

Effect of nitrobenzene on initiator-fragment incorporation radical polymerization of divinylbenzene with dimethyl 2,2'-azobisisobutyrate

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Abstract

The polymerization of divinylbenzene (DVB) with dimethyl 2,2'-azobisisobutyrate (MAIB) was conducted at 70 and 80 °C in benzene in the presence of nitrobenzene (NB) as a retarder. When the concentrations of DVB, MAIB, and NB were 0.45, 0.50, and 0.50 mol/l, respectively, the polymerization proceeded without any gelation to yield soluble polymers. The polymer yield (up to 65%) and the molecular weight ($M_n = 1.5\text{--}4.2 \times 10^4$ at 70 °C and $1.3\text{--}3.9 \times 10^4$ at 80 °C) increased with time. The polymer formed in the polymerization at 80 °C for 4 h consisted of the DVB units with (4 mol%) and without double bond (41 mol%), methoxycarbonylpropyl group as MAIB-fragment (48 mol%), and NB unit (7 mol%). Incorporation of such a large number of the initiator-fragments as terminal groups in a polymer molecule indicates that the polymer is of a hyperbranched structure. The polymer showed an upper critical solution temperature (40 °C on cooling) in an acetone-water [14:1 (v/v)] mixture. The results of MALLS and viscometric measurements and TEM observation supported that the polymers formed in the present polymerization have a hyperbranched structure. The polymerization system at 70 °C involved an ESR-observable nitroxide radical formed by the addition of polymer radical to the nitro group of NB. The polymerization was kinetically investigated in dioxane. The initial polymerization rate (R_p) at 70 °C was expressed by $R_p = k[\text{MAIB}]^{0.5}[\text{DVB}]^{0.9}[\text{NB}]^{-0.4}$. The kinetic results were explained on the basis of the reversible addition of polymer radical to NB and the termination between the polymer radical and the nitroxide radical. The overall activation energy of the polymerization was 27.8 kcal/mol.

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1. Introduction

In recent years, hyperbranched polymers as dendritic polymer have aroused a great deal of research interest because of their unique structures and unusual properties such as globular and cavity-containing shapes, a large number of terminal groups, high solubility, low solution viscosity, and no crystallization compared with linear polymers [1–6].

Some radical-mediated polymerizations have been included among a large variety of approaches developed for the syntheses of hyperbranched polymers. A typical radical polymerization aimed at the hyperbranched polymer

synthesis is the self-condensing radical polymerization of vinyl monomers carrying additionally an initiating group (inimer) [1–3,5,6]. Soluble hyperbranched polymers can be also given by the radical copolymerization of vinyl monomer with other multivinyl monomers, when the polymerization is kept below the gel point by limiting the polymer conversion or by controlling the concentration of multivinyl monomer [1].

In our previous papers [7–11], we proposed the initiator-fragment incorporation radical polymerization (IFIRP) for a convenient one-pot synthesis of soluble hyperbranched polymers. IFIRP is a radical polymerization of multivinyl monomer using high initiator concentrations where a large number of initiator-fragments are incorporated as terminal groups in the resulting hyperbranched polymer through initiation and primary radical termination. Although radical polymerization of multivinyl monomer usually proceeds with gelation to yield insoluble crosslinked polymer, the use of much higher initiator concentrations causes the resulting

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polymer to be soluble owing to great decrease in the polymer molecular weight by much increased termination rate. The decrease in the molecular weight and hence the increase in the solubility of the resulting polymer are expected to be enhanced by the presence of a retarder so that the multivinyl monomer can be used at higher concentrations and the initiator can be done at lower concentrations.

When divinylbenzene (DVB) was polymerized using dimethyl 2,2'-azobisisobutyrate (MAIB) as initiator at high concentrations in benzene, an IFIRP was found to proceed without gelation to give soluble hyperbranched polymer [12]. On the other hand, nitrobenzene (NB) is well known to act as a retarder in the radical polymerization of styrene (St) [13]. So, here we have investigated the effect of NB on the IFIRP of DVB with MAIB in benzene.

The present paper describes the results on the IFIRP behavior of DVB in the presence of NB and characterization of the resulting polymers.

2. Experimental

2.1. Materials

DVB (supplied by Nippon Steel Chemical Co., Ltd) was a mixture of *m*- and *p*-isomers (2:1) and used after distillation. MAIB (supplied by Otsuka Chemical Co., Ltd) was recrystallized from methanol. Benzene was treated by sulfuric acid and distilled. Other solvents were used after distillations.

2.2. Polymerization

The polymerization of DVB with MAIB in benzene in the presence of NB was carried out in a degassed and sealed glass tube at a given temperature. The resulting polymer was isolated by pouring the polymerization mixture into a large excess of *n*-hexane. The consumption of the vinyl groups of DVB was in situ measured as a function of time by Fourier transform-near infrared (FT-NIR) spectroscopy, where the polymerization was performed in a degassed and sealed Pyrex tube (5-mm diameter) in a custom-made aluminum furnace with an FT-FIR measurement system [14].

2.3. Measurements

The conversion of DVB was measured with a Jasco INT-400 spectrometer equipped with a mercury–cadmium telluride detector. The consumption of the vinyl groups was monitored by the absorbance at around 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) at 55°C . Gel permeation chromatography (GPC) was performed at 40°C using a Tosoh

HLC-8220 GPC chromatograph (columns; TSK-Gel super HZM $\times 2$, [polymer] = 1 mg/l, 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 by employing polySt standards for calibration. The GPC–multiangle laser light scattering (MALLS) measurements were performed by Shoko Company Ltd, using a Shodex HPLC chromatograph (columns; Shodex KF-806L, [polymer] = 1.7 mg/ml, flow rate = 1.0 ml/min, eluent; THF) equipped with a Wyatt Technology DAWN EOS with laser operating at 690 nm and a Shodex RI-101, where dn/dc (0.161 ml/g) was separately determined by a differential refractometer (Optilab DSP; Wyatt Technology Corp.) The optical transmittance of a polymer solution was monitored at 500 nm as a function of temperature with a Jasco V-550 spectrometer, where a temperature change rate of $0.5^\circ\text{C}/\text{min}$ was used. The viscosity of the polymer solution in benzene 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 $10^\circ\text{C}/\text{min}$. Differential scanning calorimetric (DSC) curve was obtained with a Shimadzu DSC 50 (under N_2 , heating rate = $10^\circ\text{C}/\text{min}$). 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. Transmission electron microscopic (TEM) observation was performed by Sanyo Chemical Industries, Ltd with a Hitachi-7100 electron microscope at an accelerating voltage 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 under vacuum and stained with ruthenium dioxide.

3. Results and discussion

3.1. Polymerization of DVB with MAIB in the presence of NB

The polymerization of DVB as an excellent crosslinker with MAIB was conducted in benzene at 70 and 80°C in the presence of NB. The results obtained are shown in Table 1. The polymer yield was estimated based on the total weight of DVB and MAIB considering N_2 -elimination on the MAIB decomposition. This is because the initiator-fragments from MAIB were incorporated as a main component into the resulting polymer as described below.

At first, the DVB concentration was changed at fixed

Table 1
Polymerization of DVB with MAIB in benzene in the presence of NB

Run	Temperature (°C)	[DVB] (mol/l)	[MAIB] (mol/l)	[NB] (mol/l)	Time (h)	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n
1	80	0.35	0.50	0.50	4.0	39	2.5	2.6
2	80	0.40	0.50	0.50	4.0	49	3.6	4.0
3	80	0.45	0.50	0.50	4.0	58	3.9	7.9
4 ^a	80	0.50	0.50	0.50	4.0	66	n.d.	n.d.
5	80	0.45	0.001	0.50	4.0	3	n.d.	n.d.
6	80	0.45	0.010	0.50	4.0	18	n.d.	n.d.
7	80	0.45	0.10	0.50	4.0	41	2.3	2.8
8	80	0.45	0.20	0.50	4.0	64	3.6	9.6
9	80	0.45	0.30	0.50	4.0	69	3.6	10.5
10	80	0.45	0.40	0.50	4.0	67	3.9	11.1
11 ^a	80	0.45	0.50	0.20	4.0	61	n.d.	n.d.
12 ^a	80	0.45	0.50	0.30	4.0	84	n.d.	n.d.
13 ^a	80	0.45	0.50	0.40	4.0	78	n.d.	n.d.
14	80	0.45	0.50	0.50	1.0	11	1.3	1.6
15	80	0.45	0.50	0.50	1.5	28	2.0	2.2
16	80	0.45	0.50	0.50	2.0	42	2.1	5.0
17	80	0.45	0.50	0.50	2.5	53	3.1	7.5
18	80	0.45	0.50	0.50	3.0	55	3.2	7.2
19	80	0.45	0.50	0.50	5.0	59	3.5	7.8
20	80	0.45	0.50	0.50	8.0	65	3.9	11.2
21	70	0.45	0.50	0.50	1.0	2	n.d.	n.d.
22	70	0.45	0.50	0.50	2.0	11	1.5	1.7
23	70	0.45	0.50	0.50	3.0	28	1.6	2.6
24	70	0.45	0.50	0.50	4.0	38	2.3	4.0
25	70	0.45	0.50	0.50	5.0	52	3.3	9.2
26	70	0.45	0.50	0.50	6.0	55	3.8	10.8
27	70	0.45	0.50	0.50	9.0	62	3.8	10.0
28	70	0.45	0.50	0.50	12.0	64	4.2	10.5

n.d., not determined.

^a System displayed gelation.

concentrations of MAIB (0.50 mol/l) and NB (0.50 mol/l) in the polymerization at 80 °C (runs 1–4). Gelation took place in the polymerization at a DVB concentration as high as 0.50 mol/l, while the polymerization at not more than 0.45 mol/l of the DVB concentration proceeded homogeneously without any gelation to give soluble polymer. Thus, the presence of NB of 0.50 mol/l as retarder increased the upper limit of the DVB concentration under no gelation conditions to 0.45 mol/l compared to 0.25 mol/l in the absence of NB as reported elsewhere [12]. The polymer yield increased with increasing DVB concentration. The molecular weight and molecular weight distribution (M_w/M_n) of the resulting polymer increased with polymer yield. These tendencies are similar to those in the polymerization in the absence of NB [12].

Next, the MAIB concentration was varied keeping the concentrations of DVB and NB constant at 0.45 and 0.50 mol/l, respectively (runs 3, 6–10). The polymerizations at all the MAIB concentrations (0.001–0.50 mol/l) here used proceeded with no gelation, although the polymer yields were very low at lower MAIB concentrations (runs 5, 6). On the other hand, in the absence of NB, gelation was reported to take place at the MAIB concentrations lower than 0.20 mol/l [12]. The polymer yield increased with the initiator concentration in the presence of NB, while it decreased

with the MAIB concentration in the absence of NB. The M_n and M_w/M_n values of the polymer again showed a tendency to increase with the polymer yield.

At last, the concentration of NB as retarder was changed with constant concentrations of DVB (0.45 mol/l) and MAIB (0.50 mol/l) (runs 3, 11–13). The polymerization at the NB concentration of 0.50 mol/l proceeded homogeneously, while the use of the lower retarder concentrations caused gelation.

Thus, the use of the high crosslinker concentration and low retarder concentration reasonably resulted in observation of gelation. The polymer yield in the presence of NB was considerably higher than that previously observed in the absence of NB [12].

The homogeneous polymerization of DVB with MAIB in the presence of NB was in more detail examined at 70 and 80 °C in benzene, where the concentrations of DVB, MAIB, and NB were 0.45, 0.50, and 0.50 mol/l, respectively. As shown in Fig. 1, the polymer yield initially rapidly increased with time and slowly over 2.5 h up to 65% at 80 °C and over 8 h up to 64% at 70 °C. The leveling yield is considerably higher and the time for leveling yield is doubly or longer in the presence of NB than in the absence [12]. This is because of retarding effect of NB. The molecular weight ($M_n = 1.5$ – 4.2×10^4 at 70 °C and 1.3 – 3.9×10^4 at 80 °C) and the

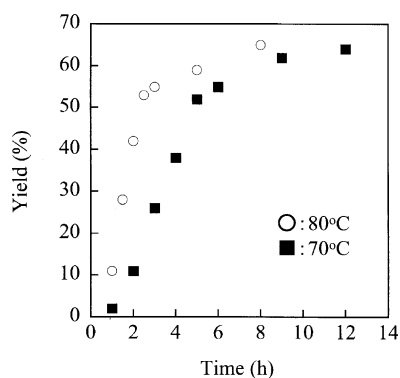


Fig. 1. Time–yield curves in the polymerization of DVB with MAIB at 70 and 80 °C in benzene in the presence of NB: [DVB]=0.45 mol/l, [MAIB]=0.50 mol/l, [NB]=0.50 mol/l.

polydispersity ($M_w/M_n=1.7\text{--}10.8$ at 70 °C and 1.6–11.2 at 80 °C) increased with time, namely the polymer yield (runs 3, 11–20, 21–28 in Table 1).

3.2. Kinetic study of the homogeneous polymerization of DVB with MAIB in the presence of NB

The homogeneous polymerization of DVB with MAIB was kinetically studied in dioxane in the presence of NB

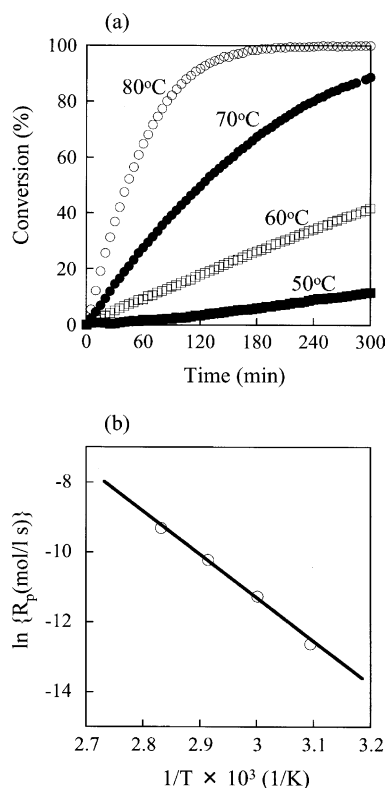


Fig. 2. (a) Time–conversion curves for the polymerization of DVB with MAIB at different temperatures in dioxane in the presence of NB and (b) Arrhenius plot of the initial polymerization rate (R_p): [DVB]=0.45 mol/l, [MAIB]=0.50 mol/l, [NB]=0.50 mol/l.

under no gelation conditions. The conversion of the vinyl groups of DVB was in situ monitored by FT-NIR.

Fig. 2(a) shows the time–conversion curves for the vinyl groups of DVB observed in the polymerization at different temperatures, where the concentrations of DVB, MAIB, and NB were 0.45, 0.50, and 0.50 mol/l, respectively. As can be seen from the figure, the vinyl groups of DVB were almost completely consumed in 2.5 h at 80 °C, well corresponding to the above observation that the polymer yield leveled over 2.5 h at 80 °C. Thus, the leveling phenomenon resulted from the consumption of the vinyl groups of DVB, suggesting that the relatively low polymer yields above observed come from the inefficient use of the initiator and/or the low molecular products which were soluble in *n*-hexane containing a small amount of benzene (the polymerization solvent).

The initial polymerization rate (R_p) was estimated from the time–conversion curve for the vinyl groups of DVB. The two vinyl groups of the DVB monomer are expected to have a different reactivity. The reactivity of the firstly reacting vinyl group is higher than that of the remaining one. So, R_p here estimated is based mainly on the consumption of the firstly reacting vinyl group of DVB.

Fig. 2(b) presents the Arrhenius plot of R_p estimated from the time–conversion curves in Fig. 2(a). From the slope of the plot, the overall activation energy of the polymerization was calculated to be 27.8 kcal/mol. This value is considerably higher than those (20 kcal/mol) of the azobisisobutyronitrile (AIBN)-initiated polymerizations of St and methyl methacrylate (MMA) [15]. Similar activation energies are reported for the decompositions of AIBN and MAIB [16].

The effect of the MAIB concentration on R_p was examined at 70 °C keeping the concentrations of DVB and NB constant at 0.45 and 0.50 mol/l, respectively, where the MAIB concentration was changed from 0.025 to 0.50 mol/l. The obtained result is shown in Fig. 3(a). Thus, R_p is proportional to the 0.5th order of the initiator concentration. Fig. 3(b) presents the relationship between the DVB concentration and R_p at 70 °C observed when the DVB concentration was varied from 0.10 to 0.45 mol/l at fixed concentrations of MAIB of 0.50 mol/l and of NB of 0.50 mol/l. R_p increases in proportion to the 0.9th power of the monomer concentration. Fig. 3(c) shows the dependence of R_p on the NB concentration at 70 °C observed when the NB concentration was changed from 0.20 to 1.0 mol/l fixing the concentrations of DVB and MAIB at 0.45 and 0.50 mol/l. R_p varies in proportion to the -0.4 th order of the retarder concentration.

From the above results, R_p at 70 °C is apparently expressed by the following equation;

$$R_p = k[\text{MAIB}]^{0.5}[\text{DVB}]^{0.9}[\text{NB}]^{-0.4} \quad (1)$$

Except for the contribution of NB, the apparent rate equation is closely similar to that for the ideal radical polymerization involving bimolecular termination, although

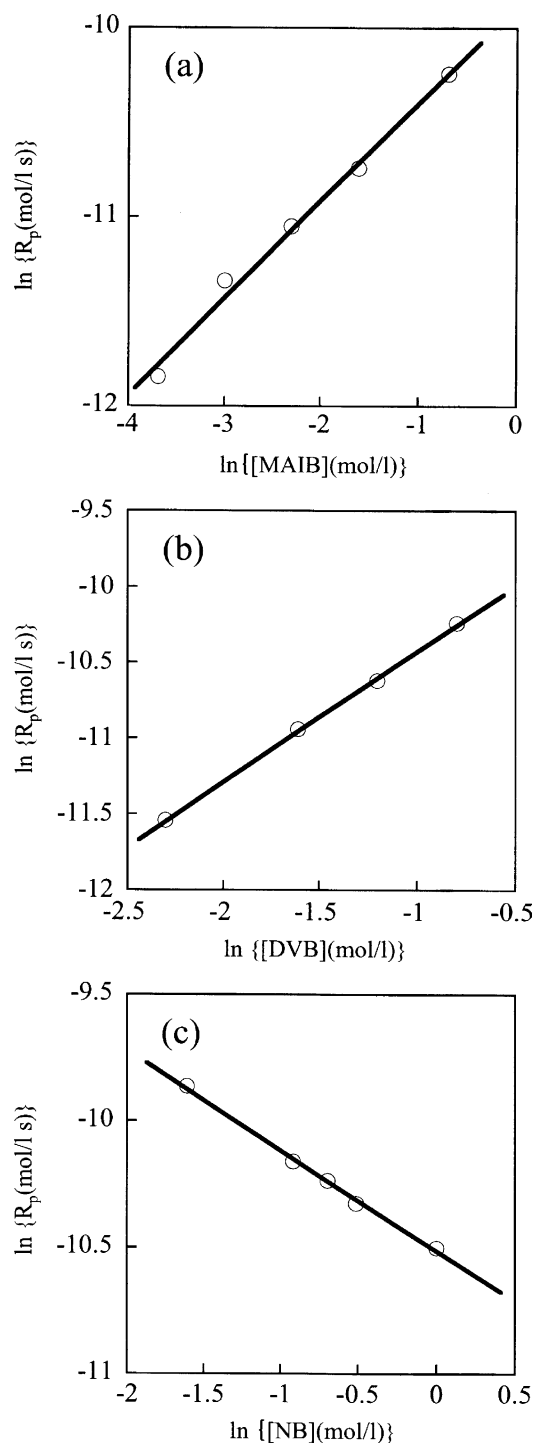
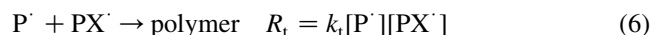
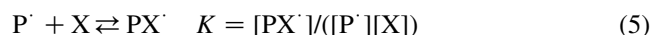


Fig. 3. Dependence of the initial polymerization rate (R_p) on (a) the MAIB concentration, (b) the DVB concentration, and (c) the NB concentration in the polymerization of DVB with MAIB at 70 °C in dioxane in the presence of NB: $[\text{DVB}] = 0.45 \text{ mol/l}$ and $[\text{NB}] = 0.50 \text{ mol/l}$ for (a), $[\text{MAIB}] = [\text{NB}] = 0.50 \text{ mol/l}$ for (b), $[\text{DVB}] = 0.45 \text{ mol/l}$ and $[\text{MAIB}] = 0.50 \text{ mol/l}$ for (c).

the present polymerization is expected to involve many elementary reactions because of the presence of retarder and the use of high initiator concentrations, leading to the complicated kinetics.

The rate equation can be simply explained by considering the following elementary reactions:



where I represents MAIB, R^\cdot is the primary radical from MAIB, M is DVB, X is NB, P^\cdot is the propagating poly(DVB) radical, and PX^\cdot is the NB-ended polymer radical. R_d , R_i , R_p , R_t , k_d , k_i , k_p , and k_t are the rates and rate constants of the elementary reactions. K is the equilibrium constant of reaction (5). $R_i = 2k_d f[\text{I}]$, where f is the initiator efficiency. NB is reported to retard the polymerization of St but have little effect on the polymerizations of MMA and methyl acrylate as electron-accepting monomers [13]. The primary radical from MAIB is closely similar in structure to the MMA propagating radical and hence is considered to attack exclusively DVB without having to do with NB (Eq. (3)) in the early stage of the polymerization.

Assuming stationary concentrations of P^\cdot and PX^\cdot , we obtain Eq. (7).

$$2k_d f[\text{I}] = k_t[\text{P}^\cdot][\text{PX}^\cdot] \quad (7)$$

Substituting $[\text{PX}^\cdot] = K[\text{P}^\cdot][\text{X}]$ [from Eq. (5)] in Eq. (6) yields Eq. (8) and then Eq. (9).

$$2k_d f[\text{I}] = k_t K [\text{P}^\cdot]^2 [\text{X}] \quad (8)$$

$$[\text{P}^\cdot] = \left\{ \frac{2k_d f[\text{I}]}{k_t K [\text{X}]} \right\}^{0.5} \quad (9)$$

So, we obtain Eq. (10) as the rate equation, which is closely similar to Eq. (1) obtained from the above kinetic study.

$$R_p = k_p[\text{P}^\cdot][\text{M}] = \left\{ \frac{2k_d f}{k_t K} \right\}^{0.5} k_p [\text{I}]^{0.5} [\text{M}] [\text{X}]^{-0.5} \quad (10)$$

3.3. ESR study on the polymerization of DVB with MAIB in benzene in the presence of NB

The polymerization of DVB with MAIB in the presence of NB was investigated in benzene at 70 °C by ESR, where the concentrations of DVB, MAIB, and NB were 0.45, 0.50, and 0.50 mol/l, respectively. Fig. 4(a) presents the ESR spectrum observed during the polymerization (15 min). A closely similar spectrum was reported to be observed in the photoreaction of NB in THF and was assigned to radical I formed by trapping of THF radical by NB (Eq. (11)), where the following coupling constants were reported; $A_N = 15.00 \text{ G}$, $A_{o,p-H} = 3.10 \text{ G}$, and $A_{m-H} = 1.08 \text{ G}$ [17]. The ESR spectrum observed above is assignable to radical II

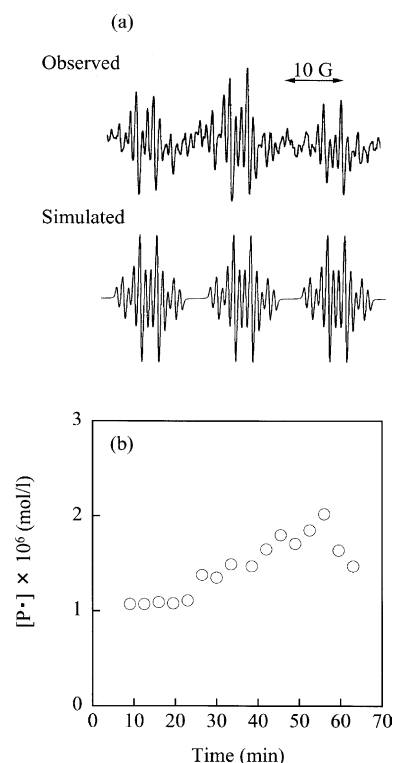
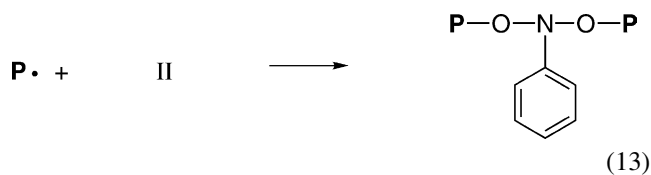
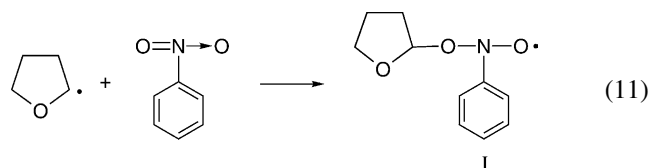


Fig. 4. (a) ESR spectrum observed in the polymerization of DVB with MAIB at 70 °C in benzene for 15 min in the presence of NB and the simulated spectrum and (b) time-profile of the total radical concentration ($[TR\cdot]$): [DVB]=0.45 mol/l, [MAIB]=0.50 mol/l, [NB]=0.50 mol/l.

formed by the reaction of NB with the polymer radical ($P\cdot$) (Eq. (12)). As mentioned above, the primary radical from MAIB firstly attacks DVB followed by propagation. The resulting propagating polymer radical adds to NB. A simulated spectrum obtained using $A_N=17.00$ G, $A_{o,p-H}=3.10$ G, and $A_{m-H}=1.08$ G is also shown in Fig. 4(a) and is in considerably good agreement with the observed one although the intensity of central part of the observed spectrum is somewhat larger than those of both sides. Eq. (12) is suggested to be reversible under the polymerization conditions from the above kinetic results. Radical II can capture another polymer radical (Eq. (13)), corresponding to Eq. (6), [13]. Fig. 4(b) shows the time-profile of the total radical concentration ($[TR\cdot]$) estimated from the spectrum. Thus $[TR\cdot]$ was almost independent of time in the early stage of the polymerization, indicating the stationary states of the radicals involved in the polymerization system. This finding supports the validity of the above assumption in the kinetic study.



3.4. Characterization of the resulting polymers

The solubility of the polymer was examined which was formed in the polymerization of DVB (0.45 mol/l) with MAIB (0.50 mol/l) at 80 °C in benzene for 4 h in the presence of NB (0.50 mol/l) (run 3 in Table 1). The polymer was soluble in benzene, toluene, ethyl acetate, THF, acetone, chloroform, and *N,N*-dimethylformamide, but insoluble in *n*-hexane acetonitrile, dimethyl sulfoxide, methanol, ethanol, and water. Thus, the polymer formed in the presence of NB showed closely similar solubility behavior to that formed in the absence of NB [12].

The polymer formed in the presence of NB was observed to show an upper critical solution temperature (UCST) in an acetone–water [14:1 (v/v)] mixture. Fig. 5 shows the temperature effect on the transmittance of a polymer solution [1% (wt/v)] on cooling and heating, where the polymer formed at 80 °C for 5 h (run 19) was used. Only a little thermal hysteresis was observed, resulting probably from the lack of intermolecular entanglements for the hyperbranched polymer.

When UCST was defined as temperature at which the transmittance became 50%, the UCST was estimated to be 39 °C on cooling and 40 °C on heating.

Fig. 6 presents the ^1H NMR spectra of the polymers formed in the polymerization at 80 °C in benzene for 1 and

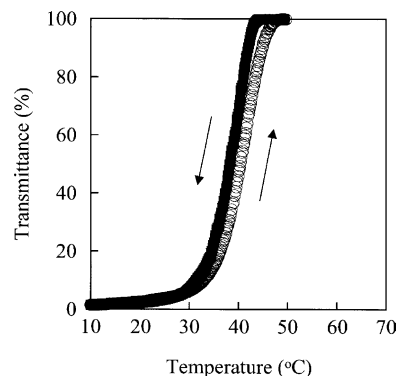


Fig. 5. Temperature effect on the transmittance of a polymer [1% (wt/v)] solution in an acetone–water [14:1 (v/v)] mixture on cooling (■) and heating (○). The polymer was obtained in the polymerization of DVB (0.45 mol/l) with MAIB (0.50 mol/l) at 80 °C in benzene for 5 h in the presence of NB (0.50 mol/l).

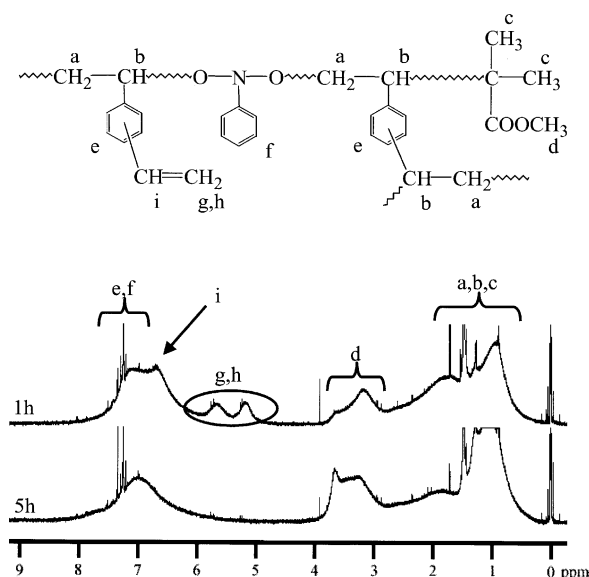


Fig. 6. ^1H NMR spectra of the polymers formed in the polymerization of DVB with MAIB at 80°C in benzene for 1 and 5 h in the presence of NB: $[\text{DVB}] = 0.45 \text{ mol/l}$, $[\text{MAIB}] = 0.50 \text{ mol/l}$, $[\text{NB}] = 0.50 \text{ mol/l}$.

5 h, where the concentrations of DVB, MAIB, and NB were 0.45, 0.50, and 0.50 mol/l (runs 14, 19 in Table 1). Peak assignments are denoted in the figure. Thus, the polymers consisted of the DVB units with and without an unreacted double bond and methoxycarbonylpropyl groups as initiator-fragment. The absorption due to the double bond reasonably decreased in intensity with time. The polymers were found to contain nitrogen by elemental analysis, indicating that the NB units were also incorporated into them.

The composition of the resulting polymers was determined from the carbon and nitrogen contents. The fraction ratio of the DVB units with and without the unreacted double bond was estimated using the peak areas of vinyl and phenyl protons. Fig. 7 shows the composition of the polymers formed in the polymerizations at 70°C (runs 21–28 in Table 1) and 80°C (runs 3, 14–20) at different times, where the concentrations of DVB, MAIB, and NB were 0.45, 0.50, and 0.50 mol/l, respectively. With respect to the polymers formed 80°C , the fraction of (38–0 mol%) the DVB unit with a double bond expectedly decreased with time and completely vanished in 8 h. That (25–42 mol%) of the DVB unit without the double bond, instead, increased with time. The content of the methoxycarbonylpropyl group as MAIB-fragment increased with time from 31 mol% at 1 h to 51 mol% at 8 h. On the other hand, the fraction (6–8 mol%) of NB was almost independent of time. Similar results were also observed for the polymers formed at 70°C . The polymer formed in the polymerization at 80°C for 8 h (run 20 in Table 1) consisted of the DVB without double bond (42 mol%), methoxycarbonylpropyl group as MAIB-fragment (51 mol%), and NB unit (7 mol%). The yield with respect to the DVB monomer in this polymerization was estimated to be 84% from the polymer yield (run 20 in

Table 1) and the mole fraction of DVB unit incorporated. The yield of 84% was rather lower from judging from the fact that the DVB double bond was completely consumed as shown in Fig. 2. This comes from polymer-missing during working up and/or formation of *n*-hexane-soluble part.

As described above, a large number of the methoxycarbonylpropyl groups as initiator-fragment were observed to be incorporated as terminal groups in the resulting polymers, indicating that an IFIRP also proceeds in the present polymerization in the presence of NB as retarder. The existence of many terminal groups in a polymer molecule means that the polymer has a hyperbranched structure. If NB is incorporated in the polymer in the manner described in Eqs. (5) and (6), the DVB double bonds are completely consumed, and all terminal groups are methoxycarbonylpropyl group, the molar ratio of the DVB unit to the methoxycarbonylpropyl group should be 1/2. However, this was not the case (ratio = $42/51 > 1/2$) for the polymer formed at 80°C for 8 h (run 20 in Table 1), suggesting that cyclic structures by intramolecular crosslinking can be also contained.

The molecular weight of a resulting polymer was also measured by GPC–MALLS. The polymer used was formed in the polymerization at 80°C for 1.5 h (run 15 in Table 1), where the concentrations of DVB, MAIB, and NB were 0.45, 0.50, and 0.50 mol/l. The M_w value was estimated to be 3.1×10^5 . The M_w value by GPC–MALLS was much higher than that (0.44×10^5) by GPC. Similar results were reported for many dendritic polymers, resulting from the small hydrodynamic radii due to their compact hyperbranched structures [7–12,18–23].

A benzene solution of the same polymer was examined viscometrically at 30°C . Fig. 8 shows the plot of the reduced viscosity (η_{red}) against the polymer concentration (C). Thus, the η_{red} values were very low and almost independent of C despite of considerably high M_w (3.1×10^5). As a result, a very low intrinsic viscosity ($[\eta] = 0.09 \text{ dl/g}$) was given for the polymer. These viscometric behaviors also support that the polymer is of compact hyperbranched structure, since the hyperbranched polymers are well known to show low solution viscosity because of lack of intermolecular entanglements [1–12,21,24–26].

Fig. 9 presents a TEM image of the same polymer subjected to the MALLS measurements. The individual polymer molecules were observed as nanoparticles of 5–10 nm diameter.

Thermal degradation behavior of the polymer formed in the polymerization at 80°C for 5 h (run 19 in Table 1) was investigated by TG. The thermal degradation began at 200°C and showed maximal rates at 220, 375, and 446°C . The DSC curve of the same polymer showed an endothermic peak at 55°C , corresponding to the glass transition temperature. On the other hand, the polymer formed in the absence of NB showed no glass transition in the temperature range from 25 to 200°C as previously reported [12].

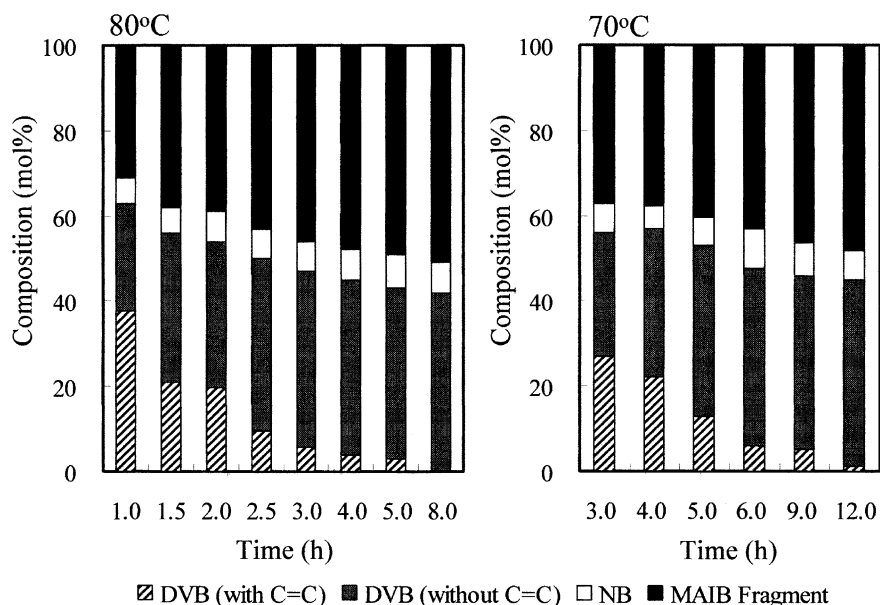


Fig. 7. Composition of the polymers formed in the polymerization of DVB with MAIB at 70 and 80 °C in benzene at different times in the presence of NB: [DVB] = 0.45 mol/l, [MAIB] = 0.50 mol/l, [NB] = 0.50 mol/l.

4. Conclusions

The effect of NB as a retarder on the IFIRP of DVB with MAIB was examined at 70 and 80 °C in benzene. When [DVB], [MAIB], and [NB] were 0.45, 0.50, and 0.50 mol/l, respectively, the polymerization proceeds with no gelation to yield soluble polymers. The yield (up to 65%) and M_n value ($1.5\text{--}4.2 \times 10^4$ at 70 °C and $1.3\text{--}3.9 \times 10^4$ at 80 °C by GPC) of the polymer increase with time. The resulting polymers contain a high fraction of methoxycarbonylpropyl group as initiator-fragment (31–51 mol%) and also 6–9 mol% of NB unit. The existence of many terminal groups in a polymer molecule means that the polymer is of a hyperbranched structure. DVB monomers are incorporated

as the units with (0–38 mol%) and without an unreacted double bond (25–44 mol%). The results of MALLS and viscometric measurements and TEM observation support that the resulting polymers have a hyperbranched compact structure. The homogenous polymerization system at 70 °C involves an ESR-observable nitroxide radical (II) formed by the addition of the polymer radical to the nitro group of NB. R_p at 70 °C in dioxane is given by $R_p = k[\text{MAIB}]^{0.5}[\text{DVB}]^{0.9}[\text{NB}]^{-0.4}$. The kinetic result can be explained in terms of the reversible addition of the polymer radical to NB and the termination between the polymer radical and the nitroxide

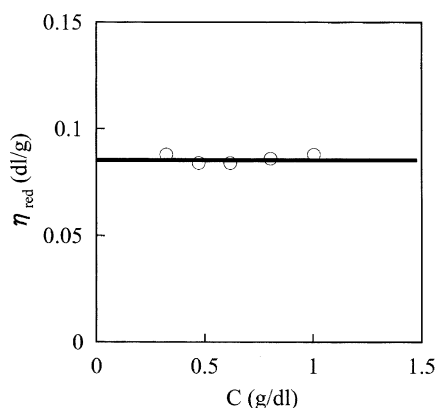


Fig. 8. Relationship between reduced viscosity (η_{red}) and the polymer concentration (C) at 30 °C in benzene for the polymer formed in the polymerization of DVB with MAIB at 80 °C in benzene for 1.5 h in the presence of NB: [DVB] = 0.45 mol/l, [MAIB] = 0.50 mol/l, [NB] = 0.50 mol/l.

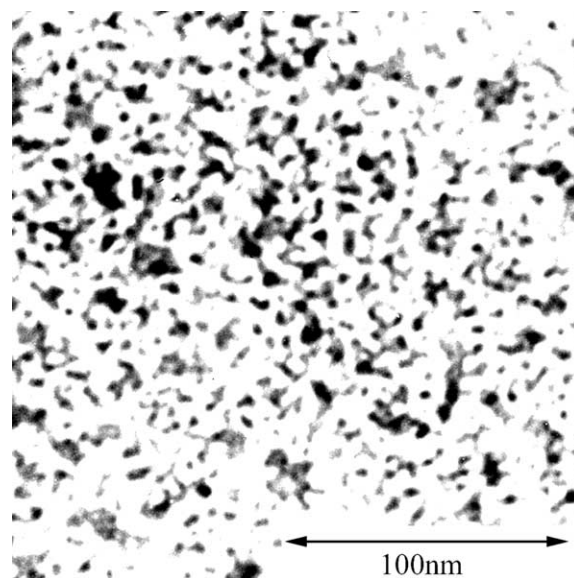


Fig. 9. TEM image of the polymer formed in the polymerization of DVB with MAIB at 80 °C in benzene for 1.5 h in the presence of NB: [DVB] = 0.45 mol/l, [MAIB] = 0.50 mol/l, [NB] = 0.50 mol/l.

radical (II). The overall activation energy of the polymerization is 27.8 kcal mol.

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