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ORIGINAL PAPER

Modeling of precipitation polymerization II: calculation of macroradicals concentrations in the continuous and dispersed phases

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Abstract According to Hunkeler model, precipitation polymerization of acrylic acid in organic media takes place simultaneously in the both dispersed and continuous phases. In this research, a model is presented based on mass balances of individual species. Hence, concentrations of macroradicals and polymer chains, in different chain lengths, were calculated in the both phases. Number- and weight-average degrees of polymerization and their distributions were concluded in the both dispersed and continuous phases. Calculation of macroradicals concentration was conducted with quasi-steady state approximation (QSSA) as well as without QSSA (based on the governing differential equations). Macroradical precipitate as soon as reaching to critical chain length. Moreover, precipitation is the main termination reaction in the continuous phase. Polymer with critical chain length is the most populated species in the dispersed phase. Comparison of theoretical and experimental results is in good agreement. QSSA theory gives better results than without QSSA theory because occlusion of macroradicals in the dispersed phase does not occur in the precipitation polymerization of water-soluble monomers in the organic media. This article has proved that the polydispersity index (PDI) of polymer product in the precipitation polymerization of acrylic acid in toluene that follows simultaneous polymerization model is less than that of PDI in the other free radical polymerization methods. Centrifugation method was used to sediment fine polymer particles. The yield of reaction was increased by sedimentation process.

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List of symbols

c	Continuous phase
d	Dispersed phase
I	Initiator
$[I]$	Initiator concentration (mol/L)
k_{cr}	Critical chain length for solubility of macroradicals in the continuous phase
k_d	Rate constant for the thermal decomposition of initiator (min^{-1})
k'_d	Rate constant for the monomer-enhanced decomposition of initiator (L/mol min)
k_p	Rate constant for the chain propagation (L/mol min)
k_{tc}	Rate constant for the chain termination by combination (L/mol min)
k_{td}	Rate constant for the chain termination by disproportionation (L/mol min)
$k_{tr,M}$	Rate constant for the chain transfer to the monomer (L/mol min)
$k_{tr,S}$	Rate constant for the chain transfer to the solvent (L/mol min)
k_v	Rate constant for the change of particle kind (min^{-1})
M	Monomer
$[M]$	Monomer concentration (mol/L)
$\overline{M}_n$	Number-average molecular weight (g/mol)
$\overline{M}_w$	Weight-average molecular weight (g/mol)
PDI	Polydispersity index
P_i	Dead polymer containing i monomer unit
R_0^*	Primary radical
R_i^*	Macroradical containing i monomer unit
$\Re_i$	Rate of initiation (mol/L min)
S	Solvent
V'_P	Molar volume of polymer (L/mol)
$\overline{X}_n$	Number-average degree of polymerization
$\overline{X}_w$	Weight-average degree of polymerization
ϕ_1	Volume fraction of primary particles
ϕ_2	Volume fraction of secondary particles
ϕ_c	Volume fraction of continuous phase
ϕ_d	Volume fraction of dispersed phase
φ	Partition coefficient between continuous and dispersed phase
$[\eta]$	Intrinsic viscosity (L/g)
λ	Conventional moment for macroradicals
λ^*	Finite moment for macroradicals
μ	Conventional moment for dead polymers
μ^*	Finite moment for dead polymers
ς	Probability of propagation reaction

Introduction

In semi-heterogeneous methods, such as precipitation and dispersion polymerizations, reaction is initiated in the homogeneous phase (continuous) upon adding the initiator. Then, the system becomes heterogeneous as the formed polymer precipitate into solid particle. Consequently, polymerization is assumed mainly occurs inside the precipitated polymer particles [1, 2].

In the precipitation and dispersion polymerization, there are four theories (model) for loci of polymerization reactions; solution polymerization model (all of the polymerization reactions take place in the continuous phase) [3–7], surface polymerization model (initiation take place in the continuous phase but propagation and termination occurs in the thin layer on the surface of the polymer particles) [8, 9], interior polymerization model (initiation take place in the continuous phase but propagation and termination occur in the polymer particles) [10–13], and simultaneous polymerization model (polymerization reactions are able to occur simultaneously in the both dispersed and continuous phases) [14–22].

Bouhendi et al. [22] have presented method of finite molecular weight moment to calculate number- and weight-average degrees of polymerization in the continuous phase of the precipitation polymerization that follows simultaneous polymerization model. According to that study, moment equations have been presented as follows:

$$\frac{\mathrm{d}\mu_0^*}{\mathrm{d}t} = \left[k_{\mathrm{tr,M}}[M] + k_{\mathrm{td}}[R]\right][R]\left(\varsigma^{n-1} - \varsigma^{m-1}\right) + \frac{1}{2}k_{\mathrm{tc}}[R]^2 \left(\varsigma^{-1} - 1\right)\left\{\varsigma^{n-1}\left[n - 1 + (1-\varsigma)^{-1}\right] - \varsigma^{m-1}\left[m - 1 + (1-\varsigma)^{-1}\right]\right\} \tag{1}$$

$$\frac{\mathrm{d}\mu_1^*}{\mathrm{d}t} = \left[k_{\mathrm{td}}[R] + k_{\mathrm{tr,M}}[M]\right]\left\{\varsigma^n\left[n + (1-\varsigma)^{-1}\right] - \varsigma^m\left[m + (1-\varsigma)^{-1}\right]\right\}[R]\varsigma^{-1} + \frac{1}{2}k_{\mathrm{tc}}[R]^2(1-\varsigma)\varsigma^{-2}\left\{\begin{array}{c}\varsigma^n\left[n^2 + \left(2(1-\varsigma)^{-1}+1\right)\left(n + (1-\varsigma)^{-1}\right)\right] \\ -\varsigma^m\left[m^2 + \left(2(1-\varsigma)^{-1}+1\right)\left(m + (1-\varsigma)^{-1}\right)\right]\end{array}\right\} \tag{2}$$

$$\frac{\mathrm{d}\mu_2^*}{\mathrm{d}t} = \left(k_{\mathrm{tr,M}}[M] + k_{\mathrm{td}}[R]\right)\left\{\begin{array}{c}\varsigma^n\left[n^2 + 2(1-\varsigma)^{-1}\left(n + (1-\varsigma)^{-1}\right)\right] \\ -\varsigma^m\left[m^2 + 2(1-\varsigma)^{-1}\left(m + (1-\varsigma)^{-1}\right)\right]\end{array}\right\} + \frac{1}{2}k_{\mathrm{tc}}[R]^2(1-\varsigma)\varsigma^{-1}\left\{\begin{array}{l}\varsigma^n\left\{n^3 + \left(3(1-\varsigma)^{-1}+1\right)\left[n^2 + 2(1-\varsigma)^{-1}\left(n + (1-\varsigma)^{-1}\right)\right]\right\} - \\ \varsigma^m\left\{m^3 + \left(3(1-\varsigma)^{-1}+1\right)\left[m^3 + 2(1-\varsigma)^{-1}\left(m + (1-\varsigma)^{-1}\right)\right]\right\}\end{array}\right\} \tag{3}$$

where $\mu^*$is the finite moments for dead polymer chains and ς is the probability of propagation reaction.

There are two defects in the previous study [22] that we have been compelled to present a new method to calculate all polymerization features in the both phases: (1) The yield of polymerization in the beginning of reaction was immeasurable and (2) The polydispersity index (PDI) of polymer formed in the dispersed phase that

were measured by experimental data were less than that of PDI that were calculated by modeling.

In this article, first, modeling was performed with quasi-steady state approximation (QSSA) and without QSSA (governing differential equations). Concentrations of all macroradicals and polymer chains, whose chain length is less than critical value in the both phases, were calculated. Second, polymerization was conducted in laboratory setup, the method of centrifugation was used for purification of polymer product and third, this method was compared with the method of finite moment and the advantages of the new method was investigated.

Polymerization mechanism

In this research, like the previous one [22], it was assumed that all polymerization reactions (initiation, propagation, and termination) take place simultaneously in the both dispersed and continuous phases. Moreover, polymerization occurred isothermally and there are no changes in volume [21, 22]. The chain transfer reactions to polymer and initiator were neglected in the both dispersed and continuous phases [21, 22].

The reactions in the continuous and dispersed phase are

$I_j \xrightarrow{k_{\mathrm{dj}}} 2R_{0,j}$	Initiator decomposition
$I_j + M_j \xrightarrow{K'_{\mathrm{dj}}} R^*_{1,j} + R^*_{0,j}$	Monomer enhanced decomposition of initiator
$R^*_{0,j} + M_j \xrightarrow{k_{\mathrm{pj}}} R^*_{1,j}$	Initiation
$R^*_{i,j} + M_j \xrightarrow{k_{\mathrm{pj}}} R^*_{i+1,j}$	Propagation
$R^*_{i,j} + M_j \xrightarrow{k_{\mathrm{tr,Mj}}} R^*_{1,j} + P_i$	Transfer to monomer
$R^*_{i,j} + S \xrightarrow{k_{\mathrm{tr,Sj}}} S^* + P_i$	Transfer to solvent
$R^*_{i,j} + R^*_{r,j} \xrightarrow{k_{\mathrm{tdj}}} P_i + P_r$	Termination by disproportionation
$R^*_{i,j} + R^*_{r,j} \xrightarrow{k_{\mathrm{tcj}}} P_{i+r}$	Termination by combination

where I, M, R^*_0, R^*_i, S, P_i are initiator, monomer, primary radicals, macroradicals-containing monomer unit, solvent, and dead polymer-containing monomer unit, respectively, and j could be either "d" or "c" that stands for dispersed and continuous phases, respectively.

Mass transfer between continuous and dispersed phases could be represented by the following form, showing mutual possible mass transfer:

$$\beta_{\mathrm{c}} \overset{\varphi_\beta}{\leftrightarrow} \beta_{\mathrm{d}}$$

where β corresponds R^*_{in}, R^*, M, P, and $I\,\varphi$ are the partition coefficient between continuous and dispersed phases and calculated as follows:

$$\varphi_\beta = \frac{[\beta]_c}{[\beta]_d} \tag{4}$$

Precipitation of macroradicals in the continuous phase, which is a termination reaction in the continuous phase [26]:

$$R^*_{c,k_{cr}-1} + M_c \xrightarrow{k_p} Rc^*_{c,k_{cr}} \xrightarrow{k_d} R^*_{d,k_{cr}} \xrightarrow{k_t^*} \text{Inert}$$

where k_{cr} is critical chain length for macroradical precipitation [23]. This termination reaction is very fast and the polymer chains with $i = k_{cr}$ form primary particle of dispersed phase.

Process modeling

In the polymerization of water-soluble monomers such as acrylamide and acrylic acid, the rate constant for the monomer-enhanced decomposition of initiator, $k_d^{'}$ is much greater than rate constant for thermal decomposition of initiator, k_d. The rate of monomer-enhanced decomposition of initiator is at least 15 times larger than the rate of thermal decomposition [26]. Then, the rate of initiator consumption can be written as:

$$\frac{d[I]}{dt} = -\left(k_d^{'}[I]_c[M]_c\phi_c + k_d^{'}[I]_d[M]_d\phi_d\right) \tag{5}$$

where ϕ_c and ϕ_d are volume fractions of dispersed and continuous phases and were calculated by Eqs. 6–8 [11, 12]:

$$\phi_d = 1 - \phi_c = \phi_1 + \phi_2 \tag{6}$$

$$\frac{d\phi_1}{dt} = \frac{dp}{dt}[M]_0 V_P^{'} - k_v\phi_1 \tag{7}$$

$$\frac{d\phi_2}{dt} = k_v\phi_1 \tag{8}$$

where ϕ_1 and ϕ_2 are volume fractions of primary particles (primary nucleus) and secondary particles, respectively. In Eqs. 7 and 8, $V_P^{'}$, k_v, and p are molar volume of polymer, rate constant for changing particle kind and monomer conversion, respectively.

Monomer is consumed by propagation and chain transfer to monomer reactions, in the both continuous phase and polymer particles. Mass balance for monomer is

$$\frac{d[M]}{dt} = -\left[k_p[M]_c[R]_c\phi_c + k_p[M]_d[R]_d\phi_d\right] - \left[k_{tr,M}[M]_c[R]_c\phi_c + k_{tr,M}[M]_d[R]_d\phi_d\right] \tag{9}$$

Macroradicals and dead polymer concentrations could be obtained by following equations:

$$\frac{d[R_0]_j}{dt} = k'_d[I]_j[M]_j - k_i[M]_j[R_0]_j = 0 \quad (10)$$

$$\frac{d[R_1]_j}{dt} = k'_v[I]_j[M]_j - k_p[M]_j[R_1]_j - (k_{tc} + k_{td})[R_1]_j[R]_j \quad (11)$$

Mass balance for macroradicals and dead polymer containing n monomer unit are

$$\frac{d[R_n]_j}{dt} = k_p[M]_j\left([R_{n-1}]_j - [R_n]_j\right) - k_t[R_n]_j[R]_j - \left(k_{tr,M}[M]_j + k_{tr,S}[S]_j\right)[R_n]_j \quad (12)$$

$$\frac{d[P_n]_j}{dt} = k_{td}[R_n]_j[R]_j + \frac{1}{2}k_{tc}\sum_{m=1}^{n}[R_m]_j[R_{n-m}]_j + (k_{tr,M}[M]_j + k_{tr,S}[S]_j)[R_n]_j \quad n > 1 \quad (13)$$

In the previous study, Eqs. 1–3 were proved by solving Eqs. 12 and 13 using finite moment method and the averages degree of polymerizations were calculated by solving differential equations 1–3, 5, and 7–9, and so on [22].

Calculation of macroradicals and dead polymer chains concentrations in the continuous phase

In the continuous phase, length of marcoradical and polymer could be up to 2081 (k_{cr}) [23]. However, in dispersed phase, length of macroradical and polymer could be up to infinity. According to quasi-steady state assumption (QSSA), the rate of termination is equal to the rate of initiation, and then the total concentrations of macroradicals are constant. Therefore, in Eqs. 11 and 12, accumulation terms are zero therefore, in the continuous phase; Eqs. 11 and 12 were rewritten as

$$2k'_d[I]_c[M]_c - k_p[M]_c[R_1]_c - (k_{tc} + k_{td})[R_1]_c[R]_c = 0 \quad (14)$$

$$k_p[M]_c\left([R_{n-1}]_c - [R_n]_c\right) - k_t[R_n]_c[R]_c - \left(k_{tr,M}[M]_c + k_{tr,S}[S]_j\right)[R_n]_c = 0 \quad (15)$$

Then, the concentrations of radical with unity chain length and macroradicals with n repeating unit in the continuous phase can be written as

$$[R_1]_c = \frac{2k'_d[I]_c[M]_c}{k_p[M]_c + (k_{tc} + k_{td})[R]_c} \quad (16)$$

$$[R_n]_c = \frac{k_p[M]_c[R_{n-1}]_c}{k_p[M]_c + (k_{tc} + k_{td})[R]_c + \left(k_{tr,M}[M]_c + k_{tr,S}[S]_c\right)} \quad (17)$$

where $2 \le n \le 2081$ in the continuous phase. Therefore, there are 2081 algebraic equations for calculating macroradicals concentrations and 2081 differential equations for calculating concentrations of polymer chains in the continuous phase.

Calculation of macroradicals and dead polymer chains concentrations in the dispersed phase

For calculating macroradicals concentration in the dispersed phase, two cases have been assumed:

Case I: according to quasi-steady state assumption, the rate of termination is equal to the rate of initiation in the dispersed phase too, and then the macroradicals concentration could be calculated in the dispersed phases by Eqs. 16 and 17 where the number of repeating unit was less than critical value (k_{cr}). According to partitioning step definition, these macroradicals are able to transfer to the continuous phase. Equation 13 was used to calculate the concentration of polymer chains with repeating unit less than critical value in the dispersed phase.

The overall concentration of macroradicals and polymer chains with repeating unit more than k_{cr} were calculated by the method of finite moment when $k_{cr}+1 \le n < \infty$:

$$\frac{d\lambda_0^{\infty}}{dt} = \Re_i + \left[-k_p[M]_d\left(\varsigma^{-1}-1\right) + k_{tr,M}[M]_d + k_t[R]_d\right][R]_d\left(-\varsigma^{k_{cr}}\right) - \left[k_p[M]_d + k_{tr,M}[M]_d + k_t[R]_d\right](1-\varsigma)[R]_d \tag{18}$$

$$\frac{d\lambda_1^{\infty}}{dt} = \Re_i + \left[k_p[M]_d\left(\varsigma^{-1}-1\right) + k_{tr,M}[M]_d + k_t[R]_d\right]\left\{\varsigma^{k_{cr}+1}\left[k_{cr}+1+(1-\varsigma)^{-1}\right]\right\} - \left[k_p[M]_d + k_{tr,M}[M]_d + k_t[R]_d\right](1-\varsigma)[R]_d \tag{19}$$

$$\frac{d\lambda_2^{\infty}}{dt} = \left[-k_p[M]_d\left(\varsigma^{-1}-1\right) + k_{tr,M}[M]_d + k_t[R]_d\right] \times \left\{-\varsigma^{k_{cr}+1}\left[(k_{cr}+1)^2 + 2(1-\varsigma)^{-1}\left(k_{cr}+1+(1-\varsigma)^{-1}\right)\right]\right\} + \Re_i - \left(k_p + k_{tr,M}\right)[M]_d(1-\varsigma)[R]_d - k_t(1-\varsigma)[R]_d^2 \tag{20}$$

And

$$\frac{d\mu_0^{\infty}}{dt} = \left[k_{tr,M}[M]_d + k_{td}[R]_d\right][R]_d\left(\varsigma^{n-1}\right) + \frac{1}{2}k_{tc}[R]_d^2\left(\varsigma^{-1}-1\right)\left\{\varsigma^{k_{cr}}\left[k_{cr}+(1-\varsigma)^{-1}\right]\right\} \tag{21}$$

$$\frac{d\mu_1^{\infty}}{dt} = \left[k_{td}[R]_d + k_{tr,M}[M]_d\right]\left\{\varsigma^{k_{cr}+1}\left[k_{cr}+1+(1-\varsigma)^{-1}\right]\right\}[R]_d\varsigma^{-1} + \frac{1}{2}k_{tc}[R]_d^2(1-\varsigma)\varsigma^{-2}\left\{\varsigma^{k_{cr}+1}\left[(k_{cr}+1)^2 + \left(2(1-\varsigma)^{-1}+1\right) \times \left(k_{cr}+1+(1-\varsigma)^{-1}\right)\right]\right\} \tag{22}$$

$$\frac{d\mu_2^{\infty}}{dt} = \left(k_{tr,M}[M]_d + k_{td}[R]_d\right)\left\{\varsigma^{k_{cr}+1}\left[(k_{cr}+1)^2 + 2(1-\varsigma)^{-1}\left(k_{cr}+1+(1-\varsigma)^{-1}\right)\right]\right\} + \frac{1}{2}k_{tc}[R]_d^2(1-\varsigma)\varsigma^{-1}\left\{\varsigma^{k_{cr}+1}\left\{(k_{cr}+1)^3 + \left(3(1-\varsigma)^{-1}+1\right) \left[(k_{cr}+1)^2 + 2(1-\varsigma)^{-1}\left(k_{cr}+1+(1-\varsigma)^{-1}\right)\right]\right\}\right\} \tag{23}$$

where $[R]_d = \sum_{i=k_{cr}}^{\infty}[R_i]_d$, $k_t = k_{tc} + k_{td}$, and $\Re_i = k_d'[I][M]$ are the rate of initiation reaction. The method of finite molecular weight moment [22] was used to derive Eqs. 18–23.

Therefore, there are 2081 algebraic equations and 2085 differential equations for calculating the concentrations of macroradicals and polymer chains in the dispersed phase.

Case II: QSSA may not be used for precipitation polymerization of acrylic acid in the dispersed phases because, macroradicals may be occluded in the dispersed phase and rate of termination was decreased in this phase. In the precipitation and dispersion polymerizations, macroradicals occlusion may be occur in the polymer particles. According to this theory, rate of termination is decreased in the dispersed phase, 2. Then, whole set of differential equations (4166) must be solved in the dispersed phase.

One of alternative approach is to consider distinct species such as different length of macroradical and polymer chains. This is a new approach in order to analyze polymerization system due to huge number of differential equation. Therefore, mentioned equations form a set of ordinary differential equations consisting 8332 equations. Lack of computing ability in normal computers is a drawback of this approach. Consequently, this massive set of differential equations are solved by HP Server Pentium intell 4×2.3 GHz. Hence, two distinct approaches could be applied as solution technique.

By solving those equations, number distributions of degree of polymerization (x_i) were calculated by [24]:

$$x_{i,j} = \frac{[P_i]_j}{N_j}, \quad N_c = \sum_{i=2}^{k_{cr}} [P_i]_c \quad \text{Continuous phase}$$

$$N_d = \sum_{i=2}^{k_{cr}} [P_i]_d + \mu_0^{\infty} \quad \text{Dispersed phase} \tag{24}$$

Then, the number-average degree of polymerization in the both dispersed and continuous phases were calculated by [24]:

$$\overline{X}_{n,c} = \sum_{i=2}^{k_{cr}} x_{i,c} i \overline{X}_{n,d} = \int_2^{\infty} x_{i,d} i \tag{25}$$

Weight distribution of degree of polymerization and weight average degree of polymerization were calculated by:

$$w_{i,j} = \frac{i x_{i,j}}{\overline{X}_{n,j}} \tag{26}$$

$$\overline{X}_{w,c} = \sum_{i=1}^{k_{cr}} w_{i,c} i \quad \overline{X}_{w,d} = \int_{i=2}^{\infty} w_{i,d} i \tag{27}$$

The desired kinetic constants and other necessary parameters of acrylic acid are listed in Table 1.

Table 1 Kinetic constants

Parameter	Value	Ref.
$k_d^{'}$	13.2×10^{-3} L/mol min	[21]
k_p	108×10^{3} L/mol min	[21, 25, 26]
k_{td}	58.8×10^{4} L/mol min	[21, 23]
$k_{tr,M}$	162 L/mol min	[21, 23]
k_v	0.18×10^{-3} s^{-1}	[11, 12]
k_{tc}	0	[21, 23]
$k_{tr,S}$	0	[21, 23]
$[M]_0$	1.252 mol/L	–
$[I]_0$	8.5 mmol/L	–
V_P	0.052 L/mol	[11, 12]
φ_I	1	[21]
φ_M	1	[21]
φ_{R^*}	1	[21]
k_{cr}	2081	[21, 23]

φ_I, φ_M are constant and do not depend on conversion

φ_{R^*} is constant and do not depend on conversion and macroradical chain length

Experiment

Reagents and procedures

Reagents and procedures were explained in Reference [22] by Bouhendi et al.

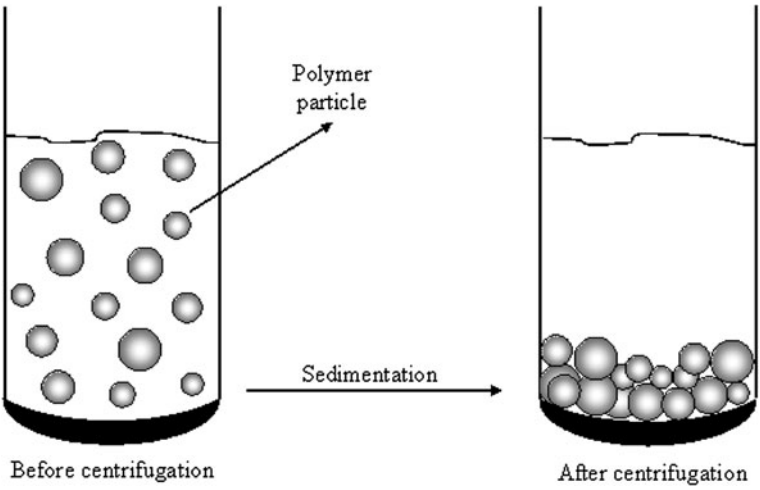
Purification process

The centrifugation method was used to separate very fine particle from diluent. 20 mL toluene was immersed in the reactor to dilute the reaction mixture; the mixture was immersed in the centrifugation tube. The centrifuge apparatus was Denly-BS 400, the process were done at 1500 rpm and the process time was 30 min. According to Scheme 1, the mixture has been in two phases because of particles sedimentation. The lower phase (polymeric product) was immersed in a vacuum oven at 50 °C for 12 h, and then the monomer conversion was measured using a gravimetric method.

Molecular weights measurements

Ubbelohde viscometer is a good method to calculate number- and weight-average molecular weights of water-soluble polymers [21], and then molecular weight measurements were carried out by Ubbelohde dilution viscometer. The number- and weight-average molecular weights of precipitated polymers were calculated by following equations [27]:

$$[\eta]_1 = 15.47 \times 10^{-3} \overline{M}_n^{0.9} \tag{28}$$



Scheme 1 Purification process by sedimentation

Table 2 The results of experiments: $[I]_0$ = 8.5 mmol/L and $[M]_0$= 1.252 mol/L

Time (min)	Conventional method [22]					Centrifugation				
	Yield	$\overline{M}_n$ (g/mol)	$\overline{X}_n$	$\overline{M}_w$ (g/mol)	$\overline{X}_w$	Yield	$\overline{M}_n$ (g/mol)	$\overline{X}_n$	$\overline{M}_w$ (g/mol)	$\overline{X}_w$
10	–	–	–	–	–	0.47	47268	656.5	87264	1212
15	–	–	–	–	–	0.52	47232	656	87120	1210
20	0.61	47088	654	87120	1210	0.68	46944	652	86400	1200
30	0.70	47088	654	87120	1210	0.80	46800	650	86040	1195
50	0.92	46152	641	86400	1200	0.93	46008	639	86184	1197
60	0.95	45432	631	84816	1178	0.96	45360	630	84960	1180

$$[\eta]_2 = 124 \times 10^{-3}\overline{M}_w^{0.5} \tag{29}$$

Result and discussions

Table 2 shows experimental results of this article. These experimental results were compared with the experimental results of previous article [22]. The yield of reaction was increased by centrifugation method because centrifugation method sediment not only coarse particles but also tiny ones, there fore polymer product was increased. The yield of reaction at 5 and 10 min could be measured by the centrifugation method; however, those yields of reactions could not have been measured in the previous study [22].

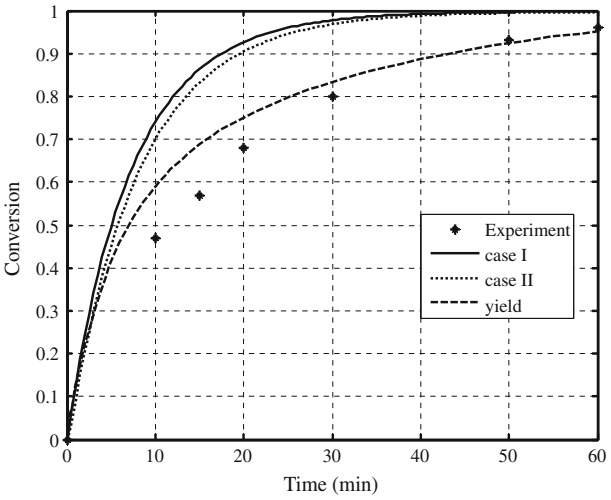


Fig. 1 Monomer conversion and yield of reaction versus time

Figure 1 shows monomer conversion versus time. Deviation between experimental data and models could be contributed to purification process of polymer product. Low molecular weight polymers in the continuous phase exit during rewashing of the product by diluent. Because diluent (nonsolvent) is able to dissolve remained monomer, initiator, and low molecular weight polymers (oligomers) that were formed in the continuous phase and were remained in that phase.

The monomer conversions that were measured by experimental data are less than that of conversions that were calculated by the model. Therefore, it is possible to calculate yield of reaction by meaning of gravimetric method. It is assumed that polymer particles (dispersed phase) and polymer chains with critical chain length in the continuous phase cannot dissolve in the diluent during purification process of product. Hence, there are some oligomers in the dispersed phase that cannot be removed from this phase because they are occluded in the polymer particles. Then, the yield of reaction is defined as

$$\text{Yield} = \frac{\left(\phi_{\text{d}} \sum_{i=2}^{2081} i[P_i]_{\text{d}} + \phi_{\text{c}} \sum_{i=2080}^{2081} i[P_i]_{\text{c}} + \frac{\phi_{\text{c}}}{\phi_{\text{P}}} \sum_{i=2}^{2080} i[P_i]_{\text{c}}\right)}{[M]_0} \tag{30}$$

The first term of Eq. 30 is polymer chains that are formed in dispersed phase, the second term is the polymer chains with critical chain length that are formed in continuous phase and form primary nucleus of dispersed phase, and the third term is the polymer chains that are formed in continuous phase and transfer to the dispersed phase.

Monomer conversion in case II is less than that of conversion in case I; as a result, the concentration of macroradicals in case I is more than that of concentration in case II.

Mathematical modeling is able to calculate rate of polymerization and number- and weight-average degree of polymerization [11, 12, 21]. Moments equations are

able to calculate cumulative concentration of polymers and macroradicals. This method calculates separately concentration of all polymer chains and macroradicals in the both phases. Therefore, the concentration of polymer chains with critical chain length in the both phases is presented in this research. $P_{k_{cr}\text{exit}}$ is the concentration of polymer chains with critical chain length in the continuous phase. It is formed either by precipitation reaction (termination) of a macroradical with critical chain length in the continuous phase. These polymer chains precipitate from continuous phase and form primary particles of dispersed phase. $P_{k_{cr}\text{prod}}$ is the concentration of polymer chains with critical chain length in the dispersed phase. It is formed by bimolecular termination in the dispersed phase and remained in that phase [11, 12]. Then, the concentration of polymer chains with critical chain length in the dispersed phase is sum of the $P_{k_{cr}\text{exit}}$ and $P_{k_{cr}\text{prod}}$. According to Fig. 2, $P_{k_{cr}\text{exit}}$ is more than $P_{k_{cr}\text{prod}}$; as a result, the main polymer chains with critical chain length are formed in the continuous phase and termination by precipitation dominates bimolecular termination in the continuous phase. $P_{k_{cr}\text{exit}}$ is decreased and $P_{k_{cr}\text{prod}}$ is increased by increasing monomer conversion. This behavior is due to decreasing monomer concentration in the continuous phase and increasing it in the dispersed phase because of increasing volume fraction of dispersed phase. Moreover, $P_{k_{cr}\text{prod}}$ in the both cases are similar but $P_{k_{cr}\text{exit}}$ in case II is more than $P_{k_{cr}\text{exit}}$ in case I. Consequently, bimolecular termination in case I is more than that of termination in case II.

The present method is able to calculate number- and weight-average degrees of polymerization, separately, in the both continuous and dispersed phases. Moreover, it is able to compute number- and weight-average degrees of polymerization, separately. Figures 3 and 4 show number- and weight-average degrees of polymerization versus monomer conversion. Experimental results are in good

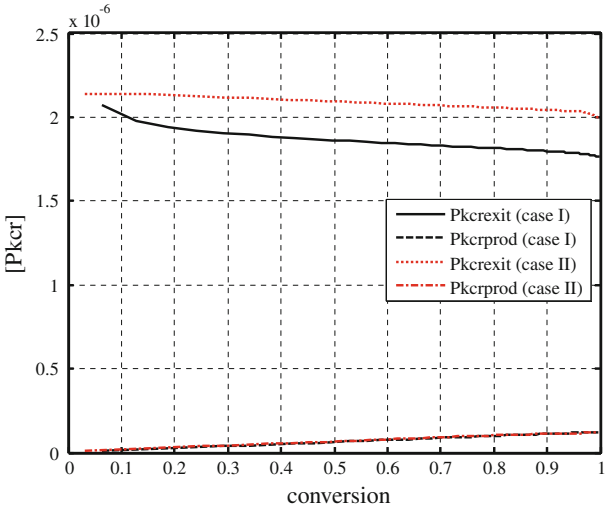


Fig. 2 Concentration of polymer chains with critical chain length as a function of conversion in the both phases

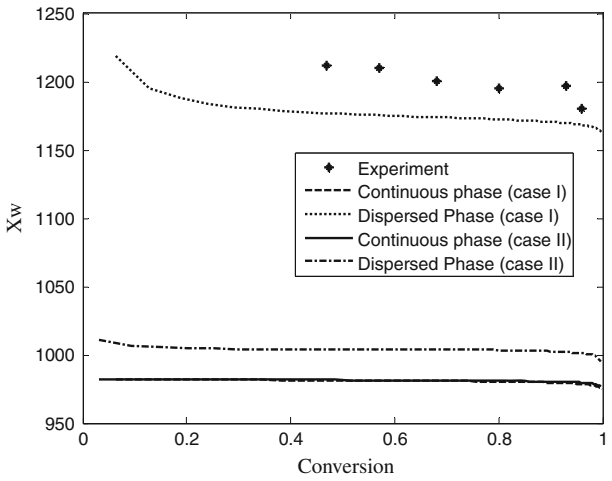


Fig. 3 Weight-average degree of polymerization as a function of conversion for dispersed and continuous phases

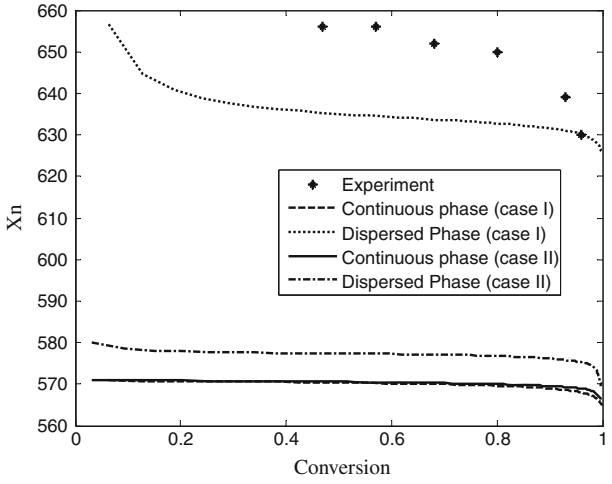


Fig. 4 Number-average degree of polymerization as a function of conversion for dispersed and continuous phases

agreement with number- and weight-averages degrees of polymerization in the dispersed phase. In Fig. 3, $\overline{X}_n \approx 1180 - 1212$ was measured by experiment and $\overline{X}_n = 1180$ was calculated by the model. The deviation is about 2.5%, this deviation is negligible. Therefore, place of experimental data in this range is somehow misleading.

Experimental results are in good agreement with number- and weight-average degrees of polymerization that was calculated by case I. However, results of case II deviate from experimental results. Therefore, case I is able to predict behavior of

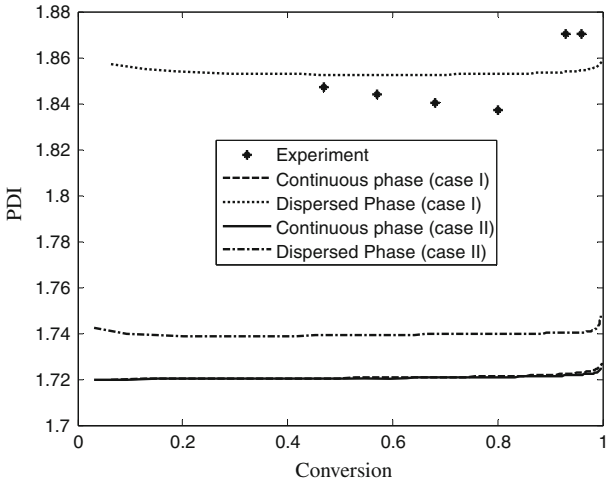


Fig. 5 PDI of polymer formed in the both continuous and dispersed phases

precipitation polymerization of acrylic acid in toluene. It means that, there is no hindrance for macroradicals termination in the dispersed phase. In the other words, the macroradicals occlusion in the dispersed phase does not happen in the precipitation polymerization of acrylic acid in toluene.

A grateful result that was observed by this modeling method is shown in Fig. 5. PDI of polymer formed in the both phases was shown in this figure. The PDI of polymer formed in the continuous phase are less than 2. In free radical polymerization, the PDI value is equal to 2 when disproportionation is main termination reaction; however, in the precipitation polymerization, termination by precipitation dominates conventional termination (disproportionation) in the continuous phase and there are not polymer chains with repeating unit more than critical value in the continuous phase (Fig. 6). Therefore, the molecular weight distribution is narrow in the continuous phase. PDI value is less than 2 for also the dispersed phase, because the polymer chains with $i = k_{cr}$ that had been formed in the continuous phase formed primary particles of dispersed phase, therefore the concentration of polymer chains with critical repeating unit is very high in the dispersed phase (see the sharp peak in the $x_i - i$ graph of dispersed phase in the Fig. 6). Therefore, PDI value of polymer chains in the dispersed phase, in the other words, PDI value of polymer product is less than PDI value of other free radical polymerization method. Bunyakan et al. [21, 23] did not calculate PDI value; they have assumed that this value was equal to 2. The other researcher did not calculate PDI value, and then for the first time, this article present the PDI value in the precipitation polymerization of water-soluble monomer in the organic media is less than that of value by the other free radical polymerization methods.

Figure 6 shows number and weight degree of polymerization distributions that were calculated by Eqs. 24 and 26 versus chain length for the both dispersed and continuous phases. It is observed that precipitation polymerization similar to homogeneous polymerizations follows Scholtz–Flory distribution function.

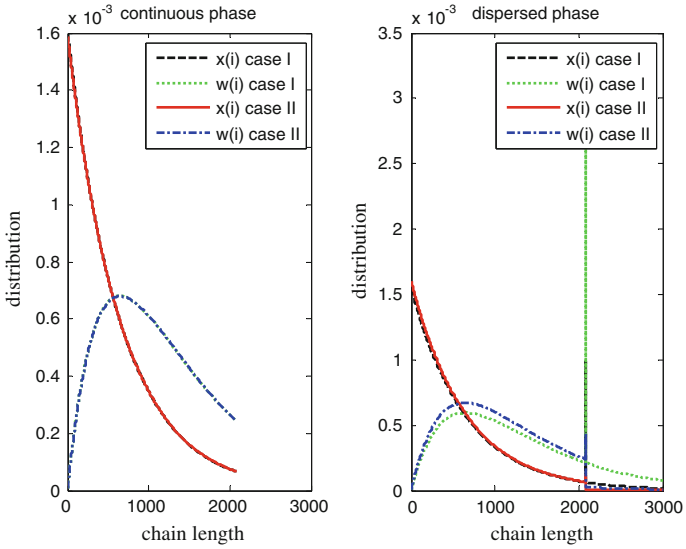


Fig. 6 Degree of polymerization distributions at the end of reaction time as a function of chain length in the both continuous (*left*) and dispersed (*right*) phases

Scholtz–Flory distribution function explains degree of polymerization distribution in the continuous and dispersed phases in this article. Cases I and II has the same distribution functions in the continuous phase and the same number degree of polymerization distribution in the dispersed phase. In the precipitation polymerization, number and weight degree of polymerization distributions have a sharp peak at critical chain length ($i = k_{cr}$) in the dispersed phase because termination by precipitation is the main reaction in the continuous phase, the polymer chains with critical chain length precipitate from continuous phase and form primary particles of dispersed phase. Therefore, polymer chains, with $i = k_{cr}$, are accumulated in the dispersed phase. By increasing the weight average degree of polymerization in the dispersed phase, a bimodal distribution appears in the plot of w_i versus i [28]. Precipitation polymerization of Vinylidene fluoride in supercritical carbon dioxide has a bimodal distribution in the continuous process too [20].

Comparison between (finite) moment method (M.M.) [22] and this new method

Figures 7 and 8 present a comparison between the two methods. According to Fig. 7, the number- and weight-average degrees of polymerization of polymer formed in the continuous phase that were calculated by the method of M.M. are equal to those of averages degrees of polymerization that were calculated by this article. It means that, the finite moment method are able to compute the polymer chains with critical chain length that were left the continuous phase, therefore the finite moment method is a perfect method to investigate polymerization features in the continuous phase.

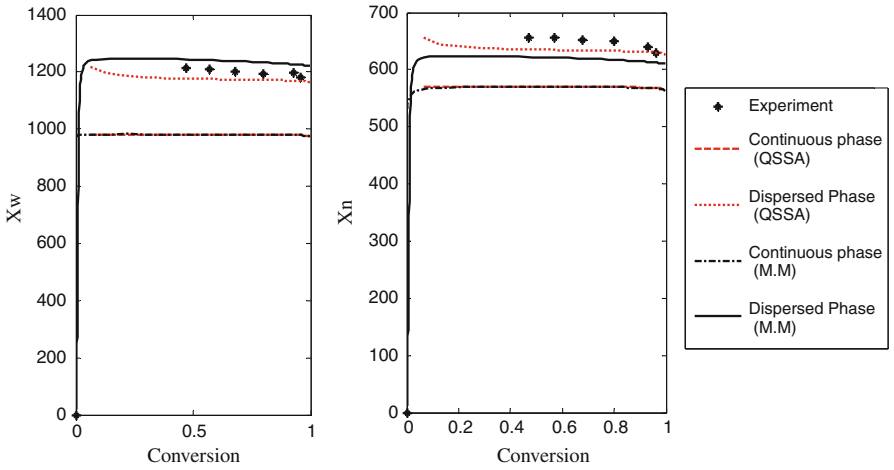


Fig. 7 Number- and weight-average degrees of polymerization that was calculated by M.M. method and the new method

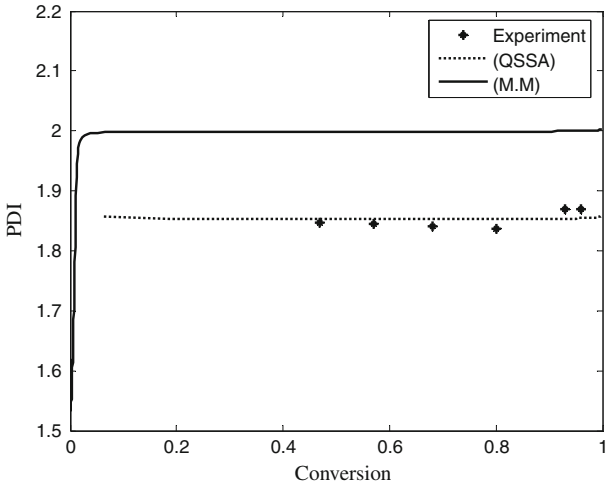


Fig. 8 PDI value versus conversion that was calculated by the M.M. method and the new method

In the dispersed phase, the weight average degree of polymerization that was calculated by moment method is more than that of degree of polymerization that was calculated in this article; however, the number-average degree of polymerization that was calculated by moment method is less than that of degree of polymerization that was calculated in this article.

According to previous study result, there is no limitation (precipitation reaction) for macroradicals propagation in the dispersed phase; M.M. methods were able to compute the number- and weight-average degrees of polymerization of polymer formed in the dispersed phase. This method was not able to compute the averages molecular weight of low molecular weight oligomers ($i = k_{cr}$) that were added to

the disperse phase; however, those oligomers were calculated when the concentration of all polymer chains with various repeating unit was computed in this article. These oligomers with critical repeating unit cause increasing the number-average degree of polymerization and decreasing the weight average degree of polymerization in the continuous phase.

The other reason that investigates degree of polymerization difference is due to macroradicals transfer between two phases. Macroradicals are able to transfer between two phases, Eq. 4 defines the macroradical concentration ratio between two phases. In the previous study, the concentration of macroradicals in the dispersed phase was calculated by the conventional moment method [22]. The moment method was able to calculate overall concentration of macroradicals in the dispersed phase. It was not able to calculate separately the concentration of macroradicals with $i < k_{cr}$ (or $i < k_{cr}$) in the dispersed phase. Therefore, it had been assumed that all macroradicals in the dispersed phase are able to return to the continuous phase. However, in this article the concentration of all macroradicals in the dispersed phase were calculated separately, therefore the macroradicals with $i < k_{cr}$ in the dispersed phase were able to return to the continuous phase and the macroradicals with $i \geq k_{cr}$ were remained in the dispersed phase because of insolubility of that macroradicals. It was shown clearly in Fig. 6 that the concentration of polymer chains with $i < k_{cr}$ in the continuous phase is more than that of concentration in the dispersed phase. Scholtz–Flory distribution function shows that the concentration of short polymer chains was more than that of long polymer chains in the dispersed phase, meaning that the exit of low molecular weight oligomers from dispersed phase does not affect clearly on that concentration in the dispersed phase, therefore the polymer formed in the dispersed phase (1180) is less than critical chain length value (k_{cr}).

According to mentioned results, the deviation between experimental results and the number- and weight-average degrees of polymerization that was calculated by the new modeling method is less than that of deviation that was calculated by the moment method and the PDI value that was calculated by the new method was fitted with experimental data and is less than that of PDI that was calculated by moment method (Fig. 8).

Disadvantage of the new method

In this article, the concentrations of all of macroradicals and all of polymer chains in the continuous phase and the concentrations of macroradicals and polymer chains with repeating unit $i < k_{cr}$ in the dispersed phase were calculated by a lot of algebraic and/or differential equations, the number of those equations are increased by increasing k_{cr} value, therefore solving a lot of algebraic and differential equations is difficult and time consuming.

Conclusions

The proposed method like the method of molecular weight moments is able to calculate separately polymerization features in the both dispersed and continuous

phases such as concentration of all polymer chains and macroradicals in the both phases. Number- and weight-average degrees of polymerization distributions could be computed in the dispersed and continuous phases. The deviation between experimental results and number- and weight-average degrees of polymerization that was calculated by the new method, is less than that of deviation that was calculated by the moment method and the PDI value that was calculated by the new method was fitted with experimental data and is less than that of PDI that was calculated by moment method. The PDI of polymer formed in the precipitation polymerization is less than that of PDI by the other free radical polymerization methods because of accumulation of polymer chains with critical repeating unit in the dispersed phase.

Degree of polymerization distribution for precipitation polymerization is similar to the Scholtz–Flory distribution function but has a sharp peak at critical chain length in the dispersed phase because the polymer chains with critical chain length formed the primary particles of dispersed phase. According to this study, case I is adapted with experimental data. Then QSSA is a good assumption for precipitation polymerization of water-soluble monomer in organic media, therefore occlusion phenomena do not occur in the dispersed phase.

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