

# Production of nanoparticles of methyl methacrylate and butyl methacrylate copolymers by microemulsion polymerization in the presence of maleic acid terminated poly(*N*-acetylenimine) macromonomers as cosurfactant

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## Abstract

In this study, MMA/BMA copolymer nanoparticles were synthesized in oil-in-water microemulsions that were stabilized by sodium dodecyl sulphate (SDS) and initiated by potassium persulphate KPS. Maleic acid terminated poly(*N*-acetylenimine) (PNAEI) with two different chain lengths was also included in the recipe, as a cosurfactant and a comonomer. FTIR and <sup>1</sup>H-NMR proved incorporation of the macromonomer in the structure. High polymerization yields were achieved upto 98%. The viscosity average molecular weights of the copolymers were in the range of 2.77–5.50 × 10<sup>5</sup>. The glass transition temperatures of these copolymers were between 50.0 and 63.9 °C. The average diameter of nanoparticles were in range of 40–96 nm. It was possible to produce nanoparticles smaller than 100 nm and with narrower size distributions by using much lower concentrations of SDS by including the macromonomers in the microemulsion polymerization recipe.

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## 1. Introduction

Many publications have appeared dealing with microemulsion polymerization since 1980 [1–16]. Microemulsions are used in the pharmaceutical, cosmetic and oil industry, as well as for textile finishing, as detergents, and as adsorbents in the environmental management. Microemulsion is an isotropic, optically transparent or

translucent, and thermodynamically stable dispersion of *nanoparticles* which forms spontaneously by mixing two ordinarily immiscible liquids (i.e., water and oil) and surfactant, with or without an alcohol as cosurfactant. Because of their well defined nature, microemulsions have been used as potential media for polymerization to prepare nanosize thermodynamically stable lattices which are not easily obtained from other systems. The polymer latex obtained from microemulsion polymerization is a liquid with lower viscosity compared to those resulted from other systems.

Anionic [1–6], cationic [6–12] or even nonionic [6,7] emulsifiers are usually used as surfactant in

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microemulsion polymerization. However, surfactant always creates drawbacks in the final application such as poisoning effect for biological systems. The use of macromonomers/macroiinitiators (which also act as co-surfactants) is an alternative to overcome this drawback, to increase monomer to surfactant ratio and to produce latexes with smaller particle sizes. This subject was studied by several groups [1,2,6]. Capek et al. studied fine emulsion of alkyl methacrylates including polyoxyethylene macromonomers. The addition of macromonomer was found to decrease the rate of polymerization and the molecular weight as well.

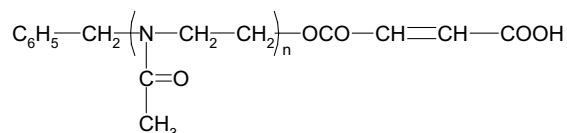
In microemulsion polymerization, most papers are focused on styrene (St) [1–4], alkyl methacrylates [2,3,5] or their combinations (copolymers) [1,10]. In our previous study, we have polymerized methyl and butylmethacrylates in oil-in-water microemulsion systems, in the presence of a poly(*N*-acetylenimine) (PNAEI) macromonomer with cinnamoyl end group. In the present study, methyl and butylmethacrylate were copolymerized in the presence of poly(*N*-acetylenimine) macromonomers with maleic moieties (MA<sub>*n*</sub>, *n* = DP<sub>PNAEI</sub>) [17], having two different chain lengths (*n* = 15 and 25). The copolymers prepared were characterized by Zeta Sizer, DSC, FTIR, and NMR techniques.

## 2. Experimental

### 2.1. Materials

The monomer methyl methacrylate (MMA) (Aldrich, USA), of commercial grade, was treated with an aqueous solution of NaOH (10%) to remove the inhibitor. Butyl methacrylate (BMA) (Aldrich, USA), monomer of commercial grade, was used as purchased. Ultrapure distilled/deionized water was used as the dispersion medium in all experiments. Sodium dodecyl sulphate (SDS) and potassium persulphate (KPS) were used as the emulsifier and initiator, respectively, without further purification.

The macromonomer, poly(*N*-acetylenimine) (PNAEI) with maleic acid with two different molecular weights (MA-15 and MA-25), with the following formula was prepared as previously reported [17], which was introduced in the recipe in order to reduce the amount of anionic emulsifier.



The PNAEI macromonomers were synthesized by the end-capping of the living poly(*N*-acetylenimine)

with maleic acid, as a nucleophile, in the presence of a macromolecular proton scavenger [17]. The functionalization efficiency (F%), calculated, as a ratio of the end-group functionality determined from <sup>1</sup>H-NMR data and the theoretical end-group functionality, was in the range of 92–96%.

The following signals were obtained: H-NMR (CDCl<sub>3</sub>): δ (ppm) = 9 (s, 1H, COOH), 7.3 (s, 5H, C<sub>6</sub>H<sub>5</sub>), 6–6.25 (d, 2H, CH=CH), 3–3.8 (s, 4H, CH<sub>2</sub>–CH<sub>2</sub>–N), 1.8–2 (s, 3H, CH<sub>3</sub>–CO–N) and FTIR (KBr): 2940 (aromatic CH group for C<sub>6</sub>H<sub>5</sub>), 2800 (–COOH carboxylic acid, ν broad), 1740 (C=O stretching), 1630 (tertiary amides). In elemental analysis, N content was found as 14% and 15.1% for MA-15 and MA-25, respectively.

### 2.2. Microemulsion polymerization

The polymerizations were realized in an oil-in-water (o/w) system. The microemulsion polymerization recipes are given in Table 1.

In a typical procedure, a selected amount of SDS (in the range of 0.0005–0.0040 g/ml), 0.002 g/ml (or 0.004 g/ml) of the macromonomer, and 1.25 g of the comonomer mixture (MMA/BMA ratio: 50/50, by weight) were added to 50 ml distilled water, in a 100 ml Pyrex reactor. Prior to polymerization, initiator was added to the solution and nitrogen gas flowed through the medium for about 1–2 min to remove dissolved oxygen. The vessel was then placed in a shaker, in a temperature control bath, and polymerization was realized at constant temperature of 75 °C for 6 h. Latex particles were cleaned by washing with methanol and water several times to remove the surfactant and the unreacted monomers.

### 2.3. Characterization

FTIR spectra of the nanoparticles were obtained by using an FTIR spectrophotometer (Shimadzu, Model: FTIR-8000 series, Japan) with KBr (IR grade)-nanoparticle mixtures in powder form.

For NMR analysis, the dried nanoparticles were dissolved in CDCl<sub>3</sub>, <sup>1</sup>H-NMR spectra were recorded in a NMR spectrometer (Bruker spectropin Avance Ultra-shield, Germany–Sweden) working at 400 MHz at room temperature. The sample concentration in CDCl<sub>3</sub> was 1% (w/v).

The polymerization yield was determined gravimetrically and calculated with the formula, where *w<sub>p</sub>* is the weight of the obtained dried part (nanoparticles) of the latex and *w<sub>m</sub>* is the weight of the comonomers (MMA/BMA) introduced in reaction.

$$\text{Polymerization yield (\%)} = (w_p/w_m) \times 100$$

Thermal transitions were obtained by using a differential scanning calorimeter (DSC) (Shimadzu, Model DSC-50,

Table 1  
Polymerization recipe

Experiment no.	SDS concentration (g/ml) $\times 10^{-4}$	Macromonomer concentration (g/ml) $\times 10^{-3}$	SDS/Monomer weight ratio $\times 10^{-3}$
<i>Only with SDS as surfactant (without PNAEI)</i>			
1	20	0	8
<i>With SDS and PNAEI-15</i>			
2	40	2	16
3	20	2	8
4	10	2	4
5	5	2	2
6	20	4	8
<i>With SDS and PNAEI-25</i>			
7	40	2	16
8	20	2	8
9	10	2	4
10	5	2	2
11	20	4	8

Japan). Nitrogen was used as the sweeping gas. The samples (5–10 mg) were heated at a scan rate of 5 °C/min from 25 to 200 °C followed by rapid cooling.

Viscosity measurements were used to obtain average molecular weights of the polymers produced in this study. Viscosities of the polymer solutions with different concentrations (0.1–1.0 g/dl) were measured with a capillary viscometer (Ubbelohde viscometer) in a constant temperature water bath, at  $25.0 \pm 0.1$  °C. The Mark–Houwink equation was used to calculate the viscosity average molecular weights:

$$[\eta] = K.M_v^a$$

The  $K$  and  $a$  values for PMMA and PBMA are  $5.5 \times 10^{-5}$  and  $4.9 \times 10^{-5}$ ; 0.79 and 0.78, respectively [18]. Since the initial ratio of the comonomers was 50/50, for the copolymers synthesized in this study, the average values  $K$ :  $5.2 \times 10^{-5}$  and  $a$ : 0.785 were used.

The average particle size and the particle size distributions were determined by Zeta Sizer (Malvern Instruments, Model 3000 HSA, France), without washing.

### 3. Results and discussion

In this study we attempted to copolymerize MMA and BMA in microemulsion in the presence of SDS, as the main surfactant, and PNAEI-15 and PNAEI-25 macromonomers as cosurfactants.

For all the investigated polymerization systems, stable latexes were obtained. In most cases, prior the polymerization, the medium was a transparent liquid, while after polymerization the latex obtained was bluish

and clear. No precipitation was observed in about one year storage period.

#### 3.1. Properties of copolymers

Two FTIR spectra are presented in Fig. 1, one for the MMA/BMA copolymer (prepared without using macromonomers), and the other obtained by including macromonomer (PNAEI-25) in the polymerization recipe. Both spectra are very similar and the following peaks can be identified,  $\text{cm}^{-1}$ : 2875–2987 CH stretching in  $\text{CH}_2$  and  $\text{CH}_3$  groups, 1732 (s) C=O stretching, 1400–1500  $\text{CH}_2$  scissor vibration, 1388 doublet twist bands for  $\text{CH}_3$  deformation, 1273–1000 C–O–C vibration in ester groups, 993 (w) C–C stretching of main chain, 845 CH out of plane deformation, 749  $\text{CH}_2$  rocking, 400–586 C–O bending. Note that the only difference on the spectra of the copolymers prepared with the macromonomer is the sharp band centered at  $1637 \text{ cm}^{-1}$ , ascertained to the carbonyl from the tertiary amide groups coming from PNAEI.

Representative  $^1\text{H}$ -NMR spectra for the MMA/BMA copolymers prepared without macromonomers, and by including the PNAEI-25 macromonomer in the polymerization recipe are given in Fig. 2A and B, respectively. We could identify signal at 3.88 ppm which belongs to the ester methyl methacrylate (A representing MMA) resonance and another signal at 3.52 ppm which belongs to the ester methyl [19] (B representing BMA) resonance. Another new peak belongs to the amide methyl appeared at 2.1 ppm in the NMR spectra, ascertained to the included macromonomer. Note that, the final comonomer ratios are lower than the initial comonomer ratios due to the different reactivity ratios of MMA and BMA [21].

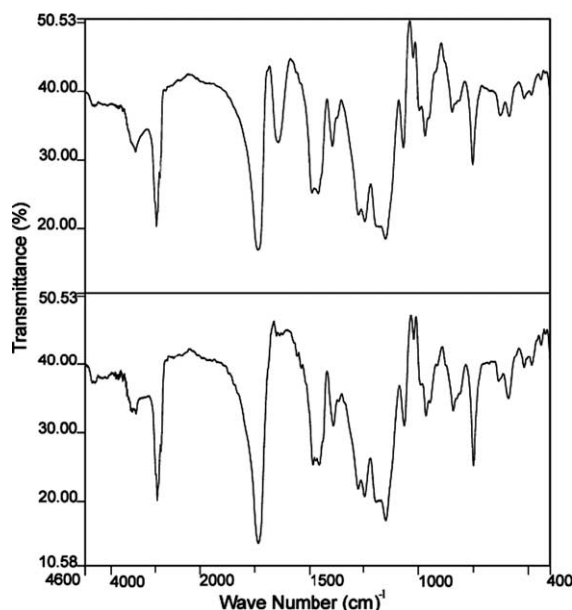


Fig. 1. Representative FTIR spectra of poly(MMA/BMA) copolymers synthesized: (A) with SDS and PNAEI-25 as the cosurfactant and (B) only with SDS as the main surfactant.

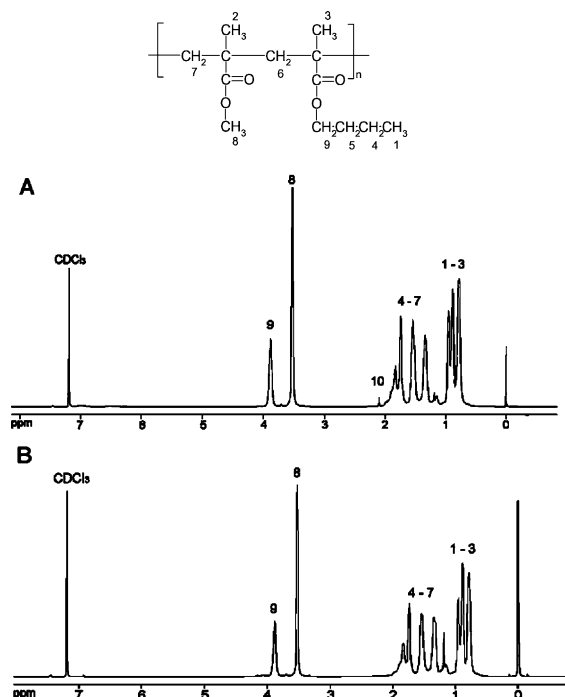


Fig. 2. Representative  $^1\text{H}$ -NMR spectra of poly(MMA/BMA) copolymers synthesized: (A) with SDS and PNAEI-25 as the cosurfactant and (B) only with SDS as the main surfactant.

Table 2 gives the polymerization yield, viscosity average molecular weights, and glass transition temperatures of the produced copolymers. Polymerization yields were determined from the total amount of comonomer used and the amount of polymer obtained as described before. As seen here, yields are over 80%, and quite comparable with the literature data. For the use of water soluble initiators lower conversions were reported [1,15,16], but by using organic phase soluble initiators (such as AIBN) much higher polymerization yields can be reached, even up to 95% [11,13,16,20].

As seen in Table 2, the viscosity average molecular weights of the produced copolymers were about  $2.77\text{--}5.50 \times 10^5$ , which were also in the limits reported in the related literature [9]. Use of the cosurfactant with SDS, especially PNAEI-15, caused an increase in the viscosity average molecular weight.

Thermal transitions were analyzed by DSC. All the copolymers produced showed only glass transition temperatures ( $T_g$ ) (no melting points), which means that they were all amorphous. The poly(MMA/BMA) 50/50 produced without macromonomers exhibited a  $T_g$  value about  $50^\circ\text{C}$ . Note that the  $T_g$  for PNAEI is about  $75^\circ\text{C}$  [22]. However, the  $T_g$  values of the similar copolymers synthesized in presence of macromonomers were higher and were in the range of  $52.2\text{--}63.9^\circ\text{C}$ , in accordance with the PNAEI grafts length (Table 2).

### 3.2. Properties of nanoparticles

Microemulsion polymerization of MMA/BMA 50/50 (by weight) were conducted by changing the main surfactant, SDS concentrations in the range of  $5 \times 10^{-4}$  to  $4 \times 10^{-3}$  g/ml. Two parallel sets of studies were performed, without or with cosurfactant PNAEI macromonomers with two different chain lengths (PNAEI-15 and PNAEI-25). The characterization of the polymer nanoparticles was performed with a Zeta Sizer. Table 3 gives the size and the polydispersity indexes of the nanoparticles. Particle diameters of these polymer latexes were in the range of 40–96 nm, with a variation coefficient of 0.03–0.2. As expected that the average size of the nanoparticles decreased significantly with increasing SDS concentration [1]. A SDS/monomer mass ratio lower than about 1.0 shifts the polymerization from microemulsion to miniemulsion or even to classical emulsion limits (at lower values). Note that in order to obtain stable latexes the amount of SDS/monomer in microemulsion formulation should be around 1–3, which is quite high [1,3]. This high concentration of SDS is a drawback that can be considerably restrict the potential uses of microemulsion polymerization since high solid contents and low surfactant amounts are usually desirable for most applications [23]. Including PNAEI macromonomer in the

Table 2  
Copolymer properties

Experiment no.	SDS concentration (g/ml) $\times 10^{-4}$	Macromonomer concentration (g/ml) $\times 10^{-3}$	Polymerization yield (%)	$T_g$ (°C)	$M_v (\times 10^5)$
<i>Only with SDS as surfactant (without PNAEI)</i>					
1	20	0	90.3	50.0	3.10
<i>With SDS and PNAEI-15</i>					
2	40	2	82.9	52.2	5.20
3	20	2	92.9	56.8	5.50
4	10	2	93.4	56.7	3.32
5	5	2	78.2	53.8	4.91
6	20	4	98.1	54.9	4.73
<i>With SDS and PNAEI-25</i>					
7	40	2	98.8	63.9	4.35
8	20	2	89.6	57.1	4.66
9	10	2	97.3	57.3	2.77
10	5	2	95.5	53.4	4.42
11	20	4	97.6	57.4	3.28

Table 3  
Nanoparticle properties

Experiment no.	SDS concentration (g/ml) $\times 10^{-4}$	Macromonomer concentration (g/ml) $\times 10^{-3}$	Particle size (nm)	Polydispersity index (–)
<i>Only with SDS as surfactant (without PNAEI)</i>				
1	20	0	53.4	0.214
<i>With SDS and PNAEI-15</i>				
2	40	2	38.7	0.118
3	20	2	48.3	0.061
4	10	2	86.9	0.119
5	5	2	92.1	0.033
6	20	4	43.8	0.124
<i>With SDS and PNAEI-25</i>				
7	40	2	39.5	0.099
8	20	2	48.4	0.106
9	10	2	74.9	0.063
10	5	2	96.3	0.042
11	20	4	40.1	0.098

recipe caused further pronounced decrease in the average particle size. It can be seen from Table 3, particle size reductions are 9.55% for MA-15 and 9.36% for MA-25, these values become 17.98% for MA-15 and 24.9% for MA-25 when the macromonomer amount doubled. Even at very low SDS concentrations ( $5 \times 10^{-4}$  g/ml) the particle size was lower than 100 nm (experiments 5 and 10, Table 3) which was actually the main target of this study. Macromonomer with longer chain length (PNAEI-25) was more relatively more effective for reducing the size of the particles comparing to the one with shorter chains (PNAEI). The particle size distribution was also narrower when PNAEI macromonomers were used for the production of the nanoparticles, which may also

be considered an important advantage for application.

#### 4. Conclusions

In this study we investigated the effects of macromonomers of poly(*N*-acetylenimine) (PNAEI) as cosurfactant on the size of poly(MMA/BMA) nanoparticles produced by microemulsion polymerization using SDS as a main surfactant. It was possible to produce nanoparticles smaller than 100 nm and with narrower size distributions by using much lower concentrations of SDS by including these macromonomers in the microemulsion polymerization recipe.

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