

Microgel formation in emulsion polymerization

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Abstract

A typical behavior of microgel formation in emulsion polymerization, where a sufficient amount of crosslinker exists and no coagulation of particles occurs, is considered both theoretically and experimentally. It was found that the crosslinked polymer formation in emulsion polymerization is significantly different from that in homogeneous media. The important characteristics can be summarized as follows. (1) The crosslinking density level is fairly high even from very early stages of polymerization, (2) the weight-average molecular weight increases just linearly with monomer conversion, and (3) the formed molecular weight distribution (MWD) is rather narrow and the distribution shifts to larger molecular weights with preserving the narrow profile as polymerization proceeds. In a typical microgel formation in emulsion polymerization, each polymer particle essentially consists of a single crosslinked polymer molecule once stable polymer particles are formed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Microgel; Emulsion polymerization; Molecular weight distribution

1. Introduction

Emulsion polymerization with a sufficient amount of crosslinkers, such as divinyl monomers, produces microgels whose size is usually below 100 nm. Microgels have found a wide variety of commercial applications, including rheology control additives for paints, ink and adhesive agents [1]. On the other hand, however, at present the mechanistic understanding of the microgel formation is not satisfactory, and they are usually produced after trying many different formulations and processes empirically. In this article, we try to shed new light on the microgel formation in emulsion polymerization, especially by focusing our attention on the differences with that obtained from corresponding bulk polymerization.

The theoretical description of emulsion polymerization is a kind of *never-beginning story*, because the particle nucleation mechanism has not been established yet [2,3]. However, after the nucleation period, the overall picture of the kinetics of emulsion polymerization is relatively well understood. The locus of polymerization is the polymer particles whose size is in the submicrometer range. The monomer droplets whose diameters are in the range 1–10 μm essentially act as a monomer reservoir, i.e. monomer is transferred from the monomer droplets into

the polymer particles to replace that which has reacted, as long as monomer droplets exist. Note that in emulsion crosslinking polymerization, the polymer particles often coagulate during polymerization especially when the amount of crosslinker (mole fraction of divinyl monomer in the case of vinyl/divinyl copolymerization) is large. However, we consider the cases without particle coagulation in the present article.

According to this simplified picture, one notices that crosslinking emulsion polymerization differs from corresponding bulk polymerization in at least two ways. First, because a separate monomer reservoir exists in the reaction system, the polymer concentration in the reaction locus is higher than that for the corresponding bulk polymerization. It is known that the polymer concentration in the polymer particles in the presence of monomer droplets varies only weakly with the size of polymer particles for many polymerization systems [4], including some crosslinked polymer systems [5–7]. In free-radical crosslinking polymerization, the polymer molecules formed inside polymer particles are reactive for crosslinking reactions, and therefore, a higher polymer concentration leads to a higher probability of chain connection.

Another important feature of emulsion polymerization, in contrast to the bulk polymerization, is that the locus of polymerization, i.e. the polymer particle, is extremely small. It has long been recognized that a microgel formed in emulsion polymerization possesses only supermolecular

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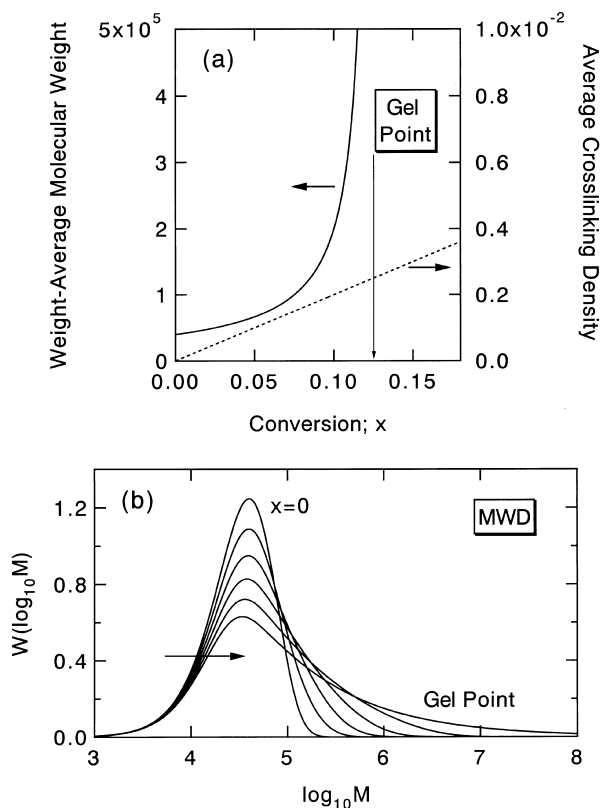


Fig. 1. Developments of average crosslinking density, weight-average molecular weight (a), and MWD (b) during crosslinking copolymerization in homogeneous media under Flory's simplifying assumption.

size and weight [8]. It is known that smaller polymer #2particles are formed in emulsion polymerization containing divinyl monomers [9,10] compared with those without crosslinkers. As an example, suppose that the final particle diameter is 50 nm, then the molecular weight of a polymer particle is 4×10^7 g/mol, which would be soluble in a good solvent and could be used for the size exclusion chromatography (SEC) aiming at determining the molecular weight distribution (MWD).

On the basis of the theoretical investigation where the classical chemical kinetics are assumed to be valid and the crosslinking reaction rate is proportional to the concentrations of polymer radicals and pendant double bonds, we have shown [5,11] that the crosslinked polymer formation in emulsion polymerization can differ significantly compared with corresponding bulk systems due to the above mentioned effects. For example, it was shown that while the average crosslinking density in homogeneous polymerization increases with polymerization, the crosslinking density level in emulsion system is fairly high even from a very early stage of polymerization. This difference can be rationalized as follows. In homogeneous polymerization, the polymer concentration in the early stage of polymerization is very low, resulting in a low crosslinking reaction rate. The crosslinking density level in homogeneous polymerization becomes higher in the later stages as the polymer

concentration becomes higher. On the other hand, in emulsion polymerization, the polymer concentration in the polymer particle, which is the locus of polymerization, is high even from the beginning of polymerization, resulting in a higher crosslinking reaction rate. This theoretical prediction agrees well with experimental investigation [7]. Therefore, the first important characteristic of emulsion polymerization can be stated that the average crosslinking density level is fairly high even from very early stages of polymerization. In addition, it was shown theoretically that the formed MWD could be significantly different from that in bulk systems [11].

Recently, Matsumoto et al. [12–14] have reported a series of experimental results concerning emulsion crosslinking polymerization, and showed that the MWD development differs significantly from corresponding bulk polymerization. It is well known that the true MWD for nonlinear polymer molecules cannot be determined by using SEC, however, they used the SEC with on-line multiangle laser light scattering (MALLS). Therefore, their MWDs are expected to be close to the true MWDs. In this article, we compare the experimental data reported by Matsumoto et al. and those of our own with the theoretical predictions, and try to clarify unique characteristics of microgel formation in emulsion polymerization.

2. Experimental

The monomers styrene, divinylbenzene and allyl methacrylate were purified by distillation. Sodium lauryl sulfate and potassium persulfate of extra pure grade were used without further purification as emulsifier and initiator, respectively.

The reactor used was a 400 ml cylindrical glass vessel with a dished bottom, equipped with a four-bladed paddle-type impeller. After the desired amounts of water, emulsifier and monomer mixture were fed to the reactor, the dissolved oxygen was removed by bubbling nitrogen gas for 15 min. The polymerization was started by injecting aqueous initiator solution that had also been deaerated by bubbling nitrogen gas.

The monomer conversion was determined gravimetrically using methanol as precipitant. Transmission electron microscopy (TEM) was used to determine the number of polymer particles and the particle size distribution by measuring the diameter of at least 300 polymer particles.

3. Crosslinked polymer formation in homogeneous media

Before considering emulsion polymer systems, let us first highlight important characteristics of crosslinked polymer formation in homogeneous media, which results in gelation. The standard idealized picture of polymeric gelation phenomena can be described by the framework of the

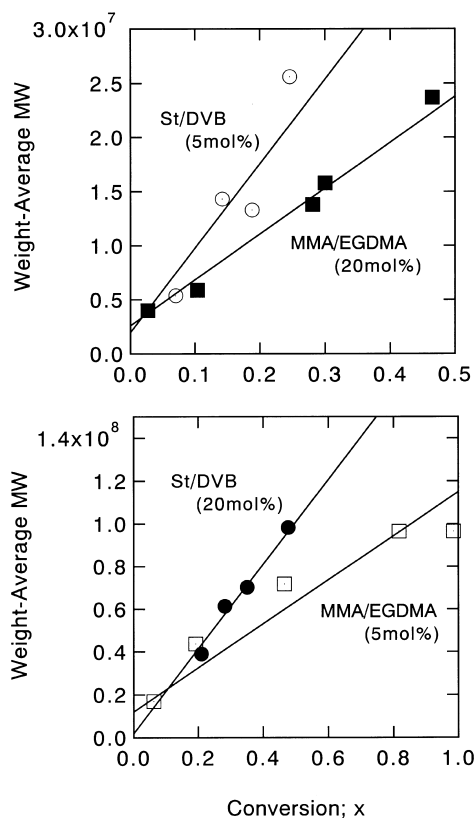


Fig. 2. Experimental results for the weight-average molecular weight development during emulsion crosslinking copolymerization of styrene (St)/divinylbenzene (DVB) and methyl methacrylate (MMA)/ethylene glycol dimethacrylate (EGDMA) [12].

Flory–Stockmayer theory [15–18], which neglects the size and structure dependence of crosslinking reactions as well as the interactions among chains. Here, we consider the crosslinked structure development during the pregelation period. We assume that the classical chemical kinetics are valid and the crosslinking reaction rate is proportional to the concentrations of polymer radicals and pendant double bonds. In the pregelation period, the weight fraction of one polymer molecule is zero in homogeneous polymerization because an infinite number of molecules are involved in the locus of polymerization. Since the concentration of pendant double bonds on its own polymer molecule is zero, the probability of ring formation within sol polymer molecule is zero. Therefore, cyclization does not occur in homogeneous polymerization during the pregelation period in the present simplified model, which leads to a ring-free model.

To illustrate important characteristics of the crosslinked polymer formation in homogeneous polymerization systems, we consider a simplified case of vinyl/divinyl copolymerization where the reactivities of all types of double bonds are equal. This condition is known as Flory's simplifying assumption. Fig. 1(a) shows the developments of average crosslinking density [19–21] (right axis) and weight-average molecular weight [16–19] (left axis), and

Fig. 1(b) shows the development of weight fraction distribution [22–25] up to the gel point. In the calculation, the following conditions are used, the initial mole fraction of divinyl monomer, $f_2^0 = 0.01$, the weight-average molecular weight and degree of polymerization of the primary chains are $\bar{M}_{wp} = 4 \times 10^4$ and $\bar{P}_{wp} = 400$, and the MWD of primary chains conforms to the most probable distribution.

Fig. 1(a) and (b) show the theoretical calculation results under an idealized condition, and in real systems the kinetic behavior does not agree perfectly with those shown in these figures. However, at least qualitatively, the important characteristics of crosslinked polymer formation in homogeneous media can be summarized as follows: (1) the average crosslinking density increases with polymerization (at least in the earlier stages of polymerization); (2) the weight-average molecular weight increases significantly as the gel point approaches and goes to infinity at the gel point; and (3) the MWD becomes broader toward gelation.

As already discussed, the average crosslinking density is high even from the beginning of polymerization in emulsion polymerization, which contrasts with the item (1) for homogeneous polymerization. We consider how the other characteristics described by the items (2) and (3) are changed in emulsion crosslinking polymerization.

4. Emulsion crosslinking polymerization

As illustrated in the introduction part (Section 1), assuming that the final particle diameter is 50 nm, the molecular weight of a polymer particle is only 4×10^7 g/mol. In emulsion polymerization, the molecular weight of primary chains could be quite large. Suppose the number-average molecular weight of primary chains is 1×10^6 . In this case, each polymer particle consists of only 40 primary chains. Therefore, all we have to do is to consider the combination of primary chains whose number is usually at most 1000. Such a small number of combination of primary chains can be simulated by using the Monte Carlo method in a straightforward manner. A Monte Carlo simulation algorithm for emulsion crosslinking polymerization was developed earlier [11].

The simulation results showed [7,11] that a significant amount of rings could be formed even when the classical chemical kinetics are valid. This can be rationalized as follows. In emulsion polymerization, because only a finite number of monomeric units are involved in a polymer particle, each polymer molecule always possesses nonzero weight fraction in the reaction locus, which allows to form rings even without considering the ring formation due to the polymer chain conformation statistics. It is expected that emulsion crosslinking polymerization leads to produce tighter polymer network compared with corresponding bulk polymerization. This prediction agrees well with the recent experimental observation [12–14] that the

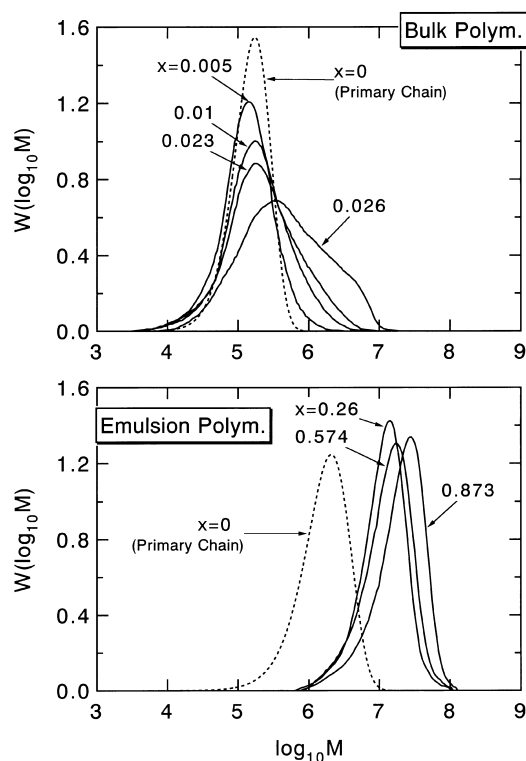


Fig. 3. MWD development in the copolymerization of St with 20 mol.% of DVB at 60°C for bulk polymerization (a) and emulsion polymerization (b). Redrawn from Ref. [12], and the dotted curves are the estimated MWD at conversion $x = 0$.

hydrodynamic volume is smaller than the crosslinked polymers formed in corresponding bulk polymerization.

4.1. Weight-average molecular weight

In a typical reaction formula to synthesize microgels in emulsion polymerization, a significant amount of crosslinker is used. According to the simulation results for such emulsion crosslinking polymerization systems [7,11], the weight-average molecular weight increases just linearly with monomer conversion, if particle coagulation can be neglected.

Matsumoto et al. reported the weight-average molecular weight (\bar{M}_w) developments for copolymerization of styrene (St)/divinylbenzene (DVB) [12], methyl methacrylate (MMA)/ethylene glycol dimethacrylate (EGDMA) [12], and homopolymerization of allyl methacrylate (AMA) [13,14]. They stated that the weight-average molecular weight increases with conversion rather gradually until leveling off at high conversions. They showed the relationship between \bar{M}_w and conversion (x) graphically, however, they used logarithmic scale for \bar{M}_w . We read the data points from their figures, and replotted them in a normal scale. The results for St/DVB and MMA/EGDMA are shown in Fig. 2. In all cases, the \bar{M}_w tends to increase linearly with conversion. The y-intercept can be interpreted as the \bar{M}_w of

polymers formed at zero conversion, which might approximately correspond to the \bar{M}_w of primary chains.

When the \bar{M}_w increases linearly with conversion, one needs to pay careful attention to the determination of gel point. If one defines the gel molecule as an insoluble fraction in a good solvent experimentally, one may just determine the molecular weight when the macromolecule becomes insoluble to the given solvent and no critical change occurs in the present type of reaction system. (Obviously, we exclude the cases where the particle coagulation occurs abruptly to form macrogels in the present context.) For instance, Matsumoto et al. reported that the gel point for the emulsion copolymerization of St with 20 mol.% of DVB at 60°C is $x_c = 0.85$ based on the finding of insoluble fraction in tetrahydrofuran (THF) [12]. However, because the \bar{M}_w increases just linearly with conversion and no coagulation of particles was observed in our experiment conducted in the same reaction condition, we think that this is not the true gel point but the point at which the formed polymer molecule becomes so large and insoluble to THF.

As discussed in this section, the theoretical prediction that the \bar{M}_w increases linearly with conversion in a typical emulsion crosslinking polymerization is supported by the experimental results.

4.2. Molecular weight distribution (MWD)

Fig. 3(a) shows the MWD development for the bulk copolymerization of St with 20 mol.% of DVB, and Fig. 3(b) shows that for the emulsion polymerization, both reported by Matsumoto et al. [12]. The reaction temperature employed was 60°C. For bulk polymerization, 0.02 mol/l of azobisisobutyronitrile (AIBN) was used as initiator. For emulsion polymerization, 0.05 mol/l-water of sodium lauryl sulfate was used as emulsifier, 0.005 mol/l-water of potassium persulfate (KPS) was used as initiator, and the monomer/water ratio by weight was 20/80.

By extrapolating \bar{M}_w -values [12] to zero conversion, the \bar{M}_w at $x = 0$, which would approximately correspond to that for the primary chains, is 1.7×10^5 for the bulk polymerization, and is 1.98×10^6 for the emulsion polymerization. Assuming that bimolecular termination by combination is dominant for the bulk polymerization, the MWD at $x = 0$ can be estimated to be [26]:

$$W(M) = \frac{4M^2}{\bar{M}_n^3} \exp\left(-\frac{2M}{\bar{M}_n}\right) \quad (1)$$

where \bar{M}_n is the number-average molecular weight and is equal to $2\bar{M}_w/3 = 1.13 \times 10^5$. The estimated MWD at $x = 0$ is shown by the dotted curve in Fig. 3(a).

On the other hand, in emulsion polymerization, if bimolecular termination by disproportionation is not dominant, the most probable distribution would be a reasonable approximation for the instantaneously formed linear polymer molecules in many cases [27–32]. Therefore, the MWD

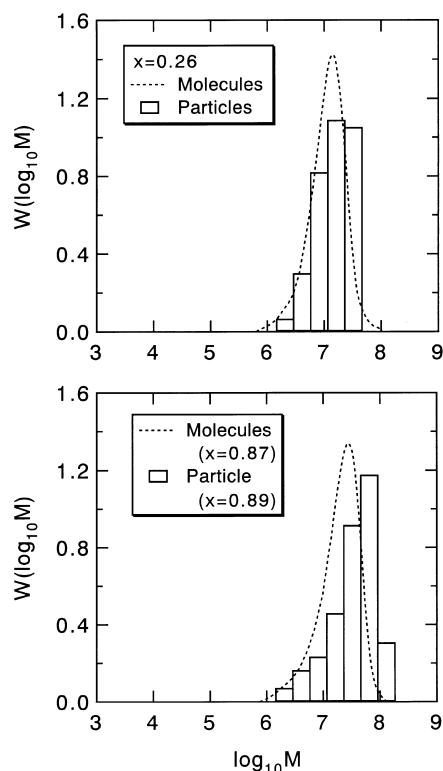


Fig. 4. MWDs of polymer molecules and dried polymer particles in emulsion copolymerization of St and DVB (20 mol.%).

at $x = 0$ could be approximated by:

$$W(M) = \frac{M}{\bar{M}_n^2} \exp\left(-\frac{M}{\bar{M}_n}\right) \quad (2)$$

where $\bar{M}_n = \bar{M}_w/2 = 9.9 \times 10^5$. The estimated MWD at $x = 0$ for emulsion polymerization is shown by the dotted curve in Fig. 3(b).

By looking at Fig. 3(a) and (b), one notices that in the case of bulk polymerization only larger polymer molecules are crosslinked to grow to larger species, while in emulsion polymerization, *all* polymer molecules including smaller polymers are crosslinked to form larger polymer molecules. The MWD becomes broader in bulk polymerization, while in emulsion system, a sharp MWD shifts to larger molecular weight as polymerization proceeds. Incidentally, the MWD profile at $x = 0.026$ for the bulk polymerization is rather distorted, which is different from that shown in Fig. 1(b). We think this type of distortion is caused by the size and structure dependence of the crosslinking reactions [33], which is not accounted for in Fig. 1(b).

“The larger grows faster” must be a basic feature of crosslinking reactions. Then, why does the MWD not become broader in emulsion polymerization? As discussed earlier, the crosslinking density is high from the beginning of polymerization, meaning that the probability that a growing primary polymer radical reacts with a pendant double bond is high from the beginning. As a consequence, a newly formed primary polymer molecule is almost always

connected to the already existing polymer molecule one after another. When a large fraction of divinyl monomer is used, it was shown that this type of molecular build-up process is the norm, rather than the exception [5,11].

As an illustration, consider a vinyl/divinyl copolymerization that satisfies Flory’s simplifying assumption. At conversion, $x = 0.1$, assuming that the weight fraction of polymer in the polymer particle is 60%, the mole fraction of pendant double bonds within the total number of double bonds in the polymer particle is 0.17. Because the reactivities of all types of double bonds are assumed to be the same, the probability that a radical inside the polymer particle reacts with a pendant double bond is equal to 0.17. Therefore, at this instant, the probability that a growing radical does *not* react with any pendant double bond at all during the addition of 20 double bonds is given by, $(1.0 - 0.17)^{20} = 0.024$. Therefore, even for a very short chain with degree of polymerization 20, the probability that this short chain is crosslinked with already existing polymer molecule is as high as 97.6%. In addition, the primary chain length is often very large in emulsion polymerization, typically being in the order of 10^4 . Even when the reactivity of pendant double bonds is quite small due to both chemical and physical effects, it is highly probable that newly formed primary chain is connected to the already existing polymer molecule one after another, resulting in forming essentially one single giant sized polymer molecule in a polymer particle on a weight basis [7,11].

If the above speculation is correct, the molecular weight distributions of polymer molecules and polymer particles represent the same distribution. We conducted the emulsion copolymerization of St with 20 mol.% of DVB under the same reaction condition as Matsumoto et al. [12]. The number of polymer particles does not change, at least, after conversion around 20%, and the value is 3.1×10^{15} particles/ml-water. Fig. 4 shows a comparison of the MWDs of polymer molecules and dried polymer particles. The particle size distribution was determined from the photographs of TEM, and the obtained distribution was converted to the MWD of polymer particles on a weight basis, setting the independent variable as the logarithm of molecular weight. As shown in Fig. 4, both distributions agree reasonably well.

According to our simulation results, the phenomenon that each polymer particle essentially consists of one single polymer molecule after the formation of stable polymer particles is expected to be observed for any emulsion crosslinking polymerization system, as long as a sufficient amount of crosslinker exists. We next examined the emulsion polymerization of allyl methacrylate (AMA), whose MWD development was reported by Matsumoto et al. [13]. For this reaction system, Matsumoto et al. reported that no gelation occurred in emulsion polymerization, while gelation occurred easily at about 4% conversion in the bulk system [13,14].

AMA possesses two different types of double bonds,

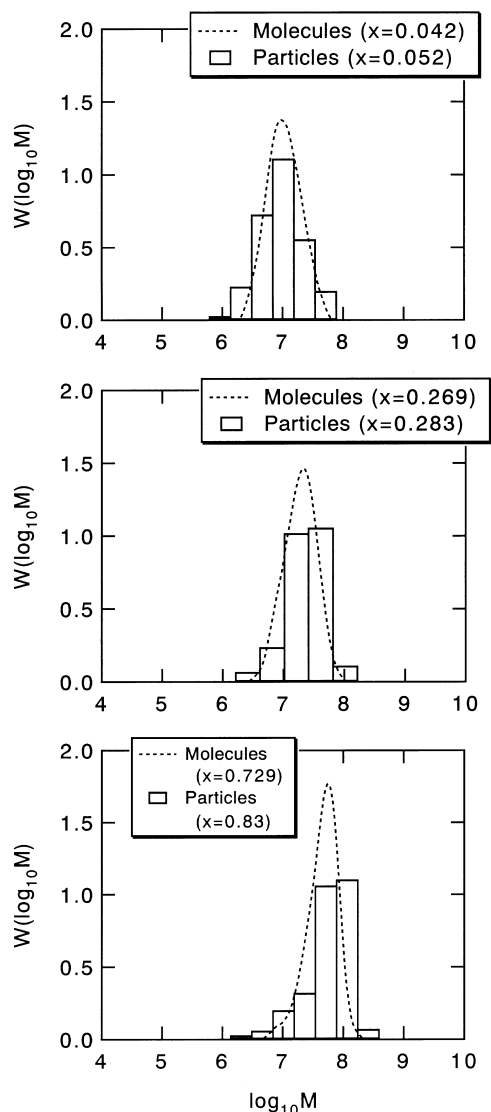


Fig. 5. MWDs of polymer molecules and dried polymer particles in emulsion polymerization of allyl methacrylate (AMA).

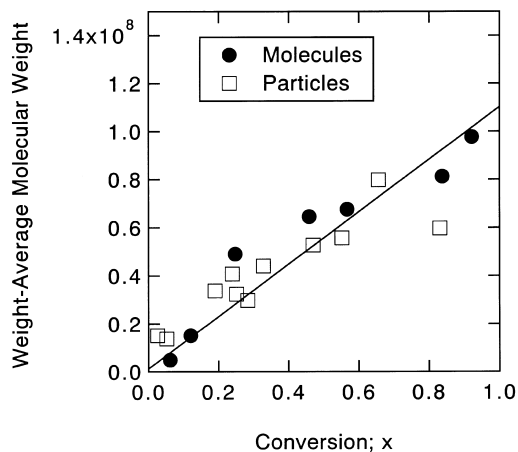


Fig. 6. Weight-average molecular weights of polymer molecules and dried polymer particles in emulsion polymerization of AMA.

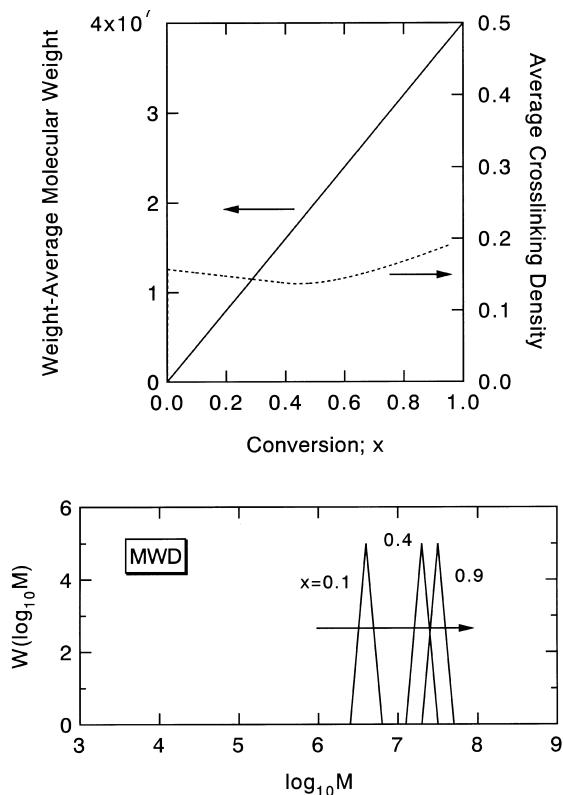


Fig. 7. Typical representation of microgel formation in emulsion polymerization. The calculation was conducted under Flory's simplifying assumption with $f_2^0 = 0.2$ and the final diameter of polymer particle 50 nm.

methacryl and allyl groups. Because the reactivity of methacryl group is much higher than allyl group, the primary polymers are mainly formed by the polymerization of methacryl groups with a large number of pendant allyl groups. The weight-average molecular weight of the primary chains [13,14] for bulk polymerization is as large as 1.26×10^6 , meaning the degree of polymerization 1×10^4 . The primary chain length for emulsion polymers is expected to be greater than or equal to that for the bulk system. A very large number of pendant allyls would exist in a primary chain. Although the reactivity of pendant allyls is very low and some fraction of pendant allyls is consumed by cyclization reactions [34], the probability of crosslinking inside the polymer particle is expected to be quite large.

We observed that the monomer droplets disappear at around the conversion 20%, and therefore, the polymer weight fraction in the polymer particle is about 20% even from very early stages of polymerization. Note that the weight fraction 20% is well over the polymer weight fraction for the corresponding bulk polymerization at the gel point, which is only 4%. In emulsion polymerization, polymer molecules are subjected to a higher probability of crosslink formation throughout the polymerization.

Fig. 5 shows the comparison of the MWDs. The MWD data of polymers were taken from Ref. [13]. The MWDs of polymer molecules coincide with those for the dried

polymer particles at any stage of polymerization. Each polymer particle essentially consists of one polymer molecule from very early stages of polymerization. This is the reason for the observation that a sharp MWD just moves toward larger molecular weight during polymerization, and that the weight-average molecular weight increases just linearly with conversion. Fig. 6 shows the weight-average molecular weights of polymer molecules and dried polymer particles. The data for polymer molecules were taken from Ref. [13]. Both molecular weights agree reasonably well, and both increase linearly with conversion.

As already shown in the Monte Carlo simulation results [7,11], there are cases where the MWD development does not follow the present picture, especially when the primary polymer chain length and/or the mole fraction of divinyl monomer is very small. However, if one admits that a standard picture of crosslinked polymer formation is represented by Fig. 1, that for the microgel formation in emulsion polymerization could be represented by Fig. 7. In the absence of particle coagulation as well as new particle formation in the later stages of polymerization, the three major features of emulsion crosslinking polymerizations are; (1) the crosslinking density level is fairly high even from very early stages of polymerization, (2) the weight-average molecular weight increases just linearly with monomer conversion, and (3) the formed MWD is rather narrow and the distribution shifts to larger molecular weights with the progress of polymerization. These three features contrast sharply with those for homogeneous polymerization.

5. Conclusions

A typical behavior of microgel formation in emulsion polymerization is considered theoretically and experimentally. A significant amount of crosslinker is usually used for the synthesis of microgels. For such cases, the probability of causing crosslinking reaction for a growing chain is high from the beginning of polymerization. A newly formed primary chain tends to be crosslinked with the already existing polymer molecule one after another, and as a consequence, each polymer particle essentially consists of one single crosslinked polymer molecule, once stable polymer particles are formed. The MWD is essentially equivalent in meaning to the particle size distribution. Therefore, the MWD does not become broader as in the case of homogeneous polymerization, but just moves toward higher molecular weight with the preservation of a sharp distribution shape, in the absence of particle coagulation as well as new particle formation. At the same time, the weight-average

molecular weight increases linearly with conversion, which is unique and differs significantly from that observed in the corresponding bulk polymerization.

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