuric acid and distilled. Other solvents were used after distillations.

Polymerization

The polymerization of DVB with MAIB in benzene was conducted in a degassed and sealed glass tube at a given temperature. The resultant polymer was isolated by pouring the polymerization mixture into a large excess of *n*-hexane. The consumption of the vinyl groups of DVB was measured in situ as a function of time by Fourier transform near-infrared (FTNIR) spectroscopy, where the polymerization was carried out in a degassed and sealed Pyrex tube (5 mm diameter) in a custom-made aluminum furnace with an FTNIR measurement system.¹³

Measurements

The conversion of DVB was estimated with a Jasco INT-400 spectrometer equipped with a mercury-cadmium-telluride detector. The consumption of DVB vinyl groups was monitored by the absorbance at about 6150 cm⁻¹, being assignable to the overtone absorption due to the stretching vibration of =C—H bonds in the vinyl groups. The ¹H NMR spectra were measured with a Jeol GX spectrometer (400 MHz). Gel permeation chromatography (GPC) was performed at 40°C, using a Tosoh HLC-8220 GPC chromatograph (columns; TSK-Gel Super HZM × 2, [polymer] = 1 mg/mL, flow rate = 0.35 mL/min) with tetrahydrofuran (THF) as eluent. From the GPC results, number-average (M_n) and weight-average (M_w) molecular weights were estimated with polystyrene standard calibration. The multiangle laser light scattering (MALLS) measurements were conducted by Shoko Co., with a Wyatt technology DAWN EOS with laser operating at 690 nm, where dn/dc (0.143 mL/g) was separately determined at 25°C in THF by a differential refractometer (Optilab DSP; Wyatt Technology). The viscosity of polymer solutions in THF was measured

with a Ubbelohde viscometer. Dynamic thermogravimetry (TG) of the polymer was performed under a nitrogen atmosphere (flow rate = 20 mL/min) with a Shimadzu TGA-50 thermogravimeter at a heating rate of 10°C/min. A differential scanning calorimetric (DSC) curve was obtained with a Shimadzu DSC 50 (under N₂, heating rate = 10°C/min). Electron spin resonance (ESR) spectra of the polymerization mixture in a degassed and sealed ESR tube were recorded with a Jeol JES-FE2XG spectrometer operating at the X band with a transverse electric wave-mode cavity. The radical concentration was determined by computer double integration of the first derivative ESR spectrum, where 2,2,6,6-tetramethylpiperidin-1-oxyl radical in the polymerization mixture without MAIB was used as a standard.

RESULTS AND DISCUSSION

Polymerization of DVB with MAIB in benzene

The homopolymerization of DVB was carried out at 70 and 80°C in benzene, using MAIB of high concentrations (0.10–0.50 mol/L) as an initiator. Table I summarizes the results observed.

When the DVB concentration was varied at a fixed MAIB concentration of 0.50 mol/L (runs 1–5), the polymerization at not more than 0.25 mol/L of the DVB concentration proceeded homogeneously at 80°C without any gelation, while the use of higher DVB concentrations (0.30 and 0.50 mol/L) caused gelation. On the other hand, when the MAIB concentration was changed fixing the DVB concentration at 0.20 mol/L (runs 6–10), the polymerization at the MAIB concentrations more than 0.30 mol/L proceeded homogeneously at 80°C, while gelation took place at lower MAIB concentrations of 0.10 and 0.20 mol/L, indicating the importance of the use of high initiator concentrations. The polymer yield (16–57% without gelation) increased with increasing DVB concentration and with decreasing MAIB concentration. The polymer yield was estimated based on the total weight of DVB and MAIB, considering N₂-elimination on the decomposition of MAIB. The molecular weight and molecular weight distribution (M_w/M_n) tended to increase with polymer yield, namely, with increasing monomer concentration and with decreasing initiator concentration.

A detailed investigation was carried out on the homogeneous polymerization at 70 and 80°C, where the concentrations of DVB and MAIB were 0.20 and 0.50 mol/L, respectively. As shown in Figure 1, the polymer yield increased with time and leveled off to about 35% over 90 min at 80°C, and to about 40% over 180 min at 70°C. The molecular weight ($M_n = 1.2$ – 4.8×10^4 at 70°C and 0.9 – 4.3×10^4 at 80°C) increased with time, namely, polymer yield (runs 2 and 10–25 in Table I). The molecular weight distribution (M_w/M_n

TABLE I
Copolymerization of DVB with MAIB in Benzene

| Run | Temperature (°C) | [DVB] (mol/L) | [MAIB] (mol/L) | Time (min) | Yield (%) | M_n (10^{-4}) | M_w/M_n |
|----------------|------------------|---------------|----------------|------------|-----------|---------------------|-----------|
| 1 | 80 | 0.15 | 0.50 | 60 | 16 | 2.6 | 3.4 |
| 2 | 80 | 0.20 | 0.50 | 120 | 34 | 2.9 | 3.3 |
| 3 | 80 | 0.25 | 0.50 | 120 | 43 | 5.1 | 6.8 |
| 4 ^a | 80 | 0.30 | 0.50 | 120 | 50 | — | — |
| 5 ^a | 80 | 0.50 | 0.50 | 120 | 66 | — | — |
| 6 ^a | 80 | 0.20 | 0.10 | 240 | 79 | — | — |
| 7 ^a | 80 | 0.20 | 0.20 | 240 | 65 | — | — |
| 8 | 80 | 0.20 | 0.30 | 240 | 57 | 6.0 | 6.3 |
| 9 | 80 | 0.20 | 0.40 | 240 | 43 | 4.3 | 4.3 |
| 10 | 80 | 0.20 | 0.50 | 240 | 35 | 2.7 | 3.5 |
| 11 | 80 | 0.20 | 0.50 | 20 | 4 | 0.9 | 1.4 |
| 12 | 80 | 0.20 | 0.50 | 30 | 12 | 1.2 | 1.5 |
| 13 | 80 | 0.20 | 0.50 | 40 | 20 | 1.5 | 2.0 |
| 14 | 80 | 0.20 | 0.50 | 50 | 25 | 1.6 | 2.0 |
| 15 | 80 | 0.20 | 0.50 | 60 | 28 | 2.3 | 1.7 |
| 16 | 80 | 0.20 | 0.50 | 75 | 34 | 4.3 | 3.7 |
| 17 | 80 | 0.20 | 0.50 | 90 | 34 | 2.7 | 4.2 |
| 18 | 70 | 0.20 | 0.50 | 50 | 4 | 1.2 | 1.6 |
| 19 | 70 | 0.20 | 0.50 | 60 | 7 | 1.3 | 1.8 |
| 20 | 70 | 0.20 | 0.50 | 70 | 10 | 1.5 | 1.8 |
| 21 | 70 | 0.20 | 0.50 | 80 | 14 | 1.7 | 2.1 |
| 22 | 70 | 0.20 | 0.50 | 90 | 19 | 1.9 | 2.5 |
| 23 | 70 | 0.20 | 0.50 | 120 | 30 | 3.4 | 3.3 |
| 24 | 70 | 0.20 | 0.50 | 180 | 39 | 4.1 | 5.6 |
| 25 | 70 | 0.20 | 0.50 | 240 | 38 | 4.8 | 7.0 |

^a System displayed gelation.

= 1.6–7.0 at 70°C and 1.4–4.2 at 80°C) was broadened with time, that is, polymer yield (runs 2 and 10–25 in Table I).

The conversion of the vinyl groups of DVB was monitored in situ by FTNIR. Figure 2 shows time-

profiles of the conversion as observed in the polymerization in dioxane at 70 and 80°C, where the concentrations of DVB and MAIB were 0.20 and 0.50 mol/L, respectively. Thus, the vinyl groups of the divinyl monomer were almost completely consumed in about

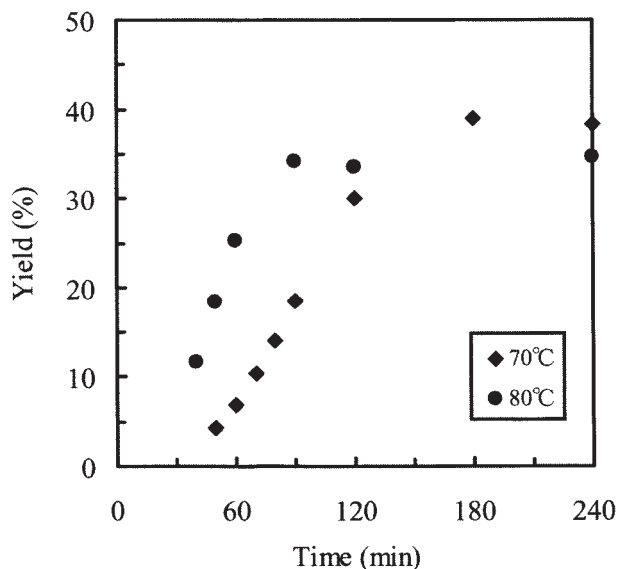


Figure 1 Time-yield curves in the polymerization of DVB with MAIB at 70 and 80°C in benzene. [DVB] = 0.20 mol/L, [MAIB] = 0.50 mol/L.

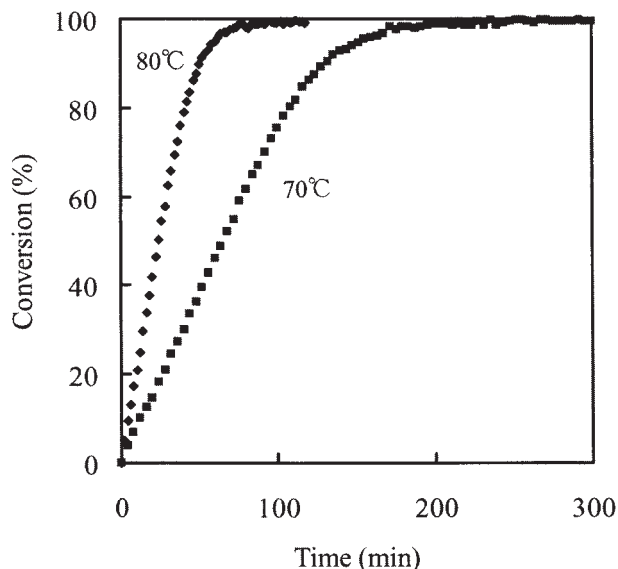


Figure 2 Time-conversion curves of DVB in the polymerization of DVB with MAIB at 70 and 80°C in benzene. [DVB] = 0.20 mol/L, [MAIB] = 0.50 mol/L.

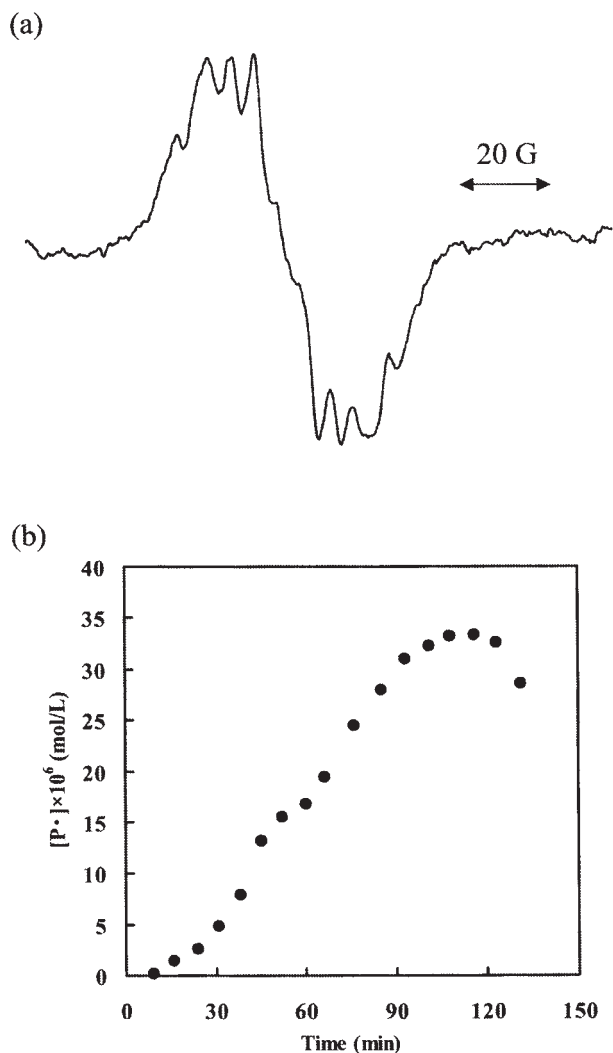


Figure 3 (a) ESR spectrum observed in the polymerization of DVB with MAIB at 80°C in benzene for 30 min and (b) time-profile of the polymer radical concentration during the polymerization. [DVB] = 0.20 mol/L, [MAIB] = 0.50 mol/L.

80 min at 80°C and in about 170 min at 70°C. These findings conform the leveling phenomenon of the polymer yield observed in Figure 1.

Figure 3(a) presents the ESR spectrum observed in the polymerization of DVB with MAIB at 80°C in benzene for 30 min, where the concentrations of DVB and MAIB were 0.20 and 0.50 mol/L. The observed spectrum is assignable to the propagating polymer radicals of DVB. The hyperfine structure is due to the hydrogens on the benzene ring of DVB. Similar hyperfine structures were also reported to be observed in the ESR spectra of the propagating polymer radicals of substituted styrenes.¹⁴ Figure 3(b) illustrates the relationship between the polymer radical concentration ($[P\cdot]$) and time. Thus, the polymer radical concentration increased with time in spite of the homogeneous polymerization. In the conventional homogeneous radical polymerization systems, the propagating poly-

mer radicals are involved in a stationary state. The accumulation of the polymer radicals observed here is due to the fact that the radicals left in the inner part of hyperbranched structure are difficult to participate in bimolecular termination. The polymer radical concentration increased up to a value as high as 3.5×10^{-5} mol/L in the polymerization for about 100 min. Such radical accumulation was also observed in other IFIRP systems which proceeded homogeneously.^{7,10,11}

Characterization of the resulting polymers

The solubility of the polymer formed in the polymerization of DVB (0.20 mol/L) with MAIB (0.50 mol/L) at 80°C in benzene for 2 h was examined (run 2 in Table I). The polymer was soluble in benzene, toluene, THF, ethyl acetate, chloroform, acetone, acetophenone, and *N,N*-dimethylformamide, and was insoluble in *n*-hexane, cyclohexane, acetonitrile, dimethyl sulfoxide, methanol, ethanol, and water.

Figure 4 shows the ¹H NMR spectra of the polymers formed in the polymerization at 80°C in benzene at different times, where the concentrations of DVB and MAIB were 0.20 and 0.50 mol/L, respectively (runs 2 and 13 in Table I). Thus, the observed peaks were considerably broad, suggesting rigid structure of the polymer. Peak assignments are given in the figure. As expected, the polymer consisted of DVB units and methoxycarbonylpropyl groups as MAIB-fragment.

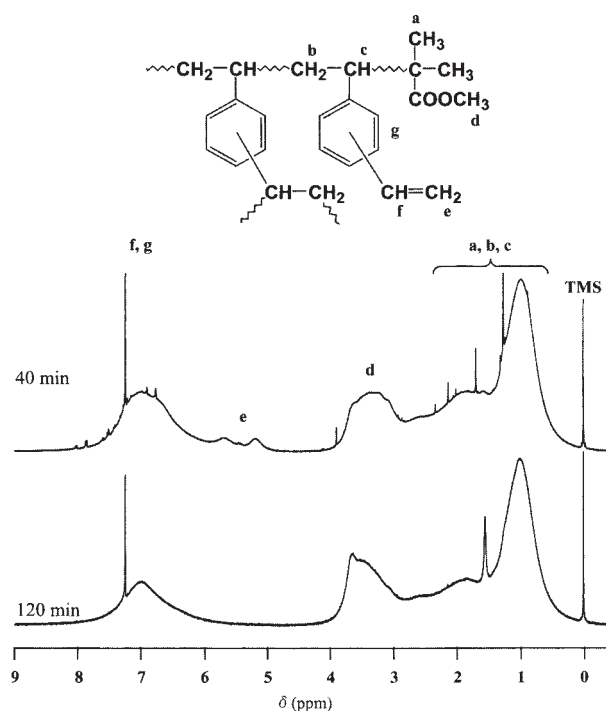


Figure 4 ¹H NMR spectra of the polymers formed in the polymerization of DVB with MAIB at 80°C in benzene for 40 and 120 min. [DVB] = 0.20 mol/L, [MAIB] = 0.50 mol/L.

The polymer formed for 40 min contained still the unreacted double bond, whereas the one formed for 120 min no longer had any intact double bond.

The composition of the resulting polymer was estimated from the carbon content by elemental analysis. The content ratio of the DVB unit with the unreacted double bond to the one without the double bond was determined using the peak areas of vinyl and phenyl

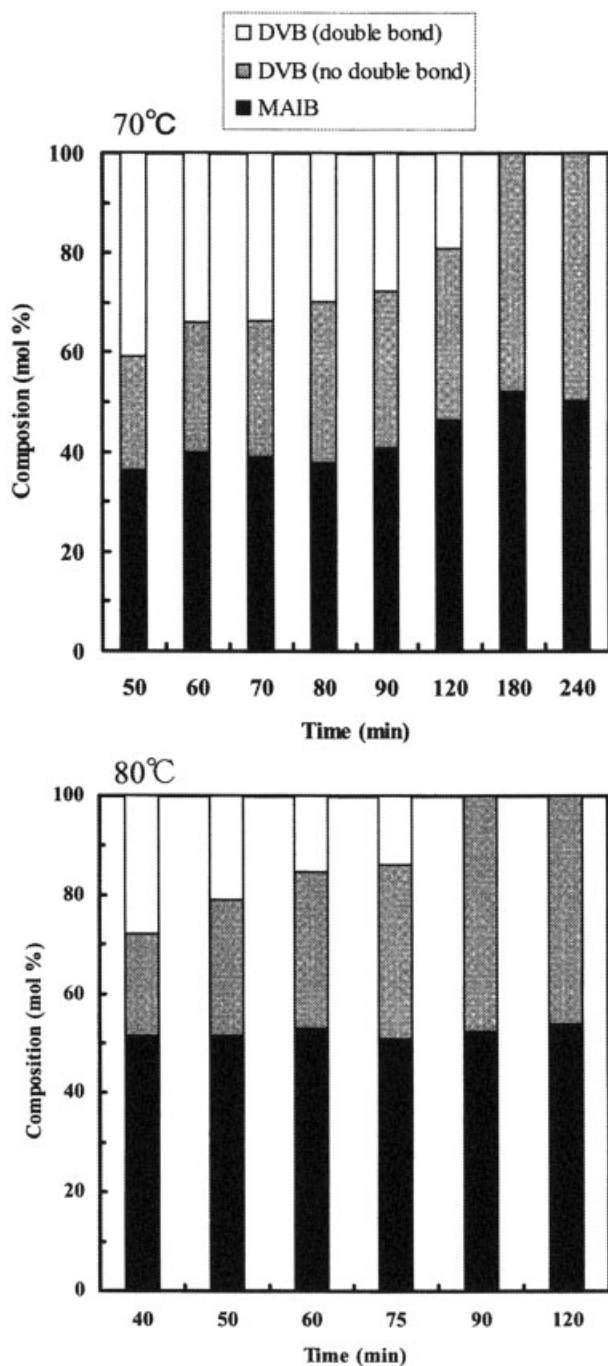
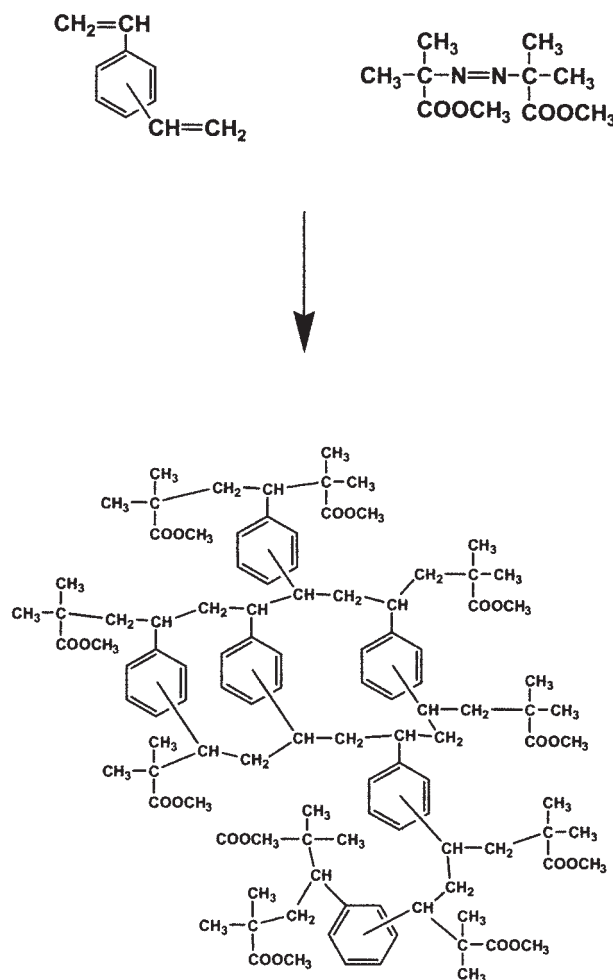


Figure 5 Composition of the polymers formed in the polymerization of DVB with MAIB at 70 and 80°C in benzene at different times. [DVB] = 0.20 mol/L, [MAIB] = 0.50 mol/L.



Scheme 1 A proposed structure of the resulting polymer.

protons. Figure 5 presents the composition of the polymers formed in the polymerization at 70°C (runs 18–25 in Table I) and 80°C (runs 2 and 13–17 in Table I) at different times, where the concentrations of DVB and MAIB were 0.20 and 0.50 mol/L, respectively.

As to the polymers formed at 70°C, the fraction (41–0 mol %) of the DVB unit with an intact double bond reasonably decreased with time and completely diminished over 180 min; instead, that (23–50 mol %) of the DVB unit without double bond increased with time. The content (36–50 mol %) of the methoxycarbonylpropyl group as initiator-fragment tended to increase with time. Similar results were also observed for the polymer formed at 80°C, although the fraction (52–54 mol %) of the initiator-fragment was almost independent of time.

Thus, a large number of the methoxycarbonylpropyl groups from MAIB were incorporated as terminal groups in the resulting polymer via initiation and primary radical termination, demonstrating that an IFIRP proceeds in the polymerization of DVB with MAIB of high concentrations. The presence of many terminal groups in a polymer molecule corresponds to

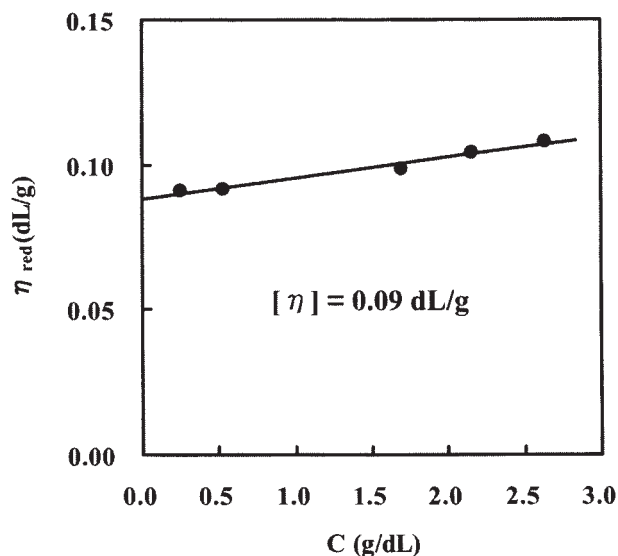


Figure 6 Relation between reduced viscosity (η_{red}) with the polymer concentration (C) at 30°C in THF for the polymer formed in the polymerization of DVB with MAIB at 80°C in benzene for 120 min. [DVB] = 0.20 mol/L, [MAIB] = 0.50 mol/L.

the fact that the polymer is of hyperbranched structure. The number (A) of branching points in a branched polymer molecule is related to the number (B) of terminal groups by $A = (B - 2)$. When the molecular weight of the polymer is large enough, A is nearly equal to B . If all the terminal groups of the polymer are the methoxycarbonylpropyl group as initiator-fragment, about 50 mol % fraction of the incorporated initiator-fragment, as described earlier, corresponds to that the polymer contains one branching point per (50/50) monomer unit. Cyclic structures by internal cyclization can also be contained. A proposed structure of the resulting polymer is depicted in Scheme 1.

The polymer formed in the polymerization of DVB (0.20 mol/L) with MAIB (0.50 mol/L) at 80°C for 2 h (run 2 in Table I) was subjected to the MALLS measurements at 25°C in THF. From the Zimm plot, M_w , radius of gyration (R_g), and 2nd virial coefficient (A_2) were estimated to be 5.0×10^5 , 14 nm, and 3.7×10^{-5} mL/g², respectively. The M_w value by MALLS was much higher than that (9.6×10^4) by GPC (Table I). Such underestimation by GPC was often observed for other dendritic polymers, including hyperbranched polymers.^{7,10–12,15–21} As a reference, a conventional linear polystyrene was also subjected to the MALLS measurements at 25°C in THF to give $M_w = 2.9 \times 10^5$, $R_g = 27.6$ nm, and $A_2 = 4.4 \times 10^{-4}$. Thus, the values of R_g and A_2 of the polymer were much lower than those of linear polystyrene, although the molecular weight of the polymer was considerably higher than that of polystyrene. These MALLS results indicate that the polymer has a compact hyperbranched structure.

The hyperbranched polymers are well known to show low solution viscosity because of lack of intermolecular entanglements.^{1–7,10–12,19,20,22–24} The polymer solution in THF was examined viscometrically at 30°C. The polymer used was the same as that subjected to the MALLS measurements. Figure 6 illustrates the relationship between the reduced viscosity (η_{red}) and the polymer concentration (C). Thus, the η_{red} values were very low (about 0.1 dL/g in the range of C as high as 0.4–2.5 g/dL) in spite of fairly large M_w (5.0×10^5). As a matter of course, the intrinsic viscosity ($[\eta]$) estimated from the plot in Figure 6 was also very low ($[\eta] = 0.09$ dL/g). These viscometric results are likewise in agreement with the fact that the polymer formed in the present polymerization has a compact hyperbranched structure.

Figure 7 presents TG and differential thermogravimetric (DTG) curves of the same polymer formed at 80°C for 2 h (run 2 in Table I). The thermal degradation of the polymer began at 280°C and exhibited maximal rates at 380 and 450°C. The residue obtained at 500°C was 33% of the initial polymer weight. The thermal behavior of the polymer was also examined by DSC. No glass transition was observed in the temperature range from 25 to 200°C. It may be due to the compact and rigid structure of the polymer.

CONCLUSIONS

The homopolymerization of DVB as an excellent crosslinker (0.20 mol/L) with MAIB proceeded homogeneously without any gelation at 80°C in benzene, when the MAIB concentrations as high as 0.30–0.50 mol/L were used, to give soluble polymers. The use of higher DVB concentrations and lower MAIB concentrations caused gelation. In the homogeneous polymerizations at 70 and 80°C at the concentrations of [DVB] = 0.20 mol/L and [MAIB] = 0.50 mol/L, the

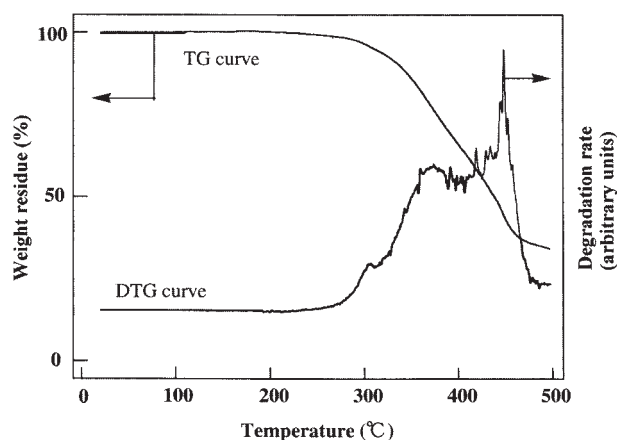


Figure 7 TG and DTG curves of the polymer formed in the polymerization of DVB with MAIB at 80°C in benzene for 120 min. [DVB] = 0.20 mol/L, [MAIB] = 0.50 mol/L.

yield and molecular weight of the polymer increased with time. The vinyl groups of DVB were almost completely consumed in about 80 min at 80°C. The homogeneous polymerization system at 80°C involved ESR-observable polymer radical, the concentration of which increased with time up to 3.4×10^{-5} mol/L. The polymer formed in the polymerization for 2 h at 80°C consisted of 46 mol % of DVB unit and 54 mol % of the methoxycarbonylpropyl group as MAIB-fragment, indicating that an initiator-fragment incorporation radical polymerization proceeds in the present polymerization. The results of the MALLS and viscometric measurements revealed that the individual polymer molecules were formed as hyperbranched polymer nanoparticles.

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