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ARTICLE

Discussion of "Greatly Delayed Gelation from Theory in Free-Radical Cross-Linking Multivinyl Polymerization Accompanied by Microgel Formation" Based on Multiallyl Polymerization

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ABSTRACT: In free-radical cross-linking (co)polymerization of common multivinyl monomers it has been conceived that the greatly delayed gelation from theory is due to microgel formation. This was discussed by pursuing the gelation in free-radical cross-linking polymerization of diallyl terephthalate (DAT) in the coexistence of a preceded cross-linking polymerization of ethylene glycol dimethacrylate accompanied by *in situ* methacrylate network-polymer-precursor (NPP) formation since in DAT polymerization the primary-polymer-chain forming reaction could be controlled by the allylic hydrogen abstraction of growing polymer radical from allyl monomer, and thus, any gel effect inducing the complication of the polymerization system is not observed at all. Thus, the preceded *in situ* methacrylate NPP formation promoted the gelation, never leading to delayed gelation. The role of high-molecular-weight NPPs ranging from an ideal NPP to a nanogel-like NPP on the gelation in DAT polymerization was then pursued by SEC-MALLS-viscometry; the addition of high-molecular-weight NPPs clearly promoted the gelation, and strikingly, the role of nanogel-like NPP was never as an inactive polymer particle leading to a delayed gelation.

Introduction

An enormous number of studies of cross-linked or thermosetting resins have been accomplished since the invention of phenolic resins by Baekeland more than 100 years ago, but even now, the network formation mechanism and the fine structure of cross-linked resins are still controversial problems because of the complexity of the reactions involved and the insolubility of the products. In particular, the free-radical cross-linking (co)polymerization of multivinyl monomers are the cases. In 1941, the gelation theory was proposed by Flory.[1] Thereafter, Stockmayer applied Flory's procedure to the special case of chain cross-linking polymerization of symmetrical divinyl monomers, i.e., Flory–Stockmayer gelation theory (FS theory).[2] Then, the pioneering experimental works were immediately performed by Walling[3] and Simpson[4] separately. Walling attempted to apply FS theory to the gelation in free-radical cross-linking monovinyl/divinyl copolymerizations, typically including methyl methacrylate (MMA)/ethylene glycol dimethacrylate (EGDMA) copolymerization, and the greatly delayed gelation from theory was observed; this was explained qualitatively on the basis of the idea that the reaction mixture consists of discrete swollen polymer molecules. Simpson treated the gelation in diallyl phthalate (DAP) polymerization; the deviation of the actual gel point from the theoretical one was ascribed to the extensive occurrence of cyclization,[5] although Walling assumed minor significance of cyclization. However, it should be pointed out that each case corresponds to a particular solution, never a general solution, for gelation in free-radical cross-linking multivinyl polymerization. That is, the weight-average length of primary polymer chain as the most crucial factor for the estimation of the theoretical gel point[2] was quite long and depended on conversion for the former Walling's case by the occurrence of gel effect[6] due to reduced or inhibited bimolecular termination or chain-length-dependent termination,[7] whereas it was quite short for the latter Simpson's case by the occurrence of monomer chain transfer characteristic of allyl polymerization.[8]

Thereafter, many papers have been published, especially including EGDMA,[7b,9−18] divinylbenzene (DVB),[19−26] and diallyl dicarboxylates[16b,27−30] as typical divinyl monomers. The importance of cyclization leading to the formation of microgel-like particles has been emphasized.[31] The predictions of classical FS theory[2] have been tested for the establishment of a network by free-radical cross-linking polymerization.[18] The discussion on the cross-linking mechanism and the characterization of network microstructure have been extended to the development of kinetic gelation models.[32] The latter two research groups have dealt with the copolymerization of MMA with EGDMA, the historical copolymerization system which was first investigated in 1945 by Walling.[3] Similarly, styrene/DVB copolymers have been under investigation for more than 50 years because of their commercial importance as the resins for size-exclusion chromatography (SEC) and ion exchangers.

On the other hand, we have been concerned with the network formation in the free-radical cross-linking (co)polymerization of multivinyl monomers, especially those including diallyl esters and dimethacrylates, by focusing our attention on the mechanistic discussion of the deviation from FS theory.[33] That is, the reasons for the greatly delayed gelation in diallyl polymerizations were discussed mechanistically in detail, and then the discussion was satisfactorily extended to a deep understanding of network formation in common cross-linking multivinyl polymerizations. Notably, the most significant difference between multiallyl and multivinyl cross-linking polymerizations is in the length of the primary polymer chain which has a crucial influence on gelation as is evident from FS theory.[2] In diallyl polymerization only the

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oligomeric primary polymer chain is formed, and moreover, its length is advantageously kept constant because a well-known degradative monomer chain transfer[8] or allylic hydrogen abstraction of growing polymer radical is an essential chain-forming reaction in allyl polymerization.[34] This situation is completely different from an ordinary cross-linking multivinyl polymerization accompanied by the gel effect[6] which is induced as a result of reduced bimolecular termination, resulting in an enlargement of primary polymer chain length, eventually leading to microgel formation.[11,12,14,24,26,35,36] Therefore, the oligomerization of neopentyl glycol dimethacrylate, a sparingly cyclopolymerizable divinyl monomer, was conducted in bulk in the presence of lauryl mercaptan (LM) as a chain transfer agent in order to reduce the primary polymer chain length to a comparable order in diallyl polymerization.[37] The gelation behavior was compared with diallyl terephthalate (DAT) polymerization as a typical example of multiallyl polymerizations. Thus, no substantial difference was observed between multiallyl and multivinyl polymerizations in the case where the primary polymer chain lengths were adjusted to be comparable.

As is evident from the above discussion, the network formation through multiallyl polymerization or multivinyl oligomerization in the presence of a chain transfer agent apparently seems to be quite different from the ordinary cross-linking multivinyl polymerizations in the absence of a chain transfer agent leading to microgel formation. The most significant difference is in the primary-polymer-chain forming reaction. In the former case, the chain-forming reaction is controlled by the advantageous monomer chain transfer characteristic of allyl polymerization or the hydrogen abstraction of growing polymer radical from a chain transfer agent, keeping the primary polymer chain length constant, whereas the latter is not the case of controlled chain-forming reaction since a sterically hindered bimolecular termination between growing polymer radicals complicated by intermolecular and intramolecular cross-linkings induces the gel effect,[6] leading to an enlargement of the primary polymer chain length. That is, in free-radical cross-linking multiallyl polymerization, only oligomeric linear or looped NPP is formed at an early stage of polymerization, as completely opposed to the case of common cross-linking multivinyl polymerization where high-molecular-weight network polymer precursor (NPP) as highly swollen polymer molecule is presumed to be formed.[3,38] With the progress of polymerization, an enhanced occurrence of intermolecular cross-linking enlarges the NPP from a linear to a branched form. This branched NPP grows further to give highly branched NPP with conversion, and eventually gelation occurs as a result of indefinitely large-sized network polymer formation.[1] The structure of the highly branched NPP consisting of oligomeric primary polymer chains seems to be core−shell type dendritic or nanogel-like[39] as the tree model is proposed for network formation.[1] Thus, our mechanistic discussion of network formation based on multiallyl polymerization is in the category of a classical FS theory.[2] The validity of FS theory was confirmed by conducting the free-radical cross-linking monovinyl/divinyl copolymerizations[40] under the polymerization conditions in which the significance of the thermodynamic excluded volume effect and intramolecular cross-linking, the respective primary and secondary factors for the greatly delayed gelation,[33a] was removed; thus, the polymerization conditions were adjusted as follows: (a) a small amount of cross-linker and a high monomer concentration and (b) a small amount of chain transfer agent should be required to estimate a high theoretical gel point and to keep the primary polymer chain length constant, respectively. We extended the above discussion of network formation mechanism to the preparation of novel amphiphilic polymers,[41] as the precursors of the homogeneous cross-linked monovinyl/divinyl copolymers, and, furthermore, amphiphilic network polymers[42] biased toward the ideal network polymer governed by FS theory.

In the present article, we proceeded further to a deeper understanding of the inhomogeneous network polymer formation biased toward the microgel greatly deviated from FS theory. That is, as is well-known, microgel is usually formed before gel point conversion,[11,12,14,24,26,35,36] or a highly swollen polymer molecule is presumed to be formed even at an early stage of polymerization,[3,38] in common cross-linking multivinyl polymerization. However, the true nature of microheterogenization before the gel point conversion is not clarified yet, but still a lot of open questions remained with numerous speculations. Thus, the detailed experimental work should be required for a deeper understanding of microgel formation because the clarification of polymerization characteristics of microgel-like NPP is significantly related not only to the delayed gelation but also closely to the mechanical properties of cross-linked resin or thermoset. Since the weight-average length of primary polymer chain is crucial in the mechanistic discussion based on FS theory,[2] we need to focus on the real role of high-molecular-weight NPP on the gelation in free-radical cross-linking polymerizations of multivinyl monomers under controlled primary-polymer-chain forming reaction where there is no gel effect, i.e., without complicating the cross-linking polymerization system. Accordingly, the gelation in free-radical cross-linking polymerization of DAT as a typical multiallyl monomer governed by FS theory was explored as follows: (1) in the coexistence of a preceded cross-linking polymerization of EGDMA as a common multivinyl monomer accompanied by *in situ* methacrylate NPP formation and (2) in the presence of a variety of vinyl-type NPPs ranging from an ideal NPP to a nanogel-like NPP which were prepared separately. Here, the primary-polymer-chain forming reaction could be controlled by the allylic hydrogen abstraction of growing polymer radical from allyl monomer, and moreover, the real role of high-molecular-weight NPP on the gelation was pursued by size-exclusion chromatography (SEC) with both multiangle laser light scattering (MALLS) and viscosity detectors. Notably, SEC-MALLS-viscometry is a multidetection system providing not only the molecular-weight distributions but also the correlations of both the weight-average molecular weight versus elution volume and the intrinsic viscosity versus molecular weight of fractionated samples, being useful as a powerful tool for pursuing the reaction behavior of the high-molecular-weight NPP in the cross-linking polymerization system.

Experimental Section

Materials. Allyl benzoate (ABz), DAT (Daiso Co., Ltd., Osaka, Japan), benzyl methacrylate (BzMA), EGDMA (Kyoeisha Chemical Co., Ltd., Nara, Japan), MMA, and allyl methacrylate (AMA) (Wako Pure Chemical Industries, Ltd., Osaka, Japan) as monomers were purified by vacuum distillation under nitrogen. 2,2′-Azobis(isobutyronitrile) (AIBN) (Wako Pure Chemical Industries, Ltd.) and benzoyl peroxide (BPO) (Nippon Oil Co., Ltd., Aichi, Japan) as initiators were purified by conventional methods. Dioxane and methyl benzoate (MBz) (Wako Pure Chemical Industries, Ltd.) as solvents were purified by distillation. LM (Wako Pure Chemical Industries, Ltd.; extra pure reagent commercially available) as a chain transfer agent was used without further purification.

Polymerization. Polymerization was carried out in a glass ampule containing the required amounts of monomers, solvent, and initiator. The ampule was degassed three times by the usual freezing and thawing technique under a vacuum and then sealed off. It was then placed in a thermostat regulated at required temperatures. After a predetermined reaction time, the polymer was precipitated by pouring the reaction mixture into a large excess of hexane containing a small amount of 4-*tert*-butylpyrocatechol as

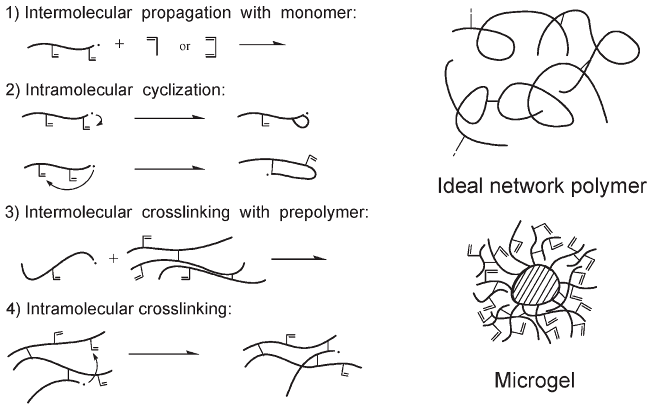

Figure 1. Reaction scheme for the network formation processes in the free-radical cross-linking monovinyl/divinyl copolymerization, forming two extreme structures of network polymers as an ideal network polymer and a microgel.

an inhibitor. The purification of the polymer was done by reprecipitation from a tetrahydrofuran (THF)−precipitant system. The gel fraction of the polymer at conversions beyond the gel point was separated by extracting the sol fraction with THF.

Measurements. The weight-average molecular weights (M_w), rms radii of gyration ($\langle S^2\rangle_z^{1/2}$), and second virial coefficients (A_2) of the resulting polymers were measured by light scattering (LS). The LS measurements were carried out in THF at 30 °C with an Otsuka Electronics DLS-7000 dynamic light scattering spectrophotometer over the angular range between 30° and 150°, using unpolarized light of a wavelength of 632.8 nm. The resulting polymers were also subjected to SEC-MALLS-viscosity measurement in order to estimate the correlation of intrinsic viscosities ($[\eta]$) versus M_w by SEC using a triple detector system set in the direction of flow. This system consisted of viscometer, MALLS device, and a differential refractometer in sequence. The SEC-MALLS-viscosity measurements were carried out at 40 °C in THF using a three-column Shodex GPC KF-806 L at polymer concentrations of 0.1−0.5% (w/v) and at a flow rate of 1 mL/min. The MALLS device was a DAWN model F (Wyatt Technology Corp., Santa Barbara, CA); the laser beam had a wavelength of 632.8 nm and was focused on a 67 μL flow cell. A Wyatt ViscoStar (Wyatt Technology Corp.) was employed as the viscometer.

Results and Discussion

Microgel Formation Leading to Delayed Gelation from FS Theory. As is discussed in the Introduction for multiallyl polymerization or multivinyl oligomerization in the presence of a chain transfer agent, we could simplify the ordinarily complicated reaction scheme for the network formation processes in free-radical cross-linking multivinyl polymerization under the condition where the primary-polymer-chain forming reaction is controlled. Typically, in a free-radical cross-linking monovinyl/divinyl copolymerization, the network formation processes essentially involve four reactions of a growing polymer radical (see Figure 1): intermolecular propagation with two types of monomer; intramolecular cyclization leading to the formation of ring or loop structures; intermolecular cross-linking with a preformed NPP to form an effective cross-link, eventually leading to the gel; and intramolecular cross-linking leading to the formation of multiple cross-links, the locally extensive occurrence of which would induce microgelation.

Then, the network structure of the resulting network polymer could be designed by controlling these elementary reactions. The intermolecular cross-linking is the key reaction for the control of gelation as the formation of three-dimensional network of indefinitely large size, whereas the key reaction for controlling the network structure is the intramolecular cross-linking that leads to the formation of multiple cross-links generating the net structure of the network polymer. As extreme cases, we can illustrate two typical structures of network polymers in Figure 1 as an ideal network polymer governed by FS theory and a microgel greatly deviated from the theory, although the structures of the actual network polymers would be between the two extreme cases. The present article is concerned with the latter microgel formation.

First, we may need to discuss briefly on microgelation.[33a] The intramolecular cross-linking could tend to occur locally because the formation of the cross-link unit induces the decrease of the interaction between polymer segment and solvent or the increase of the interaction between polymer chains leading to an enhanced occurrence of intramolecular cross-linking. Thus, the locally enhanced occurrence of intramolecular cross-linking accompanied by microsyneresis could lead to the formation of a microgel having a highly cross-linked microdomain which may induce microphase inversion. Here, the microgel is conceived as consisting of both core and shell parts of high and low cross-link densities, respectively, although it is soluble due to a strong interaction of the shell part with solvent overcoming the presence of the core part, just like a microsolid, having quite a weak interaction with the solvent. That is, it is a highly shrunken molecule having a much lower interaction with the solvent as compared with a linear polymer of the same molecular weight. This molecular size shrinkage and lowered interaction force will be reflected as the lowering of $\langle S^2\rangle_z^{1/2}$ and A_2, respectively.

A deep understanding of microgel formation up to the gel-point conversion is very important for the elucidation of three-dimensional network formation mechanism and molecular design of network polymers with high performance and high functionality. However, the true nature of microheterogenization before gelation is not clarified yet, and the detailed experimental work is still required. Here it should be recalled that the gelation occurs as a result of indefinitely large-sized network polymer formation, or it is induced by the formation of the gel that is insoluble in all solvents. In other words, the molecular-weight distribution of NPP obtained in the multivinyl polymerization would be broadened with conversion as a result of a stepwise occurrence of intermolecular cross-linking between primary polymer chains, and some chains would be significantly larger than the number-averaged ones. Eventually, a high-molecular-weight NPP reaches an indefinitely large-sized network polymer that induces gelation. As a matter of course, the relative extensiveness of the occurrence of intramolecular cross-linking between different primary polymer chains would change the high-molecular-weight NPP form from a highly swollen ideal-network-polymer-like to a shrunken tiny microgel-like (see Figure 1). Thus, since in the discussion of gelation the intermolecular cross-linkability of high-molecular-weight NPP should play a crucial role, the main purpose of the present work is to discuss experimentally the real role of high-molecular-weight NPP on the network formation in free-radical cross-linking multivinyl polymerization, especially focused on the gelation.

Does a Discrete Swollen Polymer Molecule Formed at an Early Stage of Cross-Linking Multivinyl Polymerization Inevitably Delay the Gelation? Always, the pioneering work will give us a strong impact: As mentioned in the Introduction, Walling[3] attempted to apply FS theory, first, to the gelation in free-radical cross-linking monovinyl/divinyl copolymerizations, and the greatly delayed gelation from

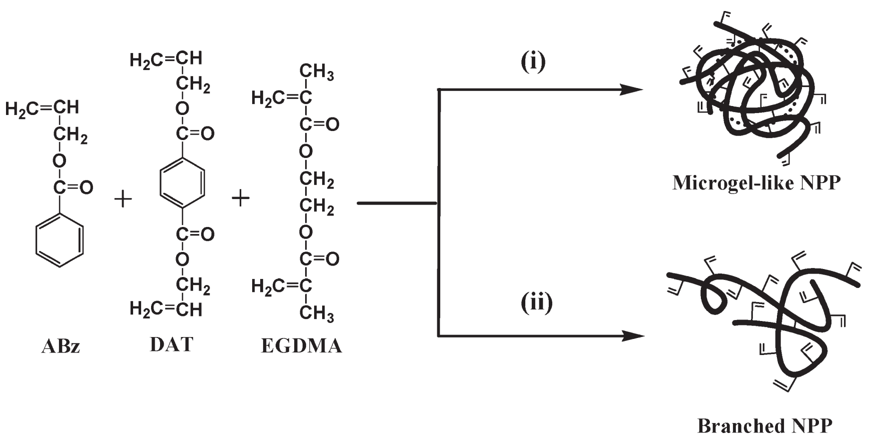

Figure 2. Cross-linking ABz/DAT/EGDMA terpolymerization accompanied by a preceded microgel-like or branched methacrylate NPP formation in the presence of (i) a rather large amount or (ii) a small amount of EGDMA.

theory was observed. This was explained qualitatively on the basis of the idea that the reaction mixture consists of discrete swollen polymer particles, originating in the following solvent effect on gelation. The solution copolymerizations of MMA with EGDMA were carried out in benzene and ethyl acetate, and the gelation was clearly delayed in ethyl acetate as a poor solvent. In order to interpret the results, the reaction mixture is pictured as consisting of polymer molecules as discrete masses or spheres, highly swollen by, and floating in, the solvent, the rate of diffusion of which is slow compared with the rate of polymer chain growth. As polymerization proceeds, new spheres are continuously generated. Cross-linking of polymer molecules generally occurs by a growing sphere becoming attached to one which is already formed. Consequently, the swelling factor of the sphere significantly influences the occurrence of cross-linking, thus leading to the delayed gelation in a poor solvent as a result of the reduction in the swelling factor.

In contrast, our mechanistic discussion[33a] on the reasons for the greatly delayed gelation in free-radical cross-linking multivinyl polymerizations demonstrated the significance of the thermodynamic excluded volume effect on the intermolecular cross-linking reaction between growing polymer radical and NPP, especially at high molecular weight; this will be extended to the expectation that the gelation should be delayed in a good solvent as opposed to Walling's result. Notably, in Walling's experiments the gel point was taken as the point when a bubble would no longer rise in the solution, and the primary polymer chain length was approximated by the degree of polymerization of poly(MMA) obtained under the same polymerization conditions although the molecular weight was determined viscometrically. In this connection, Flory pointed out that the values used by Walling for the weight-average degree of polymerization are unfortunately unreliable.[43]

So we rechecked the gelation in the same copolymerization system: The gel point was determined from the gel formation curve obtained by the sol–gel fractionation, and the primary polymer chain length was estimated by extrapolating the conversion dependence of the weight-average molecular weight, measured by light scattering, of NPP to zero conversion. We reached the conclusion that the gelation was clearly delayed in a good solvent as a result of the thermodynamic excluded volume effect.[44]

Cross-Linking Multiallyl Polymerization Preceded by *in Situ* Microgel-like Methacrylate NPP Formation.[45] As mentioned in the Introduction, the gelation behavior of free-radical cross-linking multiallyl polymerization is completely opposite to the case of common multivinyl polymerization. Thus, the combination of both cross-linking polymerization systems could provide us useful information for a deep understanding of network formation in free-radical cross-linking multivinyl polymerization. First, we tried to pursue the gelation behavior in free-radical cross-linking ABz/DAT/EGDMA terpolymerization. One of the reasons why this terpolymerization system was chosen is based on our previous experimental result that ABz/DAT copolymerization is governed by FS theory.[40a] As another reason, the coexistence of EGDMA polymerization is expected to induce a preceded *in situ* methacrylate NPP formation. Since the copolymerizability of allyl monomer (M_1) with methacrylate monomer (M_2) is very poor (DAP(M_1)/MMA(M_2) copolymerization:[46] $r_1 = 0.057$ and $r_2 = 35.0$ at 80 °C), the preceded EGDMA cross-linking polymerization could produce *in situ* a microgel-like (or nanogel-like) NPP. Figure 2 depicts schematically a preceded methacrylate NPP formation at an early stage of polymerization: (i) in the presence of a rather large amount of EGDMA, the microgel-like NPP formation occurs easily, whereas (ii) in the presence of a small amount of EGDMA, microgelation does not occur and, instead, branched poly(ABz-*co*-DAT-*co*-EGDMA)-NPP with rather longer primary polymer chains could be formed.

Thus, we can check whether the microgelation leads to the delayed gelation[3,38] or not. In addition, whether the methacrylate NPP with enlarged primary polymer chains promotes the gelation or not will be another interesting research subject.

Figure 3 shows the dependence of gel point on EGDMA content for free-radical cross-linking ABz/DAT/EGDMA (molar ratio ABz/DAT = 95/5) terpolymerizations with different amounts of EGDMA as a typical example.

Here terpolymerization was carried out in bulk in a total volume of 5 mL of three monomers using 0.2 mol/L BPO at 80 °C. Gelation was promoted with an increase in EGDMA content, and notably, the drastic change was observed when the addition of EGDMA reached close to 3 mol %. With more than 3 mol % of EGDMA, the gel point became less than 10%, and also the reaction mixture became turbid before gelation. These results clearly demonstrate a preceded *in situ* microgel-like methacrylate NPP formation in the presence of a rather large amount of EGDMA as we expected. Then, the cross-linking ABz/DAT/EGDMA (molar ratio ABz/DAT = 90/10) terpolymerizations were examined in more detail, and thus, the cross-linking terpolymerization processes were summarized roughly as follows. With more than 3 mol % of EGDMA, the cross-linking EGDMA

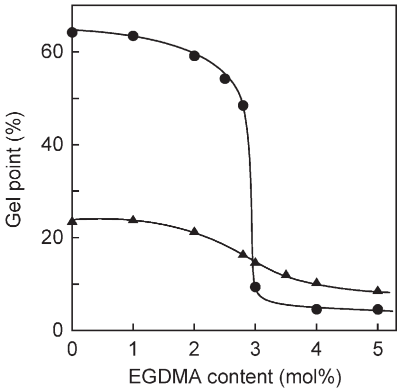

Figure 3. Dependence of gel point on EGDMA content in free-radical cross-linking (●) ABz/DAT/EGDMA (molar ratio ABz/DAT = 95/5) terpolymerizations and (▲) DAT/EGDMA copolymerizations under the following polymerization conditions: in bulk, [BPO] = (●) 0.2 and (▲) 0.1 mol/L, 80 °C.

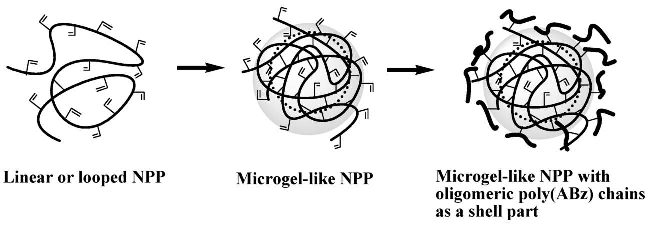

Figure 4. A rough sketch of cross-linking ABz/EGDMA copolymerization processes leading to the formation of nanogel- or microgel-like methacrylate NPP.

polymerization preferentially occurred to induce *in situ* microgel-like methacrylate NPP formation. Then, the microgel-like NPPs could collide each other, eventually leading to the gelation. On the contrary, with less than 3 mol % of EGDMA, the preceded *in situ* microgelation could not occur, and instead, poly(ABz-*co*-DAT-*co*-EGDMA)-NPP with rather longer primary polymer chains was formed, leading to the promoted gelation. In conclusion, the preceded *in situ* methacrylate NPP formation promoted the gelation in ABz/DAT(90/10) copolymerization, never leading to the delayed gelation.

Next, we tried to characterize in more detail microgel-like methacrylate NPPs mentioned above. Here, the cross-linking ABz/EGDMA copolymerization was chosen in order to simplify the cross-linking ABz/DAT/EGDMA terpolymerization system consisting of two types of cross-linkers, EGDMA and DAT, by removing the cross-linking reaction via DAT. We may illustrate roughly the cross-linking ABz/EGDMA copolymerization processes under the controlled chain-forming reaction due to monomer chain transfer to ABz in Figure 4.

At the initial stage of polymerization a linear poly(ABz-*co*-EGDMA)-NPP or looped poly(ABz-*co*-EGDMA)-NPP formed through intramolecular cyclization with abundant pendant methacryloyl groups is obtained. With the progress of polymerization, an enhanced occurrence of intramolecular cross-linking preceded by intermolecular cross-linking leads to the formation of microgel-like NPP with abundant pendant methacryloyl groups. This microgel-like NPP grows further by the copolymerization with ABz, where methacryloyl groups at the surface of microgel-like NPP can copolymerize with ABz to form the shell part consisting of oligomeric poly(ABz) chains. The resulting microgel-like NPP with a microsolid-like core has a poor interaction with ABz monomer as solvent, and thus, these can collide each other, eventually leading to the gelation. This system may be useful for pursuing *in situ* methacrylate microgel formation. Thus, the characterization of microgel-like methacrylate NPPs obtained by the cross-linking ABz/EGDMA copolymerization was done by SEC-MALLS-viscometry. The intrinsic viscosity ratio, $[\eta]_{\mathrm{NPP}}/[\eta]_{\mathrm{Linear}}$, that the $[\eta]$ values of NPPs were divided by those of the corresponding linear poly(vinyl benzoate) with a same molecular weight, as a measure of branching,[47] tended to decrease with an increase in EGDMA content. The structures of microgel-like methacrylate NPPs obtained at a rather high content of EGDMA were typically exemplified by the lowest $[\eta]_{\mathrm{NPP}}/[\eta]_{\mathrm{Linear}}$ values of methacrylate NPPs (molar ratio ABz/EGDMA = 98/2 and 96.9/3.1) obtained at 5.6 and 4.7% conversions reached 0.086 and 0.035 ($M_w = 2.98 \times 10^6$ and 9.04×10^6), respectively. Also, microgel-like NPP formation was confirmed by light scattering measurement, being reflected as the lowering of $\langle S^2 \rangle_z^{1/2}$ and A_2 values.

Considering the results obtained above, DAT was then copolymerized with EGDMA. Gelation was clearly promoted by the addition of EGDMA (see Figure 3), i.e., by a preceded *in situ* methacrylate NPP formation. Especially, more than 3 mol % of EGDMA, interestingly, the gel point of DAT/EGDMA system is higher than that of ABz/DAT/EGDMA system. Notably, the gel formation curves were not specific compared with ABz/DAT/EGDMA terpolymerization. That is, in the case of ABz/DAT/EGDMA terpolymerization, when a large amount of EGDMA were added, gel conversion did not increase beyond the gel point because the microgel particles formed at the early stage of polymerization collided each other to form aggregate. In contrast, in DAT/EGDMA copolymerization, even when a large amount of EGDMA was added, the gel conversion increased with the progress of polymerization beyond the gel point, being similar to the case of DAT homopolymerization. Thus, as a matter of course, cross-linking EGDMA polymerization preferentially occurs to induce a preceded *in situ* microgel-like methacrylate NPP formation with more than 3 mol % of EGDMA even in DAT/EGDMA copolymerization. However, the characteristic feature of DAT/EGDMA copolymerization is to introduce poly(DAT) chains with abundant allyl groups at the surface of microgel-like NPP in place of poly(ABz) chains for ABz/EGDMA copolymerization (see Figure 4). So, the interaction of microgel-like methacrylate NPP with DAT as solvent would be improved with the progress of polymerization, and instead, the collision between microgel-like NPPs could be suppressed, leading to the delayed gelation. On the other hand, any preceded *in situ* microgelation did not occur by adding less than 3 mol % of EGDMA. Instead, poly(DAT-*co*-EGDMA)-NPP with enlarged primary polymer chains was formed, leading to the promoted gelation. In conclusion, the preceded *in situ* methacrylate NPP formation promoted again the gelation in DAT polymerization. Now, we may illustrate roughly the cross-linking DAT/EGDMA copolymerization process as is depicted in Figure 5.

At an early stage of polymerization microgel-like particles would be formed. The tiny particle has abundant pendant methacryloyl and allyl groups in the shell part or at the surface of particle, and so the particle can easily copolymerize with DAT, leading to the promoted gelation.

Promoted Gelation in DAT Polymerization by the Addition of High-Molecular-Weight NPP with Pendant Methacryloyl Groups. As is evident from the above discussion, the preceded *in situ* methacrylate-NPP formation promoted the gelation in DAT polymerization, never leading to the delayed gelation even when microgelation occurred. In order to

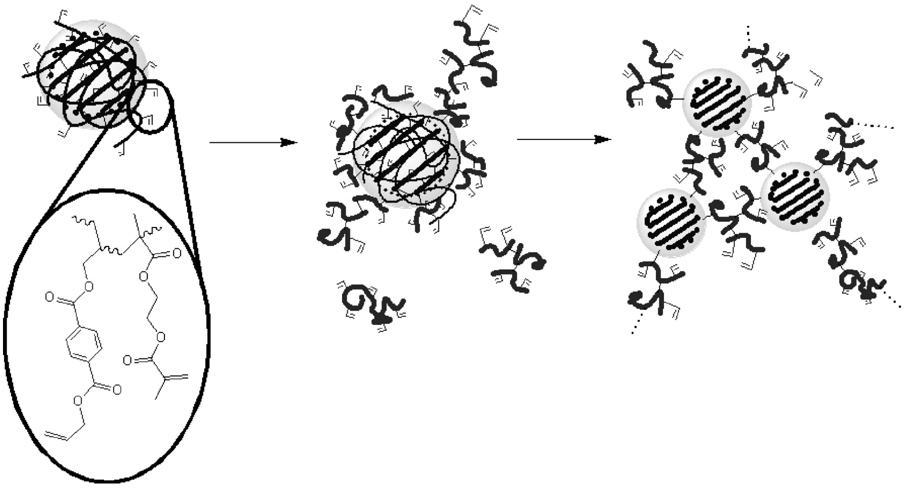

Figure 5. A rough sketch of cross-linking DAT/EGDMA copolymerization processes leading to the promoted gelation.

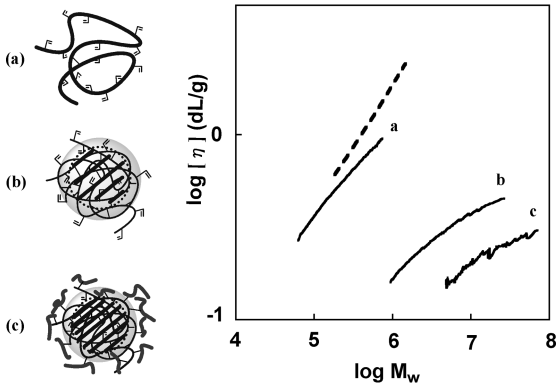

Figure 6. Images of three types of methacrylate-NPPs with pendant methacryloyl groups, i.e., (a) looped NPP, $\mathbf{A}_{\mathrm{Me}}$, (b) nanogel-like NPP, $\mathbf{B}_{\mathrm{Me}}$, and (c) nanogel-like NPP, $\mathbf{C}_{\mathrm{Me/ABz}}$, with poly(ABz) chains at the surface of particle and their double-logarithmic plots of [η] versus M_w, along with a dotted line of linear polystyrene.

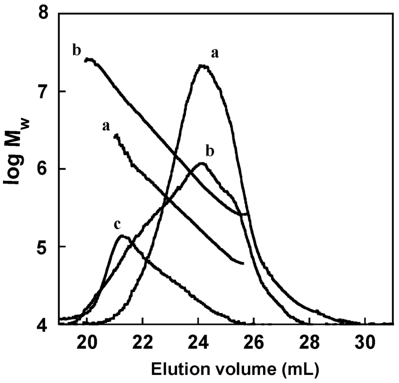

Figure 7. RI-monitored SEC curves and correlations of M_w versus elution volume (see Figure 6).

discuss in more detail the real role of high-molecular-weight NPP on the gelation in free-radical cross-linking multivinyl polymerization, the gelation in DAT polymerization was explored in the presence of a variety of vinyl-type NPPs ranging from an ideal NPP to a nanogel-like NPP as is illustrated in Figure 6.

First, three types of methacrylate NPPs with pendant methacryloyl groups, i.e., (a) looped NPP ($\mathbf{A}_{\mathrm{Me}}$), (b) nanogel-like NPP ($\mathbf{B}_{\mathrm{Me}}$), and (c) nanogel-like NPP with poly(ABz) chains at the surface of particle ($\mathbf{C}_{\mathrm{Me/ABz}}$), were prepared separately according to the aforementioned procedure[45] as follows: (a) MMA/BzMA/EGDMA (66/30/4) terpolymerization was conducted in MBz at a dilution of 1/5 using 0.02 mol/L AIBN in the presence of LM ([LM]/[total monomer] = 1/750) for 30 min at 50 °C, providing crude looped NPP obtained at 5.9% conversion. The recovered looped NPP was fractionated into three fractions from the THF−methanol system, and then, the middle fraction was collected to provide $\mathbf{A}_{\mathrm{Me}}$. (b) Similarly, MMA/BzMA/EGDMA (66/30/4) terpolymerization was conducted in MBz at a dilution of 1/8 for 50 min, providing crude nanogel-like NPP obtained at 11.8% conversion. The recovered nanogel-like NPP was subjected to a similar fractionation to give the corresponding middle fraction as $\mathbf{B}_{\mathrm{Me}}$. (c) MMA/BzMA/EGDMA (60/30/10) terpolymerization was similarly conducted in MBz at a dilution of 1/8 for 50 min, providing nanogel-like NPP obtained at 12.5% conversion. The fractionation of the recovered nanogel-like NPP was performed similarly to give the middle fraction which was subsequently subjected to the post-copolymerization with abundant ABz monomer (feed ratio (w/w) NPP/ABz = 1/99) using 0.1 mol/L BPO for 60 min at 80 °C; thus, the nanogel-like NPP with poly(ABz) chains at the surface of particle, $\mathbf{C}_{\mathrm{Me/ABz}}$, was obtained at 7.4% ABz conversion. The structural specificities of $\mathbf{A}_{\mathrm{Me}}$, $\mathbf{B}_{\mathrm{Me}}$, and $\mathbf{C}_{\mathrm{Me/ABz}}$ thus obtained were confirmed by the corresponding correlation lines of [η] versus M_w as a reflection of the remarkably reduced viscosities from $\mathbf{A}_{\mathrm{Me}}$ to $\mathbf{B}_{\mathrm{Me}}$ and to $\mathbf{C}_{\mathrm{Me/ABz}}$ as shown in Figure 6. Also, Figure 7 shows RI-monitored SEC curves and the correlations of M_w versus elution volume; notably, the correlation line shifted upward with the change of NPP structure from (a) looped to (b) particle-like.

Here it should be recalled that the intrinsic viscosity ratio, $[\eta]_{\mathrm{NPP}}/[\eta]_{\mathrm{Linear}}$, is well-known as a measure of branching.[47] Therefore, the [η] values of NPPs were divided by those of the corresponding linear polystyrene with a same molecular weight, and then, the ratios were plotted against M_w in Figure 8.

The remarkably reduced intrinsic viscosity ratios, less than 0.1, for $\mathbf{B}_{\mathrm{Me}}$ and $\mathbf{C}_{\mathrm{Me/ABz}}$ are in conformity with our expectation that the structures of $\mathbf{B}_{\mathrm{Me}}$ and $\mathbf{C}_{\mathrm{Me/ABz}}$ would be nanogel-like. Furthermore, ^{1}H NMR spectra of three types of methacrylate-NPPs were tentatively compared; the spectrum intensity assignable to backbone methyl protons became clearly weak for the nanogel-like NPP as a reflection of restricted motion of polymer chains embedded in the core part as a nanosolid.

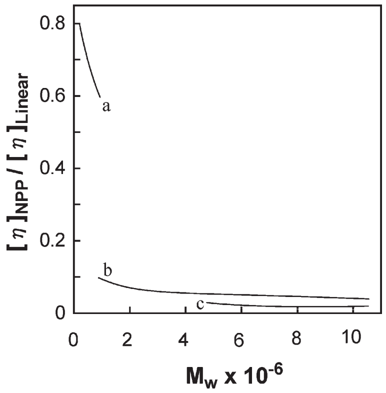

Figure 8. Plots of $[\eta]_{\mathrm{NPP}}/[\eta]_{\mathrm{Linear}}$ versus M_w (see Figure 6).

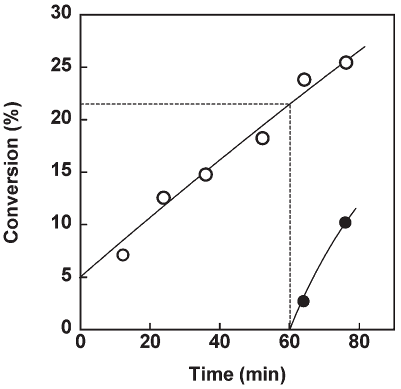

Figure 9. Conversion versus time curves for the solution DAT polymerization in MBz at a dilution of 1/2 in the presence of 5 wt % of looped NPP, $\mathbf{A}_{\mathrm{Me}}$, using 0.1 mol/L BPO at 80 °C. Open and filled symbols correspond to total and gel polymers, respectively.

Then, the addition effect of two types of methacrylate NPPs, i.e., $\mathbf{A}_{\mathrm{Me}}$ and $\mathbf{B}_{\mathrm{Me}}$, on the gelation in DAT polymerization were explored in MBz at a dilution of 1/2 using 0.1 mol/L BPO at 80 °C. As a typical example, Figure 9 shows the conversion versus time curves for the solution DAT polymerization in the presence of 5 wt % of $\mathbf{A}_{\mathrm{Me}}$, and the percentages of gel polymer are also plotted.

Notably, no gel effect[6] was observed, even beyond the gel point. The gel point was estimated to be 21.4%, being much lower than the gel point of 40.5% for the corresponding solution DAT polymerization without $\mathbf{A}_{\mathrm{Me}}$. Thus, gelation was clearly promoted by the addition of $\mathbf{A}_{\mathrm{Me}}$. Figure 10 shows the variation of SEC curves with conversion; clearly, the addition of $\mathbf{A}_{\mathrm{Me}}$ contributed significantly to the enhanced occurrence of intermolecular cross-linking leading to the gelation as a reflection of a broadened SEC curve toward a higher-molecular-weight side with conversion. Similarly, the addition of 5 wt % of $\mathbf{B}_{\mathrm{Me}}$ in the solution DAT polymerization promoted the gelation as the gel point was obtained to be 21.5%.

Figure 11 shows the addition effect of $\mathbf{B}_{\mathrm{Me}}$ that contributed significantly to the enhancement of intermolecular cross-linking leading to a promoted gelation in DAT polymerization. On the other hand, the addition of $\mathbf{C}_{\mathrm{Me/ABz}}$, i.e., nanogel-like NPP with poly(ABz) chains at the surface of particle, gave no influence on the gelation in DAT polymerization as is in line with our expectation.

Addition Effect of High-Molecular-Weight NPP with Pendant Allyl Groups. As is evident from the above discussion, the addition effect of methacrylate-NPPs or the crucial role of high-molecular-weight NPP on the free-radical cross-linking DAT polymerization was reflected by the promoted gelation. Here it should be recalled that two types of methacrylate NPPs, i.e., $\mathbf{A}_{\mathrm{Me}}$ and $\mathbf{B}_{\mathrm{Me}}$, have pendant methacryloyl groups as reactive sites for intermolecular cross-linking, but the polymerizability of methacryloyl groups is much higher than that of allyl groups. Thus, the promoted gelation may be predominantly attributable to the enhanced polymerizability of vinyl groups at the surface of particle but not to the high molecular weight of NPP.

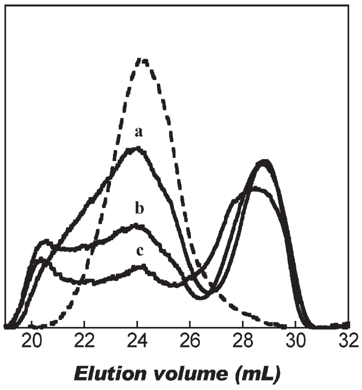

Figure 10. Variation of RI-monitored SEC curves with conversion (see Figure 9): (a) 7.0 (b) 12.2, and (c) 18.2%. Dotted line denotes an original looped NPP.

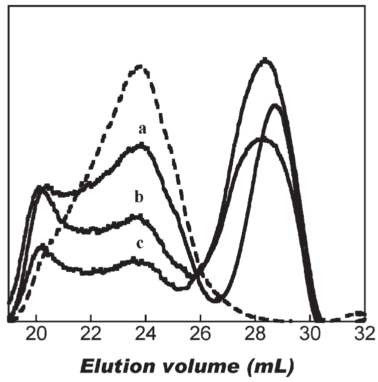

Figure 11. Variation of RI-monitored SEC curves with conversion ((a) 10.1, (b) 16.2, and (c) 20.7%) for the solution DAT polymerizations in MBz at a dilution of 1/2 in the presence of 5 wt % of nanogel-like NPP, $\mathbf{B}_{\mathrm{Me}}$, at 80 °C. Dotted line denotes an original nanogel-like NPP.

Now, we attempted to prepare two types of methacrylate NPPs with pendant allyl groups, i.e., (a′) looped NPP ($\mathbf{A'}_{\mathrm{Al}}$) and (b′) nanogel-like NPP ($\mathbf{B'}_{\mathrm{Al}}$), corresponding to $\mathbf{A}_{\mathrm{Me}}$ and $\mathbf{B}_{\mathrm{Me}}$, respectively, were prepared by partly using AMA in place of EGDMA as follows: (a′) MMA/BzMA/AMA/EGDMA (66/30/2/2) quaterpolymerization was conducted in MBz at a dilution of 1/5 using 0.02 mol/L AIBN in the presence of LM ([LM]/[total monomer] = 1/750) for 30 min at 50 °C, providing crude looped NPP obtained at 7.5% conversion. The recovered looped NPP was fractionated into three fractions from the THF−methanol system to collect the middle fraction as $\mathbf{A'}_{\mathrm{Al}}$, the SEC curve of which coincided with that of $\mathbf{A}_{\mathrm{Me}}$. (b′) Similarly, MMA/BzMA/AMA/EGDMA (66/30/2/2) quarterpolymerization was conducted in MBz at a dilution of 1/8, providing crude nanogel-like NPP obtained at 21.9% conversion. The recovered nanogel-like NPP was subjected to a similar fractionation to give $\mathbf{B'}_{\mathrm{Al}}$ as the corresponding middle fraction. The SEC curve of $\mathbf{B'}_{\mathrm{Al}}$ coincided with that of $\mathbf{B}_{\mathrm{Me}}$.

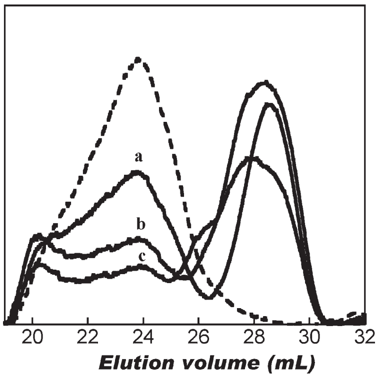

Figure 12. Variation of RI-monitored SEC curves with conversion ((a) 9.6, (b) 18.6, and (c) 23.6%) for the solution DAT polymerizations in MBz at a dilution of 1/2 in the presence of 5 wt % of nanogel-like NPP, $\mathbf{B}'_{\mathrm{Al}}$, at 80 °C. Dotted line denotes an original nanogel-like NPP.

Then, the addition effect of two types of methacrylate NPPs, i.e., $\mathbf{A}'_{\mathrm{Al}}$ and $\mathbf{B}'_{\mathrm{Al}}$, on the gelation in DAT polymerization were explored in MBz at a dilution of 1/2 using 0.1 mol/L BPO at 80 °C. Figure 12 shows a typical example of the results as the variation of SEC curves with conversion in the presence of 5 wt % of $\mathbf{B}'_{\mathrm{Al}}$; clearly, the addition of $\mathbf{B}'_{\mathrm{Al}}$ contributed significantly to the intermolecular cross-linking, leading to the promoted gelation, being similar to that of $\mathbf{B}_{\mathrm{Me}}$, although strictly speaking, a broadening tendency of SEC curve toward a higher molecular weight side with conversion was a bit less marked, shifting the gel point from 21.5% for $\mathbf{B}_{\mathrm{Me}}$ to 26.7% for $\mathbf{B}'_{\mathrm{Al}}$. In conclusion, the nanogel-like NPP clearly promoted the gelation in DAT polymerization, never leading to the delayed gelation.

Conclusions

The true nature of microheterogenization before the gel point conversion is not clarified yet, but still a lot of open questions remained. The detailed experimental work should be required for a deeper understanding of microgel formation because the clarification of polymerization characteristics of microgel-like NPP is significantly related not only to the delayed gelation but also closely to the mechanical properties of cross-linked resin. Since the weight-average length of primary polymer chain is crucial in the mechanistic discussion based on FS theory, the role of high-molecular-weight NPP on the gelation in free-radical cross-linking polymerizations of multivinyl monomers under controlled primary-polymer-chain forming reaction was pursued by SEC-MALLS-viscometry. Under the condition where the chain-forming reaction is controlled, we could simplify the ordinarily complicated reaction scheme for the network formation processes in multivinyl polymerization in which any gel effect inducing the complication of the cross-linking polymerization system is not observed at all. Since the gelation behavior of free-radical cross-linking multiallyl polymerization is completely opposite to the case of common multivinyl polymerization, both systems were combined to collect useful information for a deep understanding of network formation in free-radical cross-linking multivinyl polymerization. The gelation behavior in free-radical cross-linking ABz/DAT/EGDMA terpolymerization was pursued in order to check mainly whether the microgelation leads to the delayed gelation or not; thus, the preceded *in situ* methacrylate-NPP formation promoted the gelation, never leading to the delayed gelation. The gelation in free-radical cross-linking polymerization of DAT was examined in the coexistence of a preceded cross-linking polymerization of EGDMA accompanied by *in situ* methacrylate NPP formation; notably, the gel formation curves were not specific compared with ABz/DAT/EGDMA terpolymerization and ABz/EGDMA copolymerization. Gelation was clearly promoted by the addition of EGDMA, i.e., by a preceded *in situ* methacrylate NPP formation. Then, the role of high-molecular-weight NPPs ranging from an ideal NPP to a nanogel-like NPP on the gelation in DAT polymerization was pursued by SEC-MALLS-viscometry. Conclusively, the high-molecular-weight NPP clearly promoted the gelation, never acting as an inactive polymer particle leading to a delayed gelation.

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