

# Star-Shaped Block Copolymers. III. Surface and Interfacial Properties

HUYNH-BA-GIA, R. JÉRÔME, and PH. TEYSSIE, *Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart-Tilman, 4000 Liège, Belgium*

## Synopsis

Surface and interfacial activities of  $A(B)_2$  star-shaped block copolymers, where  $B$  is a polyoxirane block and  $A$  a polydiene or polyvinyl block, have been measured at 20°C. The surface tension of organic solvents is only slightly lowered by these copolymers, whereas a significant surface activity is noted in water. Interfacial tensions are dependent on both the nature of the organic solvent (aliphatic or aromatic hydrocarbons) and the molecular parameters of the copolymers; 50% polyoxirane seems to be the composition of maximum surface activity. The role played by the molecular architecture [ $A-B$  or  $A(B)_2$ ] of the copolymers is demonstrated. The same limiting interfacial tension is obtained on increasing the concentration of diblock ( $A-B$ ) or star-shaped block [ $A(B)_2$ ] copolymer. The limiting value is, however, attained at significantly lower concentration with the star-shaped copolymers. Their ability to fill the interface is accordingly higher.

## INTRODUCTION

Block and graft copolymers generally display characteristic and very attractive behavior resulting from the incompatibility between the chemically different sequences linked together in the same macromolecule. In the solid state, the formation of highly organized structures into mesomorphic phases has been studied,<sup>1</sup> while very useful materials such as thermoplastic elastomers,<sup>2</sup> high impact thermoplastics,<sup>3</sup> adhesives, and adherends<sup>4</sup> play a significant role in modern technology.

In solution, these copolymers have interesting colloidal and interfacial properties, much like the more classical surface-active compounds. Block and graft copolymers can be used as emulsifying agents in water-oil and oil-oil systems.<sup>5</sup> In the latter case, the oil phases are either solid and give rise to polymeric alloys,<sup>6</sup> or liquid and allow the preparation of latexes in organic media.<sup>7</sup>

More specifically, block and graft copolymers containing hydrophilic sequences linked to hydrophobic ones find applications in water-oil emulsions; the Pluronic and Tetronics resins based on oxirane and methyloxirane are commercial products, while poly(oxirane-*b*-styrene) and poly(oxirane-*g*-styrene) copolymers have been studied in the same prospects.<sup>8-11</sup> These studies have clearly demonstrated the importance of the molecular parameters of these copolymers (structure, molecular weight, composition) on their surface and interfacial activity. However, knowledge in this field relies mainly on the behavior of two well-defined molecular architectures: the diblock and triblock copolymers. This is a rather limited range and the study of new and well-controlled molecular structures could undoubtedly provide deeper understanding and more efficient mastering of this interesting field of application.

Recently, we have succeeded in the controlled synthesis of new star-shaped block copolymers with a general  $A(B)_2$  molecular architecture. Here  $A$  is a hydrophobic sequence: polyisoprene (PIP); polystyrene (PS), or poly(tertiarybutyl styrene) (PTBS). The hydrophilic sequence  $B$  is always polyoxirane.<sup>12</sup> We have now undertaken the study of the surface and interfacial properties of these new amphiphilic compounds. We report in this paper the first results obtained and compare them, as far as possible, with the behavior of diblock copolymers. We have largely considered star-shaped copolymers based on PTBS, which is still more hydrophobic than PIP and PS.

## EXPERIMENTAL

The  $AB_2$  block copolymers were prepared by oxirane polymerization from potassium naphthalene dianion-terminated PS, PTBS, or PIP. All the synthetic procedures were carried out with the precautions usual in anionic polymerization: i.e., high purity and dryness of solvents and reagents. The crude  $AB_2$  block copolymers were twice precipitated into heptane, in which homo-PTBS and homo-PIP are soluble. For PS-based copolymers, the homo-PS was extracted by diethylether until elimination was complete. Homopolyether was extracted by water or methanol from the copolymers richest in polyether. The copolymers so purified were dried under vacuum to constant weight. The complete synthetic procedure is described in Paper I of this series.<sup>12</sup> The molecular parameters of the copolymers are summarized in Table I. Surface tension ( $\gamma_{ST}$ ) was measured with a "Du Nouy" tensiometer equipped with a platinum ring 1.5 cm in diameter. The measurements were repeated at least five times and an average value was reported ( $\pm 0.5$  dyn  $\text{cm}^{-1}$ ).

TABLE I  
Molecular Parameters of  $A(B)_2$  Star-Shaped Block Copolymers

Copolymer <sup>b</sup>	$\bar{M}_n$ copolymer <sup>c</sup>	$\bar{M}_n A^c$	$\bar{M}_n 2B^d$	$A(\%)^e$	$B(\%)^e$
$I_2$	4800	2100	2700	44	56
$S_1$	6300	3000	3300	48	52
$S_2$	15,000	4800	10,200	32	68
$S_3$	18,000	4800	13,200	27	73
$S_4$	25,000	4800	20,000	19	81
$B_{11}$	5700	1900	3800	33	67
$B_{12}$	7600	1900	5700	25	75
$B_{21}$	4500	3000	1500	67	33
$B_{22}$	4900	2700	2200	55	45
$B_{24}$	8800	3000	5800	34	66
$B_{26}$	20,000	3000	17,000	15	85
$B_{27}$	60,000	3000	57,000	5	95
$B_{32}$	16,700	6550	10,150	39	61
$B_{33}$	20,000	6550	13,450	33	67
$B_{42}$	42,000	9600	32,400	23	77
$B_{51}$	53,000	15,000	38,500	28	72

<sup>a</sup>  $A$  is a polyisoprene (PIP), polystyrene (PS), or poly(*t*-butyl styrene) (PTBS) sequence, and  $B$  is a polyoxirane block (PEO).

<sup>b</sup>  $I$ : PIP(PEO)<sub>2</sub> copolymer;  $S$ : PS(PEO)<sub>2</sub> copolymer;  $B$ : PTBS(PEO)<sub>2</sub> copolymer.

<sup>c</sup>  $\bar{M}_n$  determined by vapor or membrane osmometer.

<sup>d</sup>  $\bar{M}_n$  calculated from  $\bar{M}_n$  copolymer and  $\bar{M}_n A$ .

<sup>e</sup> Calculated from <sup>1</sup>H NMR.

The PIP-based and PS-based copolymers were dissolved in water at 40–50°C. The PTBS-based copolymers, except for B26 and B27, were hardly soluble in water and the use of an intermediate solvent was therefore necessary. The copolymers were first dissolved in freshly distilled acetone (pure grade), wherein a perfectly clear solution was obtained. After addition of twice-distilled water, the acetone was completely eliminated by distillation under reduced pressure. To confirm the efficacy of this procedure, an equal amount of acetone was added to a 1% aqueous solution of PEO. The resulting solution was distilled under normal pressure until the temperature reached 100°C; 55% of the initial volume was thereby eliminated. The remaining solution of PEO was analyzed by ultraviolet spectrophotometry (Varian Techtron spectrophotometer, model 635; 1 cm path, quartz cell). It was completely free of acetone ( $\lambda_{\text{max}}$  of acetone is at 264 nm), whereas its presence in a 1% aqueous solution of PEO was still clearly detected at a concentration of 0.005%. The solutions were filtered before surface tension measurements were made.

Interfacial tension ( $\gamma_I$ ) was measured by the "sessile drop" method. Dorsey's method<sup>13</sup> was used to calculate  $\gamma_I$  by this technique which is described and commented upon elsewhere by Padday.<sup>14</sup> An accuracy of 0.2 dyn  $\text{cm}^{-1}$  has been claimed using this method for the surface tension of water (i.e.,  $72 \pm 0.2$  dyn  $\text{cm}^{-1}$ ), but the quality of the photographic prints from which the parameters of the profile of the drop are determined and the distortion of profiles for low values of  $\gamma_I$  are sources of error. Drop profiles were recorded using an optical bench photographic method. At least 6 profiles were recorded for the same drop after different times of formation (from 5 to 900 sec). The calculated  $\gamma_I$  values were independent of time and thus represented apparent equilibrium. The largest scatter of the individual measurements with respect to the average value rose to 10–15% for  $\gamma_I$  less than 5 dyn  $\text{cm}^{-1}$ . The external diameter of the syringe used was 0.71 cm and the magnification was 15 $\times$ .

The copolymers were dissolved in the organic solvent and solutions of decreasing concentrations were obtained by successive dilution.

## RESULTS AND DISCUSSION

### Surface Tension of Aqueous Solutions

In Table II, are summarized values of the surface tension  $\gamma_{ST}$  of 1% aqueous solutions of star-shaped block copolymers based on PIP, PST, and PTBS. With the exception of copolymer  $S_2$  all the results fall within a quite narrow range, whatever the nature of the hydrophobic sequence and the PEO content (higher than 5%). As both water and 1% aqueous solution of PEO ( $\bar{M}_n$  11,500) are characterized by higher surface tensions: 73.5 and 64 dyn  $\text{cm}^{-1}$ , respectively,<sup>15</sup> the surface activity of the  $A(\text{PEO})_2$  copolymers in water is evident.

TABLE II  
Surface Tension of Aqueous 1% Solutions of Star-Shaped Block Copolymers at 20°C

Copolymer	$\gamma_{ST}$ (dyn $\text{cm}^{-1}$ )	Copolymer	$\gamma_{ST}$ (dyn $\text{cm}^{-1}$ )
$I_2$	57.8	$B_{11}$	57.0
$S_1$	59.5	$B_{22}$	62.5
$S_2$	53.0	$B_{24}$	59.0
$S_4$	60.0	$B_{26}$	61.5

For PST-PEO diblock copolymers, Nakamura mentions similar results (50 to 63 dyn cm<sup>-1</sup>).<sup>10</sup> However, rather lower values of  $\gamma_{ST}$  (45 up to 58 dyn cm<sup>-1</sup>) are reported for Pluronic<sup>16</sup> and poly(oxirane-*b*-tetrahydrofuran-*b*-oxirane) copolymers.<sup>17</sup> From these two comparisons, it appears that the molecular structure of the PST-based and PEO-based block copolymers has no major effect on the  $\gamma_{ST}$  of aqueous solutions, but the highest surface activities in water are not necessarily observed for block copolymers containing the most hydrophobic sequences.

At almost constant composition, the  $\gamma_{ST}$  of 1% aqueous solutions of PTBS(PEO)<sub>2</sub> copolymers increases with the molecular weight of the PTBS sequence (Table III). Furthermore, at least for PEO content higher than 30%,  $\gamma_{ST}$  is independent of the composition when the length of the PTBS sequence is constant (Table III). Such behavior has already been mentioned for linear block copolymers<sup>10,17</sup> and accordingly it is not characteristic of the star-shaped architecture.

For low-molecular-weight homogeneous surfactants, the superficial (interfacial) area per molecule  $A_L$  can be calculated from the Gibbs law

$$A_L = - \frac{10^{16} kT}{d\gamma/d \ln C} \quad (1)$$

where  $C$  is the molar concentration of the surfactant and  $k$  is Boltzmann's constant. This equation is applicable as long as the surface is not saturated and the adsorption is reversible. As polymer adsorption is irreversible, the use of the Gibbs equation is therefore indicative only of the overall trends in the behavior of AB<sub>2</sub> copolymers. On the assumption that the surfactant molecule at the surface is spherical, the radius  $r$  of the equivalent sphere is easily calculated ( $A_L = 2\pi r^2$ ), whereas the radius of gyration ( $\langle \bar{S}^2 \rangle^{1/2}$ ) of the surfactant in solution can be approximated from Flory's relation, eq. (2), which is, however, valid only for chains obeying Gaussian statistics

$$[\eta] = 6^{3/2} \phi \langle \bar{S}^2 \rangle^{3/2} M^{-1} \quad (2)$$

where  $[\eta]$  is the intrinsic viscosity of the surfactant solution (ml g<sup>-1</sup>),  $\phi$  is a universal constant amounting to  $2.1 \times 10^{23}$ , and  $M$  is the molecular weight of the surfactant. The smaller the  $r/\langle \bar{S}^2 \rangle^{1/2}$  ratio, the more compressed is the surfactant at the interface. The ratios listed in Table IV are comparable to values (0.12–0.2) similarly calculated and reported by Nakamura for PS-PEO diblock copolymers of similar molecular weight and composition<sup>10</sup>; a third higher ratio is however observed for polyoxirane. It is recalled that the ratios calculated from eqs. (1) and (2) have only a qualitative meaning, in view of questions about the applicability of these equations to block copolymers.

TABLE III

Surface Tension of 1% Aqueous Solution of Star-Shaped Block Copolymers in Relation to Molecular Parameters (20°C)

Copolymer	PEO (%)	$\gamma_{ST}$ (dyn cm <sup>-1</sup> )	Copolymer	PEO (%)	$\gamma_{ST}$ (dyn cm <sup>-1</sup> )
B <sub>11</sub>	67	57	B <sub>21</sub>	34	61.5
B <sub>24</sub>	66	59	B <sub>22</sub>	46	62.5
B <sub>33</sub>	67	62	B <sub>24</sub>	66	59.0
B <sub>42</sub>	77	62.2	B <sub>26</sub>	85	61.5
B <sub>51</sub>	72	63.5	B <sub>27</sub>	95	63.0

TABLE IV  
Conformational State of Star-Shaped Block Copolymers at the Air/Water Interface at 20°C

Copolymer	$A_L$ (Å <sup>2</sup> )	$r$ (Å)	$\langle \bar{S}^2 \rangle^{1/2}$ (Å)	$r/\langle \bar{S}^2 \rangle^{1/2}$
I <sub>2</sub>	183	5.40	36	0.15
S <sub>1</sub>	168	5.15	36	0.14(5)
B <sub>11</sub>	139	4.70	...	...
PEO ( $\bar{M}_n = 11,500$ )	1900	17.40	42	0.41(5)

Nevertheless, no noticeable effect on the surface activity in water results from modification of the molecular architecture in the PS (or PTBS) copolymers with PEO.

### Surface Tension of Solutions in Organic Solvents

Surface tensions  $\gamma_{ST}$  of 1% solutions of A(PEO)<sub>2</sub> copolymers have been measured at 20°C, in toluene ( $\gamma_{ST} = 31$  dyn cm<sup>-1</sup>), *n*-hexane (21 dyn cm<sup>-1</sup>), *n*-dodecane (28 dyn cm<sup>-1</sup>), and decalin (34 dyn cm<sup>-1</sup>). Whatever the copolymer and the solvent used,  $\gamma_{ST}$  is only slightly decreased (less than 10%) from that of the pure solvent. The PEO sequences cannot be localized at the surface as the  $\gamma_{ST}$  of pure PEO is generally estimated to 44 dyn cm<sup>-1</sup>.<sup>18</sup> The low surface activity of the copolymers in organic solution is probably related to a partial adsorption of the surfactant micelles at the air/solvent interface, as occurs with finely dispersed minerals<sup>8,19</sup>; this problem will be discussed below.

### Interfacial Tension ( $\gamma_I$ ) in Water/Organic Solvent Systems

The  $\gamma_I$  value for the interfaces water/*n*-hexane, water/*n*-dodecane, and water/decalin has been measured without surfactant, as well as on 1% solutions of some A(PEO)<sub>2</sub> copolymers in the organic solvent. The decrease of  $\gamma_I$  due to the presence of the surfactant ( $\Delta\gamma_I$ ) is given in Table V.

The interfacial activity  $\Delta\gamma_I$  of a given A(PEO)<sub>2</sub> copolymer always decreases in the order *n*-hexane, *n*-dodecane, and decalin. In each organic solvent,  $\Delta\gamma_I$  decreases as the overall molecular weight increases in a series of PTBS(PEO)<sub>2</sub> copolymers (B<sub>11</sub> to B<sub>51</sub>, Table V). The greatest lowering of  $\gamma_I$  is observed for the water/*n*-hexane interface and the PIP based copolymer. This latter surfactant seems to be more active in hexane than the PTBS based copolymers,

TABLE V

Decrease of the Hydrocarbon/Water Interfacial Tension ( $\Delta\gamma_I$ ) by Addition of a Star-Shaped Copolymer at 20°C<sup>a</sup>

Copolymer	$\Delta\gamma_I$ (%)			
	<i>n</i> -Hexane/H <sub>2</sub> O ( $\gamma_I = 46$ dyn cm <sup>-1</sup> )	<i>n</i> -Dodecane/H <sub>2</sub> O ( $\gamma_I = 45$ dyn cm <sup>-1</sup> )	Decalin/H <sub>2</sub> O ( $\gamma_I = 35$ dyn cm <sup>-1</sup> )	Toluene/H <sub>2</sub> O ( $\gamma_I = 32$ dyn cm <sup>-1</sup> )
I <sub>2</sub>	97.5	65.5	23	95
B <sub>11</sub>	87	66.5	53	97.5
B <sub>24</sub>	81	42	48	88
B <sub>33</sub>	...	50	40.5	61
B <sub>51</sub>	77	45.5	37	45

<sup>a</sup> Concentration 1% in the organic phase.

although the contrary is observed in decalin; the nature of the hydrophobic sequence is accordingly important with respect to the organic solvent used.

The water/toluene interface has been studied in more detail. Unlike the aliphatic hydrocarbons mentioned above, toluene is not only able to dissolve PST, PTBS, and PIP but also low-molecular-weight PEO (<15,000).<sup>8</sup> The  $\gamma_I$  values in Table VI were measured using toluene solutions with different copolymer concentrations. The activity of the A(PEO)<sub>2</sub> copolymers is generally higher at the water/toluene interface than at the water/aliphatic hydrocarbon one; at 1% concentration, the B<sub>11</sub> and B<sub>24</sub> copolymers lower  $\gamma_I$  more efficiently in toluene than in aliphatic solvents (Table V). As is usually observed,<sup>8,20</sup>  $\gamma_I$  decreases as the copolymer concentration increases. The trend towards a lower limiting value is probably related to the saturation of the interface. As long as saturation is not reached,  $A_L$  values can be obtained by applying eq. (1) (Table VII). For B<sub>11</sub>, very similar  $A_L$  values are observed at both air/water and toluene/water interface (Tables IV and VII).

As expected,  $\gamma_I$  decreases when the temperature is increased (Table VIII). For 1% copolymer solutions in toluene,  $\gamma_I$  is generally reduced by one-half between 20 and 30°C. For similar PEO compositions (B<sub>11</sub>, B<sub>24</sub>, B<sub>32</sub>, and B<sub>33</sub> on the one hand and B<sub>12</sub>, B<sub>42</sub>, and B<sub>51</sub> on the other: Table IX),  $\gamma_I$  increases with the overall molecular weight of the copolymer. At practically constant length of the PTBS sequence (B<sub>21</sub>, B<sub>22</sub>, B<sub>24</sub>, and B<sub>26</sub>),  $\gamma_I$  exhibits a minimum value at about 50% PEO; this composition seems to be the most favorable as indicated by I<sub>2</sub>, S<sub>1</sub>, and B<sub>22</sub> copolymers (Table VI).

The interfacial tension must be dependent on the presence and also the con-

TABLE VI  
Toluene/Water Interfacial Tension  $\gamma_I$  at Various Concentrations of Star-Shaped Block Copolymers in Toluene (20°C)

Copolymer	Toluene/water $\gamma_I$ at different concentrations of copolymer in toluene				
	0.004%	0.04%	0.4%	1%	4%
I <sub>2</sub>	...	2.2	1.8	1.6	1.2
S <sub>1</sub>	3.0	0.1	...	...	...
S <sub>3</sub>	9.5	7.2	1.7	0.6	0.2
S <sub>4</sub>	13.2	8.5	2.0	1.6	1.3
B <sub>11</sub>	15.5	8.1	1.0	0.8	0.5
B <sub>12</sub>	13.2	7.2	1.3	1.0	0.4
B <sub>21</sub>	...	6.0	4.1	3.0	2.6
B <sub>22</sub>	9.2	0.6	a	a	a
B <sub>24</sub>	...	4.7	4.0	3.9	2.6
B <sub>26</sub>	...	...	6.5	6.9	2.0

<sup>a</sup> Too low to be measured.

TABLE VII  
Area per Star-Shaped Block Copolymer at the Toluene-Water Interface

Copolymer	$d\gamma/d \ln C$	$A_L$ (Å <sup>2</sup> )
S <sub>3</sub>	2.4	169
S <sub>4</sub>	2.2	183
B <sub>11</sub>	3.2	126
B <sub>12</sub>	2.6	155

TABLE VIII  
Effect of Temperature on Toluene/Water Interfacial Tension<sup>a</sup>

Copolymer	$\gamma_I$ (dyn cm <sup>-1</sup> )		
	20°C	25°C	30°C
I <sub>2</sub>	1.6	1.0	0.6
S <sub>4</sub>	1.6	1.4	0.7
B <sub>11</sub>	0.8	0.4	+... <sup>b</sup>
B <sub>12</sub>	1.0	0.7	0.6
B <sub>26</sub>	6.9	2.1	1.5
B <sub>33</sub>	12.5	6.4	6.4
B <sub>42</sub>	17.8	14.3	8.0
B <sub>51</sub>	17.7	11.9	9.9

<sup>a</sup> Concentration of copolymer 1% in toluene.

<sup>b</sup> Too low to be measured.

formation of the copolymer at the interface. For this reason we have sought a relationship between  $\gamma_I$  and the solvent power of the three aliphatic hydrocarbons used (nonsolvents for PEO) toward the hydrophobic sequence of the copolymers. In Table X, are gathered the solubility parameters  $\delta$  of the solvents and polymers concerned<sup>21,22</sup>: the more similar the solubility parameter of two compounds, the more favorable must be their interactions. From the analysis of Tables V and X, however, no evident conclusion can be drawn.

In Figure 1, Becher's scheme<sup>23</sup> is used to represent the localization of the individual molecules of the copolymer at the interface. Situations D, E, F are dependent on the composition of the copolymer and the nature of both the organic solvent and the hydrophobic sequence. This picture is highly idealized,

TABLE IX  
Dependence of Toluene/Water Interfacial Tension on Molecular Parameters of Star-Shaped Copolymers<sup>a</sup>

Copolymer	$\bar{M}_n$	PEO (%)	$\gamma_I$ (dyn cm <sup>-1</sup> )
B <sub>11</sub>	5700	67	0.8
B <sub>12</sub>	7600	75	1.0
B <sub>21</sub>	4500	34	3.0
B <sub>22</sub>	4900	46	<0.2
B <sub>24</sub>	8800	66	3.9
B <sub>26</sub>	20,000	85	6.9
B <sub>32</sub>	16,700	61	9.0
B <sub>33</sub>	20,000	67	12.5
B <sub>42</sub>	42,000	77	17.8
B <sub>51</sub>	53,000	72	17.8

<sup>a</sup> Concentration 1% in toluene; temperature 20°C.

TABLE X  
Solubility Parameters  $\delta$  (cal cm<sup>-3</sup>)<sup>1/2</sup>

Toluene	8.9
n-Hexane	7.3
n-Dodecane	7.9
Decalin	8.8
PIP	8.06
PTBS	8.44

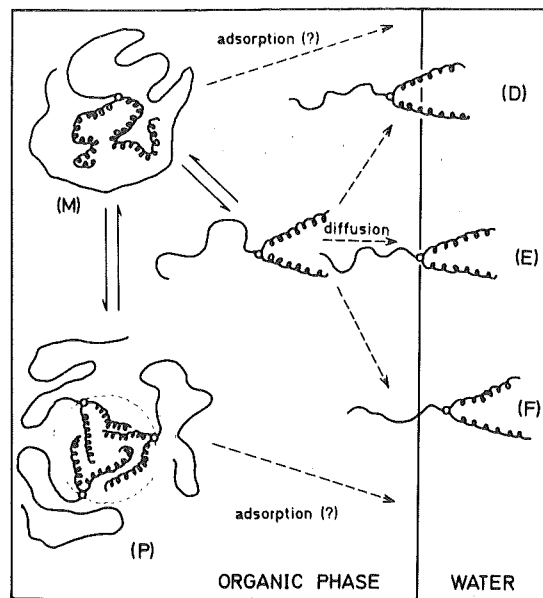


Fig. 1. Schematic description of the behavior of  $A(B)_2$  star-shaped copolymer dissolved in an organic solvent in the presence of water.

because the actual conformation of the copolymer in organic solution was not taken into account. It is well known that in a solvent selective for one sequence, a block copolymer forms monomolecular ( $M$ ) or plurimolecular ( $P$ ) micelles. The copolymer micellization in the organic phase must be controlled by the concentration, and by the interaction parameters between sequence  $A$  and sequence  $B$ , and between sequence  $A$  (and/or  $B$ ) and solvent. The more favorable the micellization, the less probable is the presence of free molecules ( $L$ ) at the interface. Along these lines, it would be possible to explain the increase of  $\gamma_I$  as the temperature decreases and the molecular weight of the copolymer increases. In the latter case, at constant weight concentration, the number of copolymer molecules decreases and, accordingly,  $\gamma_I$  is less modified. The micelles  $M$  and perhaps  $P$  can be adsorbed at the interface, as proposed by various authors<sup>8,19</sup>; this possibility is illustrated in Figure 1 and has been mentioned previously to explain the small decrease of  $\gamma_S$  in organic solvents.

TABLE XI  
Toluene/Water Interfacial Tension of Diblock and Star-Shaped Copolymers at Different Concentrations (20°C)

% PEO	Diblock copolymer			Star-shaped copolymer		
	0.04%	0.4%	1%	0.04%	0.4%	1%
33				6.0	4.1	3.0
41	1.4	0.8	1.0			
45				0.6	... <sup>a</sup>	... <sup>a</sup>
57	7.2	6.0	1.2			
66				4.7	4.0	3.9
68	8.3	4.4	3.2			

<sup>a</sup> Too low to be measured.

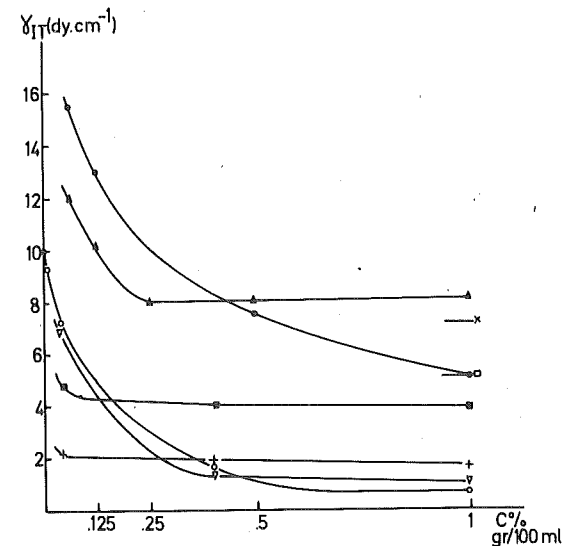


Fig. 2. Comparison of the toluene-water interfacial tension obtained from commercial surfactants and polyoxirane-based block copolymers with different molecular architecture. ( $\blacktriangle$ ) EPOL (PEO laurate;  $\overline{DP} = 6$ ); 25°C (A) ( $\bullet$ ) PS/PEO ( $\overline{M}_n = 17,700$ , 63% POE), 25°C (A) ( $\times$ ) Tween 80 (sorbitol monooleate-PEO;  $\overline{DP} = 20$ ), 20°C (B) ( $\square$ ) Span 80 (sorbitol monooleate-PEO;  $\overline{DP} = 4.3$ ); 20°C (C) ( $\blacksquare$ ) PTBS/(PEO)<sub>2</sub> ( $\overline{M}_n = 8800$ , 66% PEO); 20°C (C). ( $\nabla$ ) PTBS/(PEO)<sub>2</sub> ( $\overline{M}_n = 7600$ , 75% PEO); 20°C (C). (+) PIP(*cis*)/(PEO)<sub>2</sub> ( $\overline{M}_n = 4800$ , 56% PEO); 20°C (C). (O) PS/(PEO)<sub>2</sub> ( $\overline{M}_n = 18,000$ , 73% PEO); 20°C (C). (A) Measured with a Dognon-Abriba tensiometer; (B) pendant drop method—aqueous solution/toluene; (C) sessile drop method—toluene solution/water.

According to this picture, it seems that the micelles  $M$  and  $P$  are more favored in  $n$ -dodecane and decalin than in  $n$ -hexane and toluene. A change in the copolymer composition must affect both the position of the surfactant at the interface ( $D, E, F$ ) and the micellization equilibrium; the best composition for the PTBS(PEO)<sub>2</sub> copolymers would correspond to 50% PEO; whereas for PST-PEO diblock copolymers, 60–65% PEO are values often mentioned.<sup>8</sup>

In conclusion, the surface activity of the  $A(B)_2$  star-shaped block copolymers in organic solvents (1% concentration) at 20°C is very low whatever the solvent. Accordingly, a change in the interaction parameters between soluble hydrophobic sequences and organic solvent has no evident influence on the surface activity of the copolymer and its related conformation in solution. Once water is added to the organic solutions (1%), interfacial activity of the copolymer is observed, but this is dependent on the nature of the organic solvent. Both the presence and the conformation of the copolymer at the interface is by now very sensitive to the differences in molecular interactions between copolymer and organic solvent; but the solubility parameters alone cannot explain the differences observed.

The determining role played by the conformational state of the copolymer at the interface can also be drawn from Table XI where  $\gamma_I$  values are listed for diblock and star-shaped block copolymers containing a very similar PTBS sequence ( $\overline{M}_n = 3000$  in the star-shaped and 2700 in the diblock copolymers). From samples comparable in PEO content (66% and 68%) but with different molecular architecture, significant differences appear at low concentration (0.04%); saturation of the interface is reached more quickly with the star-shaped architecture,

whereas the  $\gamma_I$  limit value seems to be independent of this structural parameter. This observation should agree with an enhancement of the adsorption of single copolymer molecules at the interface. The plurimolecular micelle content would therefore be lower for star-shaped than for diblock copolymers, in accordance with a different efficiency in protection of undissolved sequences by the surrounding ones. Further experiments are however necessary to confirm this interesting observation.

It is also evident that direct information about the coverage of the interface by the copolymers would be very helpful; we are investigating this aspect of the problem.

Finally, Figure 2 compares the water/toluene interfacial tensions measured in the presence of various commercial surfactants and PEO based diblock<sup>8</sup> and star-shaped copolymers. The higher activity of the star-shaped block copolymers, over a broad range of concentrations, is clearly evidenced.

The authors are very much indebted to Imperial Chemical Industries for support through the first European Joint Project, including a fellowship to one of us (H.B.G.). They also thank Dr. R. Harper, Dr. G. Wiese, and Dr. T. Corner of the ICI Corporate Laboratory (Runcorn, England) for helpful collaboration in the interfacial tension measurements and fruitful discussions.

### References

1. G. E. Molau, *Block Polymers*, S. L. Aggarwal Ed., Plenum, New York, 1970, p. 79.
2. G. Holden, E. P. Bishop, and N. R. Legge, *J. Polym. Sci., Part C*, **26**, 37 (1969).
3. C. B. Bucknall, *Toughened Plastics*, Materials Science Series, Applied Science, London, 1977.
4. A. R. Carter and D. Petit, *Developments in Adhesives*, W. C. Wake Ed., Development Series, Applied Science, London, 1977.
5. G. Riess, J. Periard, and A. Banderet, *Colloidal and Morphological Behaviour of Block and Graft Copolymers*, G. E. Molau Ed., Plenum, New York, 1971, p. 173.
6. B. J. Schmitt, *Angew. Chem. Int. Ed. Engl.*, **18**, 273 (1979).
7. M. Schlienger, Ph.D. thesis, Mulhouse, France, 1976.
8. J. Nervo, Ph. D. thesis, Mulhouse, France, 1976.
9. V. H. Bartl and W. V. Bonin, *Makromol. Chem.*, **57**, 74 (1962); and **66**, 151 (1963).
10. K. Nakamura, R. Endo, and M. Takeda, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 1287 (1976).
11. F. Candau, A. S. Taromi, and P. Rempp, *C.R. Acad. Sci., Ser. C*, **283**, 453 (1976).
12. Huynh-Ba-Gia, R. Jérôme, and Ph. Teyssié, *J. Polym. Sci. Polym. Chem. Ed.*, to appear.
13. N. E. Dorsey, *J. Wash. Acad. Sci.*, **18**, 505 (1928).
14. J. F. Padday, *Surface and Colloid Science*, E. Matijevic, Ed., Wiley, New York, 1969, Vol. 1, p. 104.
15. J. E. Glass, *J. Phys. Chem.*, **72**, 4459 (1968).
16. J. R. Ceresa, *Block and Graft Copolymers*, Wiley, New York, 1976.
17. T. Kawamura, T. Takahashi, and T. Hatori, *J. Am. Oil. Chem. Soc.*, **48**, 29 (1971).
18. G. L. Gaines Jr. and G. L. Gaines III, *J. Colloid Interface Sci.*, **63**, 394 (1978).
19. P. Marie, J. Selb, and Y. Gallot, *C. R. Acad. Sci., Ser. C*, **282**, 703 (1976).
20. J. T. C. Bohm and J. Lyklema, *Theory and Practice of Emulsion Technology*, A. L. Smith, Ed., Academic, New York, 1976, p. 23.
21. *International Critical Tables*, Vol. IV, McGraw-Hill, New York, 1928.
22. J. Brandrup and E. H. Immergut, *Polymer Handbook*, Wiley Interscience, New York, 1975.
23. P. Becher, *J. Colloid Interface Sci.*, **18**, 665 (1963).

Received February 8, 1980

Accepted July 3, 1980

## Transient Decay Studies of Photophysical Process in Aromatic Polymers. I. Multiexponential Fluorescence Decays in Copolymers of 1-Vinylnaphthalene and Methyl Methacrylate

D. PHILLIPS<sup>†</sup> and A. J. ROBERTS,<sup>†</sup> *Department of Chemistry, The University, Southampton SO9 5NH, England* and I. SOUTAR, *Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh, EH14 4AS, Scotland*

### Synopsis

The considerable potential of high resolution time-resolved spectroscopic data for copolymer systems in elucidation of the intramolecular photophysical processes which occur in polymer systems is illustrated. Such information can not be gleaned solely from studies of homopolymers. Kinetic data and time resolved fluorescence spectra of copolymers of 1-vinylnaphthalene and methyl methacrylate indicate that conventional kinetic schemes are inappropriate for the description of excimer formation in 1-vinylnaphthalene polymers. Evidence is presented for the presence of an emitting species in addition to the expected monomeric and excimeric forms. The nature of this third species is discussed and photophysical kinetic schemes are proposed to describe intramolecular excimer formation in such systems. Kinetic data have been derived for the principle deactivation pathways through investigation of the observed fluorescence decays upon the intrachain concentration of aromatic species.

### INTRODUCTION

The unique opportunities afforded by macromolecules for the study of photophysical phenomena have resulted in extensive investigation of the photophysical processes occurring in such systems particularly under conditions of steady-state excitation. More recently the advent of transient excitation and time resolved spectra techniques have promised to yield considerable information about the nature of intramolecular photoprocesses in polymer species.<sup>1-11</sup>

While phenomena such as energy migration/transfer and excimer formation are widely recognized in macromolecules the nature of the interactions between the chromophores remains the subject of speculation. Information regarding the influence of factors such as chain structure, conformation and microcomposition upon processes such as intramolecular excimer formation is required. In this connection the study of copolymeric species<sup>11-22</sup> has led to an enhanced understanding of the nature of the mechanisms of intramolecular excimer formation and of the role of energy migration in such processes.

In the present paper the considerable potential of the application of transient kinetic measurements upon copolymers to problems of polymer photophysics is demonstrated for the system 1-vinylnaphthalene-co-methyl methacrylate.

<sup>†</sup> Present address: The Royal Institution, 21, Albemarle Street, London, W1X 4BS, England.