

## Reactive surfactants in heterophase polymerization

### III. Poly(ethylene oxide) macromonomers and polymerizable surfactants (surfmers) as stabilizers in styrene dispersion polymerization\*

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#### Summary

Maleic, Styrenic and Methacrylic macromonomers of poly(ethylene oxide) and related polymerizable surfactants (SURFMERS) have been used as stabilizers in the dispersion polymerization of styrene in ethanol-water mixtures. The current study looks at the polymerization yield, the particle size and the incorporation yield of the stabilizers onto the surface of the particles. The macromonomers are better suited than the corresponding SURFMERS for steric stabilization of the particles.

#### Introduction

Dispersion polymerization involves an homogeneous solution of monomer from which the polymer is precipitated as minute particles, sterically stabilized by a non-ionic surfactant (1). When the polymerization is carried out in a polar medium, such as alcohol-water mixtures, the stabilizer is often a polymeric compound, soluble in the medium, which becomes amphiphilic through grafting by the growing polymer (2). Typically, one uses rather large amounts (up to 10 % of the monomer) of polymer, such as poly(vinylpyrrolidone) which is easily grafted (3). Recently, a Japanese group (4) reported that upon replacing the polymer by a styrenic macromonomer of the same nature as the polymer (in their case poly(methyl oxazoline)) it was possible to obtain monodisperse particles of the same micron size with much less stabilizer. Some data related to the kinetics of the dispersion polymerization of styrene in the presence of methacrylic and styrenic macromonomers of poly(ethylene oxide) have recently been reported by Capek et al. (5, 6).

In part II of this series (7), we presented a rather extensive study of the dispersion polymerization of styrene in ethanol-water mixtures in the presence of a surfactant, the hydrophilic part of which was a poly(ethylene oxide) sequence attached to a hydrophobic fatty alcohol maleic hemiester (I). Stable, monodisperse micron-sized particles have been obtained also using small amounts of surfactant. However, it was found that only 3% of the polymerizable surfactant remained grafted on the particles.



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A short comparative study of several poly(ethylene oxide) macromonomers and surfactants carrying similar polymerizable groups, often referred to as SURFMERS, is presented in the current work.

## Experimental

### *Materials*

A commercially available poly(ethylene oxide) (PEO) macromonomer carrying methacrylic group was obtained from BP Chemicals. It was stabilized with hydroquinone mono methyl ether, and was thus purified after precipitation in diethyl ether. A styrenic compound was prepared using the method described by Revillon and Hamaide (8), by reacting vinyl benzyl chloride (VBC from Dow) with commercial PEO monomethylether (PEO 2000 Aldrich) in the presence of NaH. The maleic macromonomer was prepared by heating (3.5 hours at 80°C) a melt containing 41g (20.5 mmoles) of PEO 2000 and 3.35g (34.2 mmoles) of maleic anhydride. The product was purified upon reprecipitation from chloroform in diethylether, and then dried under vacuum overnight, and finally heated for 3 hours at 40°C. Another methacrylic macromonomer was prepared by reacting an excess of methacryloyl isocyanate (MAI from SNPE Chimie) with PEO 2000 in toluene (12 hours at 40°C). After distillation of the solvent, the product was redissolved in chloroform, precipitated with cold diethylether and finally dried as for the maleic macromonomer.

The corresponding polymerizable surfactants (SURFMERS) are the following :

- 1) Two maleates (1) used in Part II which were prepared by Hamaide and Zicmanis (9) from the catalytic polymerization of ethylene oxide initiated with the dodecanyl hemiester of maleic anhydride.
- 2) A styrenic SURFMER also prepared by A. Filet et al.(10) via the catalytic polymerization of ethylene oxide initiated by the condensation product of VBC with hexanediol.
- 3) The same catalytic polymerization of ethylene oxide, has also been used to produce the hydrophilic part associated with the macromonomers of poly(propylene oxide) provided by Nippon Oil and Fats (i.e an acrylic product with a short (6 units) sequence (BLEMER AP400), and a methacrylic product with a slightly longer sequence (12 units) (BLEMER PP 800)).
- 4) A block copolymer of ethylene oxide and butylene oxide was prepared through the anionic polymerization of butylene oxide (BO) initiated by PEO 2000 and naphthalene potassium, as described in the Part I of this series (11), and was reacted with a five fold excess of MAI. The reaction was carried out for 3.5 hours at 40°C, and further overnight at room temperature. The excess of MAI is destroyed with methanol, and the product is purified through precipitation with petroleum ether. The functionalization yield is 100%.

The products are characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR (Brucker 250 MHz in  $\text{CDCl}_3$ ), as well as by size exclusion chromatography (SEC) in tetrahydrofuran using a Waters instrument. The calibration is carried out from polystyrene standards (Waters). It is possible that the catalytic process used in the preparation of the PEO sequences might lead to the presence of some tiny particles of silica that could interfere with the analyses. As a result, some of the values obtained for the determination of molecular weight of the

polymers might be doubtful. The same might also be true for the critical micellar concentration (CMC).

### *Dispersion polymerization*

The dispersion polymerizations were carried out using a batch process in ethanol-water (70-30 in volume). Azobisisobutyronitrile (AIBN - Jansenn) was used as the free radical initiator (2wt% based on monomer) and styrene (Prolabo) was added in quantities such that the polystyrene content was 10% (W/W) at 100% conversion. The amount of stabilizer added was 3.1% by weight with respect to the quantity of styrene, unless otherwise specified. The reaction was carried out under nitrogen atmosphere for 24 hours at 70°C with a total volume of 180ml in the reactor, which was stirred at 250rpm. The size of the particles was determined either by a Disk Centrifuge Photosedimentometer analysis (BI-DCP Brookhaven particle sizer) or by Transmission Electron Microscopy (TEM).

## Results and discussion

The characterization of the four kinds of macromonomers are reported in Table 1. The maleate product, which is an hemiester of maleic anhydride, can be further titrated to obtain the acidic group content. The number average molecular weight from this determination corresponds to the number of ethylene oxide units of 49, in good agreement with the NMR titration. The number average molecular weight from SEC are always over estimated due to the polystyrene calibration. However, the results are in agreement with that of the PEO 2000 determined in the same conditions.

**TABLE 1 : Characterization of the poly(ethylene oxide) macromonomers**

Nature <sup>(a)</sup>	Nb of EO units	M <sub>n</sub> (NMR)	M <sub>n</sub> (SEC)	M <sub>w</sub> / M <sub>n</sub>
<b>MAL</b>	52	2 402	2 892 <sup>(b)</sup>	1.10
<b>MA</b>	51	2 344	2 934	1.03
<b>MAI</b>	48	2 255	2 630	1.10
<b>S</b>	45	2128	2529	1.09
<b>PEO 2000</b>	45	--	2585	1.07

<sup>(a)</sup> **MAL** : maleate, **MA** : methacrylate, **MAI** : methacryloyl isocyanate, **S** : styrene,  
**PEO 2000** : Poly(Ethylene Oxide) M<sub>w</sub> = 2000 g/mol

<sup>(b)</sup> in CHCl<sub>3</sub>

The results of the characterization of the SURFMERS are given in Table 2. Large discrepancies are observed between the molecular weight from NMR and from SEC. This is due to the pollution of the products with the silica catalyst residue. For that reason, NMR data seems to be more certain. The data for CMC also must be taken with

caution, except for the products which were fully soluble in water, i.e. the MAI-BO compound.

The interest of macromonomer stabilization can be seen by comparing their efficiency with that of PVP-K30 (poly(vinylpyrrolidone)), which is among the best stabilizers used (3). As shown in Table 3, less stabilizer is needed for the same particle size, and less coagulum is produced. Further, the particles are more monodisperse. Comparatively, poorer results were obtained with conventional surfactants such as ethoxylated nonylphenol, even used in a large amount.

**TABLE 2 : Characterization of the SURFMERS**

Nature	Nb of EO units	Nb of PO units	Nb of BO units	M <sub>n</sub> NMR	M <sub>n</sub> SEC	CMC mmole/L
MAL	34	--	--	1 780	1 395	1.68 10 <sup>-2</sup>
	42	--	--	2 088	1 677	6.2 10 <sup>-2</sup>
A	36	6.7	--	2 057	1 995	0.47
MA	59	15.3	--	3 370	1 520	--
MAI	45	--	8.4	2 728	3 046	0.07 <sup>(a)</sup>
S	42	--	--	2 076	880	1.73

<sup>(a)</sup> CMC of unfonctionalized diblock copolymer

**TABLE 3 : Comparative dispersion polymerization**

Stabilizer	Amount <sup>(a)</sup>	Styrene Conversion %	D <sub>n</sub> nm	D <sub>w</sub> /D <sub>n</sub>	Coagulum %
<b>Macromonomer</b>					
MA 51	1.4	100	971	1.025	0
PVP K30	3.1	85.2	979	1.13	3.9
NP 40	20	61	1 990	1.72	> 20

<sup>(a)</sup> Amount of stabilizer versus styrene

The data of dispersion polymerization with the various macromonomers and SURFMERS are reported in Table 4. Except for a few cases, the amount of stabilizer was kept as 3.1wt% based on styrene. Because most of the products have similar molecular weight, this corresponds to approximatively the same molar content. Note that satisfactory results can occasionally be obtained with smaller amounts of stabilizer (Table 3).

TABLE 4 : Results of dispersion polymerization

Nature <sup>(a)</sup>	MACROMONOMER				SURFMER					
	MAL	MA	MAI	S	MAL		A PO 6	MA PO12	MAI BO 8	S
Nb of EO units	52	51	48	45	34	42	36	59	45	42
Amount%	3.1	3.1	3.1	3.1	6 <sup>(b)</sup>	3.1	2.8	9.8	3.1	3.1
Styrene Conversion %	98	100	83	100	76.6	75	67.3	85.5	98	100
Coagulum %	0	0	0.4	0	--	3.4	67	34	0	17
D <sub>n</sub> nm	2 040	623	661	1 030	1 240	1 170	1 028	1 200	905	2 020
D <sub>w</sub> /D <sub>n</sub>	1.04	1.10	1.09	1.04	1.19	1.04	1.12	1.22	1.17	1.06
Grafted%	3.3	14.7	5.7	11.6	2.5	3.0	1.5	0.5	3.5	6.3
Adsorbed%	10.6	12.1	8.2	9.4	8.6	13	--	--	15.6	3.6
Serum%	86	73	86	79	89	84	--	--	81	90
Coverage Å <sup>2</sup> grafted	1 008	804	1 526	559	705	1 301	2 256	2 976	2 612	415
Coverage Å <sup>2</sup> adsorbed	240	440	621	415	157	247	--	--	478	264

<sup>(a)</sup> MAL : maleate, MA : methacrylate, A : acrylate, S : styrene, MAI : methacryloyl isocyanate, PO : propylene oxide, BO : butylene oxide

<sup>(b)</sup> Dispersion polymerization in ethanol-water 80-20 in volume

High conversions can be obtained with most of the products, with almost complete styrene conversion obtained when macromonomers are used. Also, when macromonomers are used, there is practically no coagulum produced. This is not the case in the presence of polymerizable surfactants despite the higher amounts of stabilizer sometimes used. It would therefore seem that macromonomers are able to confer a better stability to the particles than are polymerizable surfactants. This conclusion is reinforced if one considers both the particle size and particle size distribution, as well as the incorporation yield, which can be judged from the poly(ethylene oxide) content of the polystyrene. The particle size is generally smaller when macromonomers are used, especially if one takes the conversion into account. There is just one exception in the case of the amphiphilic maleate with the longest hydrophilic sequence. The most monodisperse particle size distribution are also observed when using the macromonomers. Finally, the incorporation yields of the stabilizers are always very limited, but the highest value is obtained for the methacrylic macromonomer, and the lowest is for the amphiphilic compound with the longest hydrophobic sequence. In addition, for each kind of reactive group, the incorporation yield is always higher when a macromonomer is used instead of the corresponding amphiphilic.

Polystyrene oligomers are produced up to a critical degree of polymerization, which should be the higher for a higher styrene content in alcohol of the reaction medium (which is actually the serum). Above this critical conversion, these oligomers are captured by the existing particles once they have been nucleated. These oligomers are able to incorporate a part of the reactive stabilizers. This copolymerization process is most probably the main route for the incorporation of the stabilizer at the surface of the particles. While these oligomers, or more precisely these copolymers, have not reached the critical degree of polymerization, they may be adsorbed onto the surface without being grafted; but the adsorbed species do participate to the stabilization. The amount of these adsorbed species is also limited for various reasons but they account for a larger part than the grafted species in most cases. However, the largest part of both the macromonomers and the polymerizable surfactants remains dissolved in the serum, which at the end of the polymerization is mainly the initial mixture of water and alcohol. One reason for this may be the initial solubility of these compounds in the final serum, and also the limitation of the molecular weight of the growing oligomers (ooligomers) because of the large amount of alcohol, which is actually a transfer agent that limits the growth of these species. In the case of the maleate (7), the species found in the serum are simply a 1-1 adduct of styrene and maleate, and also pure styrene oligomers. Most probably the 1-1 adduct results from a charge transfer complex between the two molecules which cannot grow due to the transfer reaction. In the case of acrylic, methacrylic or styrenic macromonomers and surfactants, one may expect that the copolymerization process would be more efficient, and that comb-like oligomers are produced. The resulting product can be more easily adsorbed, chiefly in the case of polymerizable surfactants.

If one takes into account the particle size of the final latexes and the amount of incorporated stabilizer, it is possible to calculate the area covered by each molecule of stabilizer. The last two columns of Table 4 give the results of this last calculation for the grafted poly(ethylene oxide) segments, and for the grafted plus adsorbed species respectively. A recent theory (12) on the modelling of dispersion polymerization stabilized by styrenic macromonomer with some amphiphilic properties, indicates that, for a PEO segment of about 50 units, the area which can be covered by random coil, i.e. with non-perturbated dimension, is about  $1100 \text{ \AA}^2$ . This value is not far from the results

obtained for most of the stabilizers except for the case of styrenic compounds. On the other hand, if one takes into account the adsorbed species, the values are much lower, and are closer to the saturation values (around  $150 \text{ \AA}^2$ ) where the conformation of the PEO chains should be a thick brush.

### Conclusion

The main conclusion of this comparative study is that hydrophilic macromonomers always give a better stabilization than amphiphilic compounds of similar structure in the case of dispersion polymerization. Such a conclusion agrees with some other studies such as those of Uyama et al. (4) who discovered for the first time that macromonomers were more efficient than high polymers in the stabilization of dispersion polymerization. The same authors have compared the behavior of similar compounds with amphiphilic properties and found that they were efficient in the case of emulsion polymerization (13). It should be interesting to try to understand the reason for this difference in behavior between the two processes. Work is in progress in our laboratory using the most powerful stabilizers for the dispersion polymerization, i.e. the methacrylic compounds.

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