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Construction of Crosslink-System-Materials Utilizing Designed Network-Polymer-Precursor Modules

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Summary: For a long time, we have been concerned with the elucidation of network formation mechanism of free-radical crosslinking (co)polymerization of multivinyl monomers. We have pursued two extreme network structures formation such as ideal and nanogel-like NPP formation. During the course of these investigations, we recognized that a network polymer may be reconsidered as a crosslink-system-material (CSM) or a giant system consisting of network polymer precursor (NPP) modules. The network polymer is not a giant molecule as a smallest unit of matter which could behave as one molecule. According to this definition, our subject may be changed from the molecular design of network polymer to the molecular design of NPP based on the free-radical crosslinking multivinyl polymerization mechanism. Then, we could construct a variety of CSMs utilizing designed NPP modules. A variety of CSM constructions are exemplified.

Keywords: crosslinking; crosslink-system-material; free-radical polymerization; multiallyl monomer; multivinyl monomer; network polymer precursor

Introduction

The gelation theory was first proposed by Flory.[1] Stockmayer applied Flory's procedure to the special case of chain crosslinking polymerization of symmetrical divinyl monomers (FS theory).[2] The pioneering experimental works were immediately performed by Walling[3] and Simpson[4] separately. However, it should be pointed out that each case corresponds to a particular solution, never a general solution, for gelation in free-radical crosslinking multivinyl polymerization. That is, the weight-average length of primary polymer chain was quite long for the former Walling's case by the occurrence of gel effect[5] due to reduced bimolecular termination, whereas it was quite short for the latter Simpson's case by the occurrence of monomer chain transfer characteristic of allyl polymerization.[6] So, we reexamined both cases by determining the primary polymer chain length using light scattering. The reasons for the greatly delayed gelation have been discussed.[7]

The primary polymer chain length is the most crucial factor for the estimation of theoretical gel point,[2,8] especially considering the following experimental result that a highly swollen polymer particle is presumed to be formed even at an early stage of polymerization.[3,9] Inevitably, it is needed to control a primary-polymer-chain forming reaction for the molecular design of network polymer precursor (NPP) since under the controlled primary-polymer-chain forming reaction, we could simplify the ordinarily complicated reaction scheme for free-radical crosslinking multivinyl polymerization. The intermolecular crosslinking 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

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crosslinking that leads to the formation of multiple crosslinks generating the net structure of the network polymer. As extreme cases, we could reach two typical structures of network polymers as an ideal network polymer governed by FS theory[2] and a microgel[10] greatly deviated from the theory. Thus, the former led to the preparation of ideal NPPs,[11] whereas the latter intramolecular crosslinking reaction was utilized for the preparation of novel net polymer[12] and nanogel-like NPPs.[13] During our continuing studies concerned with the elucidation of network formation mechanism, a simple question has been raised for the definition of a network polymer as "an indefinitely large sized, giant molecule". The network polymer is never a smallest unit of matter which could behave as one molecule. Here, we may propose that a network polymer could be reconsidered as a crosslink-system-material (CSM) or a giant system consisting of NPP modules. According to this definition, our subject may be changed from the molecular design of network polymer to the molecular design of NPP based on the free-radical crosslinking multivinyl polymerization mechanism. Then, we may construct a variety of CSMs utilizing designed NPP modules.

Why is "Crosslink-System-Material" Instead of "Network Polymer"?

At present there are a variety of synthetic polymeric materials. These polymers are roughly classified into three categories, i.e., linear, branched, and crosslinked polymers (see Figure 1).

The polymer structure would be complicated from a linear to a crosslinked form but interestingly, the crosslinked polymer with most complicated structure was the first true synthetic plastic; thus, it was "Bakelite", i.e., phenolic thermosetting resin.[14] Although around 100 years have passed since Baekeland's invention, notably, the crosslinked polymers still have many different names such as thermosetting resin, cured resin, crosslinked resin, networks, crosslinked polymer, three-dimensional polymer, network polymer, and so on. This suggests that the crosslinked polymer seemed to be quite different from the linear or branched polymer. Here it should be recalled that the molecule is defined as "a smallest unit of matter which can exist by itself and retain all its chemical properties."[15] Considering seriously the definition of molecule, the following question has been raised: "Is a network polymer in a category of molecule?" or "Is a network polymer a single giant molecule?"

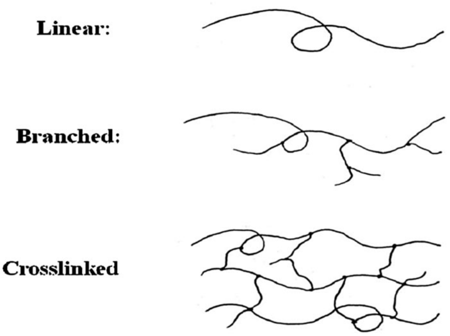
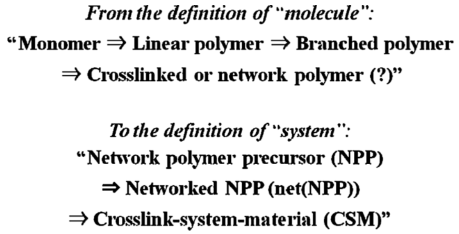


Figure 1.
Structure of linear, branched, and network polymers.

Here it is worthy to note that the system is defined as "a combination of two or more sets generally physically separated when in operation, and such other assemblies, subassemblies, and parts necessary to perform an operational function or functions."[15] The definition of system may be suitable as that of network polymer. As is seen in Figure 2, we can easily understand


From the definition of "molecule":
"Monomer ⇒ Linear polymer ⇒ Branched polymer ⇒ Crosslinked or network polymer (?)"

To the definition of "system":
"Network polymer precursor (NPP) ⇒ Networked NPP (net(NPP)) ⇒ Crosslink-system-material (CSM)"

Figure 2.
From the definition of "molecule" to that of "system".

"Monomer → Linear polymer → Branched polymer" according to the definition of molecule, but "Crosslinked or network polymer" could not be in the category of molecule. On the other hand, from the definition of system, we may easily understand "Network polymer precursor (NPP) → Networked NPP (net(NPP)) → Crosslink-system-material (CSM)". Here, both net(NPP) and CSM consist of NPP modules but their solubilities are different. That is, the net(NPP) is soluble in some solvents but the CSM is insoluble in all solvents. Conclusively, the network polymer may be reconsidered as "CSM consisting of NPP modules" instead of "an indefinitely large sized, giant molecule".

What is the origin of our idea of CSM? The idea originated in our continuing studies concerned with the elucidation of network formation mechanism of free-radical crosslinking multivinyl polymerization.[7,8] Figure 3 illustrates roughly the process of free-radical crosslinking (co)polymerization of multivinyl monomers. Here, we have two extreme cases: when the crosslinker content is high, commonly we have inhomogeneous network polymer via microheterogenization leading to microgel formation before a gel-point conversion. On the other hand, when the crosslinker content is quite low and the primary-polymer-chain forming reaction is controlled, we could reach ideal network formation without microgelation.

For a long time, we have pursued two extreme network structures formation in the free-radical crosslinking (co)polymerization of multivinyl monomers such as (1) ideal and (2) nanogel-like NPP formation. During the course of these investigations, we recognized that a network polymer may be considered as a CSM, not being a giant molecule.

Pursuit of Ideal NPP Formation

The pursuit of the variation of the molecular-weight distribution (MWD) curves with conversion is inevitable for a full understanding of free-radical crosslinking multivinyl (co)polymerization mechanism because the MWD curves of resulting NPPs should be rapidly broadened toward a higher molecular weight side with conversion as a result of exclusive occurrence of intermolecular crosslinking reaction leading to ideal network formation.[2,16] Notably, a size-exclusion chromatography (SEC) equipped with a multiangle laser light scattering (MALLS) devise (SEC-MALLS) is a very useful and efficient tool in characterizing NPP because the use of

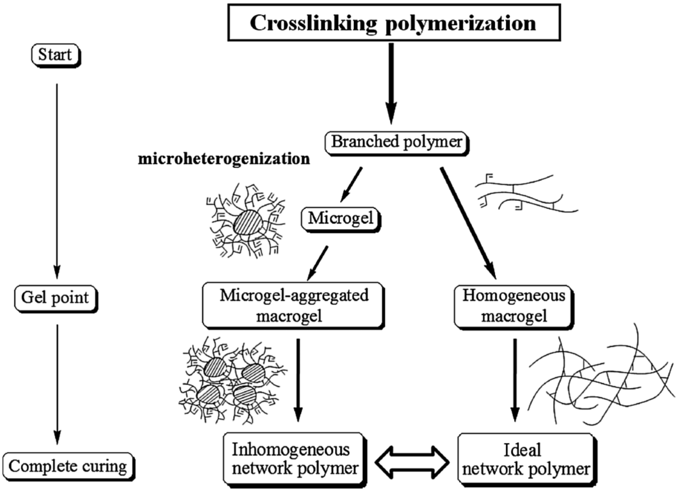


Figure 3.
A rough process of free-radical crosslinking (co)polymerization of multivinyl monomers.

MALLS enables the molecular weight and MWD to be determined directly without any calibration.[17] During the progress of our investigation, we noticed by chance that the degradation of NPPs with ultrahigh molecular weight obtained at a conversion close to the gel point occurred significantly during elution through SEC columns.[18,19] That is, the molecular weights determined by both SEC-MALLS and light scattering (LS) measurements were compared in detail. Although both results were in a good agreement within experimental errors for NPPS of moderate molecular weight less than one million, the discrepancy between both measurements became greater with further increment of molecular weight, i.e., with the progress of polymerization. The specific degradation of NPP depended on the primary polymer chain length, branched structure, and multiple crosslink or network structures as the characteristic features of NPP. Thus, Figure 4 shows the degradation of the resulting NPPs in various crosslinking monovinyl/divinyl copolymerization systems, including styrene (St)/*m*-divinylbenzene (*m*-DVB),[20] benzyl methacrylate (BzMA)/1,6-hexanediol dimethacrylate (HDDMA),[17,21] benzyl acrylate (BzA)/1,6-hexanediol diacrylate (HDDA),[22] and vinyl benzoate (VBz)/divinyl adipate (DVA).

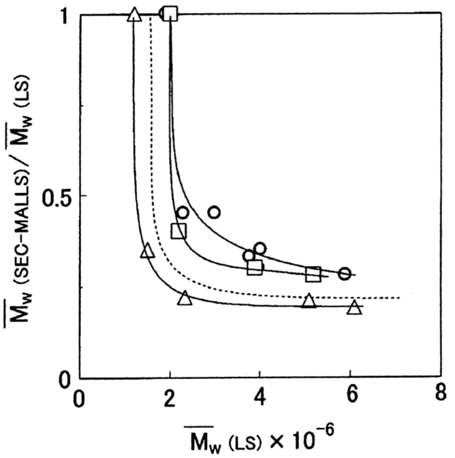


Figure 4.
Degradation of the resulting NPPs in (○) BzMA/HDDMA (99.96:0.04), (△) BzA/HDDA (99.94:0.06), and (□) VBz/DVA (99.9:0.01) copolymerizations. The dotted line corresponds to the St/*m*-DVB (99.83:0.17) copolymerization.

The degradation of the resulting NPPs occurred most remarkably for the BzA/HDDA copolymerization, which provided NPPs with the most flexible backbone chains.

In this connection, Barth and Carlin[23] reviewed the polymer shear degradation in SEC and presented guidelines involving operational parameters. High-molecular-weight polymers are fairly sensitive to shear forces, which can lead to chain scission. Because of velocity gradients generated during flow in SEC columns, a polymer becomes extended under high pressure. Bonds near the middle of the chain becomes stretched and can rupture if shear rates are great enough. As the end segments of a chain maintain their coiled shape, the maximum strain is usually focused near the center of the polymer. In general, the most probable sites of stress concentration on the polymer chain for the application of shear force are (1) side chain links to the main chain, that is, branch points; (2) crosslink points in networks; (3) points of inclusion of heteroatoms and quaternary carbon atoms; (4) dissymmetry between adjacent atoms, which promotes the rupture of the chain by stretching forces. The former two points are closely related to our vinyl-type NPPs. This kind of degradation of NPPs during elution through SEC columns suggested strongly that the polymers with ultrahigh molecular weight obtained at a conversion close to the gel point should be considered as a fragile net(NPP) consisting of NPP modules (see Figure 2). This fragile net(NPP) construction was confirmed further by the ultrasonic degradation.[24]

Pursuit of Nanogel-Like NPP Formation

Here, the following two typical cases of nanogel-like NPP formation would be exemplified as the origin of our idea of CSM. Firstly, the gel points in the free-radical polymerizations of diallyl aromatic dicarboxylates, including three isomeric diallyl phthalates such as diallyl phthalate (DAP), diallyl isophthalate (DAI), and diallyl terephthalate (DAT), were experimentally reexamined in detail[25] and discussed according to Gordon's theory.[26] Although the discrepancy between actual and theoretical gel-point conversions was quite large and, moreover, it increased in the order DAP < DAI < DAT, no substantial difference in the actual gel points was observed among the three isomeric diallyl phthalates. This interesting gelation behavior was discussed in detail,[27] in terms of the correlation between gelation and the difference in cyclization modes,[28] as well as the difference in reactivity between the uncyclized and cyclized radicals for crosslinking. Conclusively, the nonconsecutive addition in DAT polymerization led to a delayed gelation, and the cyclized radical in DAP polymerization showed an enhanced reactivity for crosslinking compared to the uncyclized radical. Then, we tried to extend our previous discussion[27] to the polymerization of triallyl trimellitate (TAT) because the chemical structure of TAT exhibits the characteristics of three isomeric diallyl phthalates. Therefore, the gel point at smaller conversion was expected in TAT polymerization, involving both abundant unreacted pendant double bonds and cyclized radicals as two significant factors responsible for an enhanced intermolecular crosslinking. However, no promoted gelation was observed in TAT polymerization when compared with DAP, DAI, and DAT polymerizations.

For a full understanding of the gelation behavior in crosslinking multiallyl polymerization, our preceding work[13] was focused on the characterization of resulting NPPs using SEC with both MALLS and viscosity detectors. SEC-MALLS-viscometry is a multidetection system providing the correlation of intrinsic viscosities ([η]) versus weight-average molecular weights (Mw) of fractionated samples; thus, it is a powerful tool for the characterization of NPPs with core-shell type dendritic structures. Notably, the microgel is conceived as consisting of both core and shell parts of high and low crosslink 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. The structures of resulting NPPs were also characterized by both correlations of [η] versus Mw and the root of mean square radius of gyration versus Mw. It is worthy to note that the structure of resulting NPPs, which consist of oligomeric primary polymer chains, as a characteristic of allyl polymerization,[6] would change with the progress of polymerization and eventually become core-shell type dendritic or nanogel-like at a conversion close to the gel point. This is inevitably related to the fact that no substantial difference in the actual gel points among DAP, DAI, DAT, and TAT polymerizations was observed. Furthermore, the nanogel-like NPPs can collide with each other to form crosslinks among NPPs, leading to the construction of a fragile net(NPP) and eventually CSM consisting of NPP modules (see Figure 5). These fragile net (NPP) and CSM constructions were confirmed further by the ultrasonic degradation.[24]

The second example is concerned with the discussion on correlation between brittleness and inhomogeneous network structure of crosslinked resins originating

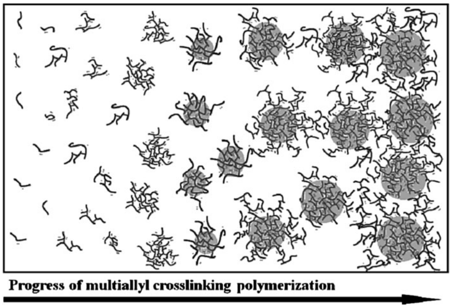


Figure 5.
Structural change of highest-molecular-weight NPP with the progress of polymerization in multiallyl crosslinking polymerization.

in specific polymerization behavior of triallyl isocyanurate (TAIC).[29] Thus, the free-radical crosslinking polymerization of TAIC was specific as compared with those of common multiallyl monomers. This is due to the steric effect on the transition state formation in the reaction at the sterically crowded, terminal reaction site of growing polymer radical caused by the sequential, bulky TAIC units, i.e., the reduced monomer chain transfer,[30] the non-terminal units effect on the cyclopolymerization of TAIC,[31] and the sequence length dependence of steric effect on the reactivity of growing polymer radical.[32]

Non-filled TAIC cured resin obtained directly by the polymerization of TAIC monomer was too brittle for practical use. This is also the case with commercially important DAP resins, and is due to the inhomogeneity of the crosslinked resins, as evidenced by electron microscopy.[33] As the inhomogenization of the resulting crosslinked polymer to form colloidal particles (quasi-microgelation) proceeded rapidly beyond the gel point, several procedures to improve the brittleness of DAP resins were developed.[34–36] These procedures, however, did not succeed in improving the toughness of TAIC resins. This clearly demonstrates the difference in the network structures of TAIC and DAP resins. Thus, the polymerization of TAIC would not always provide formation of colloidal particles, but instead introduce a rather homogeneous network, since the primary polymer chain of TAIC resin would be much more rigid than with DAP, due to very bulky side-chains. That is, the complete loss of flexibility of the polymer chain would not satisfy the prerequisite for the formation of quasi-microgels as colloidal particles in the crosslinking polymerization of TAIC. The correlation between brittleness and network structure of TAIC resins was then further discussed, especially focusing on the characterization of resulting TAIC-NPPs by SEC-MALLS-viscometry. The structure of branched TAIC-NPP is dendritic. This finding was supported by both correlations of $[\eta]$ versus M_w and $\langle S^2\rangle_z^{1/2}$ versus M_w for TAIC-NPPs.

As will be evident from the above discussion, the network structure of TAIC resin is rather homogeneous or never inhomogeneous microgel-like. The ordinary explanation that the brittleness of cured resin is caused by the inhomogeneity of network structure does not appear to be the true explanation for TAIC resin's extreme brittleness. So, an alternative explanation for the brittleness of TAIC resins is provided: the insufficient growth of the network structure of TAIC resin because of steric hindrance on the crosslinking reaction between sterically crowded growing polymer radical and pendant allyl groups belonging to the rigid primary polymer chains at the surface of core-shell type dendritic NPP. In this connection, we proposed that a network polymer should be considered as a CSM consisting of NPP modules (see Figure 6).

Molecular Design of NPPs as Modules of CSM Based on Crosslinking Multivinyl Polymerization Mechanism

As is discussed in the Introduction, we could simplify the ordinarily complicated reaction scheme for the network formation processes in free-radical crosslinking multivinyl polymerization under the condition where the primary-polymer-chain forming reaction is controlled as are the cases of multiallyl polymerization or multivinyl oligomerization in the presence of a chain transfer agent. Typically, in a free-radical crosslinking monovinyl/divinyl copolymerization, the network formation processes essentially involve four reactions of a growing polymer radical (see Figure 7): intermolecular propagation with two types of monomer; intramolecular cyclization leading to the formation of ring or loop structures; intermolecular crosslinking with a preformed NPP to form an effective crosslink, eventually leading to the gel; and intramolecular crosslinking leading to the formation of multiple crosslinks, the locally extensive occurrence of which would induce microgelation.

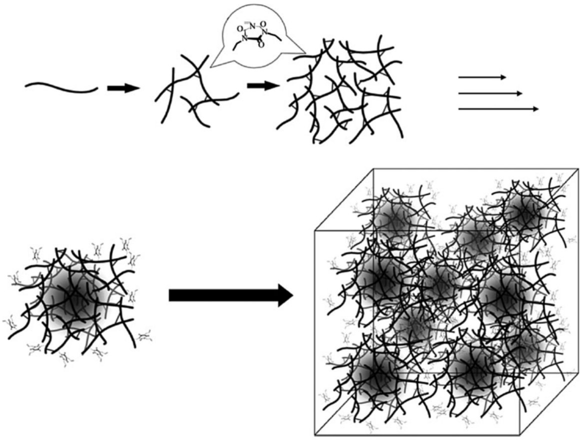


Figure 6.
A rough sketch of TAIC-CSM formation process.

Then, the network structure of the resulting NPPs and, moreover, CSM could be designed by controlling these elementary reactions. The intermolecular crosslinking is the key reaction for the control of crosslinks, whereas the key reaction for controlling the network structure is the intramolecular crosslinking that leads to the formation of multiple crosslinks generating the net structure of the NPPs. As extreme cases, we can illustrate two typical structures of CSMs in Figure 7 as an ideal CSM (A) governed by FS theory[2] and a CSM (B) consisting of nanogel- or microgel-like NPPs[10] greatly deviated from the theory, although the structures of the actual CSMs would be between the two extreme cases. Thus, the former led to the preparation of NPP modules[11] of ideal CSM, whereas the latter intramolecular crosslinking reaction was utilized for the preparation of novel net polymer[12] and nanogel-like NPPs.[13]

The former case of controlling intermolecular crosslinking has been discussed in detail: the preferential occurrence of

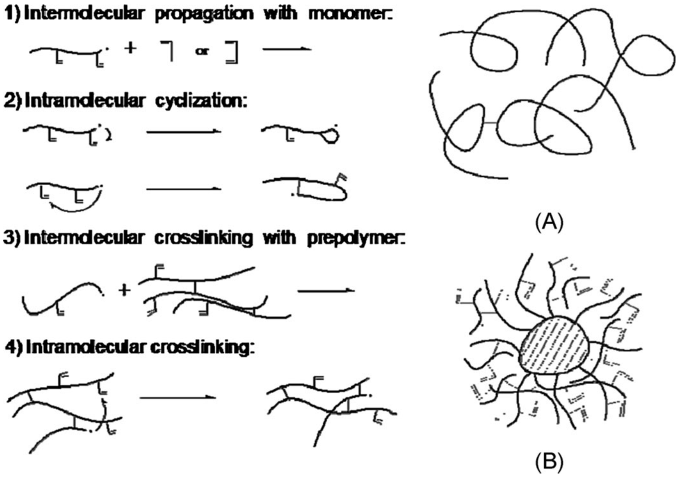


Figure 7.
Reaction scheme for the network formation processes in the free-radical crosslinking monovinyl/divinyl copolymerization mechanism under controlled primary-polymer-chain forming reaction.

intermolecular crosslinking not accompanied by any intramolecular crosslinking, i.e., governed by FS theory.[2] Thus, the crosslinking copolymerizations of St with m-DVB as a most typical monovinyl/divinyl system were discussed under the specified conditions. Notably, the occurrence of a thermodynamic excluded volume effect and intramolecular crosslinking as the primary and secondary factors, respectively, for the greatly delayed gelation in the free-radical monovinyl/divinyl copolymerizations was reduced.[20] The ratio of the actual gel point to the theoretical one reached 1.3, supporting the good applicability of FS theory. In addition, the MWD curves tailed toward a higher-molecular-weight side were observed with conversion as a reflection of preferential intermolecular crosslinking reaction leading to ideal network formation. Also, the swelling ratio of the gel obtained just beyond the gel point was very high, suggesting no microgelation up to the gel-point conversion. This kind of discussion was successfully extended to other crosslinking monovinyl/divinyl copolymerization systems, including benzyl methacrylate/1,6-hexanediol dimethacrylate[17,21] and benzyl acrylate/1,6-hexanediol diacrylate.[22] This ideal NPP formation was developed to the preparation of novel amphiphilic polymers[11] and, moreover, amphiphilic CSMs.[37–39]

As the latter case of controlling intramolecular crosslinking in the free-radical crosslinking monovinyl/divinyl copolymerization, we pursued the intramolecular crosslinking reaction to generate the net or loop structure as an origin of CSM, although the locally extensive occurrence of intramolecular crosslinking leads to microgelation.[3,40–44] Eventually, we reached the preparation of novel loop-structures containing net polymers as the ultimate precursors of CSM consisting of microgel-like NPPs. Here it should be noted that the new term, i.e., net polymer, was proposed by us;[12] thus, it is necessary to demonstrate the definition of the term "net polymer", being different from ordinary branched polymers.[45] In this connection, we may schematically depict two extreme structures of crosslinked polymer precursors as an ideal NPP (A-1) and a microgel-like NPP (B-1) (see Figure 8).

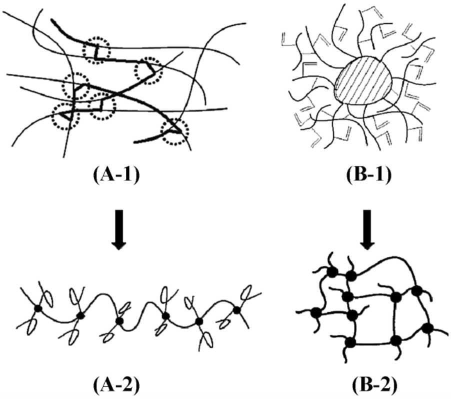


Figure 8.
Two extreme structures of crosslinked polymer precursors as (A) an ideal NPP and (B) a microgel-like NPP.

The former structure A-1 contains only one crosslink between primary polymer chains as a reflection of the preferential occurrence of intermolecular crosslinking, i.e., governed by FS theory,[2] and so, an imaginary branched polymer (A-2) could be obtained by stretching both ends, in which the bold line was assumed as the polymer backbone. On the contrary, a net polymer (B-2) could be obtained as an ultimate microgel-like NPP, reflecting the locally extensive occurrence of intramolecular crosslinking. Here, an essential requirement for B-2 is that the net polymer contains minimally one loop structure as the origin of CSM consisting of microgel-like NPPs. Notably, in free-radical crosslinking monovinyl/divinyl copolymerization α-, β-, … loop structures would be formed via intramolecular crosslinking reaction of growing polymer radical with pendant double bond belonging to different primary polymer chain as is depicted in Figure 9.

Thus, the α-loop structure could be formed via intramolecular crosslinking among three primary polymer chains, i.e., corresponding to 3-membered ring, the β-loop structure be formed via intramolecular crosslinking among four primary

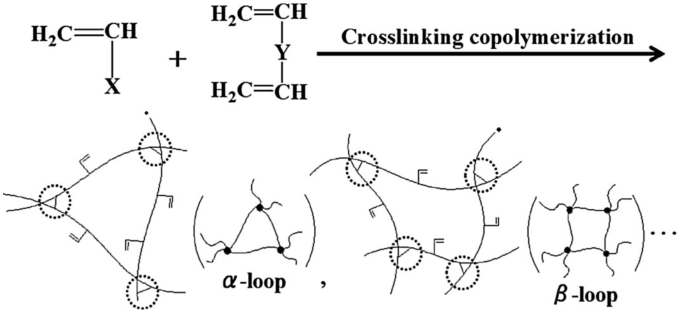


Figure 9.
A rough sketch of loop-structures formation through intramolecular crosslinking in the free-radical crosslinking monovinyl/divinyl copolymerization.

polymer chains, i.e., corresponding to 4-membered ring, and so on. The occurrence of this kind of intramolecular crosslinking reactions providing loop structures would be enhanced with conversion. As a result, α-, β-, … loop structures would be introduced into NPP not only as the isolated loop structure but also the fused loop structure containing shared primary polymer chain, i.e., corresponding to fused rings. Eventually, the ultimate precursor of CSM consisting of microgel-like NPPs would be depicted as the net polymer B-2 consisting of fused loop structures (see Figure 8) considering that the microgel-like NPP is formed by the locally extensive occurrence of intramolecular crosslinking.

Construction of Crosslink-System-Materials Utilizing Designed NPP Modules

We may reconsider a network polymer as a CSM consisting of NPP modules. Thus, we could construct novel CSMs utilizing designed NPPs as modules, providing semi-interpenetrating polymer network (IPN) involving DAT networks and linear poly(BzMA),[46] and simultaneous-IPN between polymethacrylate and polyurethane networks,[47–49] novel amphiphilic CSMs[37–39,50,51] and patchwork-type CSMs,[52] and so on.

Another example is concerned with the emulsion crosslinking (co)polymerization of multivinyl monomers,[53] especially focusing on the formation of reactive crosslinked polymer nanoparticles (CPNs) as models of microgels, with the intention of clarifying the correlation of the network structure with the reactivity of resulting CPNs which would be useful as functionalized polymeric materials. Thus, the emulsion polymerization of allyl methacrylate (AMA) was first chosen;[54] the reactive CPNs as microgel-like polymers with abundant pendant allyl groups were easily obtained. The weight-average molecular weights, the r.m.s. radii of gyration, the second virial coefficients, the intrinsic viscosities, and ^1H NMR spectra of the resulting poly(AMA)-CPNs were characteristic of microgel-like polymers. Then, the emulsion crosslinking copolymerization of AMA with alkyl methacrylates were carried out to give the reactive CPNs with different crosslink densities and different numbers of pendant allyl groups. These reactive CPNs with abundant pendant allyl groups could be utilized to construct different types of CSMs.[55]

Furthermore, considering that TAIC-NPP contains abundant pendant allyl groups, we attempted to construct novel CSMs by combining rigid TAIC-NPP with NPPs consisting of flexible chains, leading to reduction of the brittleness of TAIC resin. Also, four types of looped and nanogel-like methacrylate-NPPs with pendant methacryloyl groups or with pendant allyl groups were molecularly designed by free-radical crosslinking multiallyl/multivinyl copolymerizations as modules to construct novel CSMs.[8]

Recent development of novel hybridized materials including double network gels consisting of two different networks,[56] clay nanocomposite gels,[57] and numerous organic/inorganic hybrids may be in the category of the construction of CSMs utilizing designed NPP modules.

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