

Initiator-Fragment Incorporation Radical Polymerization of Diallyl Phthalate: Kinetics, Formation of Hyperbranched Polymer, and Iridescent Porous Film Thereof

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ABSTRACT: Diallyl phthalate (DAP) was polymerized in toluene using dimethyl 2,2'-azobisisobutyrate (MAIB) of high concentrations (0.1–0.9 mol/L) as initiator. The polymerization of DAP of 1.50 mol/L with MAIB of 0.50 mol/L proceeded homogeneously at 80°C without gelation to give soluble polymers in a high yield of 93%. Kinetic results of the homogeneous polymerization at 80°C suggest significant contributions of the degradative chain transfer and the primary radical termination as shown by the rate equation, $R_p = k [\text{MAIB}]^{0.8} [\text{DAP}]^{1.0}$ (R_p = polymerization rate). The polymer formed in the polymerization of DAP (1.30 mol/L) with MAIB (0.50 mol/L) at 80°C for 8 h consisted of the DAP units with (17 mol %) and without (47 mol %) double bond

and the methoxycarbonylpropyl group (36 mol %) as MAIB-fragment. The large fraction of the incorporated initiator-fragment as terminal group indicates that the polymer has a hyperbranched structure. The film cast from a solution of the hyperbranched poly(DAP) in tetrahydrofuran showed an iridescent color. The confocal scanning laser microscope image of the film revealed that the iridescent film contained the pores of about 1 μm arranged in an ordered array. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 408–415, 2006

Key words: radical polymerization; kinetics; hyperbranched; divinyl monomer; crosslink; viscosity

INTRODUCTION

Diallyl and multiallyl monomers such as diallyl phthalate (DAP) and diallyl diglycol carbonate (DADGC) have found various industrial applications in the production of a range of thermoset products, moldings and coatings for connectors and insulators, plastic lenses, safety shields, and so on.¹

On the other hand, we have developed the initiator-fragment incorporation radical polymerization (IFIRP) as a novel versatile approach for one-pot synthesis of soluble hyperbranched polymers, where high initiator concentrations are used in the radical homopolymerization or copolymerization of a divinyl monomer.^{2–7} In general, the radical polymerization system containing a di(multi)vinyl monomer gives an insoluble crosslinked polymer, of which the molecular weight is treated to be extremely high or infinite. However, the use of much higher initiator concentration in the polymerization of di(multi)vinyl monomer results in so great a decrease in the molecular weight that the resulting polymer ultimately becomes soluble. The soluble polymer is no longer linear, but is hyper-

branched. A large number of initiator-fragments are incorporated as terminal groups in the polymer via initiation and primary radical termination.

Here we have attempted to extend the IFIRP to DAP as an diallyl monomer, where the polymerization behavior of DAP with dimethyl 2,2'-azobisisobutyrate (MAIB) was kinetically investigated. The resulting soluble poly(DAP)s were characterized. Interestingly, the cast film from the polymer solution in tetrahydrofuran (THF) was further found to become an iridescent porous film.

The present article describes the kinetic results of the IFIRP of DAP, characterization of the resulting polymer, and formation of iridescent porous film thereof.

EXPERIMENTAL

Materials

Commercially available diallyl phthalate (DAP) was used after distillation. Dimethyl 2,2'-azobisisobutyrate (MAIB) was recrystallized from methanol. Toluene was treated with sulfuric acid and distilled. Other solvents were used after distillation.

Polymerization

Polymerizations were carried out in a degassed and sealed glass tube at a given temperature. The resulting

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TABLE I
Polymerization of DAP with MAIB at 70 and 80°C in Toluene

Run	[DAP] (mol/L)	[MAIB] (mol/L)	Temp (°C)	Time (h)	Yield (%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	Remarks
1	0.50	0.50	80	4.0	43	1.6	2.3	1.4	
2	1.00	0.50	80	4.0	72	2.5	6.6	2.6	
3	1.30	0.50	80	4.0	83	3.0	17.5	5.8	
4	1.50	0.50	80	4.0	93	4.8	55.4	11.5	
5	2.00	0.50	80	4.0	93				gelation
6	3.00	0.50	80	4.0	98				gelation
7	1.30	0.10	80	4.0	51	3.0	9.0	3.0	
8	1.30	0.30	80	4.0	74	3.1	15.2	4.9	
9	1.30	0.60	80	4.0	83	3.3	19.1	5.8	
10	1.30	0.70	80	4.0	84	4.1	24.2	5.9	
11	1.30	0.90	80	4.0	81	4.8	31.2	6.5	
12	1.30	0.50	80	0.5	24	2.1	3.6	1.7	
13	1.30	0.50	80	1.0	45	2.5	5.3	2.1	
14	1.30	0.50	80	2.0	68	2.9	9.0	3.1	
15	1.30	0.50	80	6.0	87	5.1	36.2	7.1	
16	1.30	0.50	80	8.0	85	5.4	56.2	10.4	
17	1.30	0.50	70	1.0	16	2.0	3.4	1.7	
18	1.30	0.50	70	2.0	32	2.0	4.2	2.1	
19	1.30	0.50	70	4.0	57	2.7	7.8	2.9	
20	1.30	0.50	70	6.0	64	3.5	13.7	3.9	
21	1.30	0.50	70	9.0	76	4.2	26.9	6.4	
22	1.30	0.50	70	12.0	75	4.7	45.1	9.6	

polymers were isolated by the polymerization mixtures into a large amount of *n*-hexane, dried under vacuum, and weighed. The conversion of the vinyl groups of DAP was determined *in situ* 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-NIR spectroscopic measurement system.⁸

Measurements

The conversion of the vinyl groups of DAP was monitored by the absorbance near 6150 cm^{-1} being assignable to the overtone absorption due to stretching vibration of C=C—H bonds in the vinyl groups, using a Jasco INT-400 spectrometer equipped with a mercury-cadmium-tellurium detector. ¹H spectra of the polymers were measured with a Jeol OX spectrometer (400 MHz). Gel permeation chromatography (GPC) was conducted at 40°C by using a Tosoh HLC 8220 GPC chromatograph (columns; TSK-Gel Super H-H x 2, [polymer] = 1 mg/mL, flow rate = 0.35 mL/min) with a RI detector 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 determined with polystyrene standards calibration. The multiangle laser light scattering (MALLS) measurements were carried out by Shoko, Japan, with a Wyatt technology DAWN EOS with a laser operating at 690 nm, where dn/dc (0.113 mL/g)

was separately determined in THF by a differential refractometer (Optilab DSP; Wyatt Technology, CA). The viscosity of a polymer solution in benzene was measured at 25°C, using a Ubbelohde viscometer. Dynamic thermogravimetry (TG) of the polymer was performed under a nitrogen atmosphere (flow rate = 20 mL/min) with a Shimadzu DTG 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) spectrum of the polymerization mixture in a degassed and sealed ESR tube was 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. Confocal scanning laser microscopic measurements were performed with a LEXT OLS3000 Olympus microscope with a laser operating at 408 nm.

RESULTS AND DISCUSSION

Polymerization of DAP with MAIB in toluene

The polymerization of DAP with MAIB of high concentrations (0.10–0.90 mol/L) was examined at 70 and 80°C in toluene. The obtained results are summarized in Table I. The polymer yield was calculated based on

the total weight of DAP and MAIB, considering N_2 -elimination on the MAIB decomposition, because the initiator-fragments from MAIB were incorporated as a main component into the resulting polymer as mentioned below.

Runs 1–6 presents the results observed when the DAP concentration was changed at a fixed initiator concentration of 0.50 mol/L in the polymerization at 80°C for 4 h. Gelation occurred when the DAP concentration was 2.0 and 3.0 mol/L. However, the polymerization proceeded homogeneously without gelation to yield soluble polymers when the DAP concentration was 1.50 mol/L and lower. The yield (up to 93%), molecular weight (M_n), and polydispersity (M_w/M_n) increased with increasing DAP concentration for the polymers formed under no gelation conditions. It is noteworthy that the yield of soluble polymer was as high as 93% despite the yield based on the total weight of DAP and MAIB.

The results listed as runs 3 and 7–11 were obtained when the MAIB concentration was varied, keeping the monomer concentration constant at 1.30 mol/L in the polymerization at 80°C for 4 h. No gelation was observed at all the MAIB concentrations used here. The polymer yield, molecular weight, and polydispersity tended to increase with the initiator concentration.

The homogeneous polymerization of DAP with MAIB was further investigated in detail at 70 and 80°C, where the concentrations of the monomer and initiator were 1.30 and 0.50 mol/L, respectively. As illustrated in Figure 1, the polymer yield rapidly increased with time in the early stage and became nearly flat about 85% over 5 h at 80°C and about 75% over 9 h at 70°C. The M_n and M_w/M_n values increased with time, namely with polymer yield, at both temperatures (runs 12–22 in Table I).

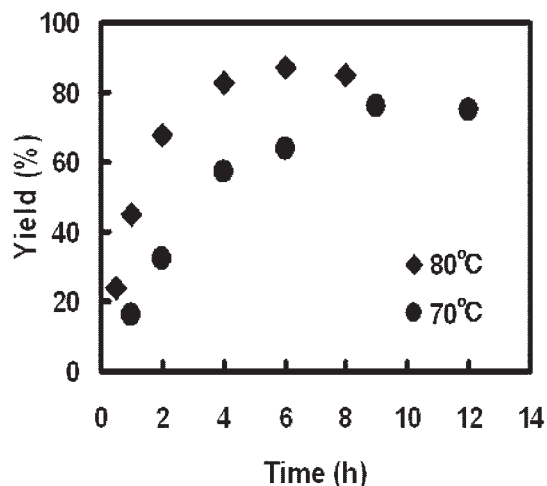


Figure 1 Time-yield curves in the polymerization of DAP with MAIB at 70 and 80°C in toluene: [DAP] = 1.30 mol/L and [MAIB] = 0.50 mol/L.

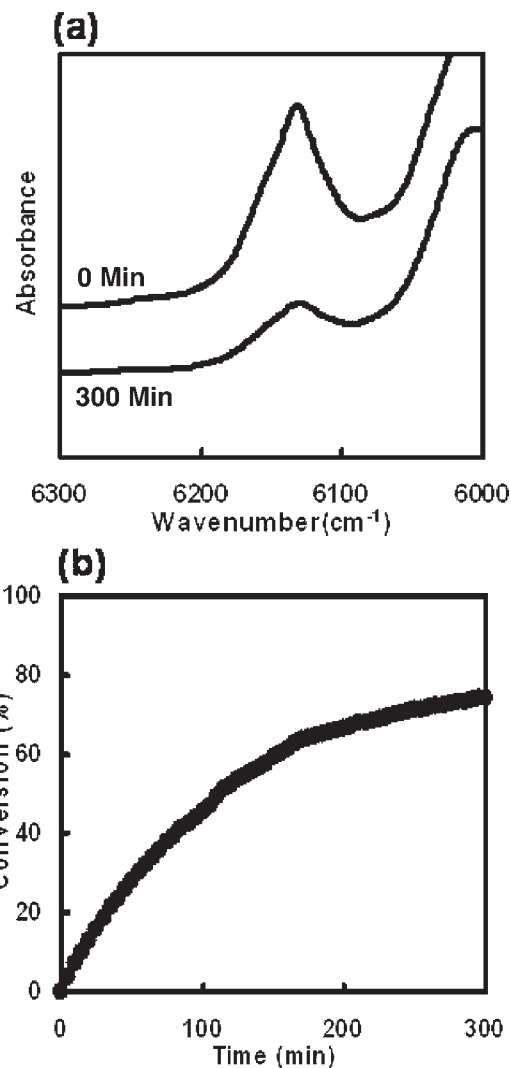


Figure 2 (a) FT-NIR spectra observed during the polymerization of DAP with MAIB at 80°C in dioxane. (b) Time-conversion curve of the vinyl groups of DAP: [DAP] = 1.30 mol/L and [MAIB] = 0.50 mol/L.

Figure 2(a) illustrates the FT-NIR spectral change during the polymerization at 80°C, where the concentrations of DAP and MAIB were the same as used in Figure 1. Figure 2(b) shows the time-profile of the double bond consumption of the DAP monomer during the polymerization. The conversion reasonably increased with time and reached about 75% in 5 h.

Kinetic study of the polymerization of DAP with MAIB

The homogeneous polymerization of DAP with MAIB was kinetically studied in dioxane. As described above, the conversion of the double bonds in the DAP monomer was estimated *in situ* by FT-NIR. Dioxane was used as solvent because it showed no absorption near 6150 cm^{-1} due to the $=C-H$ bonds. The poly-

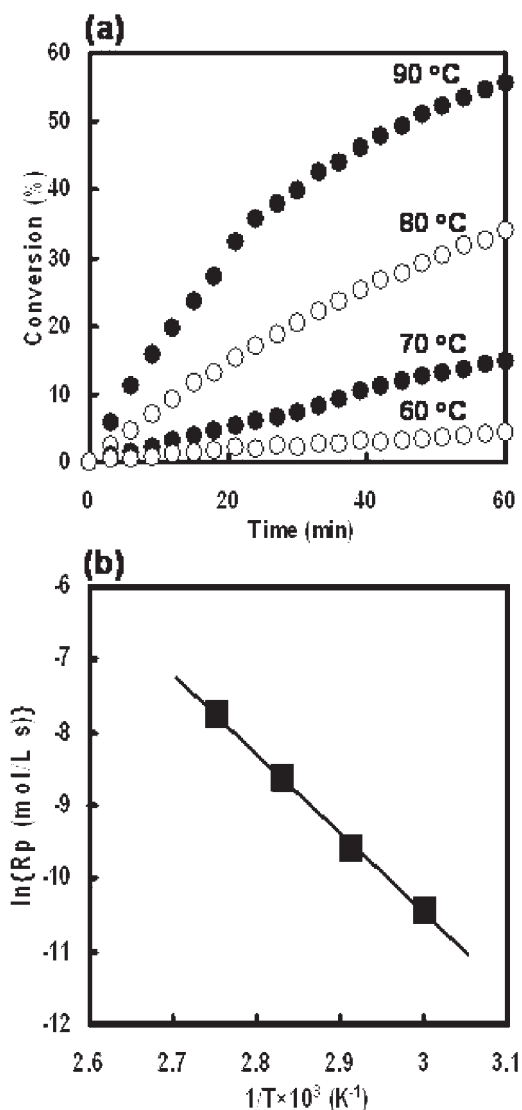


Figure 3 (a) Time-conversion curves of the DAP double bond in the polymerization of DAP with MAIB at different temperatures in dioxane. (b) Arrhenius plot of the initial polymerization rate (R_p); [DAP] = 1.30 mol/L and [MAIB] = 0.50 mol/L.

merization proceeded also without gelation in dioxane.

Figure 3(a) shows time-conversion curves for the double bonds observed in the polymerization at different temperatures, where the concentrations of DAP and MAIB were 1.30 and 0.50 mol/L, respectively. Figure 3(b) presents the Arrhenius plot of the initial polymerization rate (R_p) estimated from the time-conversion curves. From the plot, the overall activation energy of the polymerization was calculated to be 91 kJ/mol.

Figure 4(a) presents the effect of the MAIB concentration on R_p at 80°C, when the MAIB concentration was changed at a fixed DAP concentration of 1.30 mol/L. R_p was proportional to the 0.8th order of the

initiator concentration. Figure 4(b) exhibits the relationship between R_p and the DAP concentration at 80°C, when the DAP concentration was varied fixing the initiator concentration at 0.50 mol/L. R_p increased in proportion to the first order of the monomer concentration.

From the above kinetic results, R_p at 80°C is expressed by the following equation:

$$R_p = k[\text{MAIB}]^{0.8} [\text{DAP}]^{1.0} \quad (1)$$

The radical polymerizations of allylic monomers, such as allyl acetate, and allylamine, are well known to involve degradative chain transfer to the monomers, because the allylic radicals formed through abstraction of allylic hydrogen of the monomers by the

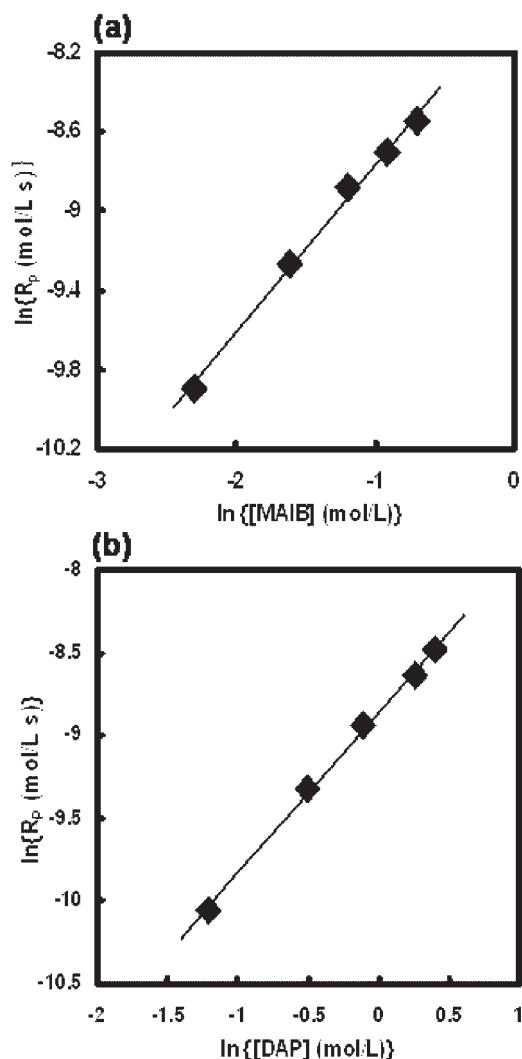


Figure 4 Dependence of the initial polymerization rate (R_p) on (a) the MAIB concentration and (b) the DAP concentration in the polymerization of DAP with MAIB at 80°C in dioxane; [DAP] = 1.30 mol/L (a) and [MAIB] = 0.50 mol/L (b).

propagating radicals are highly resonance-stabilized and too stable to reinitiate the polymerization.^{1,9} The allylic radicals undergo termination by reaction with each other, more likely, with propagating radicals. In such a case, R_p is expressed by $R_p = k [\text{initiator}]^{1.0} [\text{monomer}]^{0.9}$. Diallyl ester monomers such as DAP and DADGC were reported to show much higher polymerizability in radical polymerization compared to monoallyl ester monomers.¹⁰ In the polymerizations of DAP and DADGC with benzoyl peroxide (BPO), the order of the initiator concentration was estimated to be 0.66 at 80°C for DAP and 0.71 at 70°C for DADGC.^{10,11}

On the other hand, the primary radical termination becomes more important as the initiator concentration is higher and the reactivity of the monomer towards the primary radical is lower.^{12,13} In the present polymerization, high MAIB concentrations were used. The vinyl groups of DAP monomer are nonconjugative and hence should have a low reactivity towards the resonance-stabilized methoxycarbonylpropyl radical as the primary radical of MAIB. When all termination reactions are due to the primary radical termination, R_p is given by $R_p = k [\text{initiator}]^0 [\text{monomer}]^{2.13}$.

The kinetic results obtained here suggest significant contributions of both degradative chain transfer and primary radical termination in the present polymerization.¹⁴

Figure 5 shows ESR spectrum observed in the polymerization at 80°C for 40 min, where the concentrations of DAP and MAIB were 1.30 and 0.50 mol/L, respectively. The observed spectrum was considered to be due to the propagating polymer radical of DAP, because it was similar to those reported for the propagating radicals of allyl monomers.¹⁰

Independent of termination, using the polymer concentration ($[P\cdot]$) and R_p , the propagation rate constant (k_p) can be estimated by the following equation:

$$R_p = k_p [P\cdot] [\text{DAP}] \quad (2)$$

$[P\cdot]$ was estimated to be 4.8×10^{-7} mol/L from the ESR spectrum in Figure 6, and the instantaneous R_p at 40 min was calculated to be 7.9×10^{-5} mol/L s from

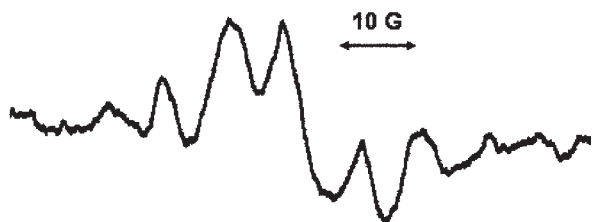


Figure 5 ESR spectrum observed in the polymerization of DAP with MAIB at 80°C in dioxane for 40 min; $[\text{DAP}] = 1.30$ mol/L and $[\text{MAIB}] = 0.50$ mol/L.

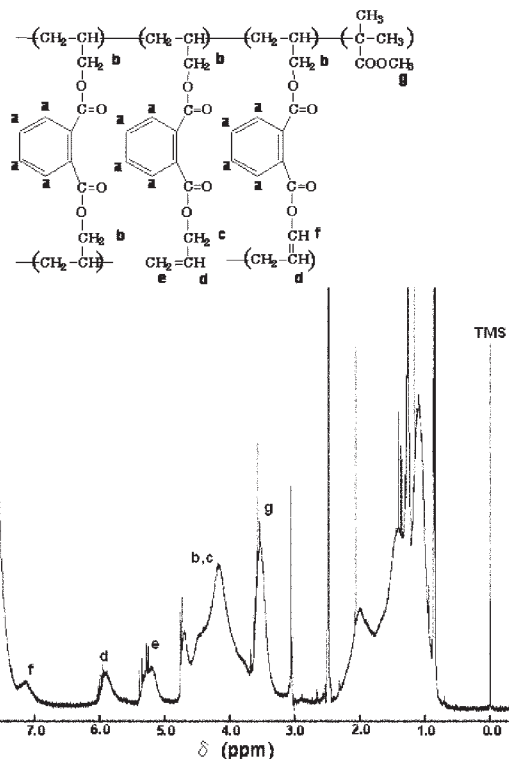


Figure 6 ^1H NMR spectrum of the polymer formed in the polymerization of DAP with MAIB at 80°C in toluene for 4 h; $[\text{DAP}] = 1.30$ mol/L and $[\text{MAIB}] = 0.50$ mol/L.

the time-conversion curve at 80°C. Using these results, k_p was determined to be 162 L/mol s at 80°C. The k_p value was similar to those reported for other diallyl monomers {DADGC: 214 L/mol s, diallyl carbonate: 305 L/mol s, diallyl isophthalate: 122 L/mol s, 2,2'-bis(allyloxycarbonyl)biphenyl: 423 L/mol s (90°C)}.¹⁰

Characterization of the resulting polymer

The solubility of the polymer formed in the polymerization of DAP (1.30 mol/L) with MAIB (0.50 mol/L) for 4 h at 80°C (run 3 in Table I) was checked. The polymer was soluble in benzene, toluene, THF, dioxane, ethyl acetate, acetone, *N,N*-dimethylformamide, and dimethyl sulfoxide, and was insoluble in *n*-hexane, cyclohexane, methanol, ethanol, and water.

Figure 6 shows ^1H NMR spectrum of the same polymer. Peak assignments are indicated in the figure. Thus, the polymer was observed to contain DAP units with and without a double bond and the methoxycarbonylpropyl group derived from MAIB.

The polymer composition was calculated from the peak areas due to the hydrogens of vinyl (5.8 ppm), phenyl (7.7 ppm), and methoxy (3.5 ppm) groups. Figure 7 shows the composition of poly(DAP)s formed at 70 (runs 17–22 in Table I) and 80°C (runs 3 and 12–16 in Table I) at different times. For the polymers

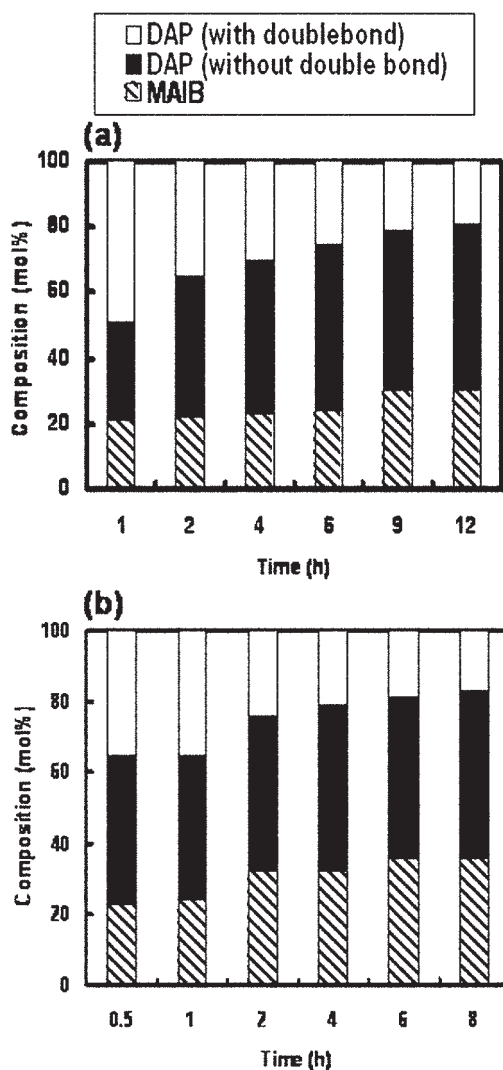


Figure 7 Composition of the polymers formed in the polymerization of DAP with MAIB at (a) 70°C and (b) 80°C in toluene at different times; [DAP] = 1.30 mol/L and [MAIB] = 0.50 mol/L.

formed at 80°C, the fraction (23–36 mol %) of the methoxycarbonylpropyl group as MAIB-fragment increased with time. Such a large number of the initiator-fragments were incorporated as terminal groups in the resulting poly(DAP)s, indicating that the polymers are of a hyperbranched structure. The content (35–17 mol %) of the DAP unit with a double bond reasonably decreased with time and still remained even after the polymerization for 8 h. This suggests that the resulting hyperbranched poly(DAP) can serve as a crosslinking reagent. The fraction (42–47 mol %) of the DAP unit without the double bond tended to increase slightly with time. The polymer formed in the polymerization for 8 h was composed of the initiator fragment (36 mol %) and DAP units with (17 mol %) and without (47 mol %) double bond. The polymers formed at 70°C showed similar tendencies for their

composition, although the fraction (30–51 mol %) of the DAP unit without double bond considerably increased with time. The polymer formed in the polymerization for 12 h was constituted of the MAIB-fragment (30 mol %) and the DAP units with (19 mol %) and without (51 mol %) double bond.

The rate constant ratio of the unimolecular cyclization reaction to the bimolecular propagation of the uncyclized radical was reported to be 8.6 mol/L, a considerably high value, for the polymerization of DAP with BPO at 80°C.¹¹ This suggests appreciable formation of cyclic structures by intramolecular cyclization during the present polymerization. The cyclic structures are included in the DAP units without double bond shown in Figures 6 and 7.

The poly(DAP) formed in the polymerization at 80°C for 4 h (run 3 in Table I) was subjected to MALLS measurements at 25°C in THF. From the Zimm plot of the observed data, M_w and radius of gyration (R_g) were estimated to be $M_w = 6.1 \times 10^4$ and $R_g = 5.1$ nm, respectively. The M_w value obtained here is considerably higher than that (1.75×10^4) by GPC. Such underestimations by GPC were reported for many dendritic polymers such as dendrimers and hyperbranched polymers, resulting from smaller hydrodynamic radii of them.^{15–18}

Owing to the lack of intermolecular entanglements, the solution viscosity of hyperbranched polymers is generally very low.^{15–21} The benzene solution of the same polymer (run 3 in Table I) subjected to MALLS measurements was examined viscometrically at 25°C. Extremely low reduced viscosity values (0.039–0.041 dL/g) were observed in the polymer concentration range of 0.3–1.0 g/dL, leading to a very low intrinsic viscosity of 0.037 dL/g. The viscometric results also support that the polymer obtained here is of compact hyperbranched structure.

From TG study of the same polymer, the thermal degradation was found to begin at about 250°C and to show a maximal rate at 380°C. The residue at 500°C was 10% of the initial polymer weight. The thermal behavior of the same polymer was also examined by DSC. A fairly sharp endothermic peak was observed at 63°C, probably corresponding to the glass transition temperature of the polymer.

Formation of iridescent porous film of poly(DAP)

The film from poly(DAP) showed iridescent color when the film was cast on a glass slide from a solution of the polymer in THF (10 mg/mL), where the polymer was obtained in the polymerization at 80°C for 4 h (run 3 in Table I). Figure 8(a) presents a digital photo of the iridescent film, the reflected color of which changed depending on the incident angle of the illuminating white light, suggesting the presence of ordered structures in the polymer film. Figure 8(b) illus-

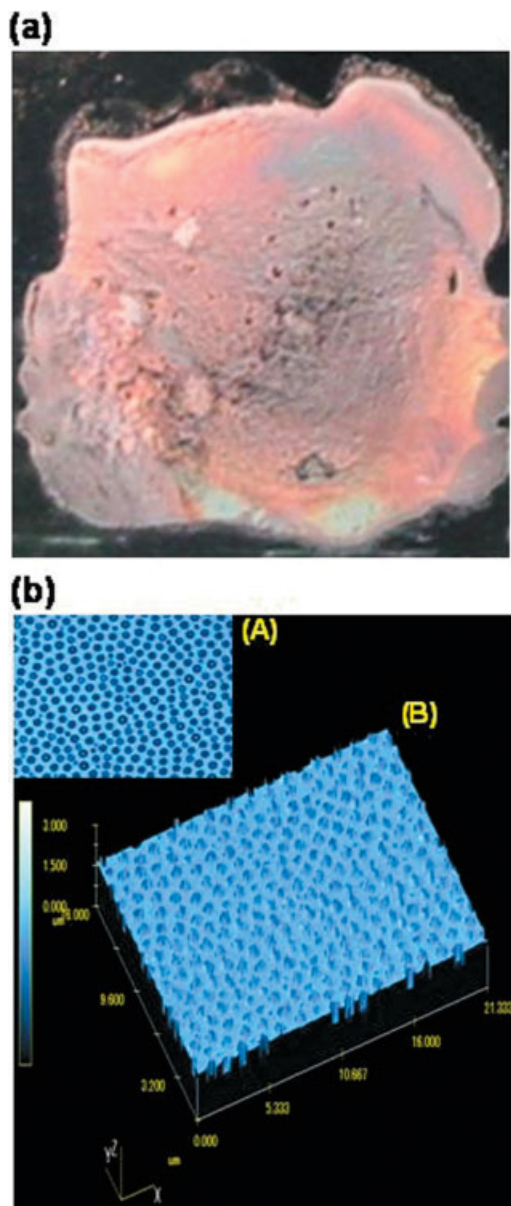


Figure 8 (a) Digital photograph and (b) confocal scanning laser microscopy image (A: intensity image; B: wire frame) of an iridescent porous film from a polymer solution in THF (10 mg/mL). The polymer was formed in the polymerization of DAP (1.30 mol/L) with MAIB (0.50 mol/L) at 80°C in toluene for 4 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

trates a confocal scanning laser microscope image of the film. Thus, the film contained the pores organized in an ordered array in a limited region with a considerably monodispersed pore size of about 1 μm . The ordered pore array is responsible for the iridescence observed for the film.^{22,23}

Star, block, and comb polymers are known to template around water droplets to form isoporous arrays when solutions of such polymers in a water-immiscible organic solvent such as carbon disulfide and chlo-

roform are cast onto a glass substrate and evaporated under a humid atmosphere (humidity level of 80% or more). After evaporation of solvent and water, the films with regular structure and pore size are formed.^{24–31} Thus, moisture frequently becomes critical for the preparation of such porous polymer films according to the method described earlier.

On the other hand, our film was prepared by casting a polymer solution onto a glass slide and drying in air under no humid conditions, although the porous structures of the film are closely similar to those of films formed under humid conditions. Further, THF used here as the solvent is miscible with water. In the present case, the formation mechanism of the porous film is considered as follows; when a certain amount of THF as the solvent is evaporated from the casting polymer solution and the solution temperature drops, a thermally induced phase separation occurs to yield the polymer-rich and polymer-poor phases.^{32,33} The polymer-poor phase becomes liquid droplets. The polymer in the polymer-rich phase then precipitates on the surface of the liquid droplets. The precipitated polymers stabilize the liquid droplets by forming a solid layer around them. Evaporation of all solvent leads to formation of a porous film.^{24–26} The hyperbranched poly(DAP) obtained here seems well suitable for stabilization of the liquid droplets.

Formation of similar microporous films from the hyperbranched polymers obtained in other initiator-fragment incorporation radical polymerization (IFIRP) systems is under study and will be published in future.

CONCLUSIONS

When the concentration of MAIB as initiator was as high as 0.10–0.90 mol/L, the polymerization of DAP (1.30 mol/L) proceeded homogeneously at 80°C in toluene without any gelation to give soluble polymers in the yield of 51–84%, based on the total weight of DAP and MAIB used. The polymerization of DAP of 1.50 mol/L with MAIB of 0.50 mol/L at 80°C for 4 h gave soluble hyperbranched polymer in a high yield of 93%. The initial polymerization rate (R_p) in the homogeneous polymerization at 80°C was given by $R_p = k [\text{MAIB}]^{0.8} [\text{DAP}]^{1.0}$, suggesting significant contributions of both the degradative chain transfer and the primary radical termination. The overall activation energy of the polymerization was 91 kJ/mol. The polymer formed in the polymerization of DAP (1.30 mol/L) with MAIB (0.50 mol/L) at 80°C for 8 h was composed of the DAP units with (17 mol %) and without (47 mol %) double bond and the methoxycarbonylpropyl group (36 mol %) as MAIB-fragment. The large fraction of the incorporated initiator-fragment as terminal group indicates that the polymer has a hyperbranched structure. The results of the MALLS and

viscometric measurements support that the polymer is of compact hyperbranched structure. The cast film from a solution of resulting poly(DAP) in THF showed iridescent colors, suggesting the presence of ordered structures in the film. The iridescent film contained the pores organized in an ordered array with a considerably monodispersed pore size of about 1 μm . Here we have shown that a film with uniform pores was formed simply by casting a solution of the hyperbranched polymer in a water-miscible solvent such as THF.

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