

Laboratory of Macromolecular Chemistry and Organic Catalysis  
University of Liège (Belgium)

## Star-shaped block copolymers. II. Microemulsions stabilizers

Huynh-Ba-Gia, R. Jérôme, and Ph. Teyssié

With 1 figure and 2 tables

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### Introduction

The increasing importance of the so-called “microemulsions” is exemplified by interesting basic studies (1–3), as well as by potential technical developments in secondary oil recovery, in lubricant, paint and varnish industry and in catalysis of hydrocarbons reactions involving hydrosoluble compounds (4).

These systems, which represent a very attractive way to dissolve in each other two otherwise non-miscible liquids (i.e. water and hydrocarbon), are obtained by adding a “cosurfactant” (usually an alcohol or an amine) to emulsions of water, hydrocarbon and ionic surfactant. However, *Riess* demonstrated recently that poly(styrene-*b*-oxirane) copolymers could act as non-ionic surfactants and lead to water-toluene microemulsions (5, 6).

A very small particle size (100–1000 Å) is responsible for translucency or transparency of these thermodynamically stable solutions. Although the term “microemulsion” is commonly used, the expression “swollen micellar solution” is more suitable to characterize the thermodynamic state of these systems (7).

### Experimental

The microemulsions were prepared, as proposed by *Rosano* (3) and *Nervo* (8), by very slow addition of the cosurfactant to the emulsion of water-toluene-surfactant, until transparency was obtained; the error relative to this procedure is about 1% (8). The copolymer is firstly dissolved in the organic solvent, water is added and a Brook-Fields mixer is used to emulsify the system; the stirring is repeated at each addition of the cosurfactant. The preparation and the characterization of the star-shaped copolymers will be published elsewhere (9).

### Results and discussion

*Riess*'s studies have put in evidence the influence of the molecular parameters of the poly(styrene-*b*-oxirane) copolymers on their efficiency in the microemulsions formation; however the molecular archi-

ture (di- or tri-block copolymers) does not seem to exert any significant influence (6, 8).

Recently, we have succeeded in synthesizing a new molecular structure also based on polyoxirane (PEO) and polystyrene (PS) or polytertiobutylstyrene (PTBS) sequences: i.e. the star-shaped copolymers PS(PEO)<sub>2</sub> and PTBS(PEO)<sub>2</sub> (9). It was therefore interesting to study the behaviour of these new block copolymers in the preparation of water-aromatic oil microemulsions.

The results, gathered in tables 1 and 2, indicate that, using isopropanol as a cosurfactant, both *O/W* (table 1) and *W/O* (table 2) microemulsions can be easily obtained. This is a very important conclusion, since the linear PEO-based diblock copolymers give only rise to *O/W* microemulsions under the same experimental conditions (water-toluene-isopropanol); this behaviour is mentioned by *Nervo* for the PS-PEO copolymers (8) and confirmed by us for PTBS and PS based diblock copolymers. The present observations are accordingly a clear-cut evidence of the determinant influence of the molecular architecture of the surfactant on the microemulsification process.

The table 1 mentions the amount of isopropanol necessary to obtain *O/W* microemulsions with different star-shaped and diblock copolymers. It is evident that the best results are obtained with copolymers containing 45 to 60% of PEO whatever their molecular structure and the use of either PS or PTBS. The nature of the hydrophobic sequence is however important as a polyisoprene-based star-shaped copolymer (*I*<sub>2</sub>) cannot similarly form toluene-water microemulsions. In conclusion the diblock and the star-shaped block copolymers based on PTBS (or PS) and PEO stabilize toluene-in-water microemulsions with the same efficiency which only depends on their molecular composition. Used at 8%, the most active copolymers largely reduce (60%) the amount of the cosurfactant necessary to obtain the complete water-toluene miscibility.

The figure 1 compares our observations to the main results reported by *Riess* and *Nervo* (5), in the case of:  
– a diblock copolymer ( $\bar{M}_n$ : 8.400, PEO: 49%)  
– a pluronic type polymeric surfactant [copolymer containing PEO and poly(propylene oxide) blocks]: PEP.

– a classical ionic surfactant (dodecyl benzene sulfonate): DBS.

Tab. 1. Microemulsification of water (50 g) and toluene (10 g) at 25 °C in the presence of isopropanol (cosurfactant) and star-shaped or diblock copolymers (surfactants)

Copolymer		Isopropanol			
Type <sup>(d)</sup>	$\bar{M}_n$ PTBS or PS	% PEO	% used <sup>(a)</sup>	ml	% <sup>(b)</sup>
– <sup>(c)</sup>	–	–	–	64	83
S3	4.800	73	8	42	54.5
B5	15.000	72	8	40	52
			4	50	65
B2	2.700	45	8	27	35
			4	45	59
S1	3.000	52	8	25	33
I2	2.100	56	8	no microemulsion	
b4	2.600	41	7	28	36
b1	2.600	57	8	30.5	40
b3	2.600	68	8	39	51
st.2	6.000	54	8	31	40
			4	47.5	62

$$(a) : \frac{\text{copolymer weight}}{60} \times 100$$

$$(b) : \frac{\text{isopropanol weight}}{60} \times 100$$

(c) : necessary amount of isopropanol to observe the complete water-toluene miscibility in the absence of surfactant.

(d) : S – B and I: correspond to star-shaped block copolymers based on styrene, tertibutylstyrene and isoprene respectively. b and st: refer to diblock copolymers based on tertibutylstyrene and styrene respectively.

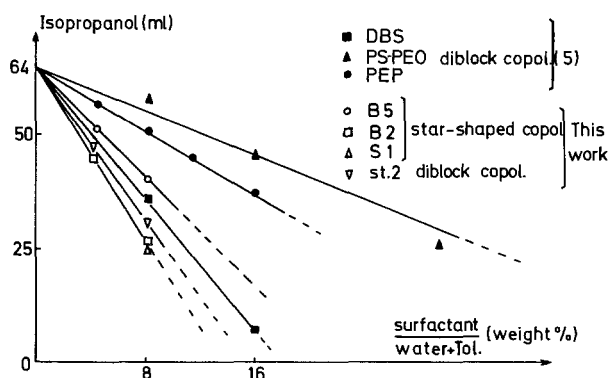


Fig. 1. Volume of isopropanol necessary for the microemulsification of water (50 g) and toluene (10 g), as a function of the concentration of different surfactants

Tab. 2. Microemulsification of water (10 g) and toluene (50 g) at 25 °C in the presence of isopropanol and star-shaped and diblock copolymers

Copolymer			Isopropanol		
Type <sup>(d)</sup>	$\bar{M}_n$ PTBS or PS	% PEO	% used <sup>(a)</sup>	ml	% <sup>(b)</sup>
– <sup>(c)</sup>	–	–	–	61	79.5
S3	4.800	73	8	54	70
S4	4.800	81	8	52	67
B5	15.000	72	8	52	67
			4	57	74
			2	59	76.5
b. & st.	(see tab. 1)		8	no microemulsion	

(a), (b), (c) and (d): see legends tab. 1.

Our copolymers have apparently the greatest efficiency. This conclusion is surprising when our st. 2 sample (table 1) and the PS-PEO diblock mentioned by *Riess* and *Nervo* are compared: their composition is very similar (54 and 49% of PEO respectively) while their activity is largely different; experimental differences (stirring, addition rate of isopropanol...) could perhaps explain this discrepancy.

The results summarized in tables 1 and 2 clearly show that *O/W* microemulsions are more easily formed than *W/O* ones; this means that the stability of the micelles formed by the surfactant in water (normal micelles) and in organic solvent (inverse micelles) is different. In other words, normal micelles are easily swollen by hydrocarbon without rupture, while inverse micelles accomodate with difficulty a larger micelles core upon addition of water. In this respect, the “branched structure” of the hydrophilic component of the PS- or PTBS-(PEO)<sub>2</sub> copolymers could favour a decrease in the packing density of the inverse micelle-forming molecules, and could explain the different behaviour of the linear and star-shaped PS/PEO block copolymers in the *W/O* microemulsification process.

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Authors' address:

Laboratory of Macromolecular Chemistry  
and Organic Catalysis  
University of Liège  
Sart-Tilman, 4000 Liège (Belgium)