DOI: 10.1002/masy.201000124

Molecular Design of Core-Shell Type Allylic Nanoparticles Based on Crosslinking Multiallyl/Multivinyl Copolymerizations

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Summary: This article is referred to the clarification of polymerization characteristics of microgel-like network polymer precursor (NPP), closely related to the inhomogeneous polymer network formation, in the free-radical crosslinking (co)polymerization of multivinyl monomers. Firstly, the gelation in free-radical crosslinking allyl benzoate/diallyl terephthalate (DAT) copolymerization governed by Flory-Stockmayer gelation theory was explored in the presence of ethylene glycol dimethacrylate (EGDMA) as a typical multivinyl monomer. Since the copolymerizability of allyl monomer with methacrylate monomer is very poor, the crosslinking EGDMA polymerization accompanied by in situ nanogel- or microgel-like methacrylate-NPP formation was preceded. Secondly, DAT polymerization was carried out with in situ inhomogeneous network formation by a preceded crosslinking EGDMA polymerization. The structures of resulting NPPs were characterized by SEC-MALLS-viscometry. Here, the preceded *in situ* methacrylate-NPP formation promoted the gelation, never leading to delayed gelation. Finally, our aforementioned discussion was extended to the preparation of novel core-shell type allylic nanoparticles based on crosslinking multiallyl/multivinyl copolymerizations.

Keywords: core-shell type allylic nanoparticle; crosslinking; gelation; multiallyl monomer; multivinyl monomer; nanogel-like network polymer precursor

Introduction

As part of our continuing studies concerned with the elucidation of network formation mechanism in free-radical crosslinking (co)polymerization of multivinyl monomers,[1,2] the present work is referred to the microgel formation because the clarification of polymerization characteristic of microgel- or nanogel-like network polymer precursor (NPP) in crosslinking multivinyl polymerization is significant in connection with the inhomogeneous polymer network formation as closely related to the mechanical properties of crosslinked polymer or thermoset. As our discussion has been based on a classical Flory-Stockmayer gelation theory (FS theory),[3,4] the validity of FS theory was confirmed by conducting the free-radical crosslinking monovinyl/divinyl copolymerizations under the polymerization conditions in which the significance of the thermodynamic excluded volume effect and intramolecular crosslinking as the primary and secondary factors, respectively, for the greatly delayed gelation was removed.[5–8] Thus, we could simplify the ordinarily complicated reaction scheme for the network formation processes in multivinyl polymerization under the controlled primary-polymer-chain forming reaction. The intermole-

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cular crosslinking is the key reaction for controlling the gelation, whereas the key reaction for controlling the network structure is the intramolecular crosslinking. As extreme cases, we can depict two typical structures of crosslinked polymers as an ideal network polymer governed by FS theory[4] and a microgel[9] greatly deviated from the theory. The idea of designing core-shell type allylic nanoparticles originated in the clarification of polymerization characteristics of microgel-like NPP.[2,10] Thus, considering the great difference in polymerizability between multiallyl and multivinyl monomers, we attempted to molecular-design novel core-shell type allylic nanoparticles through crosslinking multiallyl/multivinyl copolymerizations where the essential crosslinking multiallyl polymerization proceeded in the coexistence of a preceded crosslinking multivinyl polymerization accompanied by *in situ* nanogel-like NPP formation and the termination would be controlled by degradative monomer chain transfer characteristic of allyl polymerization.[11] Notably, the resulting core-shell type allylic nanoparticles were characterized by SEC with both multi-angle laser light scattering (MALLS) and viscosity detectors, providing not only the molecular-weight distribution but also the correlation of both the weight-average molecular weight (M_w) versus elution volume and the intrinsic viscosity ([η]) versus M_w of fractionated sample.

Experimental Part

Materials

Allyl benzoate (ABz), diallyl terephthalate (DAT), diallyl phthalate (DAP) (Daiso Co., Ltd., Osaka, Japan), ethylene glycol dimethacrylate (EGDMA) (Kyoeisha Chemical Co., Ltd., Nara, Japan), styrene (St), and divinylbenzene (DVB) (Wako Pure Chemical Industries, Ltd., Osaka, Japan) as monomers were purified by vacuum distillation under nitrogen. Benzoyl peroxide (BPO) (Nippon Oil Co., Ltd., Aichi, Japan) as an initiator was purified by a conventional method. Methyl benzoate (MBz) (Wako Pure Chemical Industries, Ltd.) as a solvent was purified by distillation.

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 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. Here the conversion is calculated on monomer basis.

Measurements

The resulting polymers were also subjected to SEC-MALLS-viscosity measurement in order to estimate the correlation of [η] 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-806L 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, U.S.A.); 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

Characteristic of Multiallyl Polymerization Compared with Common Multivinyl Polymerization

We have been concerned with the network formation in the free-radical crosslinking (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.[1,12] 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 crosslinking multivinyl polymerizations. Notably, the most significant difference between crosslinking multiallyl and multivinyl polymerizations is in the length of the primary polymer chain which has a most crucial influence on gelation as is evident from FS theory.[4] In diallyl polymerization only the oligomeric primary polymer chain is formed and, moreover, its length is advantageously kept constant because a well-known degradative monomer chain transfer[11] or allylic hydrogen abstraction of growing polymer radical is an essential chain-forming reaction in allyl polymerization.[13] This situation is completely different from a common crosslinking multivinyl polymerization accompanied by the gel effect[14] which is induced as a result of reduced bimolecular termination, resulting in an enlargement of primary polymer chain length, eventually leading to microgel formation.[9,15–22] Thus, the most significant difference between crosslinking multiallyl and multivinyl polymerization mechanisms is in the termination reaction. In the former case, the termination is controlled by the advantageous monomer chain transfer, whereas the latter is not the case of controlled termination because of a sterically hindered bimolecular termination between growing polymer radicals complicated by intermolecular and intramolecular crosslinkings. That is, in free-radical crosslinking multiallyl polymerization, only oligomeric linear or looped NPP is formed at an early stage of polymerization, as completely opposed to the case of common crosslinking multivinyl polymerization where high-molecular-weight NPP as highly swollen polymer molecule is presumed to be formed.[23,24]

Based on the above discussion, we proceeded to a deep understanding of the inhomogeneous polymer network formation biased toward the microgel greatly deviated from FS theory as follows: First, the gelation in free-radical crosslinking ABz/DAT (95/5) copolymerization[5] governed by FS theory was examined in the coexistence of a preceded crosslinking polymerization of EGDMA as a typical multivinyl monomer accompanied by in situ nanogel- or microgel-like methacrylate-NPP formation. Here it is worthy to note that the termination reaction could be controlled by the allylic hydrogen abstraction of growing polymer radical from allyl monomer. Then, DAT polymerization was carried out with a preceded *in situ* inhomogeneous network formation by crosslinking EGDMA polymerization. Finally, our discussion will be extended to the preparation of novel core-shell type allylic nanoparticles through crosslinking DAP polymerization in the coexistence of a preceded crosslinking St/DVB copolymerization accompanied by *in situ* nanogel-like NPP formation.

Crosslinking ABz/DAT Copolymerization in the Coexistence of Preceded EGDMA Polymerization Cccompanied by *in situ* Methacrylate-NPP Formation

Here, we tried to pursue the gelation behavior in free-radical crosslinking ABz/DAT/EGDMA terpolymerization. Since the copolymerizability of allyl monomer (M_1) with methacrylate monomer (M_2) is very poor[25,26] ($r_1 = 0.057$ and $r_2 = 35.0$ at 80 °C), the preceded EGDMA crosslinking polymerization could produce a nanogel- or microgel-like NPP. Figure 1 shows the dependence of gel point on EGDMA content for free-radical crosslinking ABz/DAT/EGDMA (molar ratio ABz/DAT = 95/5) terpolymerizations with different amounts of EGDMA.

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

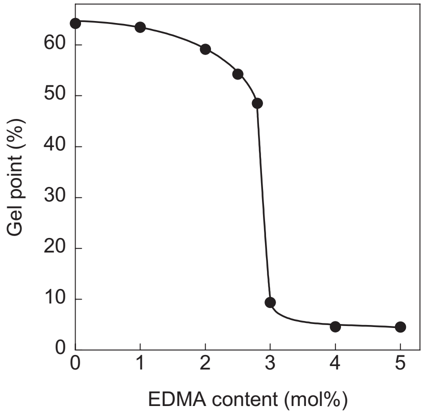

Figure 1.
Free-radical crosslinking ABz/DAT/EGDMA (molar ratio ABz/DAT = 95/5) terpolymerizations with different amounts of EGDMA (In bulk, [BPO] = 0.2 mol/L, 80 °C).

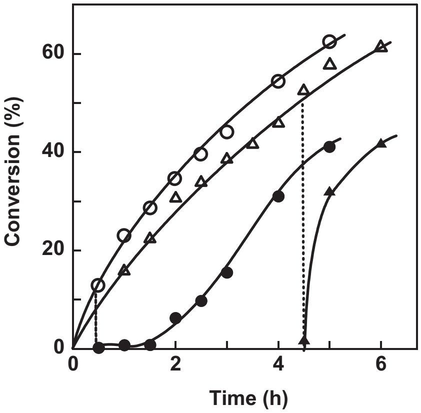

Figure 2.
Conversion versus time curves for (○,●) ABz/DAT/EGDMA(87.3/9.7/3) terpolymerizations and for (△,▲) ABz/DAT(90/10) copolymerizations (In bulk, [BPO] = 0.2 mol/L, 80 °C). Open and filled symbols correspond to total and gel polymers, respectively.

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.

Next, we examined in detail the crosslinking ABz/DAT(90/10) copolymerization in the presence of 3 mol% of EGDMA, i.e., ABz/DAT/EGDMA (87.3/9.7/3) terpolymerization. Figure 2 shows the conversion versus time curve along with the gel formation curve.

Clearly, gelation was promoted by adding 3 mol% of EGDMA and its gel formation curve was specific compared with ABz/DAT (90/10) copolymerization. Figure 3 shows the variation of SEC curves of sol fractions with conversion for the crosslinking ABz/DAT/EGDMA (87.3/9.7/3) terpolymerization beyond the gel point conversion.

The conversion dependency of SEC curves demonstrates that a higher-molecular-weight NPP, i.e., methacrylate-NPP was preferentially incorporated into the gel. By considering these results, we can summarize roughly the crosslinking ABz/DAT/EGDMA terpolymerization processes as follows. With more than 3 mol% of EGDMA, the crosslinking EGDMA polymerization preferentially occurred to induce *in situ* microgel-like methacrylate-NPP formation. Then, the microgel-like NPPs could collide with each other, eventually leading to gelation. On the contrary, with less than 3 mol% of EGDMA, the preceded *in situ* microgelation could not occur and instead, poly(ABz-co-EGDMA)-NPP with long primary polymer chains was formed, leading to a promoted gelation.

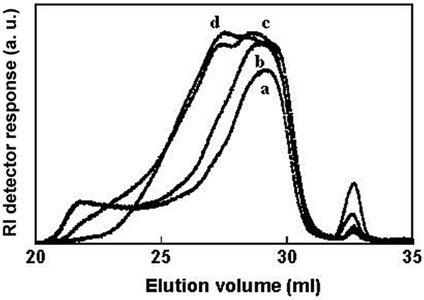

Figure 3.
Variation of RI-monitored SEC curves of sol fractions obtained beyond the gel point in ABz/DAT/EGDMA (87.3/9.7/3) terpolymerization: conversion (%), sol fraction (%); (a) 23.2, 96.7; (b) 28.8, 97.1; (c) 39.7, 75.3; (d) 44.1, 64.8.

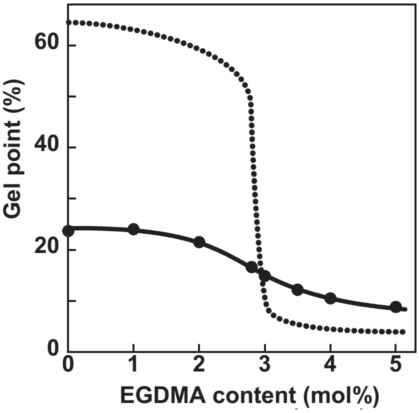

Figure 4.
Dependence of gel point on EGDMA content in DAT/EGDMA copolymerizations (In bulk, [BPO] = 0.1 mol/L, 80 °C). Dotted line corresponds to ABz/DAT/EGDMA terpolymerization (see Figure 1).

Crosslinking DAT/EGDMA Copolymerization Accompanied by a Preceded *in situ* Methacrylate-NPP Formation

Considering the results obtained above, DAT was copolymerized with different amounts of EGDMA. In Figure 4, the gel point was plotted against feed EGDMA content.

Although the gel point shifted toward a lower conversion with an increase in the EGDMA content, any drastic change was not observed as compared with the case of ABz/DAT/EGDMA terpolymerization as shown by dotted line. In addition, the gel points were obtained to be higher than those in ABz/DAT/EGDMA terpolymerizations by adding more than 3 mol% of EGDMA. Thus, in DAT/EGDMA copolymerization, crosslinking EGDMA polymerization preferentially occurred to induce a preceded *in situ* nanogel- or microgel-like methacrylate-NPP formation with more than 3 mol% of EGDMA. Characteristic feature of DAT/EGDMA copolymerization is to introduce poly(DAT) chains with abundant allyl groups at the surface of microgel-like NPP via the copolymerization with DAT. 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 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 long primary polymer chains was formed, leading to promoted gelation. Figure 5 illustrated roughly the cross-linking DAT/EGDMA copolymerization process.

At an early stage of polymerization, microgel-like particles would be formed. These tiny particles have abundant pendant methacryloyl and allyl groups in the shell parts or at their surfaces. So, the particles can easily copolymerize with DAT, leading to the promoted gelation.

Then, our aforementioned discussion was extended to the preparation of novel core-shell type allylic nanoparticles based on crosslinking multiallyl/multivinyl copolymerizations.

Molecular Design of Core-Shell Type Allylic Nanoparticles

Figure 6 demonstrates a rough guideline of the molecular design of core-shell type allylic nanoparticles.

The core part should be designed by the crosslinking (co)polymerizations of conjugated multivinyl monomers such as styryl and methacrylic monomers, while the shell part should be designed by those of unconjugated multivinyl monomers such as allylic and vinyl ester monomers. The most important point is the poor copolymerizability between two types of conjugated and unconjugated monomers. Thus, the preceded crosslinking (co)polymerizations of conjugated multivinyl monomers could make the core part, and the subsequent crosslinking (co)polymerizations of unconjugated multivinyl monomers could make the shell part. Here, considering the results obtained above, DAT or ABz/DAT monomer mixtures were replaced by DAP, and EGDMA was replaced by St/DVB mixtures because DAP, St, and DVB are commercially important monomers. Notably, the copolymerizability of allylic

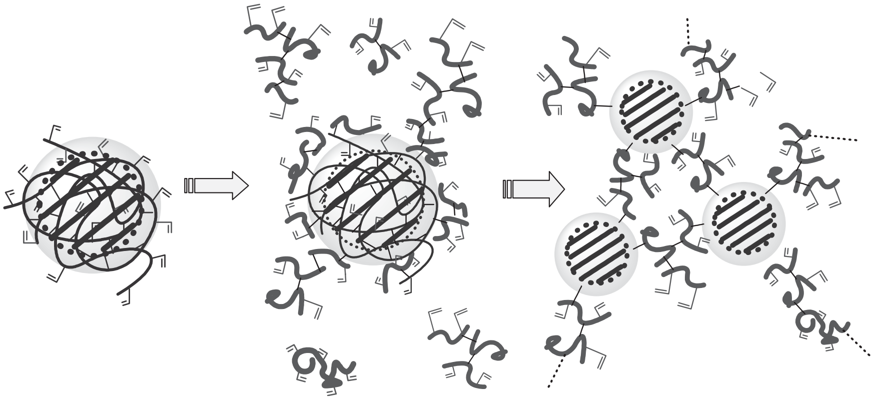

Figure 5.
A rough sketch of crosslinking DAT/EGDMA copolymerization process leading to the promoted gelation.

monomer with styryl monomer is poorer than that with methacrylic monomer,[26,27] leading to an easier construction of core part. Furthermore, the resulting St/DVB-core with a high hydrophobicity would be chemically more stable than the EGDMA-core with ester groups, providing novel amphiphilic nanoparticles by the saponification of poly(DAP) chains at the shell part to derive corresponding hydrophilic poly(allyl alcohol) ones.

Figure 7 shows RI-monitored SEC curves of NPPs obtained at an early stage (4.8%) and a late stage (33.3%) of polymerization in free-radical solution DAP/St/DVB (109/85/15) terpolymerization in MBz at a dilution of 1/3.

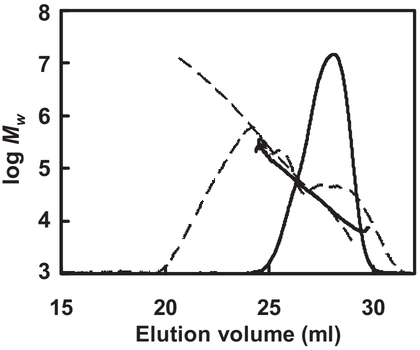

Figure 7.
RI-monitored SEC curve and correlation of M_w versus elution volume of NPPs obtained at (solid line) 4.8 and (broken line) 33.3% conversions for DAP/St/DVB (109/85/15) terpolymerization ([BPO] = 0.1 mol/L, 80 °C).

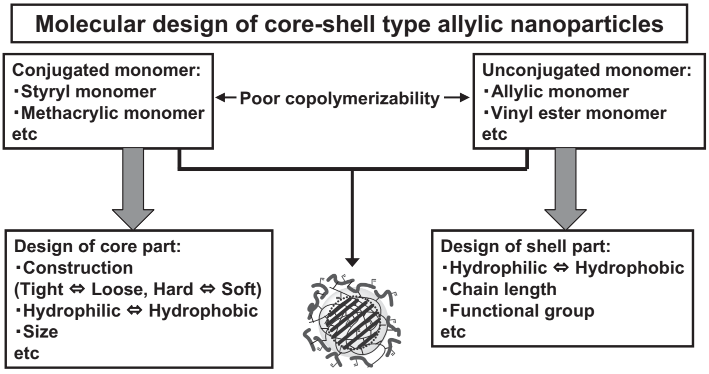

Figure 6.
A rough guideline of the molecular design of core-shell type allylic nanoparticles.

At an early stage of polymerization, the SEC curve of resulting NPP was unimodal by the preceded St/DVB copolymerization to make the core part. When the polymerization proceeded further, the SEC curve of the NPP obtained at a higher conversion was broadened toward a higher molecular weight side. This may be ascribed to the postcopolymerization of St/DVB-NPP with DAP that proceeds at the surface of St/DVB-NPP core.

The [η] values of resulting NPPs were lower than that of linear poly(St). Here it should be noted that the intrinsic viscosity ratio, $[\eta]_{NPP}/[\eta]_{Linear}$, is well-known as a measure of branching. In this connection, the [η] values of NPPs were divided by those of the corresponding linear poly(St) with a same molecular weight and then, they were plotted against M_w in Figure 8.

The intrinsic viscosity ratio tended to decrease with an increase in M_w. This is in conformity with our expectation that the structure of poly(St-co-DVB-co-DAP)-NPP obtained at a higher conversion would be core-shell type dendritic or nanogel-like. Furthermore, ABz/St/DVB and vinyl benzoate/St/DVB terpolymerizations, as well as DAP/St/DVB one, were carried out under various polymerization conditions to prepare various NPPs with different shell parts.

Finally, the surface modification of core-shell type allylic nanoparticle will be a bit discussed. Thus, the hydrophobic DAP/St/DVB-particle having poly(DAP) chains at the surface were chemically modified utilizing facile hydrolysis of ester groups of DAP units providing hydrophilic nanoparticle as follows. The ester groups belonging to poly(DAP) chains at the surface of nanoparticle were hydrolyzed to derive corresponding poly(allyl alcohol) chains. So, the surface property of nanoparticle changed from hydrophobic to hydrophilic, providing novel amphiphilic nanoparticles consisting of hydrophobic core part and hydrophilic shell part. Furthermore, our core-shell type allylic nanoparticles would be easily modified utilizing the reactivities of pendant allyl groups at their surfaces.

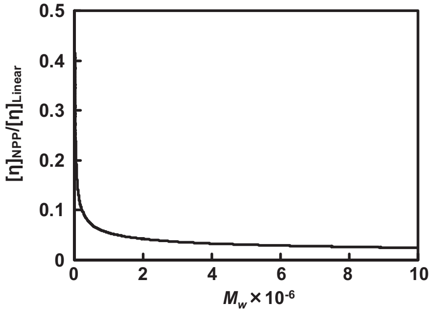

Figure 8.
Plot of $[\eta]_{NPP}/[\eta]_{Linear}$ versus M_w for the NPP obtained at 33.3% conversion (see Figure 7).

Conclusion

The free-radical crosslinking ABz/DAT/EGDMA terpolymerization and DAT/EGDMA copolymerization were preceded by *in situ* nanogel- or microgel-like methacrylate-NPP formation that promoted significantly the gelation in multiallyl polymerization, never leading to a delayed gelation. Free-radical crosslinking DAT/EGDMA copolymerization was extended to DAP/St/DVB terpolymerization to provide novel core-shell type allylic nanoparticles because DAP, St, and DVB are commercially important monomers. Notably, the copolymerizability of allylic monomer with styryl monomer is poorer than that with methacrylic monomer, leading to an easier construction of core part. The resulting St/DVB-core with a high hydrophobicity would be chemically more stable than the EGDMA-core with ester groups, providing novel amphiphilic nanoparticles by the saponification of poly(DAP) chains at the shell part to derive corresponding hydrophilic poly(allyl alcohol) ones. Furthermore, our core-shell type allylic nanoparticles would be easily modified utilizing the reactivities of pendant allyl groups at their surfaces.

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