Block Polymerisation by Interfacial Coupling of Immiscible Polymers bearing Mutually Reactive End-groups: Interfacial Activity of ω-Functionalised Polymers

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Abstract: The coupling of polymers bearing mutually reactive groups is generally prevented by the low concentration of end-groups and the immiscibility of the polymers. This can be overcome by an interfacial technique concentrating the reactive groups in the interfacial region. This paper focuses on the effect that an end-group has on the behaviour of a polymer of opposite philicity at a water–toluene interface. Measurements of the reduction in interfacial tension promoted by poly(ethylene oxide) (PEO) end-capped by a hydrophobic $C_{10}H_{18}$ group, and polystyrene (PS) terminated by an ammonium bromide group shed light on the role played by the end-group in the polymer adsorption. Values of the equilibrium interfacial tension support the conclusion that the adsorption of the hydrophilic polymer (PEO) is largely independent of the $C_{10}H_{18}$ end-group whereas the ammonium bromide effectively drives PS to the interfacial region.

1 INTRODUCTION

Research on block polymer synthesis has promoted some of the most prominent scientific and technological advances in polymer science during the last decades. The multiphase character exhibited by most of the block polymers accounts for a number of unique properties which cannot be observed when corresponding homopolymers or random copolymers are employed. For obtaining useful combinations of properties, in addition to multiphase structures, an optimum level of adhesion between the phases is also required. In neat block polymers, the phases are interconnected through covalent bonds. Block polymers involved in liquid–liquid emulsions and polymer alloys (i.e. blends of homopolymers), display surface-active properties

related to the molecular structure and composition of the blocks; they can accordingly provide adequate stability or adhesion between the phases.[1]

Block polymers can be synthesised through two main pathways:[2] techniques whereby active centres generated at the chain end(s) of polymer PA are able to initiate polymerisation of added monomer B, and techniques consisting in the coupling of two pre-formed polymers $PA(X)_n$ and $PB(Y)_m$ bearing mutually reactive end-groups X and Y (m and n both being one or more). Compared with the first approach, the second has the advantage of providing a simple way of combining blocks of quite different nature and derived from various polymerisation mechanisms. The coupling reactions can be carried out easily and they do not require the same purification level of solvent, reagents and atmosphere as ionic and coordination (co)polymerisations. Although some examples of

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industrial application are known, this very simple technique is subject to both kinetic and thermodynamic obstacles. The kinetic restriction originates in the very low concentrations of reactive end-groups engaged in slow second-order kinetics, this being quite critical when high molecular weight blocks are desirable. The other limitation is the thermodynamic immiscibility of the majority of polymer pairs especially as the molecular weight increases; an interfacial technique has been proposed as a way of overcoming this difficulty.[3] The preferential location of the mutually reactive end-groups at the interface should be an efficient way to bypass both these kinetic and thermodynamic restrictions. The key point of this concept is to dissolve selectively the two functional polymers $PA(X)_n$ and $PB(Y)_m$ in immiscible solvents in such a way that the reactive end-group X of PA (or a short segment on to which X is attached) is attracted into the solvent containing PB, and vice versa. The fundamental question to be answered should be: is a hydrophilic end-group able to drive a dissolved hydrophobic polymer towards an immiscible polar non-solvent, or vice versa, can a hydrophobic end-group of a hydrophilic polymer be adsorbed at the interface of a water–oil system? In order to clarify this question it is worth while to investigate the surface activity of hydrophobic polystyrene end-capped with a hydrophilic ammonium bromide ($PS.N^+$), and hydrophilic poly(ethylene oxide) (or polyoxirane) carrying a hydrophobic $C_{10}H_{18}$ end-group ($PEO.C_{10}$) at a water–oil interface.

For interfacial coupling to be possible the polymers must be terminated by a group able to adsorb at the interface and take part in an organic reaction. For this reason polystyrene is capped not only by the ammonium bromide group, but also by a tertiary amino group reactive towards, for example, bromine, chlorine, iodide, and acid functions; the detailed structure of the end-group is accordingly:

$$PS-(CH_2)_6-\overset{|}{\underset{|}{N}}{}^{+}\overset{Br^-}{}-(CH_2)_4N(CH_3)_2$$
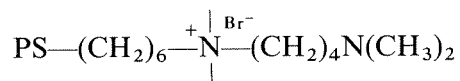
Similarly, polyoxirane is terminated by a $C_{10}H_{18}$ hydrocarbon group carrying a primary amine which is reactive towards, for example, acid chloride or isocyanate functions. Advantage has been taken of the possibility of initiating oxirane polymerisation by an aliphatic alcoholate capped by a protected primary amino group;[4] the structure of the PEO end-group, prepared in this way, is:
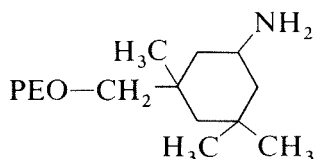
The structure of the ω-functional polystyrene ($PS.N^+$) is comparable to that of commercial ionic surfactants except for the molecular weight of the hydrocarbon chain which here ranges from 5×10^3 to 28×10^3. In these conditions, the effect of chain length on the interfacial activity can be investigated while keeping a good control of the polymer functionality. The same is true for the hydrophilic $PEO.C_{10}$ chains. This paper focuses on the effect of the ω-functional polymers on the equilibrium water–toluene interfacial tension and aims at comparing the adsorption of $PS.N^+$ and $PEO.C_{10}$ at the water–toluene interface. Accordingly, it should be a useful guide in defining the most appropriate conditions for the interfacial coupling of immiscible polymers.

2 EXPERIMENTAL

All polymers were prepared by living anionic polymerisation followed by the deactivation of the poly anions with a suitable reagent. Polymerisation was carried out with the usual precautions required in anionic polymerisation, i.e. high purity and dryness of solvents and reagents. Tetrahydrofuran (THF) and benzene were dried by refluxing over the sodium–acetophenone complex and calcium hydride, respectively. Oxirane was dissolved in benzene and the solution was successively dried over calcium hydride and n-butyllithium. Styrene and 1,6-dibromohexane were dried over calcium hydride at room temperature.

Styrene polymerisation was initiated by *sec*-butyllithium and proceeded at 25°C for 3 h. Living polystyryllithium was then deactivated by treatment with an excess of 1,6-dibromohexane. The ω-bromo-polystyrene was purified by several precipitations into methanol and reacted with an excess of N,N'-dimethylamino-1,4-butane in dimethylformamide at 80°C for 2 weeks. The final $PS.N^+$ polymer was precipitated twice in hexane and twice in methanol, respectively. Oxirane polymerisation was initiated by potassium 3-succinimidomethyl-3,5,5-trimethylcyclohexanolate in THF, and took place in sealed tubes *in vacuo* at 50°C. The details of that polymerisation technique and the hydrolysis of the imido-terminated PEO to the amino derivative are reported elsewhere.[4] The ω-functional $PEO.C_{10}$ was finally purified by precipitation into hexane. The polymerisation degree of PS and PEO was easily controlled by the monomer–initiator molar ratio.

The mean number-average molecular weight ($\bar{M}_n$) of PS and PEO was determined before and/or after functionalisation by either vapour pressure osmometry (v.p.o.) or gel permeation chromatography (g.p.c.). V.p.o. was carried out in toluene

at 37°C (Knauer apparatus). The Waters 200 chromatograph was equipped with Styragel columns (10^5, 10^4, 10^3, 500 and 100 Å), and with a refractometric detector. It was calibrated with PS and PEO standards in THF at 20°C. The amino end-groups were titrated potentiometrically in benzene–methanol (vol. ratio 9:1) by *p*-toluenesulphonic acid. The functionality (mean number of end-groups per chain) was calculated from $\bar{M}_n$ and the end-groups titration and amounted to 0·85 and 0·80 for PEO.C_{10} and PS.N^+ samples, respectively.

Interfacial tensions were measured by the 'Du Nouy' technique using a Krüss K10 type digital tensiometer. The steady-state interfacial tensions were measured at least five times and, after appropriate correlations,[5-7] an average value was calculated ($\pm 0·5$ dyn cm^{-1}). Solutions were prepared using analytical-grade toluene and water freshly distilled over $KMnO_4$, and filtered before measurement.

3 RESULTS AND DISCUSSIONS

3.1 Interfacial properties of homopolymers

Before discussing the interfacial properties of ω-functional polymers, we shall briefly summarize the behaviour of unmodified polymers as described in the literature. Few experimental investigations have been concerned with the surface or interfacial activity of homopolymers, and most of them have focused on the adsorption of hydrophilic polymers at a water–air interface, e.g. polyoxirane,[8-10] poly(acrylic acid),[11] poly(methacrylic acid),[12] poly(vinyl alcohol),[10,12-14] and polyvinylpyrrolidone.[10] The interfacial activity of poly(acrylic acid),[15] poly(vinyl alcohol),[16] and polyoxirane[17] has also been considered at a water–Hg, water–paraffin, and water–toluene interface, respectively. From this work, it is found that the linear dependence of the interfacial tension reduction on the polymer concentration sometimes exhibits a breakpoint[8,10,16] and sometimes not.[9,14,17] With one exception,[11] it is observed that the higher the molecular weight, the more important is the hydrophilic polymer adsorption, at least below a molecular weight of 10^4. Only one author has paid attention to the possible effect of temperature.[10] Finally, polystyrene is the only hydrophobic polymer for which the interfacial activity at the tetralin–air interface has been examined, and the reported surface tension reduction is very small.[13]

Statistical theories based on a surface quasi-lattice model can pretty well account for the behaviour of hydrophilic polymers, like polyoxirane, and poly(vinyl alcohol) at a water

interface. In this respect, many workers have been concerned with the chain conformation of adsorbed polymers and the thermodynamics of monomolecular adsorption.[18-31] The most widely accepted view is that the hydrophilic polymer is adsorbed by short sequences (trains) lying flat on the interface and set apart by loops, the size of which depends on solvent, temperature and chain flexibility. An important part of the chain can, however, escape from adsorption and form free tails in the bulk solution. This 'train–loop–tail' model is only valid for polymers dissolved in one phase but interacting with the other phase by atomic groups distributed along the chain. As far as hydrophobic polymers are concerned, Feigin and Napper[32] claim that purely aliphatic chains in non-polar solvents tend to avoid the interfacial layer because of conformation problems.

From a thermodynamic point of view, attention will be paid to the only approach free from any assumption about the conformation of the adsorbed macromolecules.[33-35] The molar enthalpy and free energy of adsorption are accordingly given by eqns (1) and (2), respectively,

$$\overline{\Delta G^0} = -RT \ln (m/\Pi^0) \tag{1}$$

$$\overline{\Delta H^0} = RT^2 \frac{d \ln m}{dT} \tag{2}$$

where Π^0 is a standard reduction of the interfacial tension (0·338 dyn cm^{-1}) and m is the proportionality between the interfacial tension reduction (Π) and the solute mole fraction (x_2) at very high dilution. m is usually approximated from eqn (3) which is valid in the usual range of concentrations.

$$\ln (x_2/\Pi) = \beta\Pi/kT - \ln m \tag{3}$$

where β is the interfacial area per macromolecule. m is determined by extrapolating the plot of $\ln (x_2/\Pi)$ versus Π to $\Pi = 0$.

3.2 Activity of ω-functionalised polymers at the water–toluene interface

The molecular weight of the polymers investigated was chosen to be sufficiently low to allow accurate determination of the end-group functionality but to allow a sufficiently broad range (4000–30 000) to observe a significant effect upon polymer adsorption.

The water–toluene interfacial tension reduction has been measured as a function of polymer mole fraction at different temperatures, for the PEO.C_{10} and PS.N^+ samples of various molecular weights (Tables 1 to 8). Figures 1 and 2 exemplify the dependence of Π on log C (C = concentration of polymer, g litre^{-1}) for PEO.C_{10} of two different

Fig. 1. Water–toluene interfacial tension reduction (Π) vs PEO.C_{10} ($\bar{M}_n = 4400$) concentration at different temperatures.
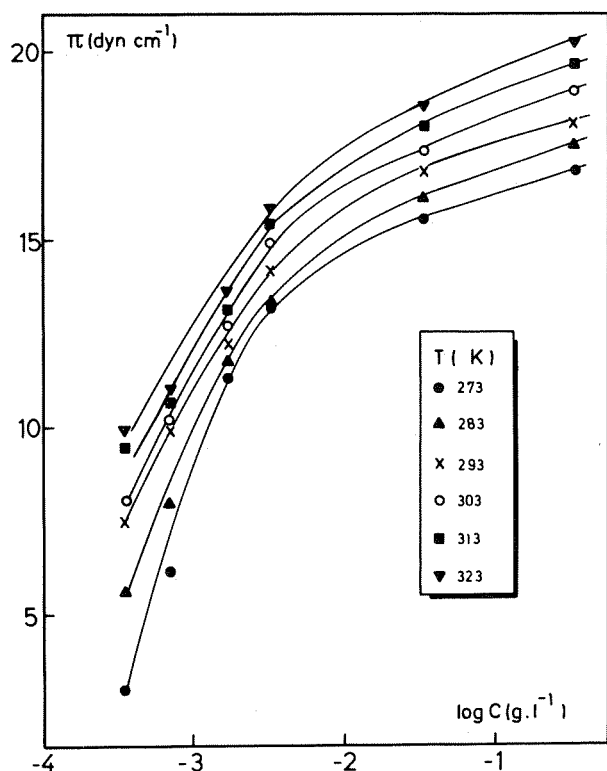

Fig. 3. Water–toluene interfacial tension reduction (Π) vs PS.N^+ ($\bar{M}_n = 5100$) concentration at different temperatures.

molecular weights. At a sufficiently high $\bar{M}_n$ (16 000; Fig. 2), the experimental curves exhibit an obvious break point; the slope change is less marked at lower $\bar{M}_n$ (4400) and higher temperatures (Fig. 1). An increase in $\bar{M}_n$ (from 4400 up to 11 000) has a
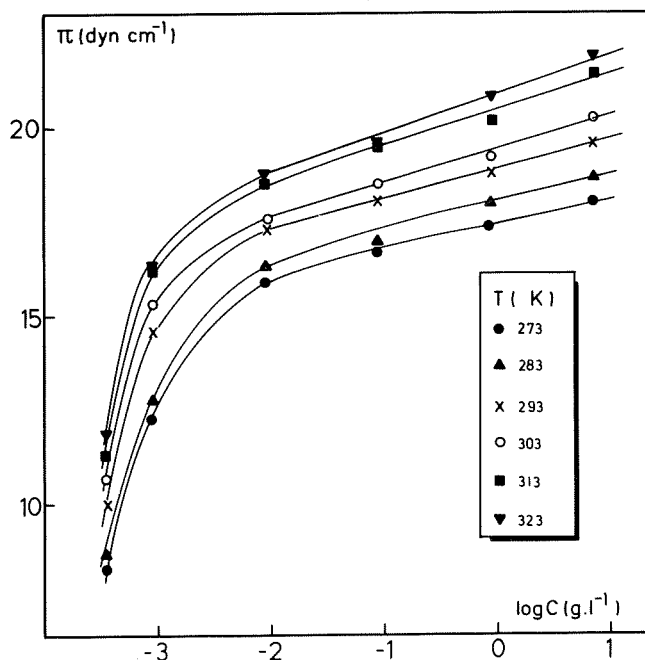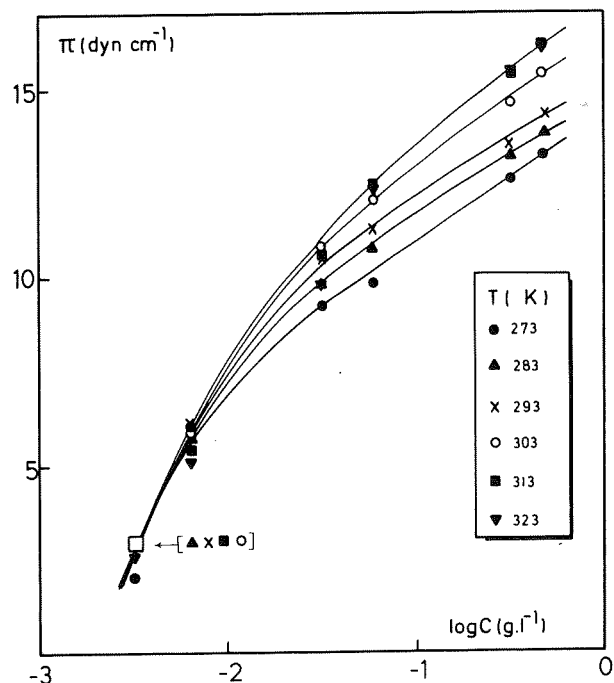
moderately beneficial effect on the interfacial activity which tends to level off at higher $\bar{M}_n$ (16 000 and 20 000) (Tables 1 to 4). This is a behaviour qualitatively similar to that reported by Glass for the unfunctionalised PEO but at the water–air interface.[10] It suggests that PEO.C_{10} is favourably adsorbed at the water–toluene interface, most likely in agreement with the largely accepted 'train–loop–tail' model for the adsorption of hydrophilic polymers. As far as PS.N^+ is concerned, the Π versus log C curves (Tables 5 to 8, and Figs. 3 and 4) are quite different from those reported for PEO.C_{10} of comparable molecular weights. In contrast to PEO.C_{10}, the interfacial tension reduction is strongly dependent on $\bar{M}_n$, and decreases as $\bar{M}_n$ increases. This observation means that the hydrophilic end-group of PS.N^+ has a decisive effect on its adsorption at the interface. As $\bar{M}_n$ increases, the

Fig. 2. Water–toluene interfacial tension rediction (Π) vs PEO.C_{10} ($\bar{M}_n = 16\,000$) concentration at different temperatures.

Table 1. Dependence of water–toluene interfacial tension reduction (Π) on temperature and PEO.C_{10} ($\bar{M}_n = 4400$) mole fraction (x_2)

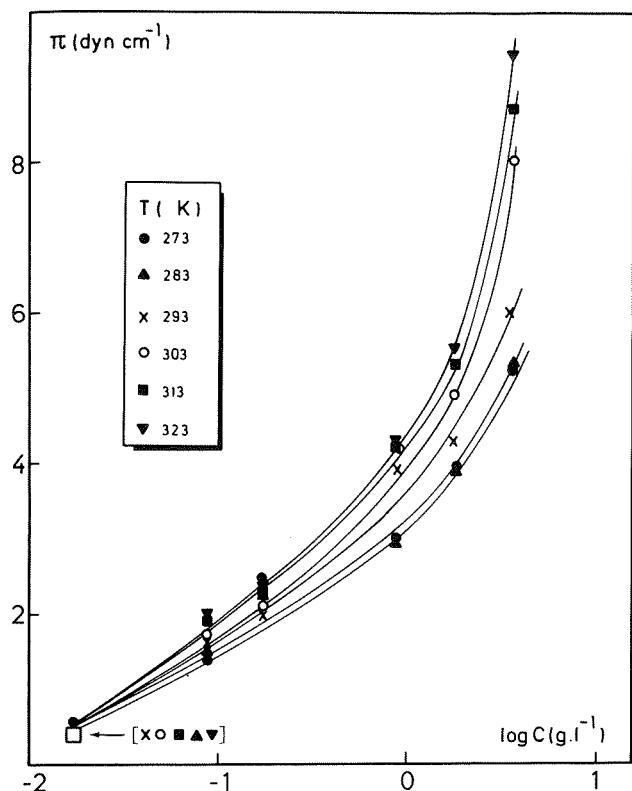| $10^6 x_2$	Π (dyn cm^{-1})					
	0°C	10°C	20°C	30°C	40°C	50°C
0·0014	3·0	5·6	7·5	8·0	9·4	9·9
0·0028	6·2	8·0	9·9	10·2	10·6	11·0
0·0069	11·3	11·8	12·2	12·7	13·1	13·6
0·0138	13·1	13·3	14·1	14·9	15·4	15·8
0·1380	15·5	16·1	16·8	17·3	18·0	18·5
1·3840	16·8	17·5	18·1	18·9	19·6	20·2

Fig. 4. Water–toluene interfacial tension reduction (Π) vs PS.N$^+$ ($\bar{M}_n = 28\,000$) concentration at different temperatures.

Table 2. Dependence of water–toluene interfacial tension reduction (Π) on temperature and PEO.C$_{10}$ ($\bar{M}_n = 11\,000$) mole fraction (x_2)

$10^6 x_2$	Π (dyn cm^{-1})					
	0°C	10°C	20°C	30°C	40°C	50°C
0·0011	9·0	10·1	11·0	11·8	12·5	13·3
0·0021	11·5	12·7	12·8	13·4	14·0	15·2
0·0066	14·2	14·9	14·9	15·6	16·2	17·1
0·0133	15·1	15·4	15·4	15·9	16·7	17·8
0·1329	16·2	16·5	16·7	17·4	18·2	19·3
1·3292	17·6	17·9	18·3	19·2	20·2	21·1

Table 3. Dependence of water–toluene interfacial tension reduction (Π) on temperature and PEO.C$_{10}$ ($\bar{M}_n = 16\,000$) mole fraction(x_2)

$10^6 x_2$	Π (dyn cm^{-1})					
	0°C	10°C	20°C	30°C	40°C	50°C
0·0004	8·2	8·6	9·8	10·6	11·2	11·8
0·0010	12·2	12·7	14·5	15·2	16·2	16·3
0·0096	15·8	16·2	17·2	17·5	18·4	18·6
0·0964	16·6	16·9	18·0	18·4	19·4	19·5
0·9644	17·2	17·9	18·7	19·1	20·0	20·7
7·7526	17·9	18·6	19·5	20·2	21·3	21·8

Table 4. Dependence of water–toluene interfacial tension reduction (Π) on temperature and PEO.C$_{10}$ ($\bar{M}_n = 20\,000$) mole fraction (x_2)

$10^6 x_2$	Π (dyn cm^{-1})					
	0°C	10°C	20°C	30°C	40°C	50°C
0·010	13·6	14·2	15·0	15·8	16·7	17·4
0·019	15·6	16·2	16·7	17·6	18·5	19·2
0·095	16·4	16·8	17·6	18·3	19·3	20·1
0·191	16·7	17·2	17·9	18·9	19·8	20·6
0·955	17·5	18·1	18·8	19·7	20·8	21·5
1·910	17·9	18·5	19·3	20·3	21·3	21·9

Table 5. Dependence of water–toluene interfacial tension reduction (Π) on temperature and PS.N$^+$ ($\bar{M}_n = 5100$) mole fraction (x_2)

$10^6 x_2$	Π (dyn cm^{-1})					
	0°C	10°C	20°C	30°C	40°C	50°C
0·065	2·0	2·9	2·9	2·9	2·9	2·6
0·130	6·0	5·8	6·1	5·7	5·4	5·0
0·651	9·2	9·8	10·5	10·8	10·5	9·7
1·190	9·8	10·7	11·2	12·0	12·5	12·3
6·510	12·6	13·2	13·5	14·6	15·3	15·3
11·940	13·2	13·7	14·3	15·4	16·2	16·0

Table 6. Dependence of water-toluene interfacial tension reduction (Π) on temperature and PS.N$^+$ ($\bar{M}_n = 9100$) mole fraction (x_2)

$10^6 x_2$	Π(dyn cm^{-1})					
	0°C	10°C	20°C	30°C	40°C	50°C
0·062	2·0	1·9	1·9	1·8	1·9	1·5
0·122	3·3	2·9	3·0	2·9	2·8	2·6
0·608	7·4	7·0	7·0	7·0	6·7	6·2
1·220	9·4	9·3	9·3	9·7	9·2	8·7
6·080	10·5	10·5	10·5	10·9	10·6	10·2
12·170	11·9	11·7	11·7	11·5	11·9	12·0

Table 7. Dependence of water–toluene interface tension reduction (Π) on temperature and PS.N$^+$ ($\bar{M}_n = 20\,000$) mole fraction (x_2)

$10^6 x_2$	Π (dyn cm^{-1})					
	0°C	10°C	20°C	30°C	40°C	50°C
0·23	1·3	1·4	1·4	1·5	1·7	1·9
0·57	2·0	1·9	2·0	2·2	2·5	2·6
1·15	3·2	3·1	3·6	3·7	3·8	3·7
5·75	4·4	4·5	4·9	5·6	5·8	5·8
11·50	4·7	4·9	5·2	6·2	6·6	6·6
23·51	5·6	5·8	6·4	7·7	9·5	11·2

Table 8. Dependence of water–toluene interfacial tension reduction (Π) on temperature and PS.N⁺ ($\bar{M}_n = 28\,000$) mole fraction (x_2)

$10^6 x_2$	Π (dyn cm^{-1})					
	0°C	10°C	20°C	30°C	40°C	50°C
0·064	0·6	0·4	0·4	0·4	0·4	0·4
0·322	1·4	1·5	1·6	1·7	1·9	2·0
0·642	2·5	2·3	2·0	2·1	2·2	2·3
3·209	3·0	2·9	3·9	4·2	4·2	4·3
6·419	3·9	3·9	4·3	4·9	5·3	5·5
13·522	5·2	5·3	6·0	8·0	8·7	9·4

hydrophilic–hydrophobic balance of PS.N⁺ steadily becomes more unfavourable and Π decreases. It can be concluded that PEO.C$_{10}$ and PS.N⁺ display significantly different surface properties. The hydrophobic terminal segment (C$_{10}$) of PEO has no dramatic effect on the adsorption of the hydrophilic polymer at the toluene–water interface, whereas the ionic end-group (N⁺) of PS tends to break its intrinsic tendency to avoid the oil–water interface.

In order to quantify the differences observed in the surface properties of PEO.C$_{10}$ and PS.N⁺, respectively, free energy and enthalpy of adsorption

have been calculated according to eqns (1) and (2) and reported in Tables 9 and 10; the resulting molar entropy (ΔS) can be found in Table 11. Although the adsorption free energy increases (in absolute value) with $\bar{M}_n$ for PEO.C$_{10}$, it decreases with $\bar{M}_n$ for the ion-capped PS. Tables 10 and 11 clearly show that the adsorption of PEO.C$_{10}$ at the toluene–water interface is essentially due to the greatly favourable entropic contribution (> 100 cal K^{-1} mol^{-1}) outmatching the unfavourable enthalpic one. In the case of PS.N⁺, the situation is quite different as both the enthalpic and entropic contributions are small but in favour of the adsorption. In the limits of validity of eqns (1) and (2), the thermodynamics of the polymer adsorption is in agreement with the qualitative meaning of the experimental curves and Glass's conclusions about the behaviour of PEO at the air–water interface.[10]

The difference in the investigated interfaces, the similarity between Glass's results and the present observations prompt us to refer to some of Glass's thermodynamic considerations. According to this author, the total entropy change upon polymer adsorption should be composed of four contributions: (i) configurational entropy associated with changes in chain conformation and ways of arranging molecules in the interfacial region compared to

Table 9. Free energy of adsorption (kcal mol^{-1})^a

Polymer ($\bar{M}_n$)	Temperature (K)					
	273	283	293	303	313	323
PEO.C$_{10}$ (4400)	$-13\cdot3$	$-14\cdot9$	$-16\cdot4$	$-17\cdot6$	$-18\cdot2$	$-19\cdot0$
PEO.C$_{10}$ (11 000)	$-16\cdot9$	$-18\cdot7$	$-20\cdot3$	$-21\cdot5$	$-22\cdot3$	$-23\cdot6$
PEO.C$_{10}$ (16 000)	$-18\cdot0$	$-18\cdot9$	$-20\cdot4$	$-22\cdot0$	$-22\cdot8$	$-24\cdot1$
PEO.C$_{10}$ (20 000)	$-21\cdot3$	$-22\cdot6$	$-24\cdot1$	$-25\cdot1$	$-26\cdot3$	$-27\cdot8$
PS.N⁺ (5100)	$-10\cdot7$	$-11\cdot4$	$-11\cdot8$	$-12\cdot1$	$-12\cdot4$	$-12\cdot6$
PS.N⁺ (9100)	$-10\cdot5$	$-10\cdot8$	$-11\cdot2$	$-11\cdot5$	$-11\cdot8$	$-11\cdot8$
PS.N⁺ (20 000)	$-9\cdot7$	$-10\cdot0$	$-10\cdot3$	$-10\cdot6$	$-10\cdot6$	$-11\cdot0$
PS.N⁺ (28 000)	$-9\cdot5$	$-9\cdot6$	$-9\cdot9$	$-10\cdot1$	$-10\cdot5$	$-10\cdot8$

^{a} 1 kcal $\equiv$ 4·184 kJ

Table 10. Enthalpy of adsorption (kcal mol^{-1})

Polymer ($\bar{M}_n$)	Temperature (K)					
	273	283	293	303	313	323
PEO.C$_{10}$ (4400)	14·7	15·8	16·9	18·1	19·2	20·6
PEO.C$_{10}$ (11 000)	15·3	16·4	17·6	18·9	20·1	21·4
PEO.C$_{10}$ (16 000)	14·1	15·2	16·2	17·4	18·5	19·7
PEO.C$_{10}$ (20 000)	11·6	12·5	13·4	14·3	15·3	16·3
PS.N⁺ (5100)	$-0\cdot8$	$-0\cdot8$	$-0\cdot9$	$-1\cdot0$	$-1\cdot0$	$-1\cdot1$
PS.N⁺ (9100)	$-1\cdot3$	$-1\cdot4$	$-1\cdot5$	$-1\cdot6$	$-1\cdot7$	$-1\cdot7$
PS.N⁺ (20 000)	$-1\cdot9$	$-1\cdot9$	$-2\cdot1$	$-2\cdot2$	$-2\cdot2$	$-2\cdot5$
PS.N⁺ (28 000)	$-2\cdot0$	$-2\cdot1$	$-2\cdot3$	$-2\cdot5$	$-2\cdot6$	$-2\cdot8$

Table 11. Entropy of adsorption (cal K^{-1} mol^{-1})[a]

Polymer ($\bar{M}_n$)	Temperature (K)					
	273	283	293	303	313	323
PEO.C$_{10}$ (4400)	103	108	114	118	120	122
PEO.C$_{10}$ (11 000)	118	124	129	133	135	139
PEO.C$_{10}$ (16 000)	117	120	125	130	132	136
PEO.C$_{10}$ (20 000)	120	124	128	130	133	137
PS.N$^+$ (5100)	36	37	37	37	36	36
PS.N$^+$ (9100)	34	33	33	33	32	32
PS.N$^+$ (20 000)	29	28	28	28	28	26
PS.N$^+$ (28 000)	28	27	26	25	25	25

[a] 1 cal ≡ 4·184 J.

the bulk of the solution; (ii) entropy arising from liberation of solvent molecules from the interface and/or from disruption of ordered arrangements of solvent molecules in that region; (iii) entropy related to the breaking of polymer–solvent interactions due to the adsorption of polymer segments; (iv) entropy of dilution of the bulk phase during the adsorption process which is, however, negligible for polymer solutions. The last three contributions favour the polymer adsorption in contrast to the first one. The enthalpy of adsorption should also be split into four contributions: (i) enthalpy resulting from disruption of polymer–solvent interactions because of adsorption; (ii) enthalpy due to polymer heterosolvent (e.g. PEO–toluene) interactions in the interfacial region; (iii) enthalpy arising from changes in polymer–solvent interactions as a consequence of the liberation of solvent molecules; (iv) enthalpy of formation of polymer–polymer interactions between adsorbed segments. Referring to Glass's views on the adsorption thermodynamics of water-soluble polymers, it turns out that the large increase in entropy upon PEO adsorption is mainly due to contributions (ii) and (iii), whereas the unfavourable enthalpic contribution should be attributable to the breakage of solvation when PEO segments come into contact with the heterophase (toluene). For the ion-capped PS chains, the adsorption enthalpy is small but favourable and is probably due to water–ionic end-group interactions, i.e. contribution (ii) wherein the polymer acts through its polar extremity. In these conditions, it is not surprising that the relative importance of the entropy contributions (ii) and (iii) has decreased.

Although the ionic end-groups of PS have a beneficial effect on the polymer adsorption, they are likely to promote a partial association of the polymer. Indeed, it is well known that, in a non-polar solvent such as toluene, ionic groups attached to a hydrocarbon polymeric backbone tend to associate into multiplets.[36]

In that respect, the apparent molecular weight of PS.N$^+$ in toluene has been compared with the number-average molecular weight of the corresponding unfunctionalised PS ($\bar{M}_n$PS). In the temperature range from 0°C to 60°C, the ratio of the viscosity-average molecular weight ($\bar{M}_v$) of PS.N$^+$ in toluene over $\bar{M}_n$PS changes from about 2·5 down to 1·5 for the four investigated PS.N$^+$ samples. As the polydispersity index of the polystyrene chains is low ($\pm$ 1·05), $\bar{M}_v$ approximates to $\bar{M}_n$. When PEO chains are characterised in the same way, $\bar{M}_v$ of PEO.C$_{10}$ in water is very close to $\bar{M}_n$ of PEO between 0°C and 60°C. It is therefore obvious that in contrast to PEO.C$_{10}$ in water, PS.N$^+$ chains partly associate in toluene through the ionic end-groups, leading to star-shaped aggregates. Accordingly, the energy required to break the ammonium bromide (N$^+$) associations partly counterbalances the gain in energy when these ionic groups interact with water; this can account for the low value of the calculated enthalpy of adsorption (Table 10). Furthermore, the entropy of adsorption is reduced by the breakage of solvation of the adsorbed ionic end-groups (contribution) (iii)) and consists mainly of dissociation of PS.N$^+$, possible changes in the chain conformation, and perturbation of the water structure in the interfacial region due to the adsorption of ammonium bromide (N$^+$) end-groups.

4 CONCLUSIONS

The comparative investigation of the interfacial activity of PEO.C$_{10}$ and PS.N$^+$ supports the view that a lipophilic end-group has no significant effect on the adsorption of PEO, whereas a hydrophilic end-group provides polystyrene with a driving force for adsorption at the same water–toluene interface. These conditions are of prime importance for devising and successfully achieving the interfacial coupling of two immiscible polymers carrying mutually reactive end-groups. Understanding the

interfacial properties of both the reactive polymers at a suitable liquid–liquid interface should be an efficient guideline in that matter.

ACKNOWLEDGEMENTS

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