

Star-Shaped Block Copolymers. IV. Emulsifying Activity in the Water–Oil Emulsions

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Synopsis

Water–organic solvents emulsions based on toluene, *n* hexane, *n*-dodecane, and decaline are stabilized by new A(B)₂ star-shaped block copolymers. B is a polyoxirane block and A a polydiene or polyvinyl one. The influence of the molecular parameters of the copolymers has been studied; low-molecular-weight (± 5000) copolymers containing 50% of polyoxirane have the originality to generate both O/W and W/O stable emulsions. The importance of the molecular architecture of block copolymers on their stabilizing efficiency has been put in evidence. For instance, 7/3 water–toluene emulsions are more efficiently stabilized by star-shaped block copolymers, whereas linear block copolymers give better results for 3/7 water–toluene emulsions.

INTRODUCTION

It is now well established that block and graft copolymers are able to stabilize oil-in-oil,^{1,2} water-in-water,³ and oil-in-water (O/W) or water-in-oil (W/O) emulsions^{4–8}; they are also suitable to prepare stable polymeric dispersions (latices) in aqueous or organic media.^{9,10} The stabilization of the O/W and W/O emulsions requires copolymers containing both hydrophilic and hydrophobic sequences; but, the hydrophilic component can be either anionic,⁸ or cationic^{6,7} or nonionic.^{4,5,11} In the latter case, graft,^{12,13} as well as di- and triblock^{4,5,14} copolymers based essentially on polyoxirane (PO) and polystyrene (PST) have been studied. Some relations between the properties of the emulsions and the molecular parameters of the copolymers have already been established, although they obviously need to be extended. A good knowledge of the basic structure–properties relationships is indeed very important in order to master more precisely the application of block and graft copolymers as emulsifiers; for instance, in the food and pharmaceutical industries and in soap and paints technology.

We have recently succeeded in the controlled synthesis of new star-shaped block copolymers with a general A(B)₂ molecular architecture; A is a hydrophobic sequence (polyisoprene:PI; polystyrene:PS; or polytertiarybutylstyrene:PTBS) and B is the hydrophilic PO sequence. Part I¹¹ of this series of articles describes the synthesis of these new amphiphilic compounds, part II¹⁵ is concerned with the efficiency of the A(B)₂ copolymers in microemulsions formation, and part III¹⁶ deals with their surface and interfacial properties. This article reports the activity of the star-shaped architecture for the stabilization of O/W and W/O emulsions, and the influence of the molecular parameters of the A(B)₂ copolymers: as well as the nature of A, molecular weight, and composition. As far as possible, comparisons with the corresponding AB copolymers will be made.

EXPERIMENTAL

The synthesis of the star-shaped block copolymers is described in part I of this series¹¹; the molecular parameters of the copolymers used are summarized in Table I.

The copolymer concentration is given in weight percent with respect to the (water + organic solvent) total volume.

The copolymer was systematically dissolved in the organic phase and, after water addition, the system was submitted to ultrasonic stirring for 4 min; after a 5-min rest, a new stirring was performed and the cycle repeated 5 times. After 2 hr, the state of the emulsions was no longer modified by further stirring.

To determine the type of emulsions water-in-oil (W/O) or oil-in-water (OW), one drop of the emulsion was added into a large volume of either water or organic solvent. A drop of a O/W emulsion was dispersed instantaneously in the water, whereas it decanted immediately in the organic solvent; the contrary was observed for W/O emulsion.

The stability of an emulsion is commonly defined by the time necessary to reach 90% of its initial volume.^{14,16,17} We observed, however, in agreement with Hallworth and Larless's results,¹⁸ that the emulsified volume percentage (R) did not necessarily tend to zero (Fig. 1), but to a finite and constant volume after a few days. The R values were accordingly measured at 20°C after 5, 10, and 15 days, and the constant limiting value reported as the criteria of stability. The reproductibility on R values is very satisfying; the accuracy ranges between 1% (for the highest R values) and ~7% (for the lowest reported values).

The mean size of the dispersed particles was determined by observation of the

TABLE I
Molecular Parameters of A(PO)₂^a Star-Shaped Block Copolymers

Copolymer ^b	\bar{M}_n Copolymer ^c	\bar{M}_n A ^c	$\bar{M}_n(2 \times \text{PO})^d$	A, % ^e	PO, % ^e
I ₂	4,800	2,100	2,700	44	56
S ₁	6,300	3,000	3,300	48	52
S ₂	15,000	4,800	10,200	32	68
S ₃	18,000	4,800	13,200	27	73
S ₄	25,000	4,800	20,000	19	81
B ₁₁	5,700	1,900	3,800	33	67
B ₁₂	7,600	1,900	5,700	25	75
B ₂₁	4,500	3,000	1,500	67	33
B ₂₂	4,900	2,700	2,200	55	45
B ₂₃	7,500	3,000	4,500	40	60
B ₂₄	8,800	3,000	5,800	34	66
B ₂₅	12,000	3,000	9,000	25	75
B ₂₆	20,000	3,000	17,000	15	85
B ₂₇	60,000	3,000	57,000	5	95
B ₃₂	16,700	6,550	10,150	39	61
B ₃₃	20,000	6,550	13,450	33	67
B ₄₁	19,000	9,600	9,400	50	50
B ₄₂	42,000	9,600	32,400	23	77
B ₅₁	53,000	15,000	38,500	28	72

^a A is a PIP, PS, or PTBS (see part I for their synthesis and characterization¹¹).

^b I or PIP(PO)₂ copolymer, S or PS(PO)₂ copolymer, and B or PTBS(PO)₂ copolymer.

^c \bar{M}_n determined by vapor or membrane osmotic pressure.

^d \bar{M}_n calculated from \bar{M}_n copolymer and \bar{M}_n A.

^e Composition in wt % calculated from ¹H NMR analysis.

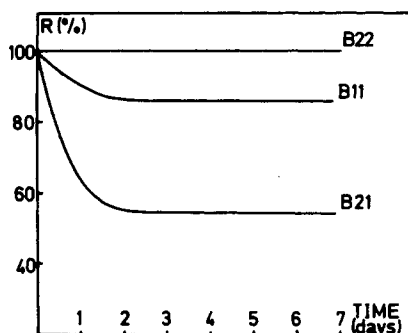


Fig. 1. General evolution of stability (R) of water-toluene emulsions with time.

emulsion under an optical microscope (Carl-Zeiss n° 61963) and computation of the numeric distribution curve of particles as a function of their size.^{19,20} The O/W emulsions were previously diluted (50 \times) with a 0.1% aqueous solution of Brij 35 (a polyoxyethylene lauryl ether), whereas a Span 80 (sorbitol ester) solution in toluene (0.1%) was used to dilute the W/O emulsions.

The interfacial tensions were measured by the "sessile drop" technique as described elsewhere.¹⁶

RESULTS AND DISCUSSION

The stability of any heterophasic system is commonly related to the amount of added surfactant¹⁴; this behavior is also observed with the star-shaped block copolymers [Table II: as explained in the Experimental section, the stability is given in terms of constant emulsified volume percentage (or R) at 20°C].

Table III correlates the stability of the water-toluene emulsions to their volume composition for different star-shaped block copolymers used at constant concentration (1%). B₂₂ is a very attractive copolymer as both O/W and W/O emulsions are highly stabilized over a broad range of phases volume ratio. To our knowledge, this result is original; in a systematic study of the emulsifying efficiency of di- and triblock copolymers based on PST and PO, Nervo has never observed such a behavior.¹⁴ However, all the other tested star-shaped block copolymers are less active and favor one type of emulsion over the other.

For a given copolymer used at constant concentration, the characteristics of

TABLE II
Stability (R) of Water-Toluene Emulsions^a in Function of Copolymer Concentration

Copolymer	R at different copolymer concentrations, %			
	0.02	0.2	1	2
S ₁	40	72 ^b	100 ^b	100 ^b
S ₃	31	46	79 ^b	100 ^b
S ₄	48	55	62	100 ^b
B ₂₁	46 ^b	52 ^b	64 ^b	65 ^b
B ₂₂	46	70 ^b	100 ^b	100 ^b
B ₂₄	49	50	60	68 ^b

^a Phases volume ratio 1/1.

^b W/O, all the other emulsions being O/W.

TABLE III
Stability (R) of Water-Toluene Emulsions in Function of Phases Volume Ratio

Copolymer, 1%	Interfacial tension, ^a dyne cm ⁻¹	R at different water-toluene volume ratios, %						
		8:2 ^b	7:3 ^b	6:4 ^b	5:5	4:6	3:7	2:8
B ₁₁	0.8	100	100	91	83 ^b	62	43	—
B ₁₂	1.0	95	94	78	71 ^b	56	38	—
B ₂₁	3.0	—	57 ^c	60 ^c	64	55	39	30
B ₂₂	<0.2	—	100	95	100	100	100	—
B ₃₂	9.0	19	40	49	65	61	40	—
B ₃₃	12.5	—	90	—	63 ^b	50	39	25
B ₄₂	17.8	100	84	78	71 ^b	54	40	—
B ₅₁	17.8	29	39	81	62 ^b	—	56	37

^a Measured at 20°C from water and 1% copolymer solution in toluene.

^b O/W, all the other emulsions being W/O.

^c $R = 100$ for a W/O emulsion (obtained by mechanical stirring).

the emulsion are also dependent on the nature of the dispersed phase: the statistical parameters of the toluene-water emulsions containing 30 and 70% of toluene, respectively, are reported in Table IV. The I₂ isoprene-based copolymer favors a decreasing particle size when water is the dispersed phase, whereas the three other copolymers display opposite behavior. Accordingly, the 1/1 water-toluene emulsion is W/O when I₂ is used as emulsifier (Table V), but O/W with S₂, B₃₃, and B₄₂ copolymers (Table III). These observations are not surprising if the copolymer composition and Bancroft's rule²¹ are considered.

The influence of the molecular parameters of the star-shaped block copolymers on the stability of the toluene-water emulsions has also been studied.

The nature of the hydrophobic sequence has been considered first, as reported in Table V, where the three copolymers studied have very similar PO content

TABLE IV
Surface and Volume-Average Diameter (\bar{D}_s and \bar{D}_v), and Mean Area per Molecule (\bar{S}_m), of Dispersed Particles in Water-Toluene Emulsions

Copolymer 1%	30% toluene			70% toluene		
	\bar{D}_s , μm	\bar{D}_v , μm	\bar{S}_m , \AA^2	\bar{D}_s , μm	\bar{D}_v , μm	\bar{S}_m , \AA^2
I ₂	2.79	3.26	33	2.42	2.86	38
S ₂	1.78	2.00	183	2.28	2.71	121
B ₃₃	2.17	2.37	211	2.32	2.69	165
B ₄₂	1.70	1.88	544	1.87	2.13	453

TABLE V
Effect of Hydrophobic Sequence Nature on Stability (R) of Water-Toluene Emulsions

Copolymer, 1%	\bar{M}_n	PO, %	Interfacial tension, ^c dyne cm ⁻¹	R at different water-toluene volume ratios, %		
				3:7 ^a	1:1 ^a	7:3 ^b
I ₂	4,800	56	1.6	100	100	100
S ₁	6,300	52	<0.2	48	100	100
B ₂₂	4,900	45	<0.2	100	100	100

^a W/O emulsion.

^b O/W emulsion.

^c Measured at 20°C, from water and 1% copolymer solution in toluene.

TABLE VI
Dependence of Stability (R) of Water-Toluene Emulsions on Molecular Composition of PTBS
(PO)₂ Copolymers Based on Same PTBS Sequence

Copolymer, 1%	PO, %	Interfacial tension, dyne cm ⁻¹	R at different water-toluene volume ratios, %		
			3:7 ^a	1:1	7:3 ^b
B ₂₁	34	3	34	64 ^a	57 ^c
B ₂₂	46	<0.2	100	100 ^a	100
B ₂₃	60	3.1	39	64 ^a	83
B ₂₄	66	3.9	38	60 ^b	89
B ₂₅	75	5.8	—	70 ^b	83
B ₂₆	85	6.9	41	42 ^b	43
B ₂₇	95	—	35	61 ^b	48

^a W/O emulsion.

^b O/W emulsion.

^c $R = 100$ for or W/O emulsion (obtained by mechanical stirring).

and molecular weight. For the different phases ratios used, the PIP- and PTBS-based copolymers both yield highly stable emulsions; the PST-based copolymer does the same except for the rich-in-toluene emulsion. A determinant influence of the hydrophobic sequence nature is, therefore, not clearly demonstrated in water-toluene macroemulsions; it will be noted that S₁ and B₂₂ form toluene-in-water microemulsions with isopropanol as cosurfactant, whereas I₂ does not.¹⁵

To correlate the stability of the water-toluene emulsions with the composition of the copolymers, a series of PTBS (PO)₂ copolymers based on the same PTBS sequence has been studied (Table VI). Too low or too high PO contents are unfavorable for stable emulsions, whereas compositions around 50% seem to be the most advantageous. For both 30 and 70% toluene emulsions, the type of

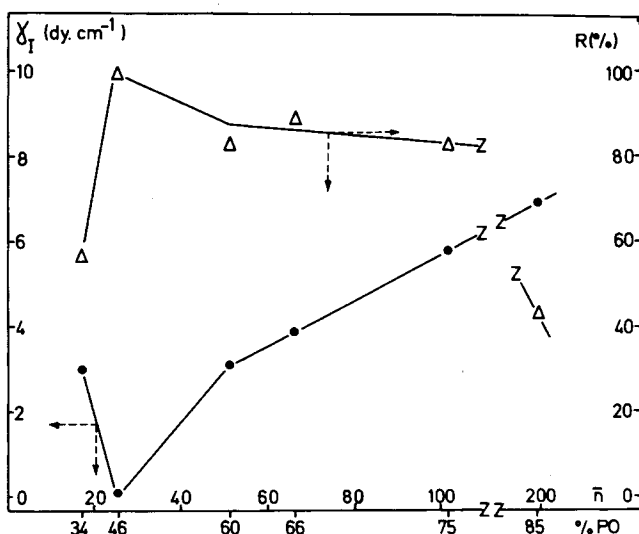


Fig. 2. Correlation between water-toluene interfacial tension (γ_I), and stability (R) of corresponding emulsions in presence of 1% series of PTBS (PO)₂ copolymers at 20°C. \bar{n} is \overline{DP} of PO sequences (linear scale); corresponding PO content of each sample is also reported (nonlinear scale).

TABLE VII
Dependence of Stability (R) of Water-Toluene Emulsions on Molecular Composition of PTBS
(PO)₂ Copolymers of Constant Molecular Weight

Copolymer, 1%	\bar{M}_n	PO, %	R at different water-toluene volume ratios, %		
			3:7 ^a	1:1	7:3
B ₂₆	20,000	85	41	42	42
B ₃₃	20,000	67	39	63	90
B ₄₁	19,000	50	42	65 ^a	67

^a W/O emulsions, all the other emulsions being O/W.

emulsions formed is independent on the PO content when higher than 33%. In agreement with Bancroft's rule, the 50% toluene-based emulsions are O/W for PO contents higher than 60%, and vice versa.

In Figure 2, a crude approximative parallelism is observed between the emulsion stability and the corresponding interfacial tension (γ_I); it is, however, dangerous to correlate systematically the stability of the toluene-water emulsions with γ_I , as shown with B₄₂ and B₅₁ for the 20 and 30% toluene emulsions (Table III).

A modification of the PO content at constant molecular weight has an effect chiefly on the stability of the 30% toluene emulsions (O/W), and a composition of about 65% of PO would be favorable (Table VII).

Once the PO percentage is kept constant, the most stable emulsions are obtained with the shortest hydrophobic sequence (Table VIII). This behavior seems to be general for di- and triblock copolymers,^{1,14,22} of course, the smaller the molecular weight, the higher the molar concentration for the same total-weight concentration. The stability of water-organic solvent emulsions has finally been studied in relation to the nature of the organic solvent: toluene, *n*-hexane, *n*-dodecane, and decaline (Table IX). Whatever the nature of the organic solvent, the I₂, B₁₁, and B₂₃ copolymers give generally the best results: these copolymers have the lowest molecular weights and PO contents.

The *n*-hexane-based emulsions have the lowest stability, in accordance with similar observations mentioned elsewhere, both for PIP-PO diblock copolymers¹⁴

TABLE VIII
Dependence of Stability (R) of Water-Toluene Emulsions on Molecular Composition of PTBS
(PO)₂ Copolymers of Constant PO Content

Copolymer, 1%	\bar{M}_n PTBS	PO, %	R at different water-toluene volume ratios, %		
			3:7 ^a	1:1	7:3
B ₁₁	1,900	67	43	83	100
B ₂₄	3,000	66	38	60	89
B ₃₃	6,550	67	39	63	90
B ₁₂	1,900	75	38	71	94
B ₂₅	3,000	75	—	70	83
B ₄₂	9,600	77	40	71	84
B ₅₁	15,000	72	56	62	39
B ₂₂	2,700	45	100	100 ^a	100
B ₄₁	9,600	50	42	65 ^a	67

^a W/O emulsions, all the other being O/W.

TABLE IX
Effect of Nature of Organic Solvent on Stability (R) of Water–Organic Solvent Emulsions

Copolymer, 1%	R at 7/3 water–solvent volume ratio, % ^a				R at 1:1 water–solvent volume ratio, %			
	Toluene	<i>n</i> -Hex.	<i>n</i> -dodec.	decaline	Toluene	<i>n</i> -hex.	<i>n</i> -dodec. ^a	decaline ^a
I ₂	90	41	78	91	100	60 ^a	79	70
B ₁₁	100	31	76	95	83 ^a	63 ^a	83	71
B ₂₃	83	33	96	96	64	59	94	74
B ₃₂	40	35	50	44	65	58	79	73
B ₄₂	84	36	57	47	71 ^a	60 ^a	81	69
B ₅₁	39	42	63	46	62 ^a	67 ^a	83	69

^a O/W emulsions; all the other emulsions being W/O.

and classical ionic surfactants.¹⁸ With 30% of organic solvent, the O/W decaline–water and toluene–water are the more stable emulsions. Once water and organic solvent are used in the same amount, the *n*-dodecane–water (O/W) and toluene–water (O/W or W/O) emulsions have a higher stability.

As the stability of an emulsion is related to hindrances to coalescence of the dispersed particles, the structure and rigidity of the interfacial film is, of course, a determinant factor, which, in turn, depends on the presence, the conformation, and the intermolecular interactions of the copolymer at the interface. Accordingly, O/W and W/O emulsions can have different stability for the same water–organic solvent copolymer system. Figure 3 shows indeed that stable W/O emulsions are obtained with low-molecular-weight copolymers containing 33–56%

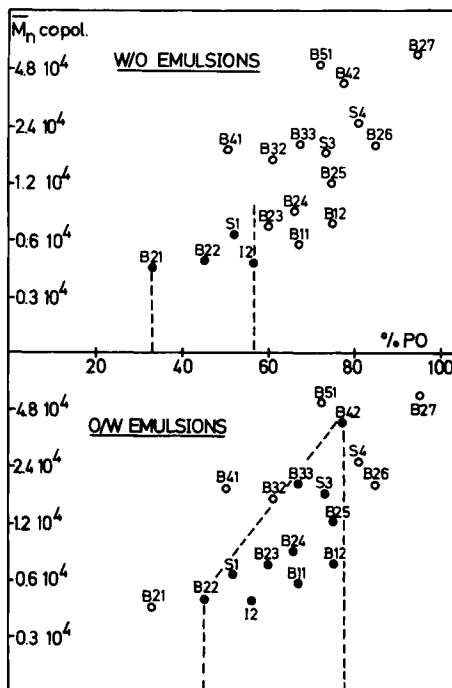


Fig. 3. Stability of W/O and O/W water–toluene emulsions in relation to molecular parameters of star-shaped block copolymers (used at 1%) at 20°C. Water–toluene volume ratio of the emulsions here reported ranges between 3/7 and 7/3. (●) Stable emulsion; (○) unstable emulsion.

TABLE X
Effect of Molecular Architecture on Stability (*R*) of Water-Toluene Emulsions

Copolymer, 1%	PO, %	<i>R</i> at different water-toluene ratios, %		
		3:7	1:1	7:3
B ₂ ^a	41			54
B ₂₂ ^b	45			100
B ₃ ^a	57	50 ^c	58 ^c	48 ^c
B ₂₃ ^b	60	39 ^c	64 ^c	83
B ₄ ^a	68	54	63	60
B ₂₄ ^b	66	38 ^c	60	89

^a Linear PTBS-PO block copolymers based on a PTBS sequence the \bar{M}_n of which = 2700.

^b Star-shaped PTBS-(PO)₂ block copolymers: see Table I.

^c W/O emulsions, all the other emulsions being O/W.

of PO, whereas for the O/W emulsions, compositions between 45 and 75% are more favorable and higher-molecular-weight copolymers are also efficient. Since there is an overlap between the two composition ranges defined here, low-molecular-weight copolymers containing 50% ($\pm 5\%$) of PO have, accordingly, the originality to generate both O/W and W/O stable emulsions (I₂, S₁, and B₂₂).

The experimental results also indicate a large range of stability for the O/W emulsions (Fig. 3): the occurrence of hydrogen links between water and PO sequences can be responsible for a pseudoreticulation of the continuous phase, and for a more effective barrier to coalescence of the dispersed particles.

In the study of water-toluene microemulsions, the importance of the molecular architecture of PO- and PTBS-containing block copolymers has been put in evidence.¹⁵ Table X compares the stability of water-toluene macroemulsions formed in the presence of 1% w/v of PTBS-PO and PTBS-(PO)₂ block copolymers based on a similar PTBS sequence and a comparable overall composition. It is interesting to note that the relative stabilizing efficiency of the linear and star-shaped block copolymers is dependent on the emulsion composition.

Water-toluene emulsions (O/W or W/O), 1/1, are indeed similarly stabilized by both molecular structures, whereas the star-shaped block copolymers are more efficient to stabilize 7/3 water-toluene emulsions and linear block copolymers give better results for 3/7 water-toluene emulsions. This observation confirms the significant role played by the molecular architecture of block copolymers in the emulsification processes; further experiments are, however, necessary to explain the specificity of this action.

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