A population balance model for miniemulsion polymerization

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Received 25 January 2003; revised received 10 October 2003; accepted 13 January 2004

Miniemulsion polymerization is mechanistically distinct from the conventional emulsion polymerization in several aspects; the most important being that the nucleation occurs in the small and stable monomer droplets. This process is being used to produce polymer latexes of unusual characteristics. The initial droplet size distribution and the final particle size distribution in miniemulsion polymerization are broad. This has not been addressed by the present models, which are based on the grosser perspectives of this system and assume monodisperse droplet size and particle size distributions. A population balance model for the miniemulsion polymerization that incorporates the particle size distribution is developed in this work. The model predictions are verified against data taken from the literature.

ICP Code: C08F 2/22

Keywords: Population balance model, miniemulsion, polymerization

Miniemulsions are comprised of relatively stable monomer droplets, in the size range of 50-500 nm, dispersed in an aqueous medium. The polymerization of miniemulsion opens the possibilities of the widely applied emulsion polymerization and provides advantage with respect to incorporation of hydrophobes, copolymerization of monomers with different polarities, homopolymerization of water insoluble monomers, and with respect to the stability of the formed latexes. Miniemulsion polymerization process is more robust to contaminants, and gives a product with a more uniform copolymer composition, high shear-stability and a wide range of final particle size distribution varying from narrow to very broad to even bimodal. In addition, miniemulsion polymerization can be used to produce a whole new range of graft copolymers. Hydrophobic comonomers have been used successfully as hydrophobes. It has been found that such systems will give a more uniform copolymer composition since the supply of hydrophobic comonomer is not mass transfer limited as in macroemulsion polymerization. Miniemulsion polymerization has been used to produce alkyl-acrylate graft copolymers that might be the basis for low volatile organic compounds alkyd coatings. This same technique can be applied to other graft copolymerizations to produce water-borne specialized coatings. Finally, miniemulsion polymerization has been found to be one of the best vehicles for carrying out living free radical polymerization. Miniemulsion polymerization has been extended to polyaddition reactions, production of armored latexes, crumpled latexes, nanocapsules and comb-like polymers. It has also been extended to high solid latexes and to continuous reactors.

The stability to these systems is usually achieved by using an anionic surfactant e.g. sodium dodecyl sulphate and a co-surfactant that is only soluble in the oil phase. The only difference between miniemulsion polymerization recipes from a typical emulsion polymerization recipe, is the presence of co-surfactant. Co-surfactants should be water-insoluble and of low molecular weight. Amphiphiles like hexadecanol, hydrophobes like hexadecane and more recently, reactive alkyl methacrylates, water insoluble dodecanethiol have been used as co-surfactants. The small size of the droplets is the result of homogenizing the monomer-water mixture to high shear that breaks the droplets into nanosizes and these droplets are stabilized against coalescence and diffusional degradation for long time by appropriate surfactant/co-surfactant combination. Coalescence may be precluded by the addition of an appropriate surfactant. Diffusional degradation, or Ostwald

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ripening can be eliminated by the addition of a small amount of co-surfactant. In recent papers\(^6,7\), the stability of the miniemulsion droplet size distribution and the nature of the initial droplet size distribution were discussed. It was concluded that the initial droplet size distribution in miniemulsion polymerization is broad and can be bimodal. The resulting particle size distribution is also very broad and also reported to be bimodal. The available models have not addressed these features of miniemulsion polymerization. They assume monodisperse droplet size and particle size distributions. In the subsequent sections, the basic features of miniemulsion polymerization process are described and, a population balance framework that incorporates these basic features and retains the full droplet size distribution and particle size distribution is given.

**Basic features of miniemulsion polymerization process**

Emulsion polymerization (both macro or conventional and miniemulsion) is essentially a process in which an aqueous dispersion of a monomer or a mixture of monomers is converted by free radical polymerization, superimposed over segregated polymerization loci into a stable dispersion of polymer particles. In a typical reactor environment, the monomer droplets, the monomer-swollen micelles, the monomer dissolved in the aqueous phase and the monomer-swollen particles compete for the aqueous phase free radicals. In conventional emulsion polymerization, the monomer droplets due to their large size (1000-10000 nm) and consequently small total surface area do not compete favourably with other loci of particle nucleation and are not considered to contribute significantly to particle nucleation. They serve primarily as reservoirs that supply monomer to the growing particles that are formed predominantly as nucleation in monomer-swollen micelles and aqueous phase. In miniemulsion polymerization, due to the small size of monomer droplets (50-500 nm), they become the predominant loci of particle nucleation and subsequent polymerization. In this size range, the total surface area of the droplets is such that the surfactant amount typically used is adsorbed predominantly on the droplets resulting in its unavailability to form micelles or to stabilize precipitated and growing oligomers in the aqueous phase. This was experimentally demonstrated for the first time in 1972 at Lehigh University\(^8\).

The formation and stabilization of droplets in the nano-size range involve pre-emulsification and emulsification steps. Pre-emulsification refers to the preparation of the homogeneous mixture of monomer, surfactant, co-surfactant and water, which are, then under high shear broken into droplets during the emulsification step. The detailed study of these steps can be found elsewhere\(^9\). Variations in these steps viz. the type and proportion of co-surfactant used, the intensity, duration and uniformity of the energy input, the type of the homogenizing device have been shown to affect the polymerization kinetics and the final latex size distribution\(^10-12\). These variations result in different droplet size distributions, which as these results demonstrate, affect the development of the particle size distribution. A direct comparison of the droplet size distribution and the final size distribution has been proven to be difficult owing to the problem of measuring the full droplet size distribution. Miniemulsion polymerization follows the kinetics of free radical polymerization superimposed on a compartmentalized medium. A kinetic feature that the miniemulsion polymerization shares with all emulsion polymerization processes is that the free radicals enter a particle intermittently. The number of radicals in a particle is determined by the balance between the rate of radical entry into, exit from and termination inside the particle\(^13\). Another kinetic feature that the miniemulsion polymerization has in common with the conventional emulsion polymerization is that monomer transport is thermodynamically governed\(^10,14-16\). Transport of monomer in a particle is very fast compared to the rate at which it is consumed inside the particle due to polymerization. This does not imply that the particle will continue to swell despite monomer being a good solvent for its polymer. The extent to which a particle can swell is governed by thermodynamics; the change in free energy of mixing is balanced by the change in free energy of expansion of interfacial area. The radical dynamics framework and the monomer transport framework for miniemulsion polymerization are presented in detail elsewhere\(^17,18\). The differences in the times at which the particles are nucleated from the droplets, and the rate at which they subsequently grow, lead to differences in their sizes. These lead to the development of the particle size distribution.

**Population balance framework**

A population balance is a balance on a defined set of dispersed entities, which accounts for the net
accumulation of such entities in a given system as a result of all phenomena that add or remove entities from the set. In order to write the population balance equations, one must choose a set of variables, the phase coordinates, whose values if known as a function of time, will suffice to describe the dynamics of the development of the dispersed entities of the system. The population balance accounts for all the important ways in which the value of each phase coordinate changes with time. These ways can be subdivided into three types: (i) Evolution: it is the event by which a phase coordinate associated with a dispersed entity changes with time, (ii) Birth or death: these are the events by which the number of dispersed entities changes either by birth of new entities or death of existing entities, (iii) Accumulation: it is the net balance of both evolution and birth/death events on the number of dispersed entities with given values of phase coordinates. The terms of the three types are collected together to give the population balance equations: Accumulation = Evolution + Birth/Death.

Phase coordinates

The phase coordinates can be broadly divided into two types: the internal coordinates and the external coordinates. The internal coordinates refer to the size, chemical composition, etc. that may vary from one dispersed entity to another. The external coordinates define the position of the dispersed entity in the reactor environment. Entities having the same internal coordinates may behave differently depending on their positions in a non-uniform continuous phase. In a well-stirred reactor, differences due to external coordinates will not be present, and only internal coordinates need to be considered. Population balance models are inherently complex and the choice of phase coordinates is important to make these models realistic as well as tractable. There have been two choices of phase coordinates in the emulsion polymerization literature\(^{19,20}\). These are the particle size description and the particle birth time description. In the particle size description, one chooses the set of internal coordinates to be any size related variable, e.g. particle diameter or volume. In the particle birth time description, one chooses the time at which the particle first appears as the internal coordinate.

Phase coordinates for miniemulsion polymerization

There are two size distributions in miniemulsion polymerization: the droplet size distribution and the particle size distribution. The entities of these distributions, the droplets and the particles, undergo various events that change their identities. The droplets evolve as a result of monomer transport from them that reduces their sizes and the droplets undergo death events due to the nucleation of new particles from them. The particles evolve as a result of growth due to polymerization and as a result of monomer transport, and they undergo birth due to nucleation.

In case one chooses volume of the particle as the internal coordinate, then the population balance equation has to be written accounting for the time variation of the net accumulation of the particles in a given volume range. The particle in a given size range will accumulate due to evolution due to particle growth. The growth accounts for both the polymerization and the swelling due to monomer transport. The smaller particles will grow to this size range from adjacent size range and the larger particles will grow out of this size range to the next bigger size range. The particle in a given volume range will also accumulate due to nucleation of a particle from a droplet in the same volume range. Thus, representation in terms of the volume, leads to the following coupling among the particles and droplets at different volume ranges: the particles in a given volume range are coupled with(i) the particles in the adjacent volume ranges (lower and upper) due to the particle growth and (ii) with the droplets in the same volume range due to particle nucleation as the droplets of a given volume will become particle of the same volume, due to nucleation. However, in case one chooses the birth time as the internal coordinate then only the second coupling exists. Particles are nucleated from different sized droplets. If the droplet size distribution is discretized into various classes and account for evolutionary and birth events in these classes, one can track particles with a given birth time arising from these classes of droplets. Further, instead of choosing the volume of the particle as the internal coordinate for the particle size distribution, if the mass of the polymer in the particle is chosen as the internal coordinate, then following simplification arises. With volume as the internal coordinate, the volume comprises of the polymer and the monomer. Both change simultaneously, one as a result of polymerization and the other as a result of both polymerization and monomer transport. Polymerization is represented by differential equations, whereas monomer transport is represented by a system of algebraic equations. In order to find
the volumetric growth rate, one needs to take the time derivative of the algebraic thermodynamic equations resulting in a system of algebraic-differential equations, whereas mass of polymer in a particle changes as a result of polymerization only for which there is a differential equation and then volume can be evaluated by finding the consequent change in the monomer amount by separately solving the algebraic equations for the thermodynamically governed monomer transport.

The resulting population balance framework for the miniemulsion polymerization can be summarized as follows. The droplet size distribution is discretized into several classes according to size. The change in the number of droplets in a given class as a result of nucleation and the change in the size of these droplets as a result of thermodynamically governed monomer transport are followed. Particle size distribution changes due to nucleation and subsequent growth of particles. Development of particle size distributions arising from each of these droplets is followed individually. The particles are thus differentiated in terms of the class of droplets from which they are nucleated and further in terms of their birth times and finally in terms of the mass of polymer in them. The size of the polymer in a particle is found by integration of the polymerization rate in a particle from its birth time to the present time. The polymerization rate incorporates monomer concentration, which is obtained by solving the thermodynamically governed monomer transport framework, and it also incorporates number of radicals in a particle, which is obtained by solving the radical dynamics framework. The solution of this framework using orthogonal collocation on finite elements will be presented in a subsequent publication. Here the population balance equations are given.

**Population balance equations**

The population balance equations, expressed in terms of the birth time \( t' \) of the particles as the internal coordinate, for the number density \( F(t',t) \) of the particles nucleated from the ith class of droplets at a rate \( R_{ni} \) is given by:

\[
\frac{\partial}{\partial t} [F(t,t)V_R]/\partial t = 0; F(t',t)V_R(at t = t') = R_{ni}(t') \quad \ldots(1)
\]

The above equation has the solution:

\[
F(t',t)V_R = R_{ni}(t') \quad \ldots(2)
\]

This implies that the number density of particles born at \( t = t' \), from the ith class of droplets, is equal to the nucleation rate corresponding to that class of droplets at \( t = t' \), and the number density will not change for \( t > t' \).

The population balance equation for the mass of polymer in the particles \( (m_p(t',t)) \) nucleated from the ith class of droplets is given by:

\[
\frac{\partial m_p(t',t)}{\partial t} = k_p \phi_m \xi_d \partial \phi / N_a \quad \ldots(3)
\]

This implies that the mass of polymer in a particle, born at \( t' \), at any time \( t \) will be given by the integration of the above equation from \( t' \) to \( t \). Any other size related variable, for example, volume of particle \( V_R \) at that time, can be obtained from:

\[
V_R = m_p / \phi_p \quad \ldots(4)
\]

**Mechanistic components of the model**

The mechanistic components of the model include (i) the initial droplet size distribution, (ii) radical dynamics framework and (iii) monomer transport framework. Stability of the miniemulsion droplet size distribution and its nature has earlier been presented in detail. For this work, based on the experimental data to be verified, a monodisperse droplet size distribution has been assumed. The radical dynamics framework has also been presented in detail elsewhere. The number of radicals in a particle are given by the balance among rates of radical entry into, termination inside and exit from the particles. In this work, the average number of radicals in all the particles equal to 0.3 has been assumed. Further the radical entry rate was modeled as:

\[
R_{ep} = k_{ep} [N_B] RV_W \quad \ldots(5)
\]

Radical entry rate coefficient has been assumed to be independent of particle size. The radical entry rate coefficients for the particles and the droplets are taken to be different. The aqueous phase radical balance neglects radical exit and aqueous phase termination and is given as,

\[
2k_d \xi_d [I] V_W - k_{ep} [N_B] RV_W - k_{ed} [N_B] RV_W = 0 \quad \ldots(6)
\]

This implies that the aqueous phase radicals generated from initiator decomposition enter the particles and the droplets. The aqueous phase radical concentration is given by:
\[ R = 2f_FI / (k_{ep}[^{N_0}] + k_{cat}[N_{D}]) \]  \( \ldots(7) \]

The rate of particle nucleation is given as the rate of radical entry into droplets:

\[ R_n = k_{cat}[N_{D}]RV_w = 2f_FI V_w k_{cat}[N_{D}] / (k_{ep}[N_0] + k_{cat}[N_{D}]) \]

Defining \( \varepsilon = k_{cat} / k_{ep} \), one gets:

\[ R_n = 2f_FI V_w \varepsilon [N_0] / ([N_0] + \varepsilon [N_{D}]) \]  \( \ldots(8) \)

In the present model, it is assumed that the monomer transport is thermodynamically governed. The chemical potentials of monomer in all the phases viz. droplets, aqueous phase and particles are equal. This may not be strictly true during the later stages of the polymerization as a result of nucleation and change in the composition of a phase as a result of polymerization are the events that disturb the pseudo-equilibrium established at a given time. One needs to associate a time framework for these events. These events necessitate the thermodynamically governed redistribution of monomer to regain the pseudo-equilibrium corresponding to the new conditions. In reality, the monomer mass transport and these events will occur simultaneously. But in the modeling framework, they are considered to occur sequentially. The above-mentioned events that necessitate a time framework are considered to occur first and are represented by differential equations and then the algebraic equations representing the thermodynamically governed monomer transport are solved. This is one advantage of representing the particle size variable as the mass of polymer in the particle. One can separate the events that require an explicit time framework from those that do not. Also, this enables the incorporation of the thermodynamic framework in its entirety to the new framework. Also, droplet-particle coalescence has not been considered because it is shown in earlier\(^6\) that for the conditions considered in experimental studies, the droplets are stable against coagulation.

It can be realized that only the amounts of monomer in various phases change during the solution of the thermodynamic framework. The chemical potentials of monomer in different phases as given by extended Flory Huggins equations are:

**Droplet phase**

\[ \mu_D = \ln \phi_{n,D} + (1 - \phi_{n,D}) + \chi_m (1 - \phi_{n,D}) \] \( \alpha / d_D \)  \( \ldots(9) \)

**Aqueous phase**

\[ \mu_a = \ln \phi_{m,a} + (1 - \phi_{m,a}) + \chi_m (1 - \phi_{m,a})^2 \]  \( \ldots(10) \)

**Particle phase**

\[ \mu_p = \ln \phi_{n,p} + (1 - \phi_{n,p}) + \chi_m (1 - \phi_{n,p})^2 \] \( + \chi_m \phi_{n,p}^2 + \phi_{c,p} \phi_{p,c} (\chi_m + \chi_m - \chi_{cp} \phi_{cp}) \] \( + \alpha / d_p \) \( \ldots(11) \)

The following changes in the representation of the various variables in the thermodynamic framework are made. The chemical potential of monomer in a droplet is expressed in terms of the three variables: the monomer volume fraction, the co-surfactant volume fraction and the droplet diameter. The chemical potential of the monomer in the droplet is represented in terms of one variable, the monomer volume fraction, by realizing that the volume fractions of the components add to 1 and the volume of co-surfactant in a droplet does not change with time (due to its insolubility) and is same as the initial volume. Thus,

\[ \phi_{n,D} + \phi_{c,D} = 1 \] \( \ldots(12) \)

\[ \Rightarrow \phi_{c,D} = 1 - \phi_{n,D} \]

\[ \pi / 6 \phi_{c,D} d_D^3 = csa \] \( \ldots(13) \)

or, \( \pi / 6(1 - \phi_{n,D}) d_D^3 = csa \)

\[ \Rightarrow d_D = [6 / \pi csa / (1 - \phi_{m,D})]^{1/3} \]

or, \( d_D = k / (1 - \phi_{m,D})^{1/3} \) \( \quad \text{where} \quad k = [6 / \pi csa]^{1/3} \)

The chemical potential of monomer in the aqueous phase can be represented in terms of one variable, the monomer volume fraction, by realizing that:

\[ \phi_{m,A} + \phi_{m,A} = 1 \] \( \ldots(14) \)

\[ \Rightarrow \phi_{m,A} = 1 - \phi_{m,A} \]
The chemical potential of monomer in a particle is expressed in terms of four variables: the volume fractions of the three components and the diameter of the particle. It can be expressed in terms of two variables: the volume fraction of monomer in the particle and the ratio of the volume of the polymer in the particle to that of the co-surfactant. The amount of co-surfactant in the droplet from which that particle was nucleated. Thus,

\[
\phi_{m,p} + \phi_{p,p} + \phi_{c,p} = 1 \quad \text{(15)}
\]

\[
\Rightarrow \phi_{c,p} = 1 - \phi_{m,p} - \phi_{c,p}
\]

\[
\phi_{p,p}/\phi_{c,p} = m_p/d_p \text{csa} = R
\quad \text{(16)}
\]

or, \((1 - \phi_{m,p} - \phi_{c,p})/\phi_{c,p} = R
\Rightarrow \phi_{c,p} = (1 - \phi_{m,p})/(R+1)
\]

and \(\phi_{p,p} = (1 - \phi_{m,p})R/(R+1)
\]

\[
\pi/6 \phi_{c,p} d_p^3 = \text{csa}
\quad \text{(17)}
\]

Thus, each phase is represented by one variable, the volume fraction of monomer in that phase. Thus, for a system consisting of \(n\) phases, there will be \(n\) variables. In order to define this system completely, one needs \(n\) equations. Equality of chemical potentials of monomer in all the phases provides \(n - 1\) equations.

The last equation is provided by the mass balance of monomer: the initial mass of monomer is equal to the sum of mass of monomer in the droplets, aqueous phase and the particles and that converted to polymer.

In our framework, the droplets are discretized into various classes and the particles are differentiated in terms of the class of droplets from which they are nucleated, the finite element to which they correspond and the collocation points. The Eqs (9)-(11) are represented by:

**Droplet of the \(i\)th class:**

\[
\mu_{D,i} = \ln \phi_{m,D,i} + (1-m_m)\phi_{p,D,i} + \chi_{mc}(1-\phi_{m,D,i})^2 + \frac{\alpha}{d_{D,i}} \quad \text{(18)}
\]

**Aqueous phase:**

\[
\mu_w = \ln \phi_{m,w} + (1-m_m)(1-\phi_{m,w}) + \chi_{mc}(1-\phi_{m,w})^2 \quad \text{(19)}
\]

**Particle from \(i\)th Class Droplet, in \(j\)th element and \(k\)th collocation point:**

\[
\mu_p = \ln \phi_{m,P_{i,j,k}} + (1-m_m)\phi_{p,P_{i,j,k}} + \chi_{mc}\phi_{c,P_{i,j,k}}^2 + \chi_{mp}\phi_{p,P_{i,j,k}}^2 + \phi_{c,P_{i,j,k}}(\chi_{mc} + \chi_{mp} - \chi_{cp} m_p) + \frac{\alpha}{d_{P_{i,j,k}}} \quad \text{(20)}
\]

After expressing these equations in terms of only monomer volume fraction as explained above, one gets:

**Droplet of the \(i\)th class:**

\[
\mu_{D,i} = \ln \phi_{m,D,i} + (1-m_m)(1-\phi_{m,D,i}) + \chi_{mc}(1-\phi_{m,D,i})^2 + \frac{\alpha}{k_{i^{1/3}}} \quad \text{(21)}
\]

**Aqueous phase:**

\[
\mu_w = \ln \phi_{m,w} + (1-m_m)(1-\phi_{m,w}) + \chi_{mc}(1-\phi_{m,w})^2 \quad \text{(22)}
\]

**Particle from \(i\)th class droplet, in \(j\)th element and \(k\)th collocation point:**

\[
\mu_p = \ln \phi_{m,P_{i,j,k}} + (1-m_m)(1-\phi_{m,P_{i,j,k}}) + \chi_{mc}(1-\phi_{m,P_{i,j,k}}) + \chi_{mp}(1-\phi_{m,P_{i,j,k}})^2 + \frac{\alpha}{k_{i^{1/3}}} \quad \text{(23)}
\]

**Overall reactor balances**

The overall reactor balances include the balances for polymer \([P]\), initiator \([I]\) and balances from the volume of reaction mixture \((V_R)\). The material balances which express the rate of change of moles of each of the species contains accumulation and reaction terms (where appropriate). The volume of the reaction mixture changes because of density differences between the monomer and the polymer.

\[
d[P]_RV_R/dt = R_p V_R \quad \text{(24)}
\]

where \(R_p \equiv \text{Rate of polymerization} = k_p \phi_M MW_M V_{MM} F(v,t) d\phi dv\).
\[ \frac{d[I]V_W}{dt} = -k_d[I]V_W \]  
\[ \frac{dV_R}{dt} = \left(\frac{1}{\rho_M} - \frac{1}{\rho_P}\right)R_p MW_M V_R \]  

\[ \text{(25)} \]
\[ \text{(26)} \]

**Numerical implementation**

The population balance Eqs (1) and (3) have been solved using the method of orthogonal collocation on finite elements\textsuperscript{21,22}. 2-3 elements with 6 collocation points each have been used for the simulations. The accuracy of the simulations is determined by requiring that the number density of particle corresponding to different collocation points correspond to monotonically decreasing nucleation rate profile and by comparing the total number of particles formed evaluated using the gaussian quadrature rule and obtained by directly integrating the rate of nucleation equation. The total number of particles evaluated through these two methods have been found to be the same for all simulations. The ordinary differential equations are integrated using Euler method. The solutions of system of algebraic equations representing the monomer transport framework are solved using the subroutine NEQNF from the IMSL Math library version 1.1.

**Validation approach**

The model predictions are compared with the experimental data taken from literature\textsuperscript{13,23}. In this work, the polymerization system consists of styrene (monomer), water, sodium dodecyl sulfate (surfactant), hexadecanol (co-surfactant), potassium persulphate (initiator) and sodium bicarbonate (buffer). The means of creating the droplet size distribution is microfluidizer. The reactions are conducted in dilatometer at a constant temperature of 70 °C. The recipe considered is given in Table 1.

The microfluidizer is known to give very fine droplet size distribution\textsuperscript{11,12} and therefore, in the present validation, it is considered to be monodisperse. The volume average diameter is taken to be 80 nm, which is close to that of the final particle size distribution at the highest initiator concentration. The basis is provided by the fact that at high initiator concentration most of the particles will be nucleated and there will be little redistribution of monomer among particles due to fast polymerization. The value of \( \varepsilon = \frac{k_{ed}}{k_{ep}} = 0.0025 \) which was obtained by matching the model prediction and the experimental data for the initial conversion-time curve for the highest initiator concentration. The thermodynamic parameters for styrene-polystyrene-hexadecanol-water system are not available. For the present simulations, those of styrene-polystyrene-hexadecane-water system as reported\textsuperscript{13,23} are used. The values of all other parameters are commonly reported values in literature. No effort was made to vary any of the parameters to fine tune the predicted values to the experimentally reported values. The values of all the parameters are given in Table 2.

**Validation results**

The comparisons of different variables with experimental data are provided in Fig. 1 and Tables 3-5. The comparison between the predicted values and the experimental values of the variation of conversion with time for different initiator concentrations is given in Fig. 1. It can be seen that model predictions are in good quantitative agreement with the experimental values for the higher initiator concentrations of 2.66, 1.33 and 0.665 mM. One possible reason for models’ under predictions at later time is due to non-inclusion of gel effect in the present model. As these predictions show, the gel effect manifests itself after 40% conversion. The model predictions at lower initiator concentrations of 0.333 and 0.133 mM differ from the experimental values even during the initial stages of the polymerization; the model predicts higher values compared to experimental values. A possible reason for discrepancy could be the presence of oxygen as inhibitor. It has been documented that the dilatometric experiments are typically started with some oxygen in the reaction mixture that results in induction period, and depending on the amount of oxygen can vary from 1 to as high as 214 min. Experimentally reported values of the number average diameter, standard deviation and polydispersity index

<p>| Table 1 — Recipe for miniemulsion polymerization |</p>
<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>5.66 mL</td>
</tr>
<tr>
<td>Water</td>
<td>17.69 mL</td>
</tr>
<tr>
<td>Sodium dodecyl sulphate</td>
<td>10 mM*</td>
</tr>
<tr>
<td>Hexadecanol</td>
<td>30 mM*</td>
</tr>
<tr>
<td>Potassium persulphate</td>
<td>2.66, 1.33, 0.665, 0.333, 0.133 mM*</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>2.66, 1.33, 0.665, 0.333, 0.133 mM*</td>
</tr>
</tbody>
</table>

*Based on water
for different initiator concentrations are compared with the predicted values, in Tables 3-5.

It can be seen that the model predictions for volume average diameters are in qualitative agreement with the experimentally reported values but are quantitatively lower. Those for standard deviation and polydispersity are higher significantly. Only 500 particles were considered for the experimentally reported distributions due to which small particles present in significantly lower proportions were not represented. For generating the particle size distribution, counting of at least 3000 particles have been recommended. Due to non-consideration or under representation of small particles, the experimentally reported average diameter values are higher and those for standard deviation and polydispersity index lower. If small-sized fraction of droplets were considered the experimental values of volume average diameters will decrease and will match the predicted values and the experimental values of the standard deviations and the polydispersity indices will increase and come closer to the predicted values. In Figs 2-5, the variations with conversion of fraction of droplets nucleated, average diameter, standard deviation and polydispersity index are given, for different initiator concentrations.

### Table 2 — Value of the parameters used in simulations

<table>
<thead>
<tr>
<th>Styrene-polystyrene</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$MW_m = 104.15 \text{ g/mol}$</td>
<td></td>
</tr>
<tr>
<td>$d_m = 0.906 \text{ g/cm}^3$</td>
<td></td>
</tr>
<tr>
<td>$d_p = 1.04 \text{ g/cm}^3$</td>
<td></td>
</tr>
<tr>
<td>$k_d(\text{at 70}^\circ\text{C}) = 425600 \text{ cm}^3/\text{mol s}$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Potassium persulfate</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$MW_i = 270.33 \text{ g/mol}$</td>
<td></td>
</tr>
<tr>
<td>$k_d = 0.000048 \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$f = 0.5$</td>
<td></td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Water</th>
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<tbody>
<tr>
<td>$MW_w = 18.0 \text{ g/mol}$</td>
<td></td>
</tr>
<tr>
<td>$d_w = 0.978 \text{ g/cm}^3$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hexadecanol</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$MW_c = 242.45 \text{ g/mol}$</td>
<td></td>
</tr>
<tr>
<td>$d_c = 0.818 \text{ g/cm}^3$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermodynamic parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_{mc} = 1.54$</td>
<td></td>
</tr>
<tr>
<td>$m_{mw} = 1.11$</td>
<td></td>
</tr>
<tr>
<td>$m_{mp} = 7 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>$\chi_{mc} = 1.69$</td>
<td></td>
</tr>
<tr>
<td>$\chi_{mw} = 7.94$</td>
<td></td>
</tr>
<tr>
<td>$\chi_{mp} = 0.35$</td>
<td></td>
</tr>
<tr>
<td>$\gamma = 3.41 \text{ dyne/cm}$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>This work</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon = k_d/k_p = 0.0025$</td>
<td></td>
</tr>
<tr>
<td>$d_d = 80 \text{ nm (monodisperse)}$</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3 — Comparison of experimental and predicted values of volume average diameters for different initiator concentrations

<table>
<thead>
<tr>
<th>[I], mM</th>
<th>Vol. Avg. Dia.\text{exp}, nm</th>
<th>Vol. Avg. Dia.\text{mod}, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.66</td>
<td>91</td>
<td>81</td>
</tr>
<tr>
<td>1.33</td>
<td>102</td>
<td>85</td>
</tr>
<tr>
<td>0.665</td>
<td>111</td>
<td>90</td>
</tr>
<tr>
<td>0.333</td>
<td>123</td>
<td>96</td>
</tr>
<tr>
<td>0.133</td>
<td>132</td>
<td>105</td>
</tr>
</tbody>
</table>

### Table 4 — Comparison of experimental and predicted values of standard deviations for different initiator concentrations

<table>
<thead>
<tr>
<th>[I], mM</th>
<th>Std. Devn.\text{exp}, nm</th>
<th>Std. Devn.\text{mod}, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.66</td>
<td>10.51</td>
<td>15.6</td>
</tr>
<tr>
<td>1.33</td>
<td>10.89</td>
<td>17.2</td>
</tr>
<tr>
<td>0.665</td>
<td>12.07</td>
<td>18.8</td>
</tr>
<tr>
<td>0.333</td>
<td>13.07</td>
<td>20.5</td>
</tr>
<tr>
<td>0.133</td>
<td>14.12</td>
<td>22.6</td>
</tr>
</tbody>
</table>

### Table 5 — Comparison of experimental and predicted values of polydispersity index for different initiator concentrations

<table>
<thead>
<tr>
<th>[I], mM</th>
<th>PD\text{Iexp}</th>
<th>PD\text{Imod}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.66</td>
<td>1.034</td>
<td>1.077</td>
</tr>
<tr>
<td>1.33</td>
<td>1.030</td>
<td>1.086</td>
</tr>
<tr>
<td>0.665</td>
<td>1.032</td>
<td>1.092</td>
</tr>
<tr>
<td>0.333</td>
<td>1.028</td>
<td>1.097</td>
</tr>
<tr>
<td>0.133</td>
<td>1.029</td>
<td>1.098</td>
</tr>
</tbody>
</table>
Conclusions

A model has been developed for the miniemulsion polymerization that for the first time incorporates the full particle size distribution. The basic features of this relatively newer process are presented. A population balance framework that retains these features has been developed in detail. Representation of initial droplet size distribution and the radical dynamics framework in the mechanistic framework are discussed in adequate detail. Monomer transport framework is developed in detail. Model predictions for variation of conversion with time for five different initiator concentrations, volume average diameter, standard deviation, and polydispersity are compared with experimental values. The reasons behind discrepancies where they exist are discussed.
There are no adjustable parameters in the model. The variation with conversion of fraction of droplets nucleated, average diameter, standard deviation and polydispersity index are also given, for different initiator concentrations. The model that we have developed provides a more realistic framework for modeling miniemulsion polymerization.

References