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Characteristic Polymerization Behaviour of Microgel-Like Poly(allyl methacrylate) Microspheres

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Summary: In the emulsion polymerization of allyl methacrylate (AMA), the reactive crosslinked polymer microspheres or microgel-like polymers with abundant pendant allyl groups were easily obtained because AMA possesses two types of vinyl groups, methacrylic and allylic double bonds, having greatly different reactivities. The resulting microgel-like poly(allyl methacrylate) microspheres (PAMA microspheres) were characterized by light scattering and viscometry. Then, the characteristic polymerization behaviour of PAMA microspheres was explored by the copolymerizations with diallyl terephthalate (DAT) and allyl benzoate (ABz).

Introduction

As an extension of our continuing studies concerned with the elucidation of the crosslinking reaction mechanism and the control of network formation in the free-radical crosslinking polymerization and copolymerization of multivinyl monomers [1], we are dealing with the emulsion crosslinking polymerization and copolymerization of multivinyl monomers, especially focusing on the formation of reactive crosslinked polymer microspheres as models of microgels [2], with the intention of clarifying the correlation of the network structure with the reactivity of resulting microspheres which would be useful as functionalized polymeric materials. Moreover, a detailed understanding of microgel is significantly required not only for the elucidation of 3-dimensional network formation mechanism, but also for the molecular design of vinyl-type network polymers with high performance and high functionality.

Microgel Formation in Monovinyl/Divinyl Copolymerization

Figure 1 shows the reaction scheme for the network formation processes in a free-radical monovinyl/divinyl copolymerization, which essentially involves four reactions of a growing polymer radical: (1) intermolecular propagation with two types of monomer; (2) intramolecular cyclization leading to the formation of small ring or large loop structures; (3) intermolecular crosslinking with the prepolymer to form an effective crosslink, eventually leading to the gel; and (4) intramolecular crosslinking leading to the formation of multiple crosslinks, the locally

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extensive occurrence of which would induce microgelation. Thus, the network structure of the resulting crosslinked polymer could be designed by controlling the elementary reactions shown in Figure 1: the intermolecular crosslinking is the key reaction for the control of gelation as the formation of a 3-dimensional network of indefinitely large size, whereas the key reaction for the control of the network structure is the intramolecular crosslinking that leads to the formation of multiple crosslinks generating the network structure of the crosslinked polymer. As extreme cases, we depict two typical structures of crosslinked polymers in Figure 2 as an ideal network polymer governed by Flory-Stockmayer gelation theory [3] and a microgel greatly deviated from the theory, although the structures of the actual crosslinked polymers would be between the two extreme cases. Furthermore, they should change from a rather homogeneous network

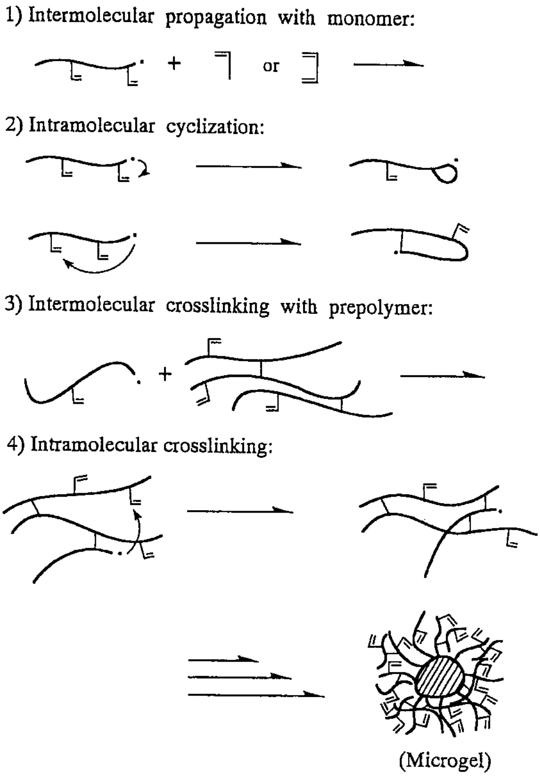

Figure 1. A reaction scheme for the network formation processes in the free-radical monovinyl/divinyl copolymerization.

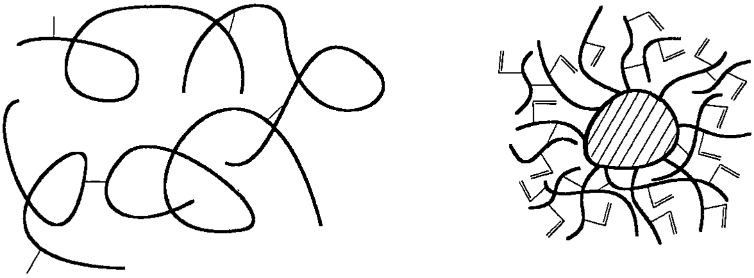
A B

Figure 2. Two extreme structures of crosslinked polymers as (A) an ideal network polymer and (B) a microgel.

structure biased toward the ideal network polymer to an inhomogeneous one biased toward the microgel according to the polymerization conditions. In addition, the distribution of inhomogeneity of the network structure would be important for the characterization of the resulting network polymers. The present article is concerned with the latter inhomogeneous network polymer or microgel; the pseudo-microgel or reactive crosslinked polymer microsphere was obtained by the emulsion crosslinking polymerization of AMA and the characteristic polymerization behaviour of resulting microgel-like PAMA was explored by the copolymerizations with DAT and ABz.

Preparation of PAMA Microspheres

The emulsion polymerization of AMA as unsymmetrical divinyl monomer was taken up [4] because we have extensively studied the polymerization of multiallyl monomers [1]; no gelation occurred, although gelation occurred easily at about 4% conversion in the bulk polymerization [5]. The resulting PAMA as prepolymers were then characterized by comparison with the prepolymers obtained in the bulk polymerization. Figure 3 shows the dependence of $\overline{M}_w$ on conversion along with that of methyl methacrylate (MMA); in contrast to the bulk polymerization where the steep increasing tendency of $\overline{M}_w$ on conversion was observed as close to the gel point, the high-molecular-weight polymer was obtained even at an early stage of polymerization and its increasing tendency with conversion was rather gradual until leveling

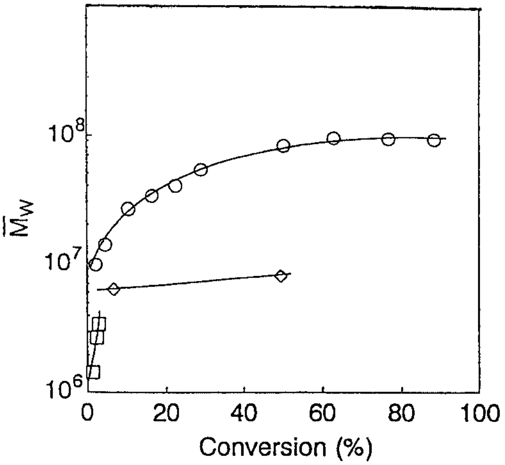

Figure 3. Dependence of $\overline{M}_w$ on conversion for the (○) emulsion and (□) bulk polymerizations of AMA, along with the emulsion polymerization of (◇) MMA.

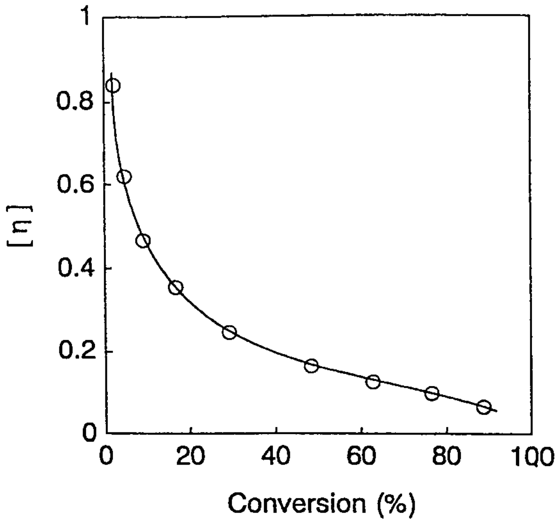

Figure 4. Dependence of [η] on conversion.

off above 70% conversion. The correlation line of $\overline{M}_w$ versus elution volume observed by SEC-MALLS for the emulsion prepolymer was cited above that for the bulk prepolymer, being ascribed to the difference in the occurrence of intramolecular cyclization, intermolecular crosslinking, and intramolecular crosslinking which result in the shrinkage of molecular size. This type of molecular size shrinkage was further reflected in the reduced values of radius of gyration, second virial coefficient A_2, and intrinsic viscosity [η]; as an example, [η] was plotted against conversion in Figure 4, suggesting the formation of microgel-like polymers. In this connection, ^{1}H NMR spectra of the resulting prepolymers were characteristic of the microgel-like polymers as a reflection of increased crosslink density with conversion, although no absorption was reported for microgel due to the complete loss of segmental motion [6]. Figure 5 shows the variation of molecular-weight distribution (MWD) curves with conversion. In the bulk polymerization, MWD curves were clearly broadened toward a higher-molecular-weight side with conversion as a reflection of intermolecular crosslinking, while only the peak shift of unimodal curves was observed in the emulsion polymerization. The residual unsaturation, i.e., a percentage of unreacted pendant allyl groups of the resulting prepolymer as compared to AMA monomer, was plotted against conversion as shown in Figure 6; it was found to be more than 80% even for the polymer obtained above 90% conversion, thus suggesting the formation of microspheres as pseudo-microgels having abundant pendant allyl groups by the emulsion polymerization of AMA.

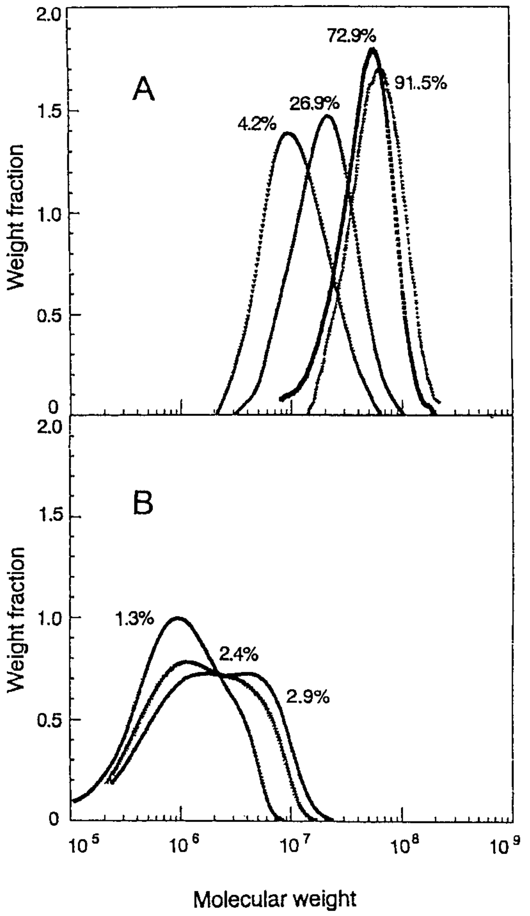

Figure 5. Variation of MWD curves with conversion in the (A) emulsion and (B) bulk polymerizations of AMA.

Thus, microgel-like PAMA microspheres, **I**~**IV**, were prepared according to our previous work [4]. That is, PAMA microspheres **I**, **II**, and **III** having different swellabilities were prepared as the polymers at ca. 80, 51, and 15% conversions, respectively, by the emulsion polymerization of AMA under the same polymerization conditions. Besides, PAMA microsphere **IV** having smaller particle size than **I** was prepared similarly, except that five-fold amount of emulsifier was employed. All PAMA microspheres are characterized as shown in Table 1 and subjected to the post-copolymerizations with DAT and ABz.

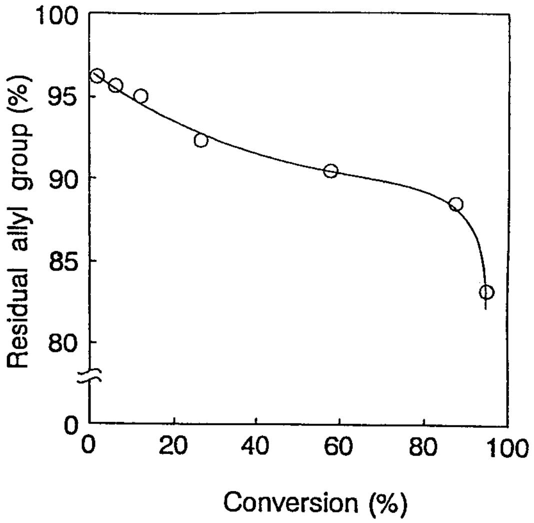

Figure 6. Dependence of residual allyl group of PAMA on conversion.

Table I. Preparation of PAMA Microspheres

PAMA microsphere	I[a]	II[a]	III[a]	IV[b]
Conversion/%	80	51	15	82
Noncyclic unit/%	89	91	94	91
$\overline{M}_w \times 10^{-7}$	7.7	7.2	2.7	7.2
$<s^2>_z^{1/2} \times 10^{-2}$/Å	2.5	2.5	2.6	2.9
$A_2 \times 10^7$/mol cm^3 g^{-2}	2.2	9.7	14	3.6
$[\eta]$/dL g^{-1}	0.10	0.18	0.41	0.14
$\overline{D}$/nm	87	62	43	56

[a] Emulsion polymerization of AMA was carried out in an ampoule 50℃ according to the following recipe: AMA, 10 g; water, 90 g; sodium dodecylsulfate (SDS), 1.3 g; and potassium peroxodisulfate, 0.03 g.

[b] Five-fold amount of SDS as an emulsifier was employed to prepare a smaller sized microsphere.

Crosslinking Polymerization of DAT in the Presence of PAMA Microspheres

The crosslinking polymerization of DAT was explored in detail in the presence of microgel-like PAMA or PAMA-microsphere [7] because in the polymerization of DAT no microgelation occurred up to the gel point [8] and PAMA microspheres obtained as reactive crosslinked polymer microspheres or microgel-like polymers with abundant pendant allyl groups [4] would be models of microgels or pseudo-microgels. Here our attention was focused on the clarification of the polymerization behaviour of microgel and, moreover, the reactivity of crosslinked polymer microspheres.

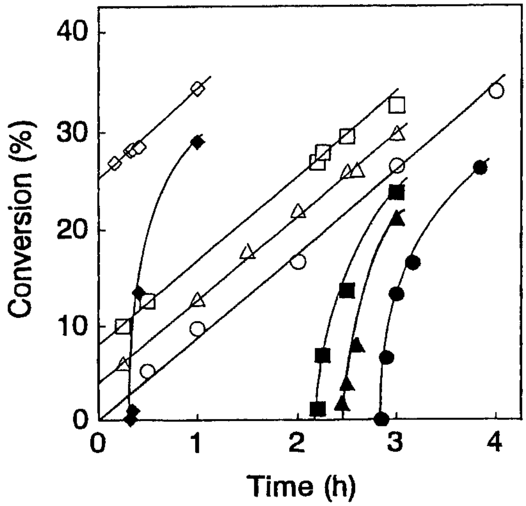

Figure 7. Conversion-time curves for the bulk polymerizations of DAT in the absence (○ , ●) and presence of (△ , ▲) 4.7, (□ , ■) 9.1, and (◇ , ◆) 25.1 wt% of **I** using 0.05 mol/L of BPO at 80℃. Open and full symbols correspond to total and gel polymers, respectively.

Figure 7 shows the conversion-time curves for the bulk polymerization of DAT in the absence and presence of PAMA microsphere **I** using benzoyl peroxide (BPO) as initiator at 80℃. No gel effect was observed, although the viscosity of the polymerization solution increased with an increase in the feed amount of microsphere. Apparently, gelation was delayed with increased amount of microsphere, in which the microsphere is assumed to act as a reactive, microgel-like prepolymer. On the other hand, gelation appeared clearly to be promoted if the microsphere were supposed to be an inactive or dead polymer for the crosslinking polymerization of DAT (see Figure 8). Then, the correlation curve would be extrapolated to ca. 26% conversion, suggesting that in the presence of 26 wt% of **I** gelation would occur

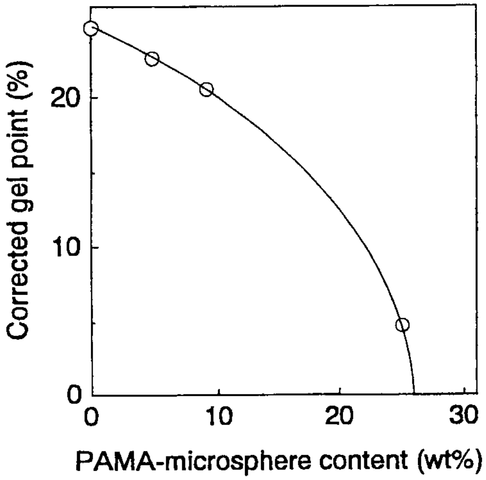

Figure 8. Dependence of corrected gel point on I content (see Figure 7).

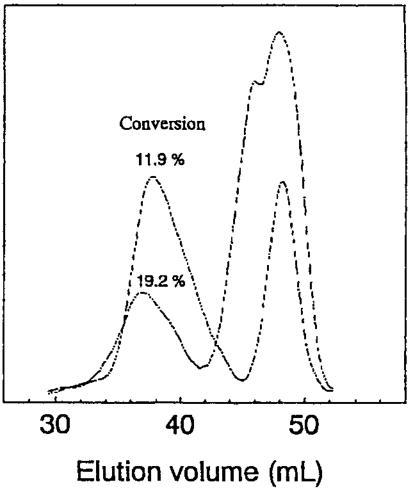

Figure 9. Variation of RI-monitored SEC curves with conversion for the polymerization of DAT in the presence of 9.1 wt% of I (see Figure 7).

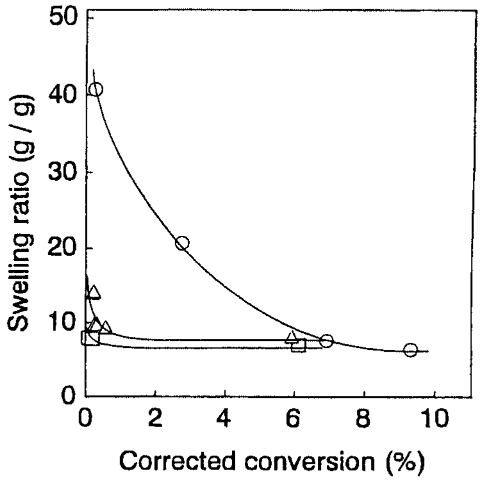

Figure 10. Decrease in swelling ratio of resulting gel in THF with the progress of polymerization beyond the gel point for the polymerizations of DAT in the absence (○) and presence of (△) 9.1 and (□) 25.1 wt% of I (see Figure 7). Conversion in the abscissa is corrected such as the corresponding gel point is 0% of conversion.

simultaneously at the start of polymerization. Figure 9 shows the variation of RI-monitored SEC curves of resulting polymers with conversion. Clearly, two peaks were observed at 11.9% conversion, which corresponds to an early stage of polymerization; this suggests that the polymerization of DAT proceeded mainly in the free space among microspheres. Then, at 19.2% conversion, the peak of the SEC curve at a low elution volume, corresponding to the PAMA microsphere, shifted toward a lower elution volume or higher-molecular-weight side; this would be ascribed to the copolymerization of the pendant allyl groups present on the surface of microsphere with DAT. This was also supported by the characterization of resulting polymers by light scattering and by ^{1}H NMR spectrum of fractionated polymer. The swelling ratios of the gels obtained in the presence of microsphere were not high even just beyond the gel points (see Figure 10), suggesting a preferential incorporation of microsphere into the gel, as opposed to DAT homopolymerization accompanied by no microgelation.

These results are discussed mechanistically as follows: In the presence of a small amount of PAMA microsphere, the wide, free space among microspheres will be a main polymerization locus of DAT and, concurrently, a small portion of DAT will copolymerize with the allyl groups present on the surface of microsphere. With the progress of polymerization, the structure of resulting prepolymer in the free space would grow to be a more branched form through crosslinking reaction, whereas the number of pendant allyl groups on the surface of microsphere, responsible for crosslinking, would increase remarkably through the copolymerization with

DAT. Eventually, the polymerization system would reach the critical point at which gelation occurs as a result of the intermolecular crosslinking reaction between microspheres. The above discussion is also verified by the promoted gelation by the use of PAMA microsphere **III** having a higher swellability for DAT monomer or having a higher copolymerizability toward DAT growing radical and, moreover, by the copolymerization with ABz in place of DAT, the copolymerization with ABz reducing the number of allyl groups at the surface of the microsphere responsible for crosslinking. Then, the post-copolymerizations of PAMA microspheres having different crosslink densities and sizes with ABz were explored in detail to clarify the characteristic polymerization behaviour of microgel-like PAMA microspheres [9].

Copolymerization of PAMA Microspheres with ABz

In the presence of PAMA microspheres, the main locus of ABz polymerization would be in the free space among microspheres, and concurrently, a small portion of ABz will copolymerize with the allyl groups present on the surface of microsphere, reducing the number of allyl groups at the surface of the microsphere responsible for crosslinking. Thus, the gelation is observed only under the polymerization condition in which the PAMA microspheres collide each other. First, we pursued the critical polymerization condition under which the gelation would be observed. Figure 11 shows the conversion-time curves for the

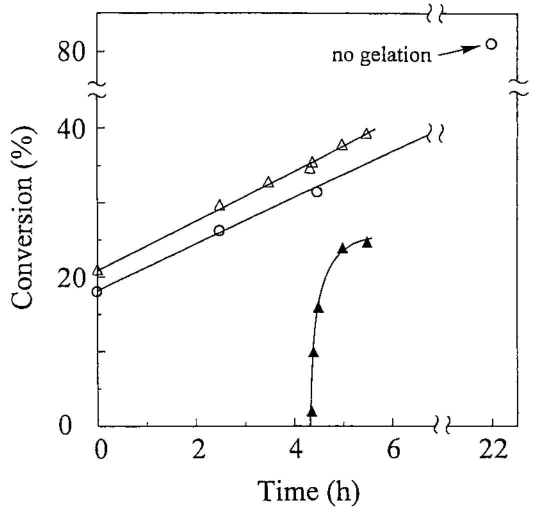

Figure 11. Conversion-time curves for the bulk copolymerizations of ABz with (○) 18 and (△ , ▲) 21 wt% of **I** using 0.05 mol/L of BPO at 80℃. Open and full symbols correspond to total and gel polymers, respectively.

copolymerizations of ABz with 18 and 21 wt% of **I**. The gel point was estimated to be 34.5% for the copolymerization with 21 wt% of **I**, although no gelation occurred for 18 wt% of **I** even when the copolymerization proceeded until 82% conversion. The critical amount of **I** required for gelation would be roughly estimated to be ca. 20 wt% since the gelation was not observed even for the copolymerization of ABz with 19 wt% of **I**.

As an extension of the above discussion to pursue the critical polymerization condition leading to gelation, we tried to explore the copolymerization of ABz with PAMA microspheres **II** and **III** in place of **I** since the A_2 and $[\eta]$ values of three kinds of PAMA microspheres increased in the order **I** < **II** < **III** (see Table 1) as a reflection of crosslink density of microsphere. The lower the crosslink density, the easier the gelation. Thus, the copolymerizations were conducted under the same conditions and the gel points were estimated to be 21.8 and 11.3%, respectively, for the copolymerizations of ABz with 18 wt% of **II** and 9 wt% of **III**. The gelation was clearly promoted in the order **I** < **II** < **III**, being in conformity with our expectation.

In addition, we examined the effect of particle size on the gelation since the surface area of PAMA microsphere would increase with decreased particle size and thus, the probability of collision between PAMA microspheres should increase, leading to an easier gelation. Here PAMA microsphere **IV** was employed in place of **I** since **IV** has a smaller size than **I** and other properties of both microspheres **I** and **IV** are similar (see Table 1). The gel point was estimated to be 23.0% for the copolymerization of ABz with 18 wt% of **IV**; obviously, the gelation was promoted with decreased particle size, in contrast with the case that no gelation occurred for 18 wt% of **I**. These are in line with the above discussion that the gelation is observed only under the polymerization condition in which the PAMA microspheres collide each other.

Then, the resulting gels were examined as the increment of gel fraction with the progress of gelation. Beyond the gel point, the sol fraction was rapidly incorporated into the gel and its tendency became to a certain extent steeper from **I** to **III** as a reflection of decreased crosslink density of PAMA microsphere. In Figure 12, the swelling ratios of resulting gels were plotted against conversion. Here the conversion is corrected such as the corresponding gel point is 0% of conversion. The swelling ratio tended to decrease gradually with the progress of polymerization beyond the gel point. Moreover, the swelling ratios became relatively higher in the order **I** < **II** < **III**. These results would support the preferential incorporation of PAMA microsphere into the gel, demonstrating again the importance of the reaction of allyl groups present on the surface of microsphere in the copolymerization of PAMA microsphere with ABz.

Finally, we discussed briefly the polymerization characteristics of microgel-like PAMA microspheres by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of the resulting PAMA/ABz

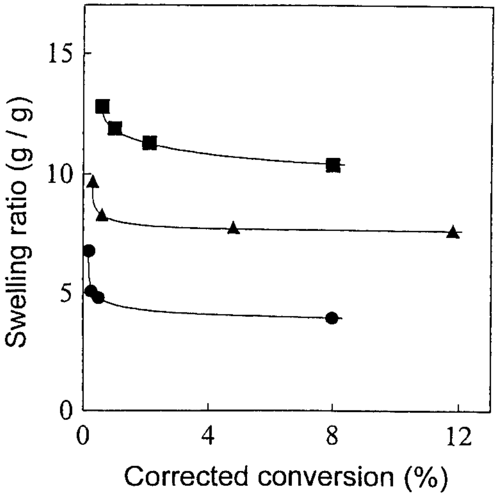

Figure 12. Decrease in swelling ratio of resulting gel in THF with the progress of polymerization beyond the gel point for the bulk copolymerizations of ABz with (●) 21, (▲) 18, and (■) 9 wt% of **I**, **II**, and **III**, respectively (see Figure 11).

copolymers clearly changed with conversion, i.e., the absorption peaks corresponding to the protons of unreacted pendant allyl groups were weakened with the progress of polymerization and, eventually, disappeared completely at 58% conversion, whereas those of benzene rings belonging to ABz units, present on the surface of microsphere, increased clearly with conversion.

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