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SOAP-FREE EMULSION POLYMERIZATION OF VINYL MONOMERS IN THE PRESENCE OF POLY(N-ACETYL IMINOETHYLENE) MACROAZOINITIATORS

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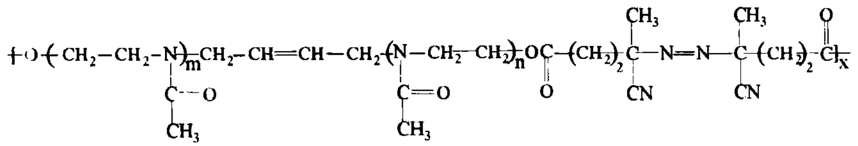
ABSTRACT

The soap-free emulsion polymerization of some hydrophobic vinyl monomers (styrene, methyl methacrylate, n-butyl methacrylate) in the presence of water soluble poly(N-acetyl iminoethylene) macroazoinitiators was investigated. The polymerization system features are controlled by the nature and concentration of both monomer and macroinitiator. The resulting block copolymers were proved to act as emulsifiers in inverse emulsion polymerizations.

INTRODUCTION

Polymer particles functionalized on the surface have received much attention in the last years, due to their possible application in both biomedical and technological fields. The technique generally used for their obtention is the soap-free emulsion polymerization of hydrophobic monomers in the presence of ionizable initiators or of hydrophilic, surface active/functional comonomers of ionic or nonionic type. Usually, statistical, graft or block copolymers, having different segments characterized by widely contrasting physical properties linked in the same chain - and therefore showing composite behaviour - are obtained from such synthetic approaches.

Recent papers report on the synthesis of micrometer sized particles with narrow size distribution, possessing poly(N-acyl iminoethylene) chains on the surface, by soap-free emulsion copolymerization of appropriate organic monomers with water soluble poly(N-acetyl iminoethylene) (PNAI) macromonomers of styryl or butadiene type [1, 2]. The high hydrophylicity and biocompatibility of poly(N-acetyl iminoethylene) [3] recommend such products for the previously mentioned purposes.



$$-\!\!\left[O\left(CH_2-CH_2-\underset{\underset{CH_3}{|}}{\underset{C=O}{\underset{|}{N}}}\right)_m CH_2-CH=CH-CH_2\left(\underset{\underset{CH_3}{|}}{\underset{C=O}{\underset{|}{N}}}-CH_2-CH_2\right)_n O\underset{\underset{O}{\|}}{C}-(CH_2)_2-\overset{CH_3}{\underset{CN}{C}}-N=N-\overset{CH_3}{\underset{CN}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}\right]_x$$

FORMULA 1

Continuing the interest in the synthesis and properties of block copolymers with poly(N-acetyl iminoethylene) sequences [4, 5], this paper presents preliminary results on the soap-free emulsion polymerization of some vinyl monomers initiated by poly(N-acetyl iminoethylene) macroazoinitiators (Formula 1).

EXPERIMENTAL

Materials

Commercially available monomers (styrene - St, methyl methacrylate - MMA and n - butyl methacrylate - BMA) and solvents (acetone, water) were purified by distillation.

Poly(N-acetyl iminoethylene) macroazoinitiators were prepared according to the literature [4]. Their characterization was previously reported [4].

Soap-free emulsion polymerization procedure

Soap - free emulsion polymerizations were typically carried out as follows. In a two necked flask purged with argon, 2.5 ml of monomer and corresponding amounts of PNAI macroazoinitiators in 50 ml of bidistilled water were magnetically stirred for 5h at 80°C and 1h at 90°C.

To obtain conversion versus time curves, one neck of the flask was capped with a rubber septum and a syringe for taking samples. The resulted latex was freezed and treated with small amounts of hydroquinone to avoid further polymerization and then with triethylamine to accelerate the coagulation. After filtration (G_4) the solid product was washed with a great amount of water and methanol to remove the eventually unreacted macroinitiator and dried in vacuum at 50°C. Monomer conversion was determined gravimetrically.

A similar procedure was used for the samples taken in the early stages of the process, before the appearance of the latex particles. After the removal of water from the filtered solution the residue was washed with ethyl ether and toluene. The toluene soluble product was characterized by ^{1}H-NMR spectroscopy.

Characterization

Particle sizes were determined with a Tesla BS 513 A transmission electron microscope (TEM). About 100 particles were considered for every systems. The number average diameter (D_n), weight average diameter (D_w) and polydispersity index (PI) were calculated with the following equations:

$$D_n = \frac{\Sigma N_i D_i}{\Sigma N_i} ; \quad D_w = \frac{\Sigma N_i D_i^4}{\Sigma N_i D_i^3} ; \quad PI = \frac{D_w}{D_n}$$

where N_i is the number of the particles with diameter D_i

The block copolymer composition was obtained from the nitrogen content determined by elemental analysis and from the ^{1}H-NMR spectra registered on a Jeol C 60 HL (60 MHz) spectrometer.

RESULTS AND DISCUSSION

No emulsifier properties could be evidenced for PNAI macroazoinitiators. Soap-free emulsion polymerization of St and BMA performed in their presence proceeded to give nanometer sized polymer particles. In contrast, that of MMA led to less stable systems and rather bulky particles (Table 1).

Further studies were concentrated on styrene, which gave the best results, in order to determine the influence of different factors on polymerization development.

Conversion levels were relatively low for the experiments performed at constant temperature. Two preparative routes were used to improve this aspect: the increase of temperature at the end of the reaction period, to allow the full decomposition of the macroinitiator (Fig. 1), and the use of acetone-water mixture (acetone/water - 40/60 v/v) as reaction medium [6, 7].

Thus, for an initial composition of the system of 0.0125g I_7/g-w and 0.045g St/g-w the conversion increased from 20% up to 60% when acetone was added, the temperature remaining the same (85°C) for 6h, and to 58%, respectively, when process conditions were modified (5h - 80°C, 1h - 90°C).

The features of the polymerization systems were dependent on macroazoinitiator characteristics and concentration. The data included in Table 1 evidence the relationship between the length of the PNAI segments in the macroinitiator and latex properties. They reveal that the best results are specific for the macroinitiators with the lower DP (I_7) of the PNAI segments. This behaviour was attributed mainly to the greater content in labile -N=N- groups in I_7 as compared to the other macroinitiators (Table 1). On the other side, the similarity with the literature data on the emulsifying properties of amphiphilic block copolymers containing PNAI hydrophilic sequences [7] suggest a possible stabilization of the system by amphiphilic oligomers eventually formed in the early stages of the process

TABLE 1

Particle size and size distribution dependence on monomer and macroazoinitiator nature in the soap-free emulsion polymerization [a].

Macroinitiator type [b]					Polymer				
No.	DP of PNAl segment	Code	$\bar{M}_w$	$\frac{\text{mmol } N_2}{\text{g sample}}$	Monomer	Yield %	D_n	$\frac{D_w}{D_n}$	Emulsion [c] stability
1	6.9	I_7	2125	1.04	MMA	20	10^4-10^5	-	-
2	6.9	I_7	2125	1.04	BMA	52	424	1.49	+
3	6.9	I_7	2125	1.04	St	17	197	1.21	+
4	21.0	I_{20}	4635	0.43	St	15	492	1.21	+
5	25.5	I_{30}	6280	0.40	St	5	335-860	-	-

[a] - Reaction conditions : 0.0075g I_7/g-w, 0.045g monomer/g-w, 5h at 80°C, 1h at 90°C, Ar.

[b] - from [4]

[c] - + stable, - unstable.

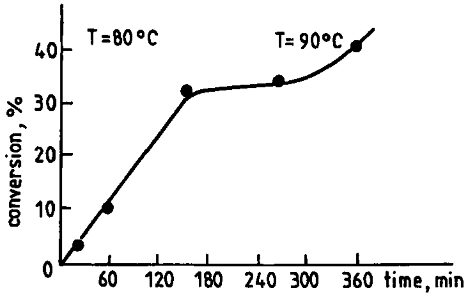


Figure 1 : Conversion *vs.* time in soap-free emulsion polymerization of styrene. Reaction conditions : 0.0125g I_7/g-w; 0.045g St/g-w; 5h at 80°C; 1h at 90°C

Their presence was experimentally confirmed. It was found that 12' from the beginning of the reaction the yield in water soluble block copolymers reached about 2%. The content in PSt sequences of these earlier products, as determined from ^{1}H-NMR spectra ($CDCl_3$), increases with time, i. e. from 10% (at t = 4') to 19.2% by weight (at t = 12'). The dependence of the reduced viscosity *versus* concentration, plotted in Fig. 2, unambigously demonstrates that this material allows micelle formation, thus suggesting a nucleation through "in situ" micellization.

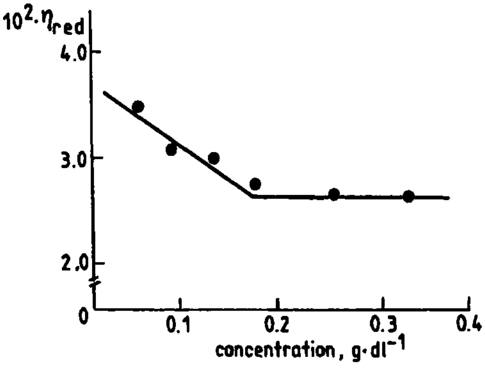


Figure 2. Concentration dependence of reduced viscosity for the dilute aqueous solution of the oligomers formed at t = 9 min. Reaction conditions: 0.0125g I_7/g-w, 0.045 St/g-w, T = 80°C.

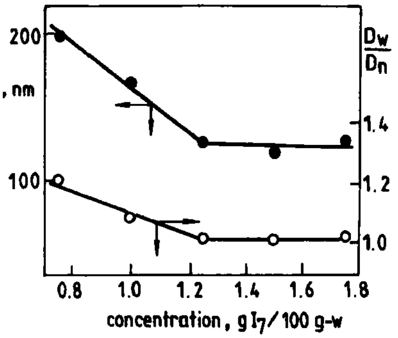


Figure 3. Particle diameter and size distribution *vs.* macroazoinitiator concentration in the polymerization of styrene. Reaction conditions: 0.045g St/g-w; 5h at 80°C; 1h at 90°C; Ar.

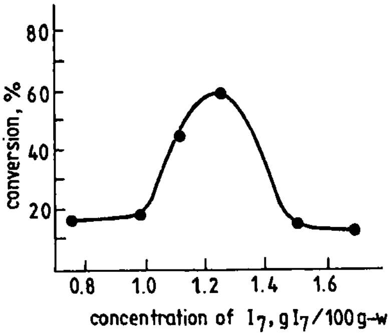


Figure 4. Conversion *vs.* macroazoinitiator concentration in soap-free emulsion polymerization of styrene (experimental conditions as in Fig. 3).

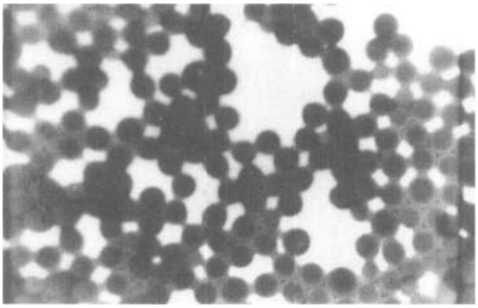


Figure 5. Electron micrograph of the latex particles Reaction conditions: 0.0125gI7/g-w; 0.05g St/g-w; 5h at 80°C; 1h at 90°C.

The effect of macroinitiator concentration upon particle size, size distribution and conversion level is shown in Figures 3 and 4. Particle size and size distribution decrease with increasing initiator concentration. Nearly monodisperse spherical particles, with the hydrophilic PNAI chains located on the surface (Figure 5) and a diameter as small as 120-130 nm could be obtained for a concentration in macroinitiator greater than 0.0125g I7/g-w.

A maximum in polymer yield was observed for the same value of 0.0125g I7/g-w. The following explanations for these last results are available :

-- the competition between the increase of nucleation rate with the initiator concentration

[8] and the concomitent increase of the content in allylic groups - with inhibitory effect - inserted in the macroinitiator backbone (see Formula 1), and
-- the usual lowering of the emulsion polymerization rate with increasing the concentration of the nonionic emulsifier [9].

The resulting amphiphilic block copolymers have molecular weights in the 10^5 range and a low content in PNAI. Such compounds might be used as emulsifiers in inverse emulsions. To exemplify, for the block copolymers with PSt and PBMA sequences, obtained for initial concentration of I_7 and monomer in the polymerization system of 0.0125g I_7/g-w and 0.045g monomer/g-w, respectively, the content in PNAI was of 18% and 21% by weight. A typical recipe for a stable emulsion using them for system stabilization would consist of the following ingredients: BMA monomer, 30 vol %, toluene/water 50/10 (v/v), 6.5 10^{-3}g $(NH_4)_2S_2O_8$/g mixture , 6.5 10^{-3}g emulsifier/g mixture (PSt/PNAI, or BMA/PNAI block copolymer). After 6h the yield was as high as 75 % and 53 %, respectively.

Further investigations on the mechanism of each peculiar mentioned case are now in progress.

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