Initiator-Fragment Incorporation Radical Polymerization of Divinyl Adipate with Dimethyl 2,2′-Azobis(isobutyrate): Kinetics and Formation of Soluble Hyperbranched Polymer

Tsuneyuki Sato,* Yukiko Arima, Makiko Seno, and Tomohiro Hirano

Department of Chemical Science and Technology, Faculty of Engineering, Tokushima University, Minamijosanjima 2-1, Tokushima 770-8506, Japan

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ABSTRACT: The polymerization of divinyl adipate (DVA) as an effective cross-linker with dimethyl 2,2′-azobis(iosbutyrate) (MAIB) was performed at 70 and 80 °C in benzene. When the MAIB concentrations as high as 0.05−0.50 mol/L were used, the polymerization of DVA (0.30 mol/L) proceeded homogeneously at 80 °C without any gelation to give soluble polymers in the yields of 45−87%. Kinetic investigation on the homogeneous polymerization at 70 °C gave the following rate equation: $R_p = k[\mathrm{MAIB}]^{0.3}[\mathrm{DVA}]^{1.7}$ (R_p = initial polymerization rate), indicating a significant contribution of the primary radical termination. The overall activation energy of the polymerization was estimated to be 26.8 kcal/mol. The polymer formed in the polymerization of DVA (0.30 mol/L) with MAIB (0.50 mol/L) at 80 °C for 4 h was composed of the DVA units without (48 mol %) and with (8 mol %) double bond and the methoxycarbonylpropyl group (44 mol %) from MAIB. The large fraction of the incorporated initiator-fragment implies that an initiator-fragment incorporation polymerization proceeded to give hyperbranched polymer in the present polymerization. The results of the multiangle laser light scattering and viscometric measurements and also transmission electron microscopic observation indicate that the polymer was of compact hyperbranched structure. The polymer showed an upper critical solution temperature (36 °C on cooling) in an acetone−water [7:40 (v/v)] mixture and also exhibited the encapsulation and transport properties for Rhodamine 6G as a dye probe.

Introduction

The radical polymerization including a divinyl monomer is well-known to give insoluble cross-linked polymer, the molecular weight of which is usually treated to be extremely high or infinite. On the other hand, in the conventional radical polymerization of a vinyl monomer, the molecular weight of the resulting polymer decreases with increasing initiator concentration, owing to increasing termination rate. These facts lead to an idea that the use of much higher initiator concentration in the polymerization of a divinyl monomer can cause so great a decrease in the molecular weight that the resulting polymer finally becomes soluble and its structure is no longer linear, but is hyperbranched.

This idea has been realized in some polymerization systems involving divinyl monomers such as divinylbenzene, ethylene glycol dimethacrylate, and divinyl adipate (DVA), where soluble hyperbranched polymers were expectedly formed.[1−4] A large number of initiator-fragments were incorporated as terminal groups in the resulting copolymers via initiation and primary radical termination, on the basis of which the polymerization was named the initiator-fragment incorporation radical polymerization (IFIRP).[1] The soluble hyperbranched polymers so far obtained by the IFIRP were formed in the polymerizations of divinyl monomers in the presence of a monovinyl monomer or a retarder.[1−4] Recently, we have found that the homopolymerization of DVA as an effective cross-linker could also yield soluble hyperbranched polymer when dimethyl 2,2′-azobis(isobutyrate) (MAIB) as initiator was used at concentrations as high as 0.1−0.5 mol/L.

The present paper describes the kinetic results of the IFIRP of DVA with MAIB in benzene and characterization of the resulting polymers.

Experimental Section

Materials. Commercially available DVA was used after distillation. MAIB was recrystallized from methanol. Benzene was treated with sulfuric acid and distilled. Other solvents were used after distillations. Rhodamine 6G (Tokyo Kasei Kogyo Co., Ltd.) was used as received.

Polymerization. Polymerizations were conducted in degassed and sealed glass tubes at given temperatures. The resulting polymers were isolated by pouring the polymerization mixtures into a large excess of *n*-hexane, dried under vacuum, and weighed. The conversion of the vinyl groups of DVA was estimated in situ as a function of time by Fourier transform near-infrared (FT-NIR) spectroscopy, where the polymerizations were carried out in degassed and sealed Pyrex tubes (5 mm diameter) in a custom-made aluminum furnace with an FT-NIR spectroscopic measurement system.[5]

Measurements. The conversion of the vinyl groups of DVA was determined with a Jasco INT-400 spectrometer equipped with a mercury−cadmium telluride detector and monitored by the absorbance at around 6200 cm^{-1} assignable to the overtone stretching vibrations of the =C−H bonds in the vinyl groups. ^{1}H NMR spectra of the polymers were obtained with a JEOL GX spectrometer (400 MHz). Gel permeation chromatography (GPC) was performed at 40 °C by 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, the number-average (M_n) and weight-average (M_w) molecular weights of the polymers were estimated with polystyrene standards for calibration. The optical transmittance of a polymer solution was monitored at 500 nm as a function of temperature with a Jasco V-550 spectrometer. A temperature change rate of 0.5 °C/min was used. The multiangle laser light scattering (MALLS) measurements were conducted by Shoko Co. Ltd. with a Wyatt

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* Corresponding author: Tel +81-88-656-7402; Fax +81-88-655-7025; e-mail sato@chem.tokushima-u.ac.jp.

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Table 1. Polymerization of DVA with MAIB at 70 and 80 °C in Benzene

run	[DVA] (mol/L)	[MAIB] (mol/L)	temp (°C)	time (h)	yield (%)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	remarks
1	0.50	0.50	80	4.00	63				gelation
2	0.40	0.50	80	4.00	50	6.14	43.0	7.0	
3	0.30	0.50	80	4.00	45	1.16	5.6	4.8	
4	0.20	0.50	80	4.00	25	0.84	1.3	1.3	
5	0.30	0.40	80	4.00	52	1.19	6.2	5.2	
6	0.30	0.30	80	4.00	59	1.38	8.8	6.4	
7	0.30	0.20	80	4.00	68	1.71	15.7	9.2	
8	0.30	0.10	80	4.00	79	1.85	23.5	12.7	
9	0.30	0.05	80	4.00	87	1.68	21.8	13.0	
10	0.30	0.01	80	4.00	93				partial gelation
11	0.30	0.50	70	0.25	23	0.86	1.6	1.9	
12	0.30	0.50	70	0.50	30	1.02	2.7	2.6	
13	0.30	0.50	70	0.75	40	1.05	3.5	3.3	
14	0.30	0.50	70	1.00	39	1.15	4.3	3.7	
15	0.30	0.50	70	2.00	42	1.24	6.4	5.2	
16	0.30	0.50	70	4.00	46	1.22	8.5	6.9	
17	0.30	0.50	70	6.00	46	1.23	9.5	7.7	
18	0.30	0.50	80	0.25	21	0.86	1.7	2.0	
19	0.30	0.50	80	0.50	30	0.92	2.4	2.6	
20	0.30	0.50	80	0.75	33	0.96	2.9	3.0	
21	0.30	0.50	80	1.00	37	1.00	3.5	3.5	
22	0.30	0.50	80	2.00	41	1.01	4.2	4.2	

Technology DAWN EOS with a laser operating at 690 nm, where d*n*/d*c* (0.100) was separately determined at 25 °C in THF by a differential refractometer (Optilab DSP; Wyatt Technology Corp.). The viscosity of a polymer solution in THF was measured at 30 °C using a Ubbelohde viscometer. Dynamic thermogravimetry (TG) of the polymer was performed under a N_2 atmosphere (flow rate = 20 mL/min) with a Shimadzu TGA-50 thermogravimeter at a heating rate of 10 °C/min. Transmission electron microscopic (TEM) observation was carried out by Sanyo Chemical Industries Ltd. on a Hitachi-7100 electron microscope at an accelerating voltage of 100 kV, where the sample was prepared by immersing a carbon-coated copper grid into a 0.01 wt % polymer solution in benzene which was dried in a vacuum and stained with ruthenium dioxide.

Results and Discussion

Polymerization of DVA with MAIB in Benzene. At first, the polymerization of DVA with MAIB of high concentrations was conducted at 80 °C in benzene for 4 h. The results observed are listed as runs 1−10 in Table 1. When the MAIB concentration was fixed at 0.50 mol/L, the use of a DVA concentration as high as 0.50 mol/L caused gelation (run l), while the polymerization proceeded homogeneously without any gelation at the less DVA concentrations of 0.20−0.40 mol/L (runs 2−4). The yield (25−50%), the molecular weight (M_n = (0.8−6.l) × 10^4 g/mol), and the molecular weight distribution (M_w/M_n = 1.3−7.0) of the resulting polymers increased with increasing DVA concentration. The polymer yield was estimated on the basis of the total weight of DVA and MAIB, considering N_2 elimination on the MAIB decomposition. On the other hand, at a fixed DVA concentration of 0.30 mol/L, the polymerization proceeded homogeneously at the MAIB concentrations of 0.05−0.40 mol/L (runs 5−9) although the use of a lower MAIB concentration of 0.01 mol/L resulted in partial gelation (run 10). The yield (52−87%), the molecular weight (M_n = (1.2−1.9) × 10^4 g/mol), and the M_w/M_n value (5.2−13.0) of the polymers increased with decreasing MAIB concentration.

Next, a detailed examination was performed for the homogeneous polymerization of DVA with MAIB at 70 and 80 °C in benzene, where the concentrations of DVA and MAIB were 0.30 and 0.50 mol/L, respectively. The results obtained are also summarized in Table 1. As shown in Figure 1a, the polymer yield at 80 °C rapidly increased with time up to about 60 min and then gradually did so. The M_n and M_w/M_n values of the polymer increased in a similar way with time, namely with polymer yield (Figure 1b). Similar results were observed at 70 °C (runs 11−17).

Kinetic Study of the Polymerization of DVA with MAIB in Benzene. The polymerization of DVA with MAIB at high concentrations was kinetically studied in benzene. The conversion of the vinyl groups of the monomer was in situ monitored by FT-NIR.

Figure 2a shows the time−conversion curves in the polymerization of DVA with MAIB at different temperatures, where the concentrations of DVA and MAIB

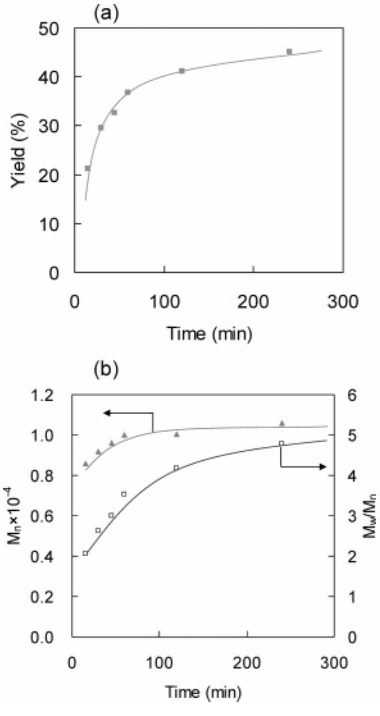


Figure 1. Time profiles of (a) the yield and (b) the molecular weight (M_n) and polydispersity (M_w/M_n) of the polymer formed in the polymerization of DVA with MAIB at 80 °C in benzene. [DVA] = 0.30 mol/L and [MAIB] = 0.50 mol/L.

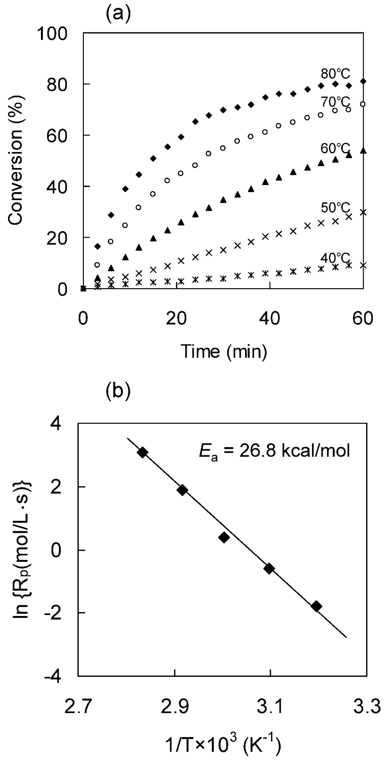


Figure 2. (a) Time−conversion curves for the polymerization of DVA with MAIB at different temperatures in benzene and (b) Arrhenius plot of the initial polymerization rate (R_p). [DVA] = 0.30 mol/L and [MAIB] = 0.50 mol/L.

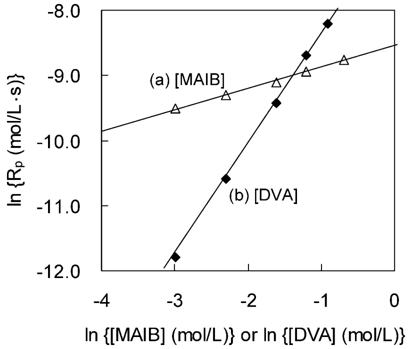


Figure 3. Dependence of the initial polymerization rate (R_p) on (a) the MAIB concentration and (b) the DVA concentration in the polymerization of DVA with MAIB at 70 °C in benzene. [DVA] = 0.30 mol/L for (a) and [MAIB] = 0.50 mol/L for (b).

were 0.30 and 0.50 mol/L, respectively. From these time−conversion plots, the initial polymerization rate (R_p) was estimated at each temperature. Figure 2b illustrates the Arrhenius plot of R_p, from the slope of which the overall activation energy of the polymerization was calculated to be 26.8 kcal/mol.

Figure 3a shows the effect of the MAIB concentration on R_p at 70 °C when the MAIB concentration was changed at a fixed DVA concentration of 0.30 mol/L. Thus, R_p increased in proportion to the 0.3 power of the initiator concentration. The observed power of 0.3 is considerably lower than 0.5 for the conventional radical polymerization involving bimolecular termination between the propagating polymer radicals. Figure 3b presents the relationship between the DVA concentration and R_p at 70 °C when the DVA concentration was varied fixing the MAIB concentration at 0.50 mol/L. R_p was proportional to the 1.7 order of the monomer concentration. This order with respect to the monomer concentration is much higher than the first order for the conventional radical polymerization.

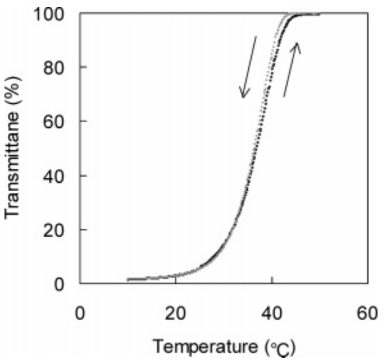


Figure 4. Temperature effect on the transmittance of a polymer [0.1 % (w/v)] solution in an acetone−water [7:40 (v/v)] mixture on cooling (←) and heating (→). The polymer was formed in the polymerization of DVA with MAIB at 80 °C in benzene for 4 h. [DVA] = 0.30 mol/L and [MAIB] = 0.50 mol/L.

From the above kinetic results, R_p at 70 °C in benzene is expressed by the following equation:

$$R_p = k[\mathrm{MAIB}]^{0.3}[\mathrm{DVA}]^{1.7}$$

The unusual rate equation is reasonably explained by considering of contribution of primary radical termination. In general, the primary radical termination becomes more predominant as the initiator concentration is higher and the reactivity of the monomer toward the primary radical is lower.[6,7] The high initiator concentrations were used in the present polymerization. The vinyl groups of DVA are nonconjugative and hence should have a low reactivity toward the resonance-stabilized methoxycarbonylpropyl radical as the primary radical of MAIB. Vinyl acetate as monovinyl analogue of DVA is reported to show a very low reactivity toward the methoxycarbonylpropyl radical.[8] When all the termination reaction is due to the primary radical termination, R_p is given by $R_p = k[\mathrm{initiator}]^0[\mathrm{monomer}]^2$.[7]

Characterization of the Resulting Polymers. There was examined the solubility for the polymer formed in the polymerization of DVA with MAIB at 80 °C in benzene for 4 h, where the concentrations of DVA and MAIB were 0.30 and 0.50 mol/L, respectively (run 3 in Table 1). The polymer was soluble benzene, toluene, acetophenone, THF, chloroform, ethyl acetate, acetone, acetonitrile, *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) and was insoluble in *n*-hexane, cyclohexane, ethanol, methanol, and water. Interestingly, the polymer showed an upper critical solution temperature (UCST) in an acetone−water [7:40 (v/v)] mixture. Figure 4 illustrates the temperature effect on the transmittance of a polymer solution [0.1% (wt/v)] on cooling and heating. Thus, little hysteresis was observed. When UCST was defined as the temperature at which the transmittance became 50%, the UCST was estimated to be 36 °C on cooling and 37 °C on heating.

Figure 5 presents the ^{1}H NMR spectra of the polymers formed in the polymerization of DVA with MAIB at 80 °C in benzene at different times, where the concentrations of DVA and MAIB were 0.30 and 0.50 mol/L (runs 3, 18, and 21 in Table 1). Peak assignments are denoted in the figure. Thus, the polymers were found to consist of DVA units with and without an intact double bond

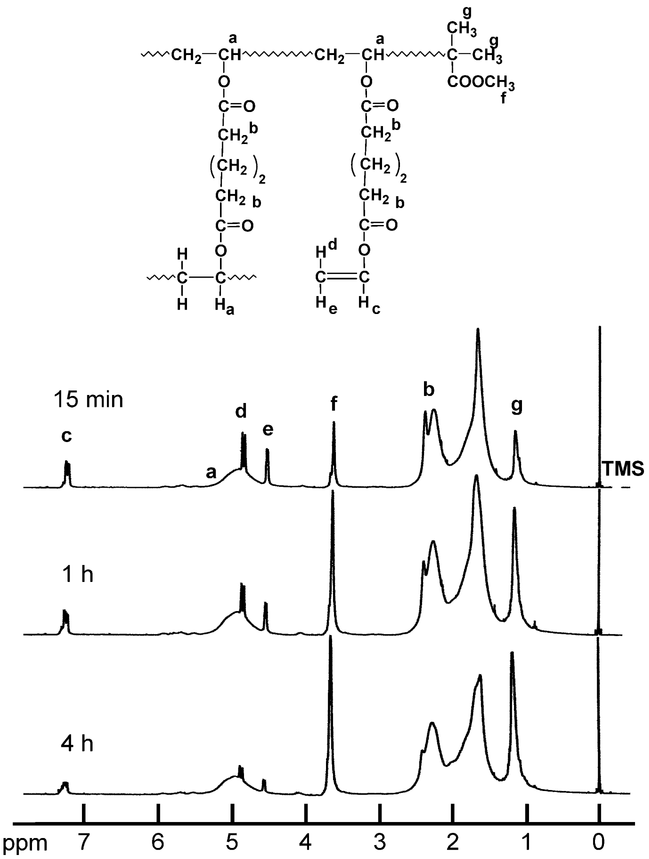


Figure 5. ^{1}H NMR spectra of the polymers formed in the polymerization of DVA with MAIB at 80 °C in benzene at different times. [DVA] = 0.30 mol/L and [MAIB] = 0.50 mol/L.

and the metoxycarbonylpropyl group derived from MAIB. The peak intensities of the vinyl protons decreased with time.

The compositions of the resulting polymers were estimated from the peak areas of vinyl (4.6 and 4.9 ppm), acyloxymethine (4.5−5.5 ppm), and methoxylcarbonyl (3.6 ppm) protons. Figure 6a shows the composition of the polymers formed at different MAIB concentrations in the polymerization at 80 °C for 4 h, where the DVA concentration was fixed at 0.30 mol/L (runs 3 and 5−9 in Table 1). As expected, the fraction (19−44 mol %) of methoxycarbonylpropyl group as initiator-fragment increased but not linearly with increasing MAIB concentration. This fact reveals that the comparatively low polymer yields observed at high MAIB concentrations resulted from the inefficient consumption of MAIB because the polymer yields were estimated by considering the weight of MAIB. The fraction (17−8 mol %) of DVA unit with an unreacted double bond tended to decrease with the MAIB concentration. Figure 6b illustrates the composition of the polymers generated at different times at 80 °C, fixing the concentrations of DVA and MAIB at 0.30 and 0.50 mol/L, respectively (runs 3 and 18−22 in Table 1). The fraction (30−8 mol %) of the DVA unit with an intact double bond reasonably decreased with time but did not completely vanish even after polymerization for 4 h at 80 °C. The residual vinyl groups are considered to be those left unreacted in the inner part of the polymer molecules. Contrarily, the content (17−44 mol %) of the initiator-fragment increased with time. The fraction (48−54 mol %) of DVA unit without double bond was almost independent of time.

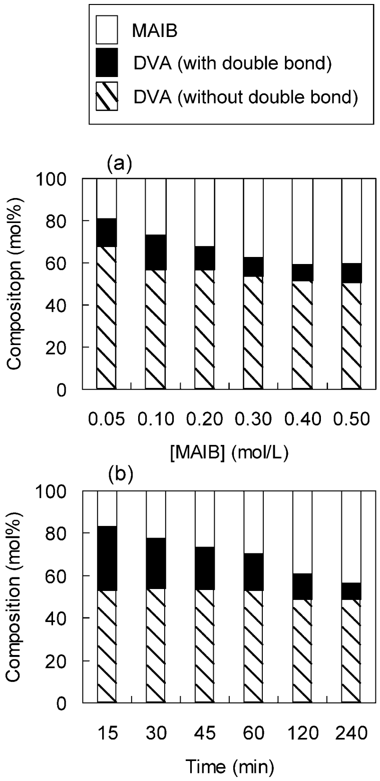
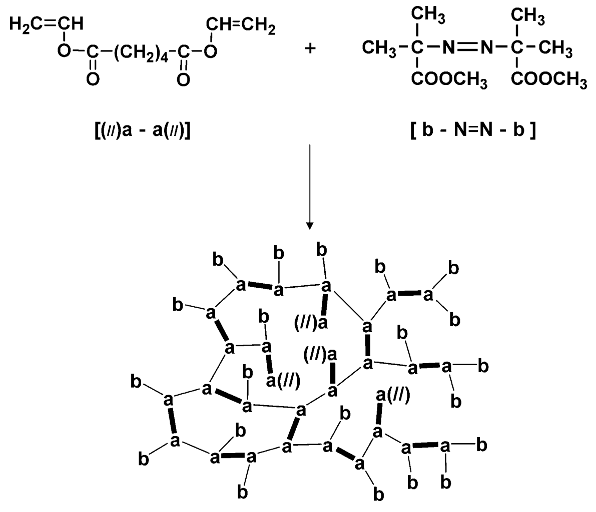


Figure 6. Composition of the polymers formed in the polymerization of DVA with MAIB at 80 °C in benzene (a) at different MAIB concentrations for 4 h and (b) at different times. [DVA] = 0.30 mol/L for (a). [DVA] = 0.30 mol/L and [MAIB] = 0.50 mol/L for (b).

Thus, a large number of the methoxycarbonylpropyl groups were incorporated as terminal groups in the resulting polymers via initiation and primary radical termination, indicating that an IFIRP proceeded in the present polymerization system. The presence of many terminal groups in a polymer molecule means that the polymer was 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 enough large, A is nearly equal to B. The polymer formed in the polymerization at 80 °C for 4 h contained the metoxycarbonylpropyl groups in the fraction of about 40 mol %. If all of the terminal groups in the polymer are the methoxycarbonylpropyl group from MAIB, the 40 mol % fraction of the incorporated initiator-fragments corresponds to that the polymer contains one branching point per 1.5 (=60/40) monomer units. Cyclic structures by internal cyclization may be also involved. A proposed structure of the resulting polymer is depicted in Scheme 1.

The polymer formed at 80 °C for 4 h (run 3 in Table 1) was subjected to MALLS measurements at 25 °C in THF. From the Zimm plot, M_w, radius of gyration (R_g), and the second virial coefficient (A_2) were estimated to be $M_w = 2.6 \times 10,^5$ $R_g = 15$ nm, and $A_2 = 7.7 \times 10^{-5}$ mL/g^2, respectively. The M_w value by MALLS was far higher than that (5.6×10^4) by GPC (Table 1). Such underestimations by GPC were often reported for other hyperbranched polymers and dendrimers, being ascribed to smaller hydrodynamic radii of those polymers.[1−4,9−15] R_g of 15 nm was much smaller compared with that (28 nm) of a conventional linear polystyrene with similar M_w (2.9×10^5) which were in the same way

Scheme 1. A Proposed Structure of the Hyperbranched Polymer Formed in the Polymerization of DBA with MAIB



determined by MALLS at 25 °C in THF, supporting the compact hyperbranched structure of the polymer. The A_2 value of the polymer was considerably lower than those (10^{-4} mL/g^2) of common linear polymers such as polystyrene and poly(methyl methacrylate) in good solvents,[16] also suggesting that the polymer is of compact globular hyperbranched structure which causes the lack of intermolecular entanglements.

THF solutions of the same polymer (run 3 in Table 1) were examined viscometrically at 30 °C. Figure 7 shows the plot of reduced viscosity (η_{red}) against the polymer concentration (C). Thus, the η_{red} values (0.06–0.08 dL/g, C = 0.4–1.1 g/dL) were very low despite moderately high M_{w} (2.6×10^5). The dendritic polymers are well-known to show low solution viscosity because of the lack of intermolecular entanglements.[1–4,9–15] As a matter of course, the intrinsic viscosity ($[\eta]$) estimated from the plot was also very low ($[\eta]$ = 0.06 dL/g). These viscometric data likewise conform to the fact that the polymer formed in the present IFIRP is of compact hyperbranched structure.

Dendritic polymers were reported to show encapsulation and transport properties for organic or metalloorganic molecules such as dyes and metalloporphyrins owing to their void-containing structures.[17–21] Such properties of the polymer formed at 70 °C for 6 h (run17 in Table 1) were preliminarily checked using Rhodamine 6G as a dye probe. The dye was soluble in water and chloroform and was only slightly soluble in toluene. When chloroform of 2.5 mL was added to 2.5 mL of a dye solution (0.01 wt %) in water, the chloroform phase became orange because a considerable portion of the dye was transferred from the aqueous phase to the organic phase. When the present hyperbranched polymer of 50 mg was dissolved in the chloroform phase, almost all Rhodamine 6G molecules were transferred to the organic phase, and hence the water phase became substantially colorless. Little distribution of Rhodamine 6G was observed in the toluene phase when toluene (2.5 mL) was added to the aqueous dye (0.01 wt %) solution (2.5 mL). On the other hand, when the hyperbranched polymer (50 mg) was dissolved in the toluene phase, a considerable fraction of the dye molecules was transferred to the organic phase, and then the toluene phase was appreciably colored orange. However, any appreciable color change was not observed in the organic and aqueous phases when a separately radically prepared poly(vinyl acetate) ($M_{\mathrm{n}} = 5.2 \times 10^4$, $M_{\mathrm{w}} = 1.1 \times 10^5$) was used in the place of the hyperbranched polymer. These results indicate the encapsulation and phase transfer properties of the present hyperbranched polymer.

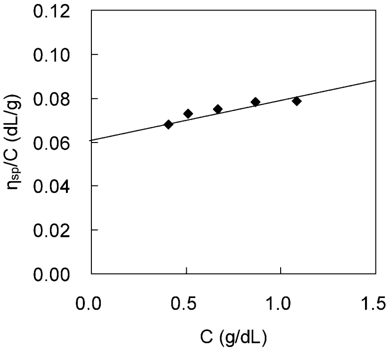


Figure 7. Relationship between the reduced viscosity (η_{red}) and the polymer concentration (C) at 30 °C in THF for the polymer formed in the polymerization of DVA with MAIB at 80 °C in benzene for 4 h. [DVA] = 0.30 mol/L and [MAIB] = 0.50 mol/L.

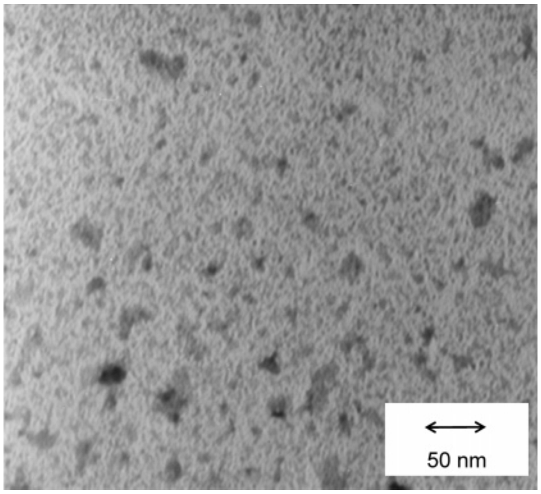


Figure 8. TEM image of the polymer formed in the polymerization of DVA with MAIB at 80 °C in benzene for 4 h. [DVA] = 0.30 mol/L and [MAIB] = 0.50 mol/L.

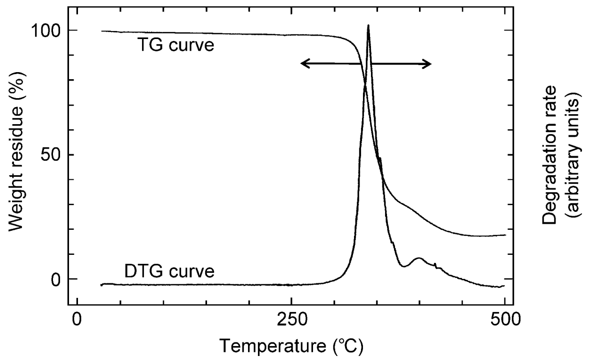


Figure 9. TG and DTG curves of the polymer formed in the polymerization of DVA with MAIB at 80 °C in benzene for 4 h. [DVA] = 0.30 mol/L and [MAIB] = 0.50 mol/L.

Figure 8 presents a TEM image of the polymer formed at 80 °C for 4 h (run 3 in Table 1). Although not clearly, nanoparticles of 8–25 nm diameter were observed. These diameters are considerably smaller than the diameter of gyration (30 nm) in THF by MALLS. So, most of particles observed by TEM were considered to be individual polymer molecules although some larger particles might be aggregates of a few polymer molecules.

Figure 9 shows TG and differential thermogravimetric (DTG) curves of the same polymer formed at 80 °C for 4 h (run 3). The thermal degradation of the polymer began at 300 °C and showed maximal rates at 340 and 400 °C. The residue at 500 °C was 18% of the initial polymer weight.

Conclusions

The polymerization of DVA as a typical divinyl monomer was performed at 70 and 80 °C in benzene using MAIB of high concentrations as initiator. When the MAIB concentrations as high as 0.05−0.50 mol/L were used, the polymerization of DVA (0.30 mol/L) proceeded homogeneously at 80 °C without any gelation to give soluble polymers in the yields of 45−87%. The initial polymerization rate (R_p) at 70 °C was given by $R_p = k[\mathrm{MAIB}]^{0.3}[\mathrm{DVA}]^{1.7}$, indicating a significant contribution of the primary radical termination. The polymer formed in the polymerization of DVA (0.30 mol/L) with MAIB (0.50 mol/L) at 80 °C for 4 h consisted of the DVA units without (48 mol %) and with (8 mol %) double bond and the methoxycarbonylpropyl group (44 mol %) as MAIB fragment. Such a large fraction of the incorporated initiator-fragment implies that an initiator-fragment incorporation polymerization proceeded and gave hyperbranched polymers in the present polymerization. The results of MALLS and viscometric measurements and TEM observation revealed that the resulting polymer was of compact hyperbranched structure. The polymer showed an upper critical solution temperature in an acetone−water [7:40 (v/v)] mixture at 36 °C on cooling and exhibited the encapsulation and transport properties for Rhodamine 6G as a dye probe.

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