Kinetics and mechanism of styrene-acrylonitrile copolymerization in micro-emulsion

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Abstract: Stable and transparent poly(styrene-acrylonitrile) latexes were produced by the polymerization of styrene-acrylonitrile in ternary o/w micro-emulsions containing sodium dodecyl sulfate as an anionic surfactant. Kinetics of copolymerization was studied at different temperatures using different concentrations of potassium persulfate and hydrogen peroxide/ascorbic acid. The suitability of existing model for homopolymerization was examined for styrene-acrylonitrile copolymerization after appropriate modification. The latexes were characterized for particle size and number of particles by dynamic light scattering and TEM. The isolated products were characterized by 1H and 13C NMR as well as by thermal analysis. The overall size of particles was found to be between 15 and 20 nm.

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INTRODUCTION

The unique properties of micro-emulsions such as low viscosity, greater stability and transparency due to uniformly dispersed smaller droplets have made them attractive media for polymerization. Polymerization of a non-polar monomer in an oil-in-water (o/w) micro-emulsion produces latex particles of <50 nm diameter, whereas particles produced from conventional emulsion polymerization are >400 nm in size. A micro-emulsion medium allows as to polymerize various monomers, which differ appreciably in their polarity and reactivity. The micro-emulsion controls the macromolecular characteristics and latex particle morphology. A considerable amount of work dealing with the kinetics of polymerization in micro-emulsion, the type of nucleation, and particle size and its distribution, has been reported for the homopolymerization of styrene,1-4 acrylamide,5 vinyl toluene,6 tetrahydrofurfuryl7 and methyl, ethyl, butyl, hexyl and 2-ethylhexyl acrylates and methacrylates.8-12 However, very few reports are available for the kinetics of copolymerization of styrene and various monomers. Monomer polarity, which controls monomer partitioning, reactivity ratios and the propagation rate constant, and initiator type, which generates the charged or neutral initiating species, are the main factors to be considered for understanding copolymerization. Zang et al13 have carried out photo-initiated copolymerization of styrene with acrylamide and have reported that photo-initiation takes place at the interface between oil and water, and that polymerization takes place in micro-emulsion droplets. Puig et al14 have reported a copolymerization of styrene with acrylonitrile in emulsion and micro-emulsion using cationic surfactant. Little attention has been given towards the mathematical models for copolymerization in a micro-emulsion medium. Mathematical models are available only for the homopolymerization of hydrophobic monomers like styrene4,15 and hexyl methacrylate12 in three-component micro-emulsion media.

In this paper we focus on the copolymerization of styrene, a hydrophobic monomer, and acrylonitrile, a partially water-soluble monomer, using charged and neutral initiating species. An attempt is also made to examine the suitability of existing mathematical models to styrene and acrylonitrile copolymerization in a micro-emulsion medium. However, in these models there are number of independent variables the values of which are not well established, and so the utility of this model for precise mechanistic hypothesis testing is compromised.

EXPERIMENTAL

Materials

Styrene from National Chemicals, India was made free from inhibitor by washing with an aqueous sodium hydroxide solution (2% w/v) and was then dried over anhydrous calcium chloride. It was further purified by passing through an alumina column and distilling under vacuum. Acrylonitrile from SRL, India was distilled under vacuum and stored at 0 °C until further use. Potassium persulfate (KPS) from Sisco Chemi-
mass was purged with nitrogen. The reactions were carried out by using KPS and H$_2$O$_2$/ascorbic acid initiating systems at various temperatures. The latexes were cooled below the Kraft temperature for the precipitation of surfactant. Most of the surfactant was removed by this process. The remaining surfactant along with copolymer was precipitated using large quantity of methanol. The traces of surfactant were removed by washing the precipitate several times with water. For study of the kinetics of copolymerization, samples were withdrawn from the reaction vessel at regular time intervals and transferred to pre-weighed glass bottles containing hydroquinone and methanol. The percentage conversion was calculated gravimetrically. In the case of the redox initiating system, sodium nitrate was also added as a radical inhibitor along with hydroquinone to arrest the polymerization.


RESULTS AND DISCUSSION

A pseudo-phase diagram was constructed for an o/w micro-emulsion containing various compositions of styrene-acrylonitrile mixtures. It was observed that, by increasing the concentration of acrylonitrile, the region of micro-emulsion increases due to the higher solubility of acrylonitrile in water. The formulation used for the study was: 5% monomer mixture, 14% SDS and 81% water. All micro-emulsions were optically transparent and no phase-separation was detected visually before or after polymerization. The microlatexes remained stable with respect to coagulation for more than six months.

Characterization

Copolymerisation was confirmed from the IR spectra of the representative sample by the appearance of bands at 3026 cm$^{-1}$ for C=C stretching from aromatic ring, at 2926 cm$^{-1}$ for C≡N stretching from acrylonitrile, at 1602 cm$^{-1}$ due to CC stretching from aromatic ring and at 700 and 760 cm$^{-1}$ due to CH bending from mono-substituted benzene. The high resonance $^1$H NMR spectrum of representative sample is shown in Fig 1(a). The signal around 2.2–1.25 ppm can be attributed to ±CH$_2$ protons of styrene and acrylonitrile backbone. The signals shown around 3.75–2.5 ppm and 4.5–4.0 ppm are attributed to CH protons from styrene and acrylonitrile, respectively. The aromatic protons from styrene show splitting into two broad bands around 6.75–6.25 ppm and 7.5–7.67 ppm due to ortho and meta-para protons, respectively. $^{13}$C NMR spectrum of representative sample is given in Fig 1(b). The quaternary carbon resonance for styrene residue appeared at 146.4–138.7 ppm and nitrile carbon resonance of acrylonitrile residue appeared at 122.5–117.5 ppm. The regions assigned for the resonance of styrene-centred triads, were: SSS, 146.4–143.7 ppm; SSA or ASS, 143.7–141.1 ppm and ASA, 141.1–138.7 ppm and those for acrylonitrile-centred triads were: SAS, 122.5–120.7 ppm; SAA or AAS, 120.7–118.8 ppm and AAA 118.8–117.5 ppm.

The glass transition temperatures of the styrene-acrylonitrile copolymers were observed in the range 108 to 118°C and were dependent on the acrylonitrile content.
concentration in the copolymer. TGA analysis showed increased thermal stability of the copolymer containing a higher acrylonitrile content. The temperatures corresponding to 10, 20, 50 and 90% degradation were 350 and 370, 375 and 390, 410 and 412 and at 420 and 430°C for polystyrene and styrene-acrylonitrile copolymer (1:1 mol/mol), respectively. The activation energies for degradation of homopolymer and copolymers calculated using Briodo's method were: 74.38 kJ mol\(^{-1}\) for polystyrene, 84.52 kJ mol\(^{-1}\) for poly(styrene-co-acrylonitrile) (2:1 mol/mol) and 87.2 kJ mol\(^{-1}\) for poly(styrene-co-acrylonitrile) (1:1 mol/mol).

**KINETICS OF POLYMERIZATION**

**Theoretical background**

Morgan *et al.* have discussed in detail the development of a theoretical model for the conversion and rate of polymerization of hexyl methacrylate. The model is based on a number of experimentally determined parameters and assumptions. We are trying to see the adaptability of this model to the copolymerisation process. No attempts have been made so far for the development of the model for copolymerization in micro-emulsion. The main factors governing kinetics of copolymerization are initiator type and concentration, monomer type and composition and tempera-
ture. To avoid the complexity of the treatment, we are considering only the type and concentration of the initiator for the comparison of experimentally obtained data and data generated theoretically for styrene-acrylonitrile copolymerization. For the micro-emulsion polymerization, two possible mechanisms of nucleation are widely discussed in literature, nucleation in monomer-swollen micelles and homogeneous nucleation. The polymerization process, as indicated below in eqn (1), depends upon the propagation rate constant, the concentration of free radicals in aqueous phase which further enter the monomer-swollen micelles, and rate as a function of conversion as

\[
\frac{dN^*}{dt} = k_p C_M N^* - k_c N_{aq}^* - k_c N_{aq}^{*2} \tag{3}
\]

where \( k_a \) and \( f \) is a conversion fraction, \( M_0 \) is an initial concentration of monomer per litre of micro-emulsion, \( N^* \) is a concentration of radicals propagating in particles, \( k_c \) is a propagation rate constant and \( C_M \) is a monomer concentration in the growing particles. For the water-soluble initiating system, the radicals are produced due to the decomposition of initiators in the aqueous phase which further enter the monomer-swollen micelles (monomer droplets), initiate the polymerization and propagate to a certain chain length, which is long enough not to escape out the micelles and thus finally convert into polymer particles. As the equilibrium partitioning or kinetically limited partitioning of monomer is governed by the propagation rate constant in micro-emulsion medium, \( k_p \), capture of free radicals by monomer swollen micelles is very fast (ie \( k_c \) is very large) and (d) all the radicals generated in the aqueous phase are captured by the monomer-swollen micelles, eqns (3) and (5) can be summarized as

\[
dN^*/dt = \rho_0 \text{ or } N^* = \rho_0 t \tag{6}
\]

Further substituting eqns (2) and (6) in eqn (1) we obtain

\[
\frac{dN^*}{dt} = \frac{k_c C_0 (1 - f) \rho_0 t}{M_0} \tag{7}
\]

As \( k_p C_0 \), \( \rho_0 \) and \( M_0 \) are constant for a given system eqn (7) can be written as

\[
\frac{df}{dt} = A t (1 - f) \tag{8}
\]

where

\[
A = k_p C_0 \rho_0 / M_0 \tag{9}
\]

This can further be solved to conversion as a function of time as

\[
f = 1 - e^{-1/2A t^2} \tag{10}
\]

and rate as a function of conversion as

\[
\frac{df}{dt} = (1 - f) \sqrt{-2A \ln(1 - f)} \tag{11}
\]

We have simulated values of \( A \) from our experimental data. A values are dependent on the initial concentration of monomer in the growing particle (\( C_0 \)), the rate of production of primary free radicals from initiator decomposition (\( \rho_0 \)), the initial concentration of monomer per litre of micro-emulsion (\( M_0 \)) and the propagation rate constant in micro-emulsion medium (\( k_p \)). The values of \( C_0 \) have not yet been directly measured. By taking the number of particles \( N_{aq}^* \) at 2% conversion to be \( 3.6 \times 10^{16} \) per ml, from the light scattering studies, and the initial concentration of monomer per litre of micro-emulsion to be 0.637 M, as
calculated from the polymerizable formulation, $C_0$ was calculated to be 6.88 M. The decomposition constant $k_d$ of KPS in aqueous phase is $4.4 \times 10^{-5} \text{s}^{-1}$. The propagation rate constant ($k_p$) for styrene-acrylonitrile in micro-emulsion medium is not reported in the literature but can be calculated from the monomer reactivity ratios of styrene-acrylonitrile in micro-emulsions using eqn (12).

Monomer reactivity ratios depend on the reaction medium. We have calculated true and apparent reactivity ratios for styrene-acrylonitrile and the distribution of acrylonitrile between micro-emulsion droplets and aqueous phase. True and apparent values reported are $r_S=0.85$ and $r_A=0.82$ and $r'_S=1.49$ and $r'_A=0.022$, respectively. The overall propagation rate constant is expressed as \(^{19,20}\)

$$k_p = \left[ \frac{1}{r_A/k_{AA}} + r_S/k_{SS}(\frac{[S]}{[A]}) \right] \times \left[ \frac{[S]([S]/[A]) + 1)}{f_S + [r_A + ([S]/[A])]} \right]$$

(12)

where $r_S$ and $r_A$ are the monomer reactivity ratios of styrene and acrylonitrile in micro-emulsion, $k_{SS}$ and $k_{AA}$ are the propagation rate constants of homopolymerization of styrene and acrylonitrile, respectively, $[S]$ and $[A]$ are the molar concentrations, and $f_S$ and $f_A$ are the mole fractions of styrene and acrylonitrile, respectively. The monomer partitioning very much affects the kinetic parameters. Because of the higher solubility of acrylonitrile in the aqueous phase the monomer reactivity ratios of styrene and acrylonitrile in the micro-emulsion are very different from those in bulk and solution polymerization. The details of monomer reactivity ratios, their distribution coefficient and sequence distribution in micro-emulsions are discussed in our earlier paper. \(^{18}\) The overall propagation rate constant $k_p$ for micro-emulsion calculated by eqn (12) was $471 \text{M}^{-1} \text{s}^{-1}$.

### Polymerization rate

The rate of polymerization and percentage conversion of equimolar styrene-acrylonitrile as a function of time depended on the initiator concentration, temperature and monomer-monomer feed composition. The effect of temperature on the rate of polymerization was studied at 65, 70 and 80°C. Fig 2 illustrates the percentage conversion versus time and the rate of polymerisation versus conversion using 0.37 mM of KPS at various temperatures. The 95% conversion was obtained within about 5 min at 80°C, but at 65°C the rate of reaction was lower and maximum conversion was observed to be 80%. This may be due to a smaller population of free radicals at 65°C. Overall, the rate of polymerization increased with increasing temperature. The results are simulated using properly selected A values at various temperatures which are given in Table 1. The theoretical conversion and rate

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Copolymer Initiator concentration</th>
<th>Temperature</th>
<th>$R_{h}$</th>
<th>$N_p \times 10^{-16}$</th>
<th>Conversion (%)</th>
<th>$A$ (simulated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1A1</td>
<td>KPS</td>
<td>0.37</td>
<td>65</td>
<td>29</td>
<td>3.95</td>
<td>80</td>
</tr>
<tr>
<td>S1A1</td>
<td>KPS</td>
<td>0.37</td>
<td>70</td>
<td>24</td>
<td>7.41</td>
<td>85</td>
</tr>
<tr>
<td>S1A1</td>
<td>KPS</td>
<td>0.37</td>
<td>80</td>
<td>22</td>
<td>10.11</td>
<td>98</td>
</tr>
<tr>
<td>S1A1</td>
<td>KPS</td>
<td>0.27</td>
<td>70</td>
<td>26</td>
<td>4.66</td>
<td>68</td>
</tr>
<tr>
<td>S1A1</td>
<td>KPS</td>
<td>0.46</td>
<td>70</td>
<td>23</td>
<td>9.11</td>
<td>92</td>
</tr>
<tr>
<td>S2A1</td>
<td>KPS</td>
<td>0.37</td>
<td>70</td>
<td>23</td>
<td>8.22</td>
<td>83</td>
</tr>
<tr>
<td>S3A1</td>
<td>KPS</td>
<td>0.37</td>
<td>70</td>
<td>20</td>
<td>13.10</td>
<td>87</td>
</tr>
<tr>
<td>S1A1</td>
<td>HP/AA</td>
<td>7.2</td>
<td>40</td>
<td>16</td>
<td>29.40</td>
<td>100</td>
</tr>
<tr>
<td>S1A1</td>
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<td>40</td>
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</tr>
<tr>
<td>S1A1</td>
<td>HP/AA</td>
<td>0.90</td>
<td>40</td>
<td>18</td>
<td>17.60</td>
<td>85</td>
</tr>
</tbody>
</table>

* Styrene:acrylonitrile = 1:1 mol ratio.

$R_h$ = hydrodynamic diameter, $N_p$ = number of particles, AA = equimolar concentration.

Table 1. Variation of size and number of latex particles and computed A values with experimental conditions in the copolymerization of styrene-acrylonitrile

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Figure 2. Effect of temperature (● 80°C, ○ 70°C, ▲ 65°C) on conversion and rate of polymerization at 0.37 mM of KPS. Symbols represent experimental values and solid curves are generated using eqns (10) and (11).
data generated from eqns (10) and (11) using selected A values given in Table 1 were used to get best fit of theoretically calculated and experimentally obtained values (Fig 2). However, a deviation was observed at higher conversion. The chosen A values increased with increasing temperature. As in eqn (9), the A values depend upon the propagation rate constant $k_p$ and rate of production of primary free radicals from initiator decomposition. With increasing temperature the number of primary free radicals generated from initiator decomposition increase resulting in increased A values. The maximum rate of polymerization was observed in the range of 30–40% conversion. By plotting the maximum rate of polymerization versus temperature the activation energy was calculated using the Arrhenius equation as 45kJ mole$^{-1}$.

Although the optimum temperature was 80°C, due to the faster rate of polymerization at 80°C, the effect of initiator concentration was studied at 70°C. The conversion-time plots for various concentrations of KPS show that the reaction rate and final conversion increase with increasing concentration of KPS. Figure 3 shows that the highest rate and percentage conversion were obtained at 0.46 mM at 70°C. It also shows that 90% conversion was achieved within about 20min. At lower concentrations the reaction was slower and the conversion was limited to 80%. As the initiator concentration increases, the number of primary free radicals increases and consequently the rate of polymerisation increases. The results are simulated using appropriate A values given in Table 1 and solid curves are generated using eqns (10) and (11) to achieve the best agreement with both conversion and rate data. The deviation observed at lower initiator concentration may be due to the lower concentration of free radicals produced in the aqueous phase affecting the previously-made assumption of fast capturing of free radicals by monomer droplets. A linear correlation was observed between concentration of initiator and A values with a correlation coefficient of 0.9969. The A values increase with increasing initiator concentration as they depend on the concentration of free radicals. The effect of initiator concentration on the rate of polymerization was studied by plotting $R_p$ versus $[\text{KPS}]$. A straight line of slope 1.1 gives the power of initiator concentration. However, according to the assumption of fast capturing (ie $k_c$ is very large) and no bimolecular termination, the dependency of the initiator concentration should be $[\text{KPS}]^{1.3}$, which is very different than that obtained for the system. This difference may be attributed to the partial solubility of acrylonitrile in the aqueous phase which leads to homogeneous nucleation. In the nucleation state, most of the radicals are either captured by micro-emulsion droplets or react with monomer molecules in the aqueous phase and grow to a critical size to become a particle. Therefore two rate constants are governing the micro-emulsion polymerization, ie rate constants for radical capture by the monomer droplets ($k_c$) and by growing and dead particles ($k'_c$). When micro-emulsion droplets have disappeared in the later stages of polymerization, the radicals captured by the growing and dead particles dominate the system and hence the above deviation is observed.

In the copolymerization of monomers having a difference in polarity the following mechanisms are involved during nucleation:

(1) production of primary free radicals from initiator decomposition,

(2) propagation of free radicals in aqueous phase to form surface-active oligomeric free radicals or to precipitate homogeneously from the aqueous phase and to form colloidal particles,

(3) capturing of free radicals by monomer swollen micelles or monomer droplets,

(4) capturing of free radicals and surface active oligomeric free radicals by growing and dead particles,

(5) termination of free radicals in the aqueous phase leading to a capture efficiency less than 100%.

The copolymerization process in micro-emulsion may be governed by the solubility of monomer in aqueous phase, the composition of the micro-emulsion, monomer-monomer feed composition, the reactivity ratios of monomers and the nature of the initiator. To examine the effect of initiator type we have studied a redox initiator system which does not produce a surface active oligomeric free radicals as KPS does. The results of conversion as a function of time and rate as a function of conversion using hydrogen peroxide/ascorbic acid at 40°C at various concentrations are given in Fig 4. It was observed that, as the concentration of initiator increased, the rate of
polymerization increased. The approximately 100% conversion was achieved within about 3 min. The results are simulated using properly selected A values given in Table 1. Solid curves were generated from eqns (10) and (11). A linear correlation was observed between concentration of initiator and A values with correlation coefficient of 0.9994. The A values increased with increasing initiator concentration as they depend on the concentration of free radicals. The effect of initiator concentration on maximum rate was studied by plotting ln$R_p$ versus ln[$\text{H}_2\text{O}_2$/[$\text{AA}$]. A straight line was observed and slope of the line gave the power of initiator concentration and was observed to be 0.58 which differed widely from that of the KPS system and is close to 0.5. As discussed earlier, the rate of polymerization shows dependency on the initiator concentration with a power of 0.5 in the case of fast capturing of free radicals by the micelles or monomer droplets and no bimolecular termination. In the redox initiation the reaction between oxidizing agent and reducing agent produces neutral OH$^-$ radicals. When the uncharged OH$^-$ free radicals propagate in aqueous phase they do not produce surface active oligomeric free radicals and hence they are easily captured by the monomer droplets or growing particles. The barrier exerted by SDS molecules on the entry of negatively charged free radicals or oligomeric free radicals generated due to the solubility of acrylonitrile in water is not observed in the case of the H$_2$O$_2$/AA system.

The effect of monomer-monomer composition was studied through the conversion as a function of time and the rate as a function of conversion at 70°C using 0.37 mM of KPS. Fig 5 exhibits the results obtained with various molar ratios of styrene to acrylonitrile. The rate of polymerization decreased with the increasing concentration of acrylonitrile. The induction period also increased with the increasing concentration of acrylonitrile. The results are simulated using properly selected A values given in Table 1. The solid curves were generated as described earlier. The A values increased as acrylonitrile concentration decreased and led to smaller chances for the homogeneous nucleation. The dependency of the rate of polymerization on monomer is calculated by plotting ln$R_p$ versus ln [styrene(S)] and ln$R_p$ versus ln [acrylonitrile (4AN)]. The straight line observed gives $R_p \propto [S]^{2.7} [4AN]^{-0.86}$.

**Particle size analysis**

Dynamic light scattering analysis showed the size of the particles were in the range 22–27 nm TEM analysis particles showed a size of 25–32 nm with a narrow distribution. The TEM analysis of the representative sample is shown in Fig 6. The particle size and size distribution decreases with increasing temperature. It must be pointed out that the size of particles also depends on the polymerization rate: the faster the polymerization the smaller the particle size.

The number of particles was calculated using the following expression,

$$N_p = 6M_0f/\pi Dn^3 \rho$$

(13)

where $f$ is a fractional conversion, $M_0$ is a initial concentration of monomer per litre of micro-emulsion, $D_n$ is a number average diameter, $N_p$ is a number of particles per cm$^3$ and $\rho$ is density of polymer. The total numbers of particles calculated at maximum conversion are given in Table 1. The variation of particle size and number of particles with time of polymerization

Figure 4. Effect of hydrogen peroxide/ascorbic acid (equimolar concentration at ● 7.2 mM, ○ 1.83 mM, ▲ 0.9 mM) on percentage conversion and rate of polymerization at 40°C. Symbols represent experimental values and solid curves are generated using eqns (10) and (11).

Figure 5. Effect of styrene-acrylonitrile mole ratio concentration ● 3:1, ○ 2:1, ▲ 1:1, on percentage conversion and rate of polymerization using 0.37 mM of KPS at 70°C. Symbols represent experimental values and solid curves are generated using eqns (10) and (11).
was examined for the copolymer synthesized using 0.37 mM of KPS at 70°C (Fig 7). As the reaction proceeded the number of particles increased and then remained constant. However, the size of the particles did not vary during polymerization. The dependency of rate of copolymerization on the number of particles was calculated by plotting \( \ln R_p \) versus \( \ln N_p \) for KPS and the redox system and were 1.05 and 0.83, respectively.

To examine the reliability of the selected A values for simulation of experimental data it is necessary to compare the values with those calculated theoretically. As discussed earlier, A values depend on \( k_pC_oM_o \) and \( p_o \). Overall, \( k_p \) and \( C_o \) were calculated as described earlier. \( k_d \) was taken from the literature assuming 80% efficiency and \( M_o \) was calculated from micro-emulsion formulation. Theoretical A values and simulated values for KPS are compared in Table 2. A good correlation was observed in calculated and simulated values.

### CONCLUSION

From the kinetic studies it was observed that the nature of the initiator and the monomer type play important role in copolymerization. In case of styrene-acrylonitrile copolymerization using KPS and \( \text{H}_2\text{O}_2/\text{AA} \), the anionic nature of the free radicals and oligomeric free radicals generated due to KPS and the solubility of acrylonitrile in water experience more resistance from the SDS molecules compared with \( \text{OH}^- \) radicals generated from \( \text{H}_2\text{O}_2/\text{AA} \). As a result the rate of polymerization shows a higher dependency on initiator concentration for KPS system. The number of particles remain constant during polymerization. However, size initially increases and then remains constant. The overall rate of polymerization can be given as \( R_p \propto [\text{KPS}]^{1.1} [N_p]^{1.05} [S]^{2.7} [\text{AN}]^{-0.86} \).

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Styrene-acrylonitrile copolymerization in micro-emulsion