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Bimodal molecular weight distribution formed in emulsion crosslinking copolymerization

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Abstract

A bimodal molecular weight distribution, first predicted theoretically in the Monte Carlo simulation of emulsion crosslinking copolymerization [Macromolecules 27 (1994) 3389], is now confirmed experimentally in emulsion copolymerization of styrene/divinylbenzene, by setting the number of divinylbenzene molecules per primary chain ca. 5. It was found that the locations of these two peaks can be controlled independently, i.e. the location of high molecular weight peak is controlled by the particle size, while that for low molecular weight peak is controlled by the chain lengths of the primary polymer molecules. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Bimodal molecular weight distribution; Emulsion polymerization; Crosslink

1. Introduction

The locus of polymerization in emulsion polymerization is the polymer particle whose diameter is in a submicron range, often less than 0.1 μm. Assuming the diameter of a polymer particle is 50 nm, then the molecular weight of this polymer particle is about 4×10^7 g/mol. Even when all polymer chains in each polymer particle form one crosslinked polymer molecule, the molecular weight distribution could be measured by the size exclusion chromatography (SEC) as long as such polymer molecules are soluble in a solvent. Further, assuming the molecular weight of a monomeric unit is 100, then the total number of monomeric units in each particle is only 4×10^5, which means that the number of primary chains is 40–4000, depending on the length of primary chains. It was shown theoretically that the polymeric network formation in these small polymer particles is substantially different from that in a homogeneous medium [1].

For example, the model calculation [1] predicts the following behavior for the cases where a significant amount of crosslinker is added, as usually employed in the microgel synthesis. (1) The molecular weight distribution (MWD) does not become broader during polymerization, as in the case of homogeneous polymerization, but it just moves toward higher molecular weight with preserving a sharp distribution shape. (2) The weight-average molecular weight increases linearly with conversion, which shows a clear contrast to the usual gelation in which it increases steeply as the reaction system approaches the gel point. Recent experimental investigations [2–4] have shown this type of behavior, and the kinetic mechanism was clarified in Ref. [5].

In Ref. [1], another interesting behavior was reported for the cases where a few crosslinkers per primary chain are used, i.e. a bimodal MWD is predicted to be formed. Experimentally, several articles reported bimodal MWD in emulsion polymerization that involves crosslinking [6] or branching [7]. However, the formation mechanism of bimodal distribution was not clarified in these articles.

Here, we clarify that a bimodal MWD can be formed in emulsion copolymerization of vinyl/divinyl monomers because of a very small size of polymerization locus. In addition, we propose a method to control each peak location independently based on the formation mechanism.

2. Theoretical backgrounds

Fig. 1 shows examples of bimodal chain length distribution (CLD) predicted in the Monte Carlo (MC) simulation [1] at three different conversion levels, x. The primary polymer molecules are assumed to follow the most probable distribution with the number-average chain length, $\bar{P}_{np} = 1000$. In C2, the reactivities of all types of double bonds are equal, while those in divinyl monomers are higher in C3.

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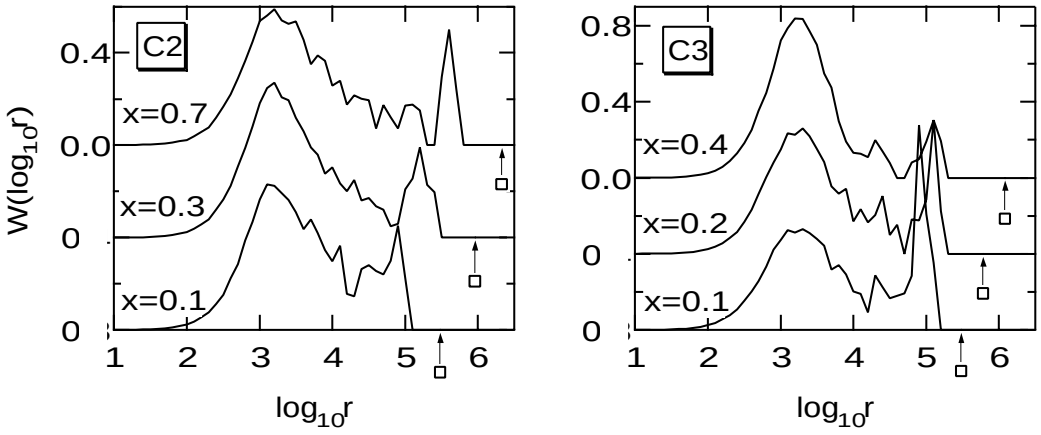

Fig. 1. Monte Carlo simulation results that show bimodal chain length distributions in emulsion copolymerization of vinyl/divinyl monomers [1]. The parameters used as well as the other property changes during polymerization can be found therein.

More details on the used kinetic parameters can be found in Ref. [1]. In Fig. 1, the independent variable is the logarithm of chain length, $\log r$, and the distribution is given on a weight basis. This type of distribution corresponds to the MWD usually obtained by SEC. The arrows indicate the total number of polymerized monomeric units in a polymer particle, which gives the upper limit for the size of a polymer molecule formed in a polymer particle.

In the MC simulation [1], it was assumed that (1) all polymer particles are formed instantaneously at $t = 0$, (2) the polymer particles are monodisperse, and (3) the polymer concentration in polymer particles is kept constant until the depletion of monomer droplets. The third assumption is a reasonable approximation for many emulsion polymerization systems [8], including crosslinking copolymerization [9,10].

Because the polymer concentration in the polymer particle is high from a very early stage of polymerization, the average crosslinking density is higher than the corresponding bulk polymerization [10,11]. Under condition C2, the average crosslinking density does not change much during the whole course of polymerization, while the average crosslinking density decreases as polymerization proceeds in C3 [1]. These types of behavior are not unusual in emulsion polymerization [10–12]. In both cases, the average crosslinking density level, $\bar{\rho}$ is close to:

$$\bar{\rho} = 1/\bar{P}_{wp} \tag{1}$$

where $\bar{P}_{wp}$ is the weight-average chain length of the primary chains.

According to the random crosslinking theory in an infinitely large reaction system [13], gelation is predicted to occur when the average crosslinking density reaches $1/\bar{P}_{wp}$. Therefore, under conditions C2 and C3, the chain connection probability is high enough to form a gel molecule if the polymerization were carried out in a homogeneous medium.

On the other hand, there exists an upper limit for the size of a polymer molecule and any polymer molecule cannot grow larger than the particle size. The crosslinking reactions between large-sized polymer molecules separated into different polymer particles are prohibited, and the partner for crosslinking reaction must be chosen within the same polymer particle. Large polymer molecules in the sharp high molecular weight peak have a potential for further growth because of a high chain connection probability, but they cannot grow further because of the limitation of small particle size. This is the reason for forming a sharp high molecular weight peak close to the particle size.

According to the MC simulation results [1] in which all pendant double bonds react ideally, the bimodal MWD is predicted to be formed when the average crosslinking density is close to $1/\bar{P}_{wp}$, namely, the number of effective crosslinkages per chain is approximately unity assuming $\bar{P}_{wp}/\bar{P}_{np} = 2$.

Incidentally, the area of high molecular weight peak decreases during polymerization in C3. Under condition C3, the average crosslinking density decreases as polymerization proceeds and primary chains formed in the later stages of polymerization are not connected effectively to the polymer molecules in the high molecular weight peak. A similar type of behavior will be shown for the styrene/divinylbenzene systems investigated in this article.

In this MC simulation, the primary polymer chains are assumed to follow the most probable distribution with $\bar{P}_{wp} = 2000$, and therefore, the peak location for the primary chain length distribution is $\log \bar{P}_{wp} = 3.3$. The locations of low molecular weight peaks shown in Fig. 1 are close to 3.3, but slightly smaller. The decrease in the peak chain length is due to the fact that larger primary chains have a better chance of being crosslinked to become a part of high molecular weight peak polymers.

In summary, according to the MC simulation results, the bimodal MWDs are expected to be formed (1) when the number of effective crosslinkages per primary chain is approximately unity, and (2) two peaks are formed at molecular weights that are close to the particle size and the

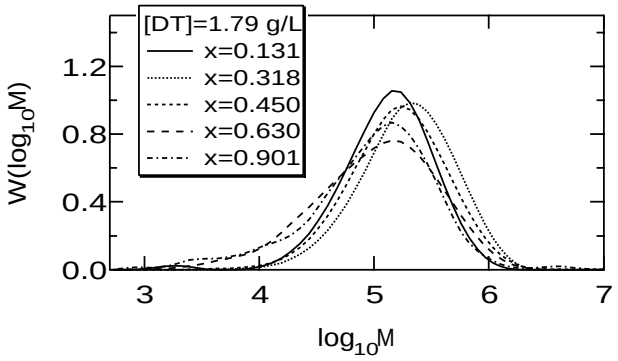

Fig. 2. Molecular weight distribution development for emulsion polymerization of styrene with chain transfer agent, [DT] = 1.79 g/l water. The monomer concentration is 250 g/l water, [SDS] = 14.4 g/l water, [KPS] = 1.35 g/l water, and the temperature is 50°C.

weight-average chain length of primary chains, respectively.

3. Experimental

The monomers, styrene and divinylbenzene, were purified by distillation. Sodium dodecyl sulfate (SDS) and potassium persulfate (KPS) of extra pure grade were used without further purification as emulsifier and initiator, respectively. The chain transfer agent, 1-dodecanethiol (DT) was used as received.

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 polymerization temperature was set to 50°C using a water bath with a thermostat.

Concentrations used were 250 g/l water for the total monomer, and 1.35 g/l water for potassium persulfate.

The monomer conversion was determined gravimetrically using methanol as precipitant. The transmission electron microscopy (TEM) was used to determine the particle size distribution by measuring the diameter of at least 300 polymer particles. The size exclusion chromatography (SEC) was used to determine the MWD, using a set of linear polystyrene standards for calibration.

4. Results and discussion

4.1. Experimental verification of bimodal MWD

We controlled the primary polymer chain length by using DT. The chain transfer constant of styrene to DT is large (≈ 19) [14]. However, because of a small mass transfer rate of DT from monomer droplets to polymer particles, the concentration of DT is much smaller than the thermodynamic equilibrium and the apparent chain transfer constant is decreased significantly [15]. In addition, because the solubility of DT in water is very low, the probability of desorption for a transfer radical is small and the number of polymer particles does not increase significantly by increasing the amount of DT.

Fig. 2 shows the MWD development when 1.79 g/l water of DT is added in styrene emulsion polymerization with 14.4 g/l water of SDS. The MWD does not change significantly up to conversion $x = 0.45$, and after that a significant amount of shorter chains are formed. Because the amount of crosslinker is rather small in our experiments, this distribution can be considered as the MWD of primary chains.

The number-average chain length for homopolymerization up to $x = 0.45$ is ca. $\bar{P}_{np} = 1000$. It would be reasonable to consider that not all crosslinkers connect polymer molecules intermolecularly, and we added divinylbenzene to the reaction system so as to make 5 crosslinkers per chain, i.e. the mole fraction of divinylbenzene, $f_2^0 = 5 \times 10^{-3}$.

Fig. 3 shows the MWD development for the copolymerization. The bimodal MWD as predicted in the MC simulation is now confirmed experimentally.

The low molecular weight peak location is smaller than that for primary polymer MWD shown in Fig. 2, as in the MC simulation results shown in Fig. 1. The apparent peak location could be further decreased by the problems in the

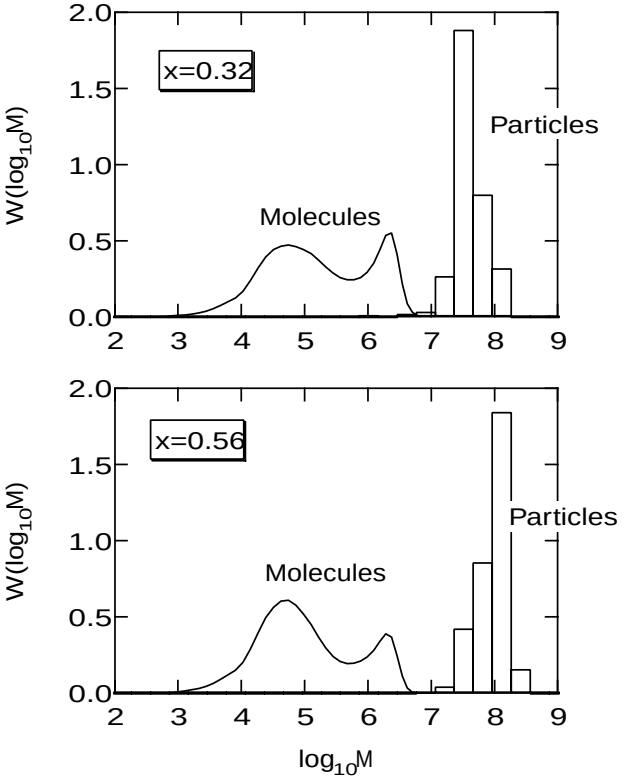

Fig. 3. Molecular weight distribution developments of polymer molecules and particles for emulsion copolymerization of styrene and $f_2^0 = 5 \times 10^{-3}$ of divinylbenzene. Other concentrations are the same as those in Fig. 2.

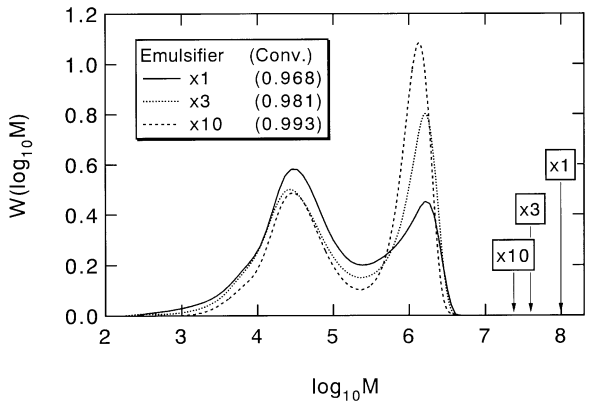

Fig. 4. Comparison of molecular weight distribution profiles when the amount of emulsifier, SDS is increased to 2× and 3× of that in Fig. 3. The arrows show the weight-average molecular weight of dried polymer particles. As the particle size decreases, the location of high molecular weight peak moves to smaller molecular weights.

SEC measurement. In the experiment, the SEC column was calibrated by linear polystyrene standards, and therefore, the obtained molecular weights may be underestimated for inter- and intramolecularly crosslinked polymer molecules.

The MWD of the dried polymer particles, determined from the measurement of particle size distribution and converted the x-axis to grams of 6.022×10^{23} polymer particles having the same diameter, is also shown in the figures. Note that the particle size distribution is clearly unimodal. By comparing Fig. 3 with the MC simulation results shown in Fig. 1, it would be reasonable to consider that the high molecular weight peak is formed due to the limitation of the particle size. In the present reaction system, the area of high molecular weight peak decreases with polymerization, similarly with C3 shown in Fig. 1, where the average crosslinking density decreases with polymerization.

4.2. Independent control of high and low molecular weight peak locations

According to the MC simulation, the location of high molecular weight peak is mainly dominated by the particle size, while the low molecular weight peak location is mainly determined by the primary chain length. Therefore, the location of these two peaks could be controlled independently.

To examine this hypothesis, first we decreased the particle size by increasing the amount of emulsifier, SDS. Fig. 4 shows the MWD at conversion $x > 0.95$. The arrows show the weight-average molecular weights of dried polymer particles, determined from the particle size distribution. The movement of high molecular weight peak location was small, but clearly it moved to smaller molecular weights, while keeping the low molecular weight peak location essentially the same.

A significant feature of Fig. 4 is that the height of high molecular weight peak becomes larger as the particle size decreases. The apparent reactivity of crosslinking reaction is enhanced in the smaller particles. This experimental finding may be rationalized as follows. In the present reaction system, the initiator radical is generated in the water phase and enters into the polymer particle. For larger particles, therefore, the pendant double bonds located in the core region of polymer particles may not be used effectively for crosslinking reaction. Smaller particles could make such inactive core region smaller, which makes the apparent reactivity of pendant double bonds larger.

Next, we increased the amount of chain transfer agent, DT, aiming at making the primary chain length smaller. We increased DT concentration to 17.9 g/l water, and found that the number-average chain length of polystyrene chain decreases to about $\bar{P}_{np} = 100$. Again, we set the amount of divinylbenzene so as to make $\bar{P}_{np} f_2^0 = 5$, i.e. the initial mole fraction of divinylbenzene, $f_2^0 = 0.05$.

Fig. 5 shows the comparison of MWDs. Because the particle size became slightly smaller when DT concentration was increased, the high molecular weight peak moves to smaller molecular weight a bit. However, it was confirmed that the low molecular weight peak moves to smaller molecular weights by making the primary chain length smaller, as expected from the theoretical argument.

It was further found that the height of low molecular weight peak becomes smaller as the primary chain length decreases. The apparent reactivity of pendant double bonds seems to become larger for smaller chains. This may be attributed to the higher mobility of smaller polymer radicals.

5. Conclusions

The theoretical prediction that the bimodal MWD could be formed in emulsion crosslinking copolymerization, by

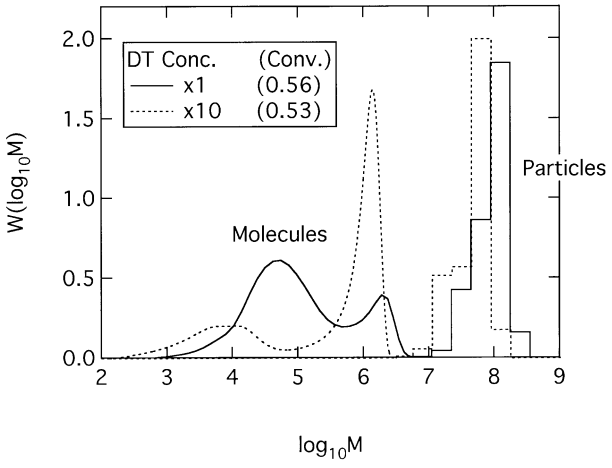

Fig. 5. Comparison of molecular weight distribution profiles when the amount of chain transfer agent is increased to [DT] = 17.9 g/l water. The mole fraction of divinylbenzene is $f_2^0 = 0.05$, and other conditions are the same as those in Fig. 2. As the primary chain length decreases, the location of low molecular weight peak moves to a smaller molecular weight.

using a small amount of crosslinker, is now confirmed experimentally. For the styrene/divinylbenzene system, we found that the bimodal MWD is formed by setting the number of crosslinker per primary chain ca. 5.

The locations of these two peaks can be controlled independently. The location of high molecular weight peak can be controlled by the particle size, and that of the low molecular weight peak by changing the primary chain length.

It was found experimentally that the apparent reactivity of pendant double bonds for crosslinking reaction becomes larger for (1) smaller particles and/or (2) smaller primary chains.

References

[1] Tobita H, Yamamoto K. Macromolecules 1994;27:3389.
[2] Nakamura K, Imoto A, Aota H, Matsumoto A. In: Preprints for the Eighth Polymeric Microsphere Symposium, 1994 Nov 9–11; Fukui, Japan. p. 37.
[3] Matsumoto A, Mori Y, Takahashi S, Aota H. Netsukokasei-Jushi 1995;16:131.
[4] Matsumoto A, Kodama K, Mori Y, Aota H. Pure Appl Chem 1998;A35:1459.
[5] Tobita H, Kumagai M, Aoyagi N. Polymer 2000;41:481.
[6] Matsumoto A, Kobayashi Y, Matsuo T, Aota H. In: Preprints for the Eighth Polymeric Microsphere Symposium, 1994 Nov 9–11; Fukui, Japan. p. 33.
[7] Starkweather Jr. HW, Han MC. J Polym Sci: Polym Chem 1992;30:2709.
[8] Gardon JL. J Polym Sci, Part A-1 1968;11:2859.
[9] Tobita H, Kimura K, Fujita K, Nomura M. Polymer 1993;34: 2569.
[10] Tobita H, Uemura Y. J Polym Sci: Polym Phys 1996;34:1403.
[11] Tobita H. Macromolecules 1992;25:2671.
[12] Ding ZY, Ma S, Kriz D, Aklonis JJ, Salovey R. J Polym Sci: Polym Phys 1992;30:1189.
[13] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press, 1953.
[14] Walling C. J Am Chem Soc 1948;70:2561.
[15] Nomura M, Suzuki H, Tokunaga H, Fujita K. J Appl Polym Sci 1994;51:21.