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## Poly[(N-Acetylimino)ethylene] Macromonomers with Maleic Moieties in the Dispersion Copolymerization with Styrene

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### ABSTRACT

Three different poly(N-acetyliminoethylene) (PNAI) macromonomers containing maleic acid moieties were tested as stabilizers for the preparation of polymer microparticles by dispersion polymerization in a polar media (alcohol/water). A comparative study on the effect of various factors, such as initiator nature and solvency of the reaction medium, on system stability and particle characteristics was performed. Styrene was used as the main monomer and ethanol, isopropanol and 2-butanol as organic solvents. Chemical and photochemical techniques were applied as initiation routes. The photoinitiators allow the synthesis of microparticles with low diameters and narrow size polydispersity in a high yield. The polymerization duration was significantly improved as compared to the methods available in the literature.

*Key Words:* Macromonomers; Poly(2-oxazoline); Dispersion polymerization; Microparticles; Styrene.

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## INTRODUCTION

Dispersion polymerization has received much attention as a simple and convenient method to prepare monodisperse polymer particles in the micron range. The dispersion polymerization of hydrophobic monomers, such as styrene and methyl methacrylate, has been extensively studied.<sup>[1-7]</sup> The reported results show that a large number of variables control the particle characteristics. Among them, the nature of the polymeric stabilizer and the solvency of the reaction medium are the most important ones. As for the polymeric stabilizers available in dispersion polymerization, four different types may be considered, i.e., homopolymers, block and graft copolymers, macromonomers and multifunctional polymers. Much of the literature reports mentioned a higher stabilization efficiency of the macromonomers.<sup>[8-10]</sup>

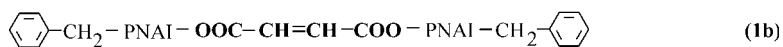
A comparative study on the effect of the structure of the polymerizable group on the stabilization efficiency of the involved macromonomers was accomplished in order to point out the importance of this aspect.

## EXPERIMENTAL

### Materials

Styrene (St) was treated with aqueous NaOH to remove the inhibitor, and then was vacuum distilled. 1,1'-Azobis(isobutyronitrile) (AIBN, Merck), benzoyl peroxide (BP, Aldrich) and the photoinitiators (2,4,6-trimethylbenzoyl diphenyl phosphine oxide, (TPO), (BASF); [(2,4,6-trimethylphenyl)carboxy-ethoxy-phenyl]phosphorus oxide (TEPO), (BASF); 2,2-dimethoxy-2-phenylacetophenone-Irgacure 651, (CIBA-GEIGY) were used as received. Ethanol (EtOH), isopropanol (PrOH) and 2-butanol (BuOH) were obtained from Merck and were used without further purification.

The macromonomers **1a-c** were synthesized according to the literature data,<sup>[11]</sup> by the coupling of the living poly[(N-acetylimino)ethylene] (PNAI) growing chains with maleic acid as a nucleophile. Their characteristics are given in Table 1.



Deionized water was used in dispersion polymerization.

*Table 1.* Macromonomers characteristics.

Macromonomer	DPn <sup>a</sup>	Functionalization <sup>b</sup> (%)
<b>1a</b>	25	93
<b>1b</b>	25	92
<b>1c</b>	25	98

<sup>a</sup> Polymerization degree for the PNAI sequence.<sup>b</sup> From <sup>1</sup>H-NMR data.

### Dispersion Polymerization

Depending on the reaction conditions, the dispersion copolymerizations were carried out under an inert atmosphere (argon), (a) in a 100 ml two-necked round bottomed flask equipped with a stopcock gas inlet, immersed in a thermostated bath or, (b) in a thermostated sealed quartz ampoule, situated at a 16 cm distance from a high-pressure mercury lamp of 500 W. Both the flask and the ampoule were equipped with a magnetic stirrer. Concentrated solutions of Irgacure 651 in the chosen polar solvent mixture, or of AIBN, BP, TPO or TEPO in styrene were prepared. The appropriate amounts of these solutions were added to the weighed comonomers (macromonomers). The reaction mixture was then completed with the required volume of solvent until a total amount of 50 ml was reached, and purged with argon for 10 min.

The resulting polymer particles were separated by centrifugation of the dispersion, purified by washing with methanol, dried in vacuum and analyzed.

### Measurements

Electron microscopy studies were performed on a TESLA BS 513A apparatus. The samples were prepared by spraying the diluted solutions of the reaction mixture (1 wt% in an ethanol/water mixture) on copper grids covered with carbon. The number average diameter ( $D_n$ ), the weight average diameter ( $D_w$ ) and the size distribution index (PI) were evaluated by analyzing the micrographs according to the following relations

$$D_n = \frac{\sum NiDi}{\sum Ni} \quad (1)$$

$$D_w = \frac{\sum NiDi^4}{\sum NiDi^3} \quad (2)$$

$$PI = D_w/D_n \quad (3)$$

where  $N_i$  is the number of particles of diameter  $D_i$  (nm).

The conversions were determined gravimetrically by precipitating the dispersion in methanol and weighing the dried polymer, or by lyophilization of the polymer particles followed by weighing.

## RESULTS AND DISCUSSION

The one step dispersion polymerization is one of the most convenient approaches for the preparation of polymer particles with narrow size distribution. The stabilization of such systems is assured by polymeric compounds.<sup>[10]</sup>

In this study we have used the three PNAI macromonomers with the previously mentioned structures, derived from maleic acid and living PNAI chains. Reaction parameters such as macromonomer concentration, initiator type and polarity of the medium were varied in order to establish the optimum conditions in obtaining particles with narrower size distribution.

### Concentration of the Stabilizer

The concentration of the macromonomer, acting both as a stabilizer and as a comonomer, strongly affects the efficiency in stabilization of the dispersion system. Table 2 contains experimental results obtained for different concentrations of macromonomer **1a** and two entries for the macromonomers **1b** and **1c**. It can be seen that the particle size decreases with increasing macromonomer amount in the polymerization system, due to the increased number of primary microparticles formed. The increase of the macromonomer content in the monomer mixture favors the improving of particle size distribution. However, after reaching a macromonomer amount specific for each system, a slight increase of particle size distribution was reported.<sup>[12]</sup> It was ascribed to the increase of the nucleation period.

In the present study, the best results were obtained for macromonomer concentration values situated in the range of 4–6 wt% relative to total monomer. The comparison with

**Table 2.** Dispersion copolymerization of styrene with PNAI macromonomers at different concentrations of the stabilizer.

Entry	Macromonomer	Amount of macromonomer <sup>a</sup>	Dn (nm)	PI
1	<b>1a</b>	1	900	1.20
2	<b>1a</b>	3	886	1.18
3	<b>1a</b>	4	809	1.07
4	<b>1a</b>	5	716	1.08
5	<b>1a</b>	6	650	1.09
6	<b>1a</b>	7	641	1.10
7	<b>1b</b>	6	768	1.17
8	<b>1c</b>	6	886	1.19

Reaction conditions: 10 wt% St, 6 wt% macromonomer with respect to total monomer, 2 wt% AIBN with respect to total monomer, 90/10 v/v ethanol/water mixture, 70°C, Ar.

<sup>a</sup> % wt with respect to total monomer.

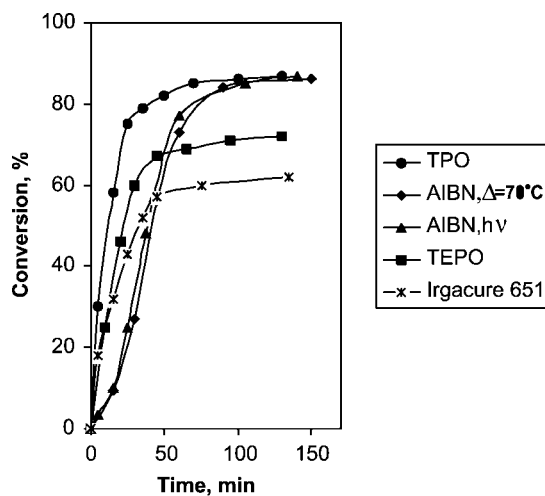
the two other macromonomers, **1b** and **1c**, (Table 2, entries 5, 7, 8) proves the decrease of the stabilization efficiency in the order: **1a** > **1b** > **1c**. This aspect was related to the different structures that imply different reactivities and a different disposal of the PNAI sequences at the particle surface.

As expected, the multifunctional compound **1c** favors the formation of coagulum. Its amount decreases with increasing macromonomer concentration. As a consequence, a value of 6 wt% macromonomer relative to total monomer was selected.

### Type of Initiator

By its solubility, decomposition efficiency and the concentration in the reaction system, the initiator controls the nucleation stage and as a consequence, the yield, particle dimension, and size polydispersity. A short initiation period avoids a secondary nucleation, yielding in monodisperse particles.

The initiation was performed by a thermal or a photochemical procedure. The initiators used were AIBN, for the thermal polymerization and AIBN, BP, TPO, TEPO, Irgacure 651, respectively, for the photoinitiated polymerization. The specific higher photodecomposition rate of the initiators as compared to the thermal one is expected to provide higher polymerization rates, higher yields, and an improved particle size polydispersity. Indeed, the conversion - time plots evidence the faster initiation through UV irradiation of the polymerization systems. As shown in Fig. 1, the kinetic curves obtained for the systems initiated with AIBN, at 70°C and by photoirradiation (35°C),



**Figure 1.** Variation of monomer conversion with the polymerization time in the presence of different initiators. Polymerization conditions: 10 wt% St, 6 wt% macromonomer **1a** with respect to total monomer, 2 wt% initiator with respect to total monomer, 90/10 v/v ethanol/water mixture, Ar; the photopolymerizations were performed at 35°C.

**Table 3.** Dispersion copolymerization of styrene with PNAI macromonomers.

Sample code	Initiator type	Mode of initiation	Time (h)	Temp. (°C)	Dn <sup>a</sup> (nm)	Dw <sup>a</sup> (nm)	PI	Yield (%)	System stability <sup>b</sup>
D <sub>1</sub>	TPO	hν	4	35	350	367	1.05	89	+
D <sub>2</sub>	TEPO	hν	4	35	455	478	1.08	65	-
foculation at 1.5 h									
D <sub>3</sub>	Irgacure 651	hν	4	35	647	712	1.10	84	+
D <sub>4</sub>	BP	hν	4	35	886	1027	1.16	70	+
D <sub>5</sub>	AIBN	hν	4	35	650	715	1.09	79	+
D <sub>6</sub>	AIBN	Δ	6	70	2820	3158	1.12	78	+

Reaction conditions: 10 wt% St, 6 wt% macromonomer **1a** with respect to total monomer, 2 wt% initiator with respect to total monomer, 90/10 v/v ethanol/water, Ar.

<sup>a</sup> by TEM.

<sup>b</sup> (+):stable, (-):unstable.

respectively, are practically superposed and have a slightly S shape, suggesting the existence of a short induction period.

The plots corresponding to the systems employing photoinitiators have higher slopes in agreement with their known rapid decomposition. The best behavior was observed in the case of TPO. The higher rate of photoinitiation at a low temperature determines the increase of the number of the generated polymer chains, yielding the increase of nuclei number. As a consequence, a greater number of particles with smaller sizes are formed, as can be seen in Table 3, the particle size dispersion being slightly improved.

### Medium Solvency

In the dispersion polymerization, monomer, initiator and stabilizer are all soluble in the dispersion medium. The medium solvency, i.e., polarity, given by the Flory–Huggins interaction parameter, drastically affects the particle size and size distribution.

The solubility of styrene in dispersion media consisting of alcohol/water mixture depends on the alcohol type, water content of the dispersion medium, and the solubility of water in alcohol. By changing the alcohol type and water content, the yield, particle size and size polydispersity can be varied in a large range. Three different alcohols, namely ethanol, isopropanol and 2-butanol were used. Table 4 contains the data obtained for these experiments.

As can be seen, the best results were obtained with ethanol, which has the highest solubility parameter. In agreement with other literature reports<sup>[1,7]</sup> the system having 2-butanol as dispersion medium gives the largest size dispersity and the lowest yield. The size of the particles is decreasing with the increase of the polarity, which facilitates the earlier precipitation of the growing chains. The increased number of formed nuclei implies lower particle dimensions.

### Alcohol/Water Ratio

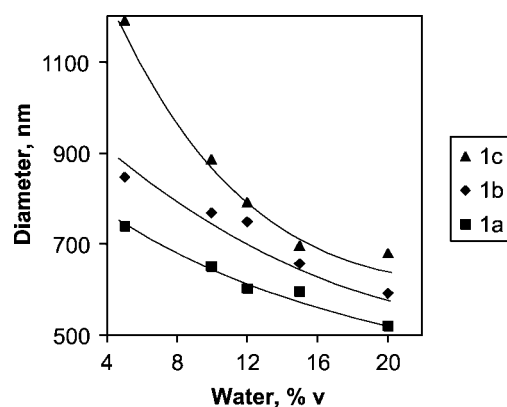
The behavior of polymerization systems stabilized with the three different polymer stabilizers was investigated for alcohol/water v/v ratios in the range of 95/5–80/20.

**Table 4.** Dispersion copolymerization of styrene with PNAI macromonomers in different polar media.

Alcohol	Solvability parameter (cal/cm <sup>3</sup> ) <sup>1/2</sup>	Dn (nm)	Dw (nm)	PI	Yield (%)
Ethanol	12.7	650	715	1.10	82
Isopropanol	11.5	716	1024	1.32	62
2-Butanol	10.8	844	1367	1.48	56

Reaction conditions: 10 wt% St, 6 wt% macromonomer **1a** with respect to total monomer, 2 wt% AIBN with respect to total monomer, 90/10 v/v alcohol/water mixture, 4 h, 35°C, Ar.

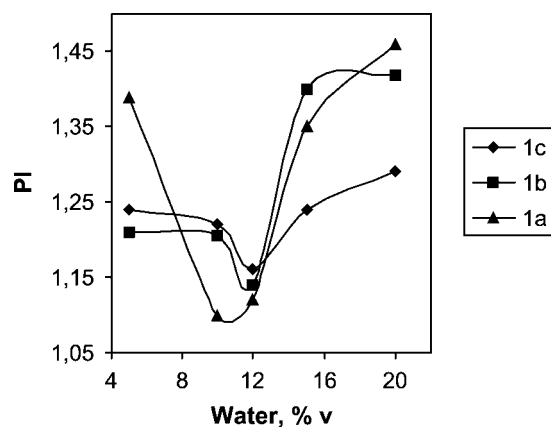




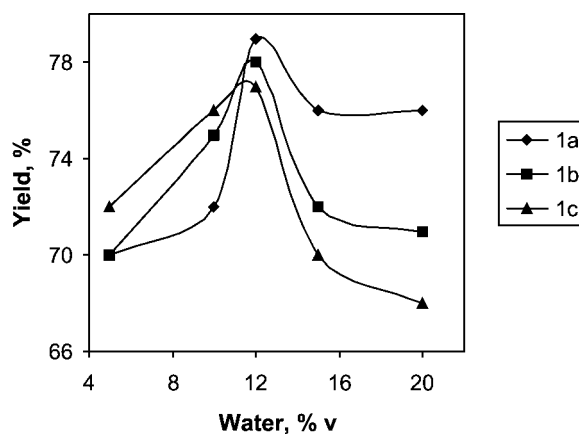
**Figure 2.** Effect of alcohol/water ratio on the particle size. Polymerization conditions: 10 wt% St, 6 wt% macromonomer with respect to total monomer, 2 wt% AIBN with respect to total monomer, 90/10 v/v ethanol/water, 4 h, Ar.

For the higher alcohol/water ratio, the polarity of the dispersion medium is diminished, favoring the solubilization of the growing polymer chains. The nucleation takes place at a relatively high average molecular weight. As a consequence, a reduced number of polymer particles are generated, giving rise to an increase of their size (Fig. 2). Higher amounts of stabilizers are required. This determines the increase of the duration for the formation of the primary particles, implying an enlarged particle size distribution.

As shown in Fig. 3, the composition of the polymerization medium yielding the narrowest size distribution is the same no matter what the macromonomer type (i.e., 10–15% v water). Kobayashi<sup>[12]</sup> and David<sup>[13]</sup> specified the same domain of narrow polydispersity for the dispersion polymerization of styrene stabilized with PNAI



**Figure 3.** Size distribution of the prepared particles as a function of alcohol/water ratio. Polymerization conditions: 10 wt% St, 6 wt% macromonomer with respect to total monomer, 2 wt% AIBN with respect to total monomer, 90/10 v/v ethanol/water, 4 h, Ar.



**Figure 4.** Dependence of the polymer yield on the alcohol/water ratio. Polymerization conditions: 10 wt% St, 6 wt% macromonomer with respect to total monomer, 2 wt% AIBN with respect to total monomer, 90/10 v/v ethanol/water, 4 h, Ar.

macromonomers with quite different polymerizable groups (styryl and cinnamoyl, respectively). This aspect suggests that the determinant role in size distribution control belongs to the medium solvency that is the most important factor of influence in dispersion polymerization. The yield presents a maximum in the same domain (Fig. 4).

## CONCLUSION

The effect of several reaction parameters (initiation type, stabilizer concentration, dispersion medium polarity) on particle size and particle size distribution in the dispersion polymerization of St in alcohol/water media was investigated. The polymerization systems were stabilized with PNAI macromonomers containing maleic acid moieties as active groups.

The comparative study of systems with different initiators proved that the known rapid photoinitiation leads to the formation of smaller particles with similar or slightly improved size distribution in relatively mild conditions (4 h, 35°C). The variation of the medium polarity by changing the alcohol/water ratio or the alcohol type yielded the increase of the particle size with increasing polarity of the medium. The optimum domain for the size distribution was found to be independent on the macromonomer type (i.e. nature and position of the polymerizable group). This behavior evidences the priority of the medium solvency as a factor of influence in the dispersion polymerization.

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