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Soluble hyperbranched copolymer via initiator-fragment incorporation radical copolymerization using a trivinyl monomer

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Abstract

The initiator-fragment incorporation radical polymerization was extended to a copolymerization system of a trivinyl monomer. The copolymerization of trimethylolpropane trimethacrylate (TMPTM) as a trivinyl monomer with α-methylstyrene (MSt) was examined at 70 and 80 °C in toluene using dimethyl 2,2′-azobisisobutyrate (MAIB) of high concentrations as initiator. When the concentrations of TMPTM, MSt and MAIB were 0.30, 0.60 and 0.50 mol/l, the copolymerization proceeded homogeneously without gelation at 80 °C to yield soluble hyperbranched copolymer in a yield of 65%. The copolymer formed for 8 h consisted of 37 mol% of the TMPTM unit, 42 mol% of the MSt unit and 21 mol% of the methoxycarbonylpropyl group as initiator-fragment, where 22% of the vinyl groups of the incorporated TMPTM units remained unreacted. The copolymer showed an upper critical solution temperature (32 °C on cooling) in a tetrahydrofuran(THF)-water [44:10 (wt/wt)]. Reflecting the hyperbranched structure, the viscosity of a copolymer solution in toluene was very low. The porous film was prepared directly by casting a THF solution of the hyperbranched copolymer on a cover glass. The copolymer molecules are radially arranged on the surface layer of the spherical pores as showed by polarized optical microscope imaging.

Keywords: Initiator-fragment incorporation radical polymerization; Trivinyl monomer; Hyperbranched polymer

1. Introduction

Recently, hyperbranched polymers have received a great deal of 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].

In our pervious papers [7–10], we proposed the initiator-fragment incorporation radical polymerization (IFIRP) as a convenient method for the one-pot synthesis of soluble hyperbranched polymers. The key-point of IFIRP is the use of high initiator concentrations in the radical homopolymerization or copolymerization of a divinyl monomer. Usually, the radical homo- or copolymerization of a divinyl monomer leads to the formation of insoluble crosslinked polymer, the molecular weight of which is treated to be extremely high or infinite. However, the use of initiator at high concentrations causes so great decrease in the molecular weight that the resulting polymer becomes soluble and is of a hyperbranched structure, where a large number of initiator-fragments are incorporated as terminal groups in the polymer through initiation and primary radical termination (IFIRP). In facts, soluble hyperbranched polymers were successfully synthesized by the homo- and copolymerizations of divinyl monomers such as divinylbenzene, ethylene glycol dimethacrylate and divinyl adipate using high initiator concentrations.

Here, we have attempted to extend the IFIRP concept to a polymerization system involving a trivinyl monomer. The copolymerization of trimethylolpropane trimethacrylate (TMPTM) and α-methylstyrene (MSt) was conducted using dimethyl 2,2′-azobisisobutyrate (MAIB) as initiator at high concentrations, in which soluble hyperbranched copolymers were formed.

The present paper describes the initiator-fragment incorporation radical copolymerization behavior of the

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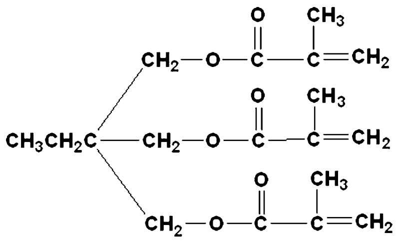
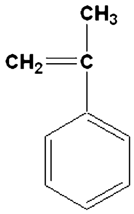
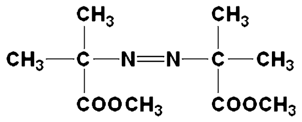
TMPTM/MSt/MAIB system and characterization of the resulting copolymer.



TMPTM



MSt



MAIB

2. Experimental part

2.1. Materials

TMPTM (supplied by Shin-Nakamura Chemical Co., Ltd) was freed from the inhibitor through washing with a 5 wt% aqueous NaOH solution. MSt was used after distillation. MAIB was recrystallized from methanol. Toluene was treated with sulfuric acid and distilled. *n*-Hexane and dioxane were used after distillation.

2.2. Polymerization

Copolymerization of TMPTM and MSt with MAIB was performed in a degassed and sealed glass tube at a given temperature. The resulting copolymer was isolated by pouring the polymerization mixture into a large excess of *n*-hexane. The conversions of the vinyl groups of TMPTM and MSt were followed in situ as a function of time by Fourier-transform near-infrared (FT-NIR) spectroscopy, where the copolymerization was conducted in a degassed and sealed Pyrex glass tube (5 mm diameter) in a custom-made aluminum furnace with an FT-NIR measurement system [11].

2.3. Preparation of porous copolymer film

A porous copolymer film was prepared directly by casting a copolymer solution in tetrahydrofuran (THF) (1 mg/ml) on a cover glass in the air at room temperature. The resulting copolymer film on the cover glass was subjected to the optical microscope observation.

2.4. Measurements

The conversions of TMPTM and MSt were estimated with a Jasco INT-400 spectrometer with a mercury–cadmium–telluride detector. The consumptions of the vinyl groups of TMPTM and MSt were monitored by the absorbance at about 6150 $\mathrm{cm^{-1}}$ being assignable to the overtone absorption due to stretching vibrations of =C–H bonds in the vinyl groups. ^{1}H NMR spectra were recorded on a Jeol GX spectrometer (400 MHz). Gel permeation chromatography (GPC) was conducted 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 THF as eluent. From the GPC results, number-average (M_n) and weight-average (M_w) molecular weights of the copolymers were estimated with

Table 1
Copolymerization of TMPTM and MSt with MAIB in toluene at 80 °C for 4 h

Run	[TMPTM] (mol/l)	[MSt] (mol/l)	[MAIB] (mol/l)	Yield (%)	$M_n \times 10^{-3}$	M_w/M_n	Remarks
1	0.10	0.50	0.50	20	2.7	1.4	
2	0.20	0.50	0.50	51	4.5	2.3	
3	0.30	0.50	0.50	70	10.3	19.0	
4	0.35	0.50	0.50	83	–	–	Gelation
5	0.40	0.50	0.50	85	–	–	Gelation
6	0.50	0.50	0.50	92	–	–	Gelation
7	0.30	0.50	0.20	58	5.7	4.7	
8	0.30	0.50	0.30	65	6.7	7.3	
9	0.30	0.50	0.40	68	7.6	10.5	
10	0.30	0.50	0.60	66	8.2	22.1	
11	0.30	0.50	0.70	61	8.1	24.3	
12	0.30	0.50	0.80	59	8.2	19.0	
13	0.30	0.50	0.90	56	7.7	16.8	
14	0.30	0.50	1.00	53	7.7	12.8	
15	0.30	0.20	0.50	70	–	–	Gelation
16	0.30	0.30	0.50	75	–	–	Gelation
17	0.30	0.40	0.50	72	–	–	Gelation
18	0.30	0.60	0.50	65	7.0	5.8	
19	0.30	0.70	0.50	58	5.0	3.7	
20	0.30	0.80	0.50	53	4.5	3.1	

polystyrene standards calibration. Electron spin resonance (ESR) spectra of the polymerization mixture were measured with a Jeol JES-FE2XG spectrometer operating at the X band with a transverse electric wave-mode cavity. The total concentration of the polymer radicals involved was determined by computer double integration of the first derivative ESR spectra, where 2,2,6,6-tetramethylpiperidin-1-oxyl radical in the polymerization mixture without MAIB was used as standard. The optical transmittance of a copolymer 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 °C/min was used. The viscosity of copolymer solutions in toluene was measured at 25 °C using a Ubbelohde viscometer. The multi-angle laser light scattering (MALLS) measurements were carried out by Shoko Co., Ltd with a Wyatt Technology DAWN with laser operating at 690 nm, where d*n*/d*c* (0.104 ml/g) was separately determined at 25 °C in THF by a differential refractometer (Optilab DSP; Wyatt Technology Corp.). Optical microscope imaging of the cast copolymer film was done with an Olympus BX50 microscope. Dynamic thermogravimetry (TG) of the copolymer 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 a nitrogen atmosphere (heating rate = 10 °C/min).

3. Results and discussion

3.1. Copolymerization of TMPTM and MSt with MAIB in toluene

The copolymerization of TMPTM as trivinyl monomer and MSt was carried out at 80 °C in toluene for 4 h using MAIB as initiator at high concentrations (0.20–1.00 mol/l). Table 1 summarizes the observed results.

The copolymer yield was estimated based on the total weight of the comonomers and the initiator used considering N_2-elimination on the MAIB decomposition. This is because the initiator-fragments were incorporated as a main component into the resulting copolymer as described below.

When the TMPTM concentration was changed fixing the concentrations of MSt and MAIB at 0.50 mol/l (runs 1–6), gelation was observed at the TMPTM concentrations higher than 0.35 mol/l, while the polymerization proceeded homogeneously without any gelation at lower TMPTM concentrations of 0.10–0.30 mol/l to yield soluble copolymers. The copolymer yield in the homogeneous polymerization increased with increasing TMPTM up to 70%. The molecular weight ($M_n = 2.7–10.3 \times 10^3$) and the molecular weight distribution ($M_w/M_n = 1.4–19$) were also enlarged with increasing TMPTM concentration.

Next, the MAIB concentration was varied keeping the concentrations of TMPTM and MSt constant at 0.30 and 0.50 mol/l, respectively (runs 3, 7–13). The polymerization proceeded without gelation in the initiator concentration range of 0.20–1.00 mol/l here used. The copolymer yield (53–70%) showed a broad maximum on varying the MAIB concentration. The M_n ($5.7–10.3 \times 10^3$) and M_w/M_n (4.7–24) also exhibited similar behaviors to the copolymer yield.

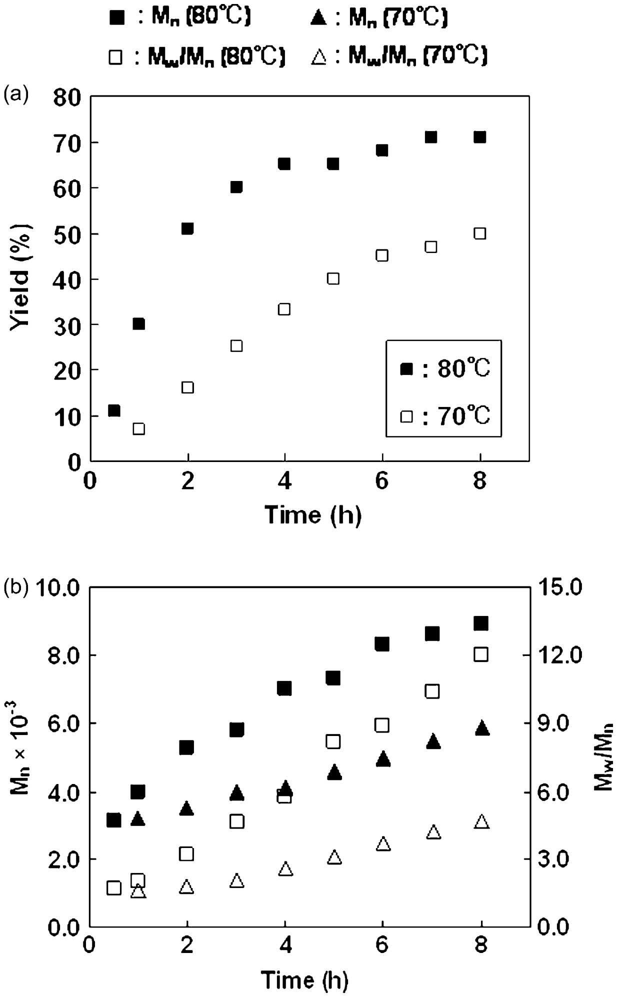


Fig. 1. (a) Time-yield curves in the copolymerization of TMPTM and MSt with MAIB in toluene at 70 and 80 °C and (b) time-profiles of M_n and M_w/M_n of the copolymer: [TMPTM] = 0.30 mol/l, [MSt] = 0.60 mol/l, [MAIB] = 0.50 mol/l.

At last, the MSt concentration was changed at fixed concentrations of TMPTM (0.30 mol/l) and MAIB (0.50 mol/l) (runs 3, 15–20). The polymerization proceeded homogeneously at higher MSt concentrations (0.50–0.80 mol/l) although the use of lower MSt concentrations (0.20–0.40 mol/l) resulted in gelation. The yield (70–53%), M_n ($4.5–10.3 \times 10^3$), and M_w/M_n 3.1–19) of the copolymer formed in the homogeneous polymerization decreased with the MSt concentration. These results come from little homopolymerizability of MSt in the usual radical polymerization.

The homogeneous copolymerization in toluene was in more detail examined at 70 and 80 °C, where the concentrations of TMPTM, MSt and MAIB were 0.30, 0.60 and 0.50 mol/l, respectively. Fig. 1(a) presents time-yield curves observed at 70 and 80 °C. The copolymer yield at 80 °C increased rapidly in the early stage of the polymerization (up to 4 h) and then the increase rate was showed down. The yield at 70 °C was considerably lower than at 80 °C. As shown in Fig. 1(b), the molecular weight increased and the molecular weight

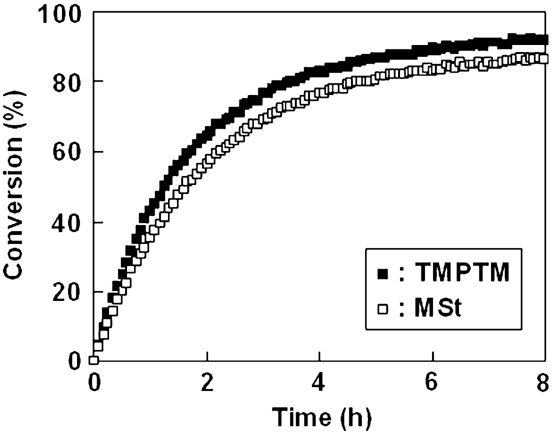


Fig. 2. Time-conversion curves of the vinyl groups of TMPTM and MSt in the copolymerization of TMPTM and MSt with MAIB in toluene at 80 °C: [TMPTM] = 0.30 mol/l, [MSt] = 0.60 mol/l, [MAIB] = 0.50 mol/l.

distribution broadened with time, namely with the copolymer yield, both at 70 and 80 °C.

Fig. 2 shows time-conversion curves for the vinyl groups of TMPTM and MSt in the copolymerization of TMPTM and MSt with MAIB at 80 °C in dioxane, in which the concentrations of TMPTM, MSt and MAIB were 0.30, 0.60 and 0.50 mol/l, respectively. The consumption of the vinyl groups was in situ followed by FT-NIR. Thus, the vinyl groups of TMPTM and MSt were consumed at similar rates, although the former somewhat more rapidly than the latter. The copolymerization for 8 h resulted in conversions of 90% for the TMPTM vinyl groups and 83% for the MSt one. These results are consistent with the monomer reactivity ratios ($r_1 = 0.42$, $r_2 = 0.22$) reported for the copolymerization of methyl methacrylate (M_1) and MSt (M_2) [12].

Fig. 3(a) illustrates ESR spectrum observed in the homogeneous copolymerization of TMPTM and MSt with MAIB at 80 °C in toluene for 5 h, where the concentrations of TMPTM, MSt, and MAIB were 0.30, 0.60 and 0.50 mol/l, respectively. The observed spectrum is considered to be overlapping of the spectra due to the propagating polymer radicals of MSt and TMPTM as methacrylate monomer [13]. Fig. 3(b) depicts the time-profile of the total polymer radical concentration ([P•]). The [P•] value gradually increased with time up to 1.2×10^{-6} mol/l at 6 h although the polymer radical concentration is well known to be almost independent of time in the conventional radical polymerization of vinyl monomers. This suggests that the polymer radicals were formed in the compact hyperbranched polymer structure.

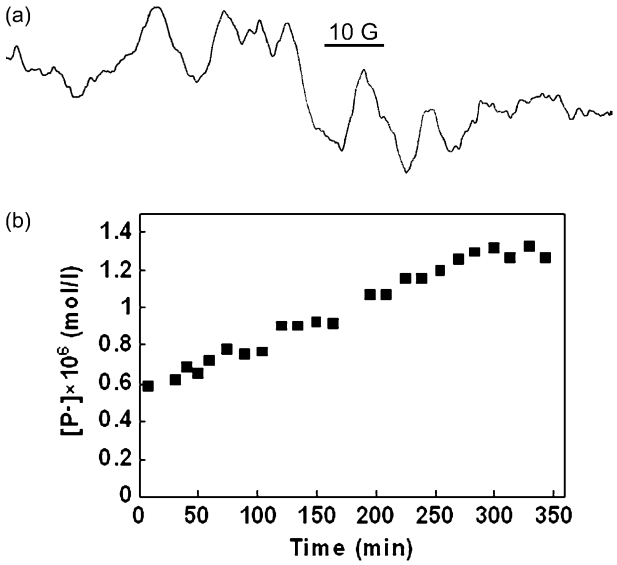


Fig. 3. (a) ESR spectrum observed in the copolymerization of TMPTM and MSt with MAIB at 80 °C in toluene for 5 h and (b) time-profile of the total polymer radical concentration ([P•]): [TMPTM] = 0.30 mol/l, [MSt] = 0.60 mol/l, [MAIB] = 0.50 mol/l.

3.2. Characterization of the resulting copolymers

Fig. 4 shows the ^{1}H NMR spectra of the copolymers formed in the copolymerization at 80 °C in toluene for 1 and 4 h, where the concentrations of TMPTM, MSt, and MAIB were 0.30, 0.60 and 0.50 mol/l, respectively. The spectra were obtained at 55 °C in $CDCl_3$. Peak assignments are given in the figure. Thus, the copolymers consisted of the TMPTM units, MSt units and the methoxycarbonylpropyl groups as MAIB-fragment. It is reasonable that the peaks of vinyl protons in the incorporated TMPTM units (5.6 and 6.2 ppm) were smaller in the copolymer formed for 4 h than in that for 1 h. The peaks *b* and *e* were not clearly resolved. So, the resonance spectra in this area (3–5 ppm) were separately measured at 150 °C in $C_6D_5NO_2$ and shown in the circle in the figure.

The composition of the resulting copolymers was determined from the peak areas due to the $–CH_2–O–$ groups (3.9–4.9 ppm) of TMPTM unit, the phenyl group (6.6–7.6 ppm) of MSt unit and the methoxy group (3.3–3.9 ppm) of methoxycarbonylpropyl group. Fig. 5(a) shows the composition of the copolymers formed at 80 °C in toluene at different initiator concentrations (0.20–1.00 mol/l) for 4 h, where the concentrations of TMPTM and MSt were 0.30 and 0.50 mol/l. The fraction (32–45 mol%) of methoxycarbonylpropyl group as initiator-fragment reasonably increased with increasing MAIB concentration, while that (30–19 mol%) the TMPTM unit decreased with the MAIB concentration. The MSt content showed a little tendency to decrease with the MAIB concentration. The use of the MAIB concentrations more than 0.70 mol/l resulted in the nearly same copolymer composition. As mentioned above, a large number of the methoxycarbonylpropyl groups as MAIB-fragments were incorporated as terminal groups in the resulting copolymers, indicating that an IFIRP proceeds in the present copolymerization to yield soluble copolymers of a hyperbranched structure.

Fig. 5(b) presents the effect of MAIB concentration on the double bond content of TMPTM unit in the copolymers. The double bond content was estimated from comparison of peak areas of the vinyl and $–CH_2–O–$ groups in the TMPMT unit. Thus, the double bond content (26–16%) somewhat decreased with the MAIB concentration.

Fig. 6(a) shows the composition of the copolymers formed at different times in the copolymerization at 80 °C in toluene, where the concentrations of TMPTM, MSt and MAIB were

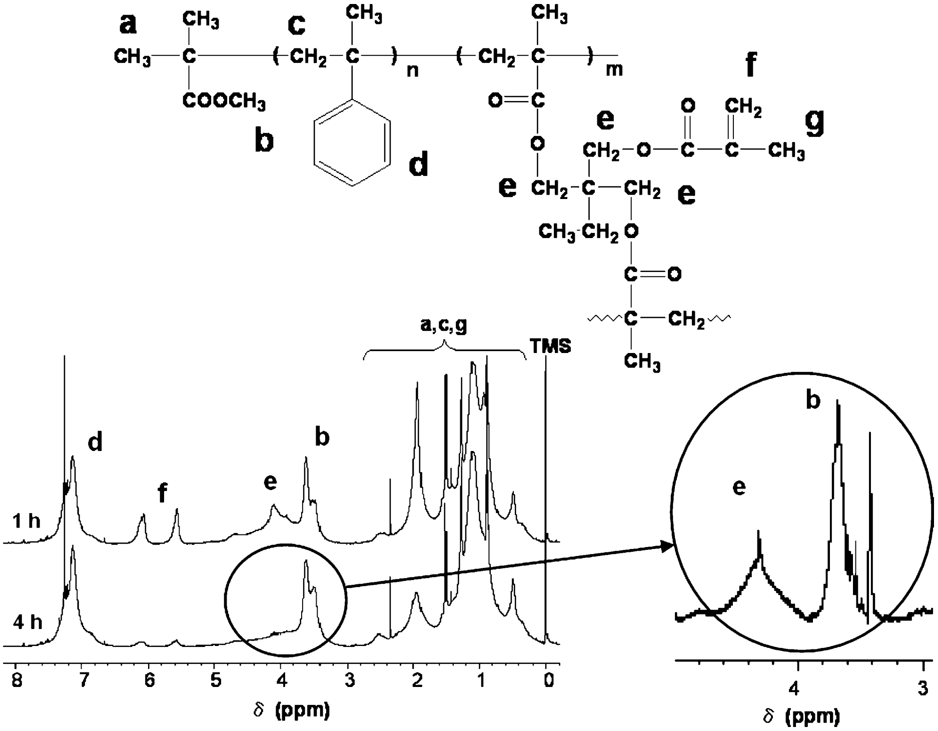


Fig. 4. ^{1}H NMR spectra of the copolymers formed in the copolymerization of TMPTM and MSt with MAIB in toluene at 80 °C for 1 h and 4 h: [TMPTM] = 0.30 mol/l, [MSt] = 0.60 mol/l, [MAIB] = 0.50 mol/l. The spectra were measured at 55 °C in $CDCl_3$. The spectrum in the circle was done at 150 °C in nitrobenzene$_{d-5}$.

0.30, 0.60 and 0.50 mol/l, respectively. Thus, the copolymer composition was not so changed with time. The MSt content (35–43 mol%) increased with time, while the TMPTM (32–21 mol%) one decreased with time. This is because TMPTM has a somewhat higher reactivity compared with MSt as described above. The fraction (33–39 mol%) of the methoxycarbonylpropyl group did not experience a significant time effect. As shown in Fig. 6(b), the double bond content (33–22%) in the TMPTM units reasonably decreased with time.

We checked the solubility of the copolymer formed in the copolymerization at 80 °C for 4 h, where the concentrations of TMPTM, MSt and MAIB were 0.30, 0.60 and 0.50 mol/l (run 16 in Table 1). The copolymer was soluble in benzene, toluene, methyl benzoate, nitrobenzene, acetone, chloroform, ethyl acetate, THF and *N*,*N*-dimethylformamide, while it was insoluble in *n*-hexane, diethyl ether, methanol, ethanol, dimethyl sulfoxide and water.

The solution viscosity of the hyperbranched polymers is well known to be very low because of the lack of intermolecular entanglements [1–10,14–17]. The resulting copolymer was examined viscometrically at 25 °C in toluene. The copolymer used was obtained in the copolymerization at 80 °C for 4 h, where the concentrations of TMPTM, MSt and MAIB were 0.20, 0.50 and 0.50 mol/l, respectively (run 2 in Table 1). The M_w value of the copolymer was separately estimated by MALLS to be 3.6×10^4 although that by GPC was 1.4×10^4 (Table 1). Such underestimations of the molecular weight by GPC were often reported for other hyperbranched polymers [7–10,14,18–20]. This comes from smaller hydrodynamic radii of the hyperbranched polymers compared to

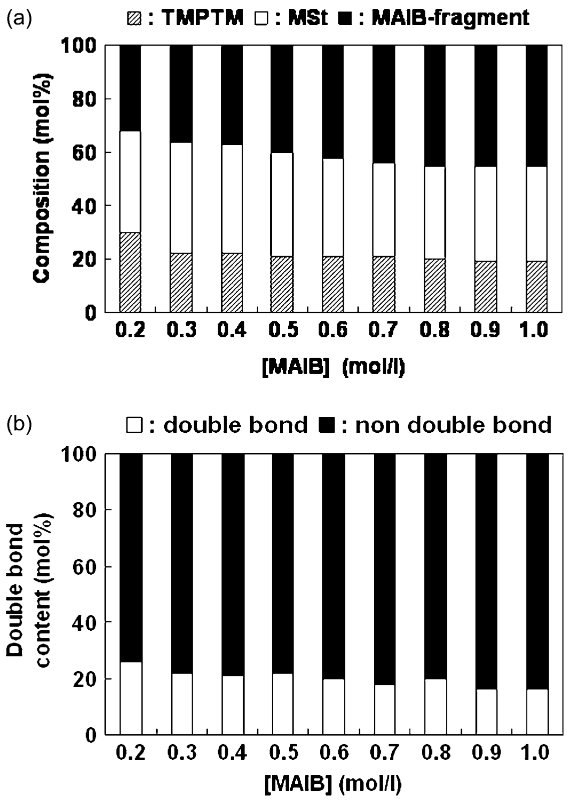


Fig. 5. Effect of the MAIB concentration on (a) the copolymer composition and (b) the double bond content in the TMPTM units of the copolymer in the copolymerization of TMPTM and MSt with MAIB in toluene at 80 °C for 4 h: [TMPTM] = 0.30 mol/l, [MSt] = 0.50 mol/l.

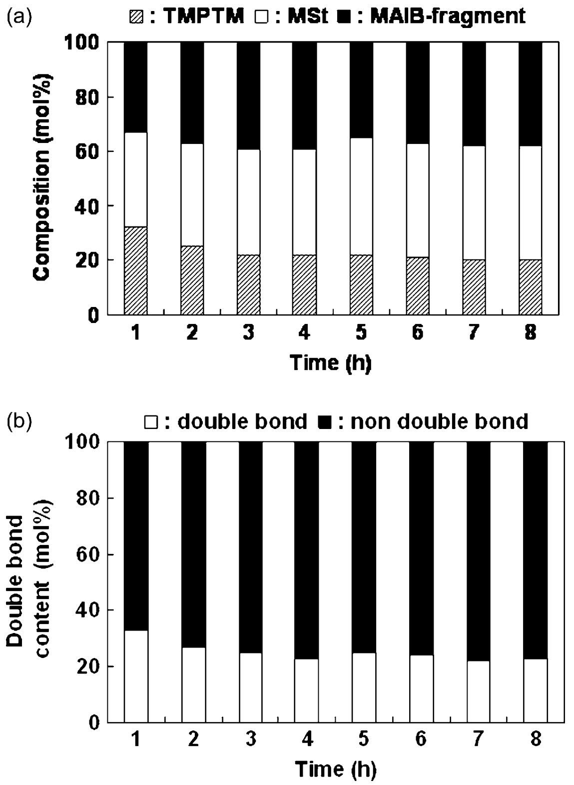


Fig. 6. Time effect on (a) the copolymer composition and (b) the double bond content in the TMPTM units of the copolymer in the copolymerization of TMPTM and MSt with MAIB in toluene at 80 °C: [TMPTM] = 0.30 mol/l, [MSt] = 0.60 mol/l, [MAIB] = 0.50 mol/l.

those of corresponding linear polymers. Fig. 7 presents the relationship between the reduced viscosity (η_{red}) and the copolymer concentration (C). Thus, the η_{red} values were very low and almost independent of the copolymer concentration (~0.04 dl/g, C = 0.4–1.0 g/dl), suggesting little interactions between the copolymer molecules. The intrinsic viscosity ([η]) was estimated to be 0.04 dl/g, an extremely low value, from the plot. These viscometric results also support that the copolymer is of a hyperbranched structure.

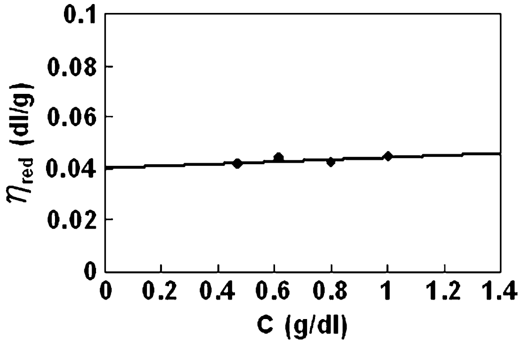


Fig. 7. Relationship between the reduced viscosity (η_{red}) and the copolymer concentration (C) at 25 °C in toluene. The copolymer was prepared in the copolymerization of TMPTM (0.20 mol/l) and MSt (0.50 mol/l) with MAIB (0.50 mol/l) in toluene at 80 °C for 4 h.

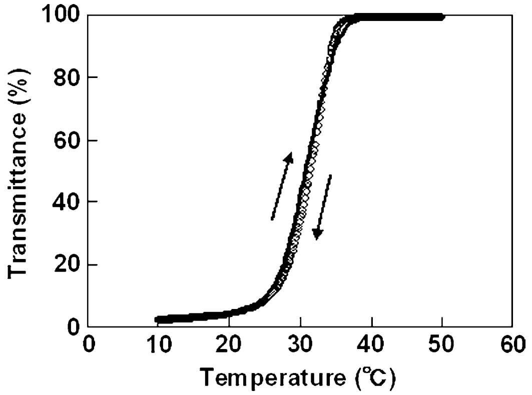


Fig. 8. Temperature effect on the transmittance of a copolymer solution (0.31 wt%) in a THF–water [44:10 (wt/wt)] mixture on cooling (←) and heating (→). The copolymer was prepared in the copolymerization of TMPTM (0.30 mol/l) and MSt (0.60 mol/l) with MAIB (0.50 mol/l) in toluene at 80 °C for 4 h.

Some hyperbranched polymers exhibited an upper critical solution temperature (UCST) in a water–organic solvent mixture, indicating that they are thermally sensitive [8–10]. Little interactions between hyperbranched copolymer molecules are expected to cause the sharp behaviors on dissolution and precipitation of the copolymer. The copolymer formed in run 18 in Table 1 showed a UCST in a THF–water [44:10 (wt/wt)] mixture. Fig. 8 illustrates the temperature effect on the transmittance of a copolymer solution (0.31 wt%) on cooling and heating. A little hysteresis was observed. Such a thermal hysteresis is reported to result from a difference in the rates of precipitation and dissolution processes [21]. In most of reported results [22–25], the rate of dissolution process is

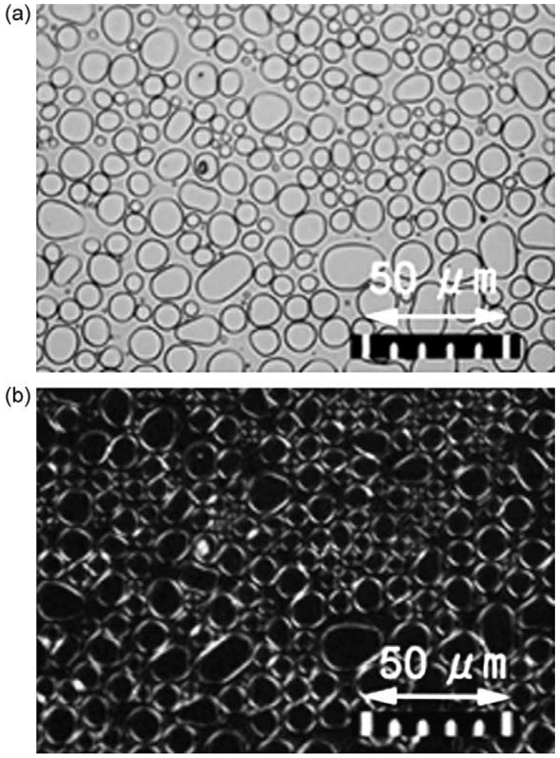


Fig. 9. Optical microscope images of a porous film from a copolymer solution in THF (1 mg/ml) under (a) bright field and (b) crossed polarizers. The copolymer was prepared in the copolymerization of TMPTM (0.30 mol/l) and MSt (0.60 mol/l) with MAIB (0.50 mol/l) in toluene at 80 °C for 4 h.

slower than that of precipitation one. On the other hand, an inverse phenomenon was observed in Fig. 8, indicating that the dissolution rate was faster than the precipitation one for the copolymer. Similar phenomena were observed for other hyperbranched polymers [26,27]. This might come from the unique structure of the hyperbranched polymers. When UCST was defined as the temperature at which the transmittance became 50%, the UCST of the copolymer was estimated to be 32 °C on cooling and 31 °C on heating.

Fig. 9 shows optical microscope images of a cast film on a cover glass from a copolymer solution in THF (1 mg/ml) under (a) bright field and (b) crossed polarizers. Here was used the copolymer obtained in the copolymerization at 80 °C for 4 h (run 18 in Table 1). Thus, the film was found to contain many pores with diameter of 3–20 μm, most of which was spherical. Further, fairly high birefringence with Maltese cross was observed for the spherical pores in the polarized optical micrograph. Maltese cross is known to be observed for spherulites formed during crystallization of polymer molecules, where the polymer molecules are radially arranged [28,29]. Here, however, the Maltese cross was only observed near the surfaces of the spherical pores [30]. These findings suggest that the copolymer molecule arrangement is highly ordered with radial packing in the surface layer of the pores [30]. Such an ordered arrangement of the copolymer molecules is worthy of remark because the copolymer has a broad molecular weight distribution ($M_w/M_n = 5.8$) and a not-defined structure. Such phenomena as pore formation and ordered arrangement might be characteristic of the hyperbranched polymers [27].

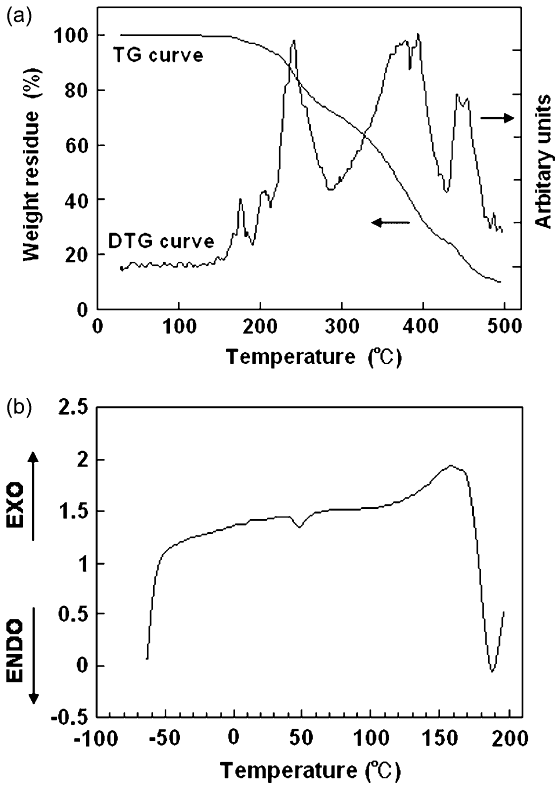


Fig. 10. (a) TG and DTG curves and (b) DSC curve of the copolymer formed in the copolymerization of TMPTM (0.30 mol/l) and MSt (0.60 mol/l) with MAIB (0.50 mol/l) in toluene at 80 °C for 4 h.

Fig. 10(a) shows TG and differential thermogravimetric (DTG) curves of the copolymer formed in the copolymerization at 80 °C for 4 h (run 18 in Table 1). The thermal degradation of the copolymer began at 150 °C and exhibited maximal degradation rates at 240, 390 and 440 °C. Thus, the copolymer was thermally not so stable and degraded through several steps. The observed thermal instability seems to come from the thermally unstable structure of poly(MSt). The residue at 500 °C was 10% of the initial polymer weight. As shown in Fig. 10(b), the DSC curve of the same polymer showed an endothermic peak at 42 °C, corresponding to the glass transition temperature.

4. Conclusions

The copolymerization of TMPTM as trivinyl monomer with MSt proceeded homogeneously without gelation at 70 and 80 °C in toluene when MAIB as initiator was used at high concentrations. When the concentrations of TMPTM, MSt and MAIB were 0.30, 0.60 and 0.50 mol/l, respectively, the copolymer yield at 80°C increased rapidly with time up to about 65% and then the increase rate of the yield was slowed down over 4 h. The copolymer formed for 8 h was composed of 37 mol% of the TMPTM unit, 42 mol% of the MSt unit and 21 mol% of the methoxycarbonylpropyl group as initiator-fragment. Twenty-two percent of the vinyl groups of the incorporated TMPTM units remained unreacted. Thus, a large number of initiator fragments were incorporated as terminal groups in the copolymer, indicating that the copolymer is of a hyperbranched structure. The copolymer showed an upper critical solution temperature in a THF–water. The viscosity of a copolymer solution in toluene was very low at 25 °C, supporting that the copolymer has a hyperbranched structure. The porous film was prepared directly by casting a THF solution of the hyperbranched copolymer on a cover glass. The polarized optical micrograph of the copolymer film suggested that the copolymer molecules are radially arranged on the surface layer of the spherical pores.

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