Colloid Polym Sci 276:297–304 (1998)

ORIGINAL CONTRIBUTION

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Functional polythiiranes 7: Surface activity of polythiiranes with PEO side chains

Received: 20 May 1997
Accepted: 25 November 1997

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Abstract Some comb-like polythiiranes with PEO side chains were prepared from the corresponding macromonomers. These new materials are amphiphiles and act as surfactants. Their surface tension and interfacial tension are measured and studied in this paper on account of their structures. The lowering of surface tension measured in polymers bearing methyl terminal group in PEO side chains, are in the same range as these observed with polymers of identical structures but different main chains. An increase of the hydrophobic units in the main chain, obtained in copolymers with methylthiirane does not significantly modified the surface tensions. Better lowering is afforded with structures bearing large alkyl groups as terminal group of PEO side chains. On the contrary, some of these macromolecules with an optimized EO content largely lower the water/xylene surface tension. The main interest of these new materials is their very low cmc and the stabilization of L_1-type microemulsions.

Key words Polymeric surfactants – polythiiranes – polyoxyethylenes – cmc – surface tension – interfacial tension – cloud point

Introduction

The synthesis of new functional polymers have received much attention in recent years [1]. Over the last few years, we have tried to synthesize new polythiiranes with functional groups in side chains by ring opening polymerization of suitable thiirane monomers. The aim was to obtain polymers with properties related to the specific feature of the sulfur atom. These polythiiranes are not water soluble and for some potential applications hydrophilic polythiiranes might be needed. Thus, in a previous work [2] we built new polythiiranes, with PEO side chains affording hydrophilic character. The link between the main chain and the side chain in these polymers is an ester function or a monothioacetal function. Statistical copolymers with methylthiirane were also prepared and studied. Then, we studied the chemical stability of these new polymers in aqueous solution in acidic or basic medium [3]. Such comb-like polymers, described in Fig. 1, with a hydrophilic part and a lipophilic part, are, in fact, amphiphiles and can act as surfactants.

In order to study the modifications of the amphiphilic properties in this series with structural changes, we also designed polymers with large alkyl terminal groups of PEO chains such as **PE10/12**, **PE10/18**, **PE20/16** from the corresponding commercial polyoxyethylene alkyl ether named Brij®. The present study is an attempt to test the surface activity and interfacial tension of these new polythiiranes. The solubilization of an hydrophobic organic molecule is depicted as due to the amphiphilic properties.

Several kinds of comb-like PEO polymers with hydrophobic backbone chains such as polystyrene [4], polymethacrylate [5, 6], polysiloxane [7], polyoxirane [8] are

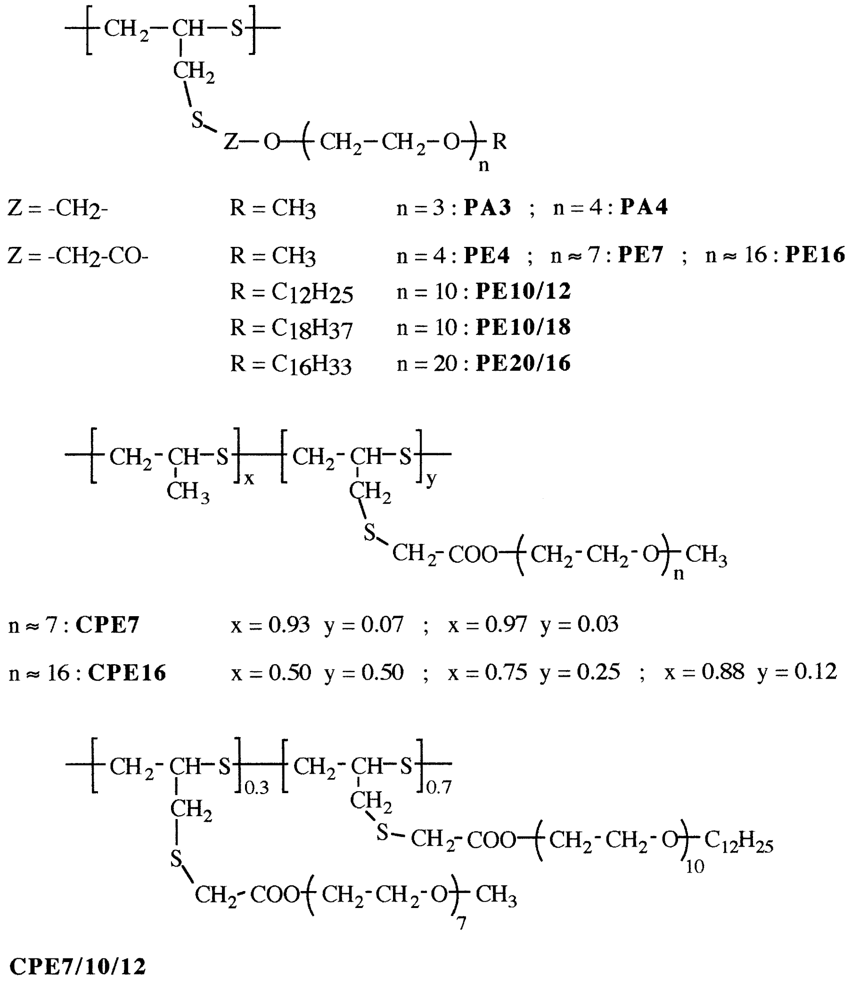

Fig. 1 Structures of the amphiphile polymers

described in the literature. They vary in hydrophobic backbone chain lengths, hydrophilic branch lengths and frequency of branches. They were obtained by direct polymerization of macromonomers as well as by grafting PEO chains on different hydrophobic backbones. Some were prepared and tested as surfactants and as emulsifiers and we compare their performances with those of PEO-polythiiranes.

Experimental

Materials

Polymers **PA3**, **PA4**, **PE4**, **PE7**, **PE16**, **CPE7**, **CPE16** were prepared by ring opening polymerization of the corresponding macromonomers. The synthesis of the macromonomers and the experimental conditions of polymerization were described previously [2]. Their molecular weights were determined by SEC-LS viscosimetry: a multidetection technique [9]. Commercial polyoxyethylene laurylether, stearylether Brij®76, and cetylether Brij®58 were used to synthesize polythiiranes with PEO alkyl side chains according to the same synthetic process. The new products were analyzed by IR, ^1H and ^{13}C NMR to confirm their structure.

Surface properties

Device

The procedure used for the measurement of the surface properties is a modified Wilhelmy plate method. An electrobalance to which a platinum plate or a stirrup [10] is hung, is connected to an amplifier and a plotter. A motor drives the stage to advance or recede the water container at a controlled speed (2 mm/min) and the measurements are conducted at 20 °C.

As soon as a solid comes into contact with an aqueous media, it supports a force which is created on the surface by the liquid meniscus. This force (F) is related to the contact angle (θ), the wetted perimeter (L) of the material and to the surface tension (γ) of the liquid according to the following relation:

$$F = \gamma L \cos\theta \ .$$

If $\theta = 0$, the surface tension of a liquid–vapor surface is reached. This method, proposed here for the determination of γ at a liquid surface, can also be applied to a liquid–liquid interface. In this last case, the contact angle is called θ_i. It is defined inside the inferior phase. At the beginning of the experiments, the plate or the stirrup is entirely immersed in this phase. The measurement of a very low interfacial tension was performed with a spinning drop tensiometer KRUSS SITE 04.

Solutions

For the preparation of the solutions, monodistilled water is used and its surface tension is 72.6 mN/m at 25 °C. Xylene was chosen as the organic phase. It is 99% pure and supplied by PROLABO. All the vessels are cleaned with sulfochromic mixture ($KMnO_4$ and sulfuric acid), rinsed with copius amount of distilled water and dried in an oven at 80 °C before use. The temperature is kept at 20 °C during the experiments and measurements.

For the preparation of liquid–liquid systems, the surfactants are dissolved in equal volumes of water and xylene. A series of such interfaces is performed at different concentrations and stirred over 48 h. Surface measurements are performed two hours after the end of shaking, either on the surface in equilibrium with its vapor, or on the liquid–liquid system.

Results and discussion

Surface tensions of homo and copolythiiranes with PEO-methyl side chains

The plots of the surface tension γ versus the logarithm of the concentration (C% w/w) are drawn in Fig. 2, for polymers with esters link **PE4**, **PE7**, **PE16**, the macromonomer of **PE4** : **M4** and a polyoxyethylene methylether ($M \approx 750$), in Fig. 3 for polymers with monothioacetal link, **PA3** and **PA4** and in Fig. 4 for copolymer **CP16** with three ratios of hydrophilic side chains. Obviously, all the

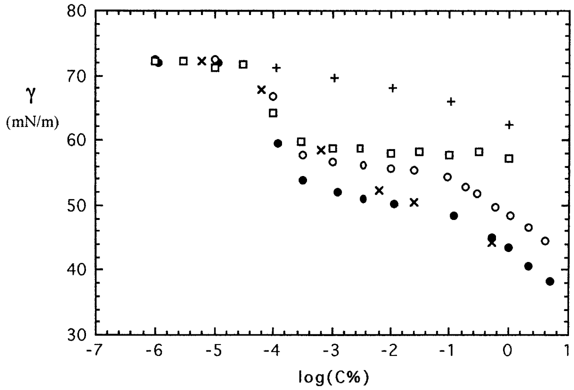

Fig. 2 Variation of surface tension with concentration at 20 °C for PE4 (●), PE7 (○), PE16 (□), polyoxyethylene monomethylether 750 (+) and thiirane monomer of PE4 (×)

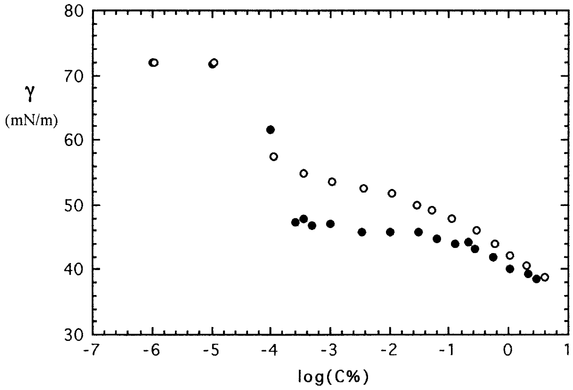

Fig. 3 Variation of surface tension with concentration at 20 °C for PA3 (●) and PA4 (○)

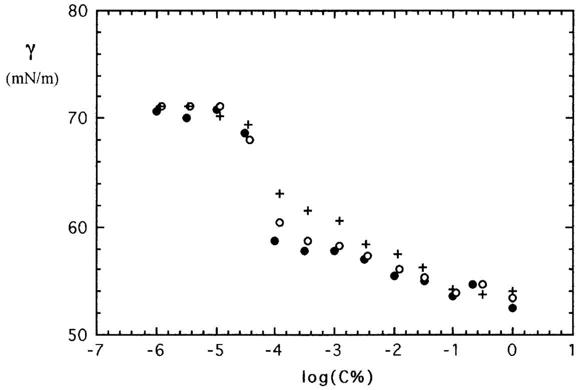

Fig. 4 Variation of surface tension with concentration at 20 °C for CPE16 50/50 (●), CPE16 75/25 (○) and CPE16 88/12 (+)

polymers exhibit surface activities from a low concentration value around 10^{-5}%, which means that adsorption occurs. This amphiphilic behavior is probably related to the polyethylenoxide group soluble in water, which plays the role of the polar part, and to an apolar part constituted by the main chains and the first atoms of the side chains: $-(CH_2-CH-(CH_2-S-Z)-S)-$.

The decrease of γ is observed for some polymers, by a plateau, which may correspond to a saturation of the interface and an aggregation of the polymer in the bulk phase, which looks like micelles. In these aggregates, the apolar domains are probably constituted by hydrophobic associations of the apolar part of the polymer.

In order to evidence the formation of the aggregates, dithizone was dissolved in the aqueous phase before adding polymers. This hydrophobic dye shows a low absorption when measured by visible spectroscopy: 0.015 at 455 nm. When polymers **PE4**, **PA4**, **PE7** were added to the solution, an increase of the absorption was observed; Figs. 5 and 6 were obtained with **PE4** and **PE7**, respectively, the **PA4** behavior being similar to **PE4** plot. They show the variation of the visible absorption versus the polymers concentration which are superimposed with the plots $\gamma = f(\log C\%)$. A significant increase of the absorption is obtained in a range of concentration corresponding to the cmc for polymer **PE4** and **PA4**. For polymer **PE7** the increase occurs at upper concentration: this could result from interactions between **PE7** and dithizone. So we may conclude that intramolecular aggregation occurs in solution corresponding to the formation of apolar domains which can solubilize hydrophobic molecules. The comparison of POE–Me750, which does not possess these apolar domains, with the corresponding polythiirane confirms this assumption. It should be interesting now to characterize the size of these aggregates by an experimental method like light scattering for instance. Nevertheless, by analogy with the classical surfactants, the saturation concentration of the interface, which corresponds to the existence of aggregates in solution, will be called cmc.

The copolymers exhibit a small plateau followed by a regular decrease. For some samples another decrease of γ is observed beyond $C = 10^{-1}$%. This transition could be related to the existence of a critical concentration from which a new structure of the micelles would occur, passing from intramolecular aggregates to intermolecular aggregates.

Table 1 summarises the main characteristics of the studied samples. The cmc are nearly thousand times as low as those of Brij® [11], probably because the formation of intramolecular polymeric micelles needs lower entropy than the formation of micelles from free chains.

It is not possible to establish a relation between the number of EO units and the cmc: owing to the polymolecularity of the main chains the aggregation process may occur at various concentrations. Tradewise, these polymers could be used as cheap surfactants as their cmc are low but their surface tension at cmc, γ_{cmc}, remain high (>45 mN/m).

The surface tensions lie in the same range for polymers with acetal link or polymers with ester link for identical side chain. As it was observed with PEO fatty alcohol [11], the surface tension of homopolymers decreases more with shorter PEO side chains: the best result is exhibited for **PA3** with three EO units. This trend is illustrated in Fig. 7 where the cloud point temperature (T_{cp}) at 1% concentration as a function of OE number is also plotted.

As for copolymers **CPE16**, γ values close to 60 mN/m were obtained whatever the composition (Table 1). This value is similar to the value of the corresponding polymer **PE16**, but the cmc value is lower. Polymethacrylates

Fig. 5 Variation of absorbance (●) at 455 nm with concentration of aqueous solutions of PE4 in contact with dithizone and variation of tension surface (○) with concentration at 20 °C for PE4 (without dithizone)

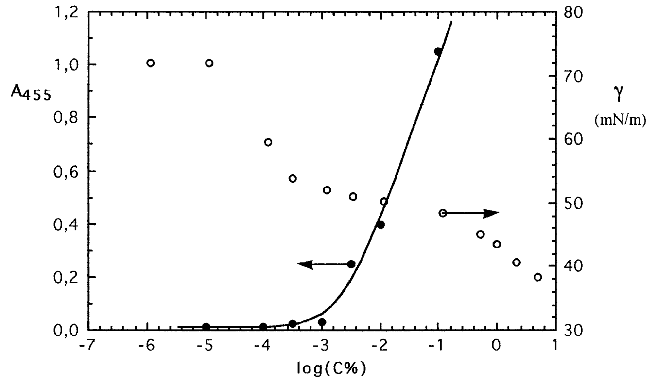

Fig. 6 Variation of absorbance (●) at 455 nm with concentration of aqueous solutions of PE7 in contact with dithizone and variation of tension surface (○) with concentration at 20 °C for PE7 (without dithizone)

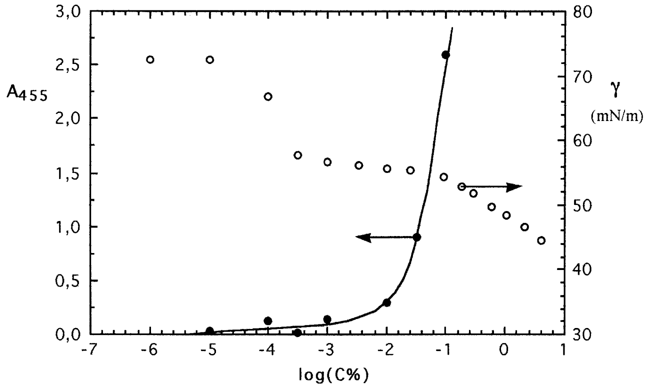

Table 1 Polymers data: light diffusion molecular weight, oxyethylene weight percentage, cloud point temperature at $C = 1\%$, critical micellar concentration, surface tension at C = cmc and $C = 1\%$ (at 20 °C); *: not detected in 20–100 °C range

Compound; $(M_W)^{LS}$	$\%_W$ OE	T_{cp} 1% [°C]	cmc [$\%_W$]	γ_{cmc} [mN/m]	γ 1% [mN/m]
PA3; (69 000)	47	21	2.5×10^{-4}	46.5	40.1
PA4; (15 000)	54	39	1.4×10^{-4}	55	42.3
PE4; (55 000)	50	35	4.0×10^{-4}	52	43.5
PE7; (150 000)	64	64	3.0×10^{-4}	56	48.3
PE16; (100 000)	80	94	3.0×10^{-4}	58	57.2
CPE16 50/50; (100 000)	72	88	1.2×10^{-4}	57.5	53.1
CPE16 75/25; (50 000)	63	84	1.3×10^{-4}	59	53.4
CPE16 88/12; (30 000)	46	75	1.1×10^{-4}	62	54.0
POEMe$_{750}$	96	*	—	—	62.5

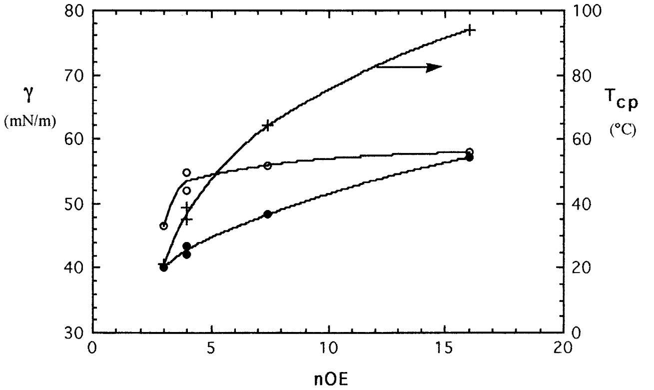

Fig. 7 Variations of tension surface at C = cmc (○) and $C = 1\%$ (●) and variation of cloud point temperature ($C = 1\%$) (+) with ethylene oxide side chains numbers

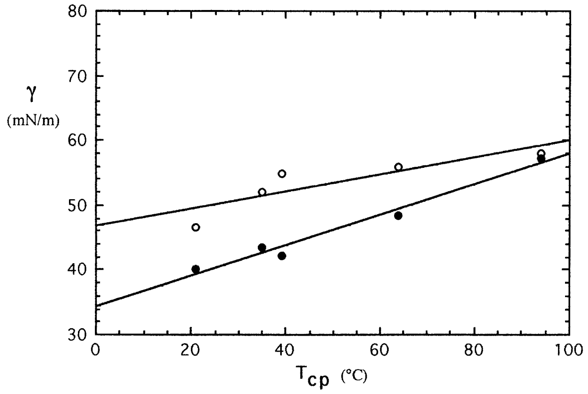

Fig. 8 Dependence of tension surface at C = cmc (○) and $C = 1\%$ (●) with cloud point temperature

with PEO side chains gave similar values of surface tensions ($\gamma = 60$ mN/m, $C = 10^{-3}\%$) [12]. This confirms that the essential factor is the length of the PEO side chains. With the copolymers we expected a variation of γ with the EO percentage and at the present time, we must conclude that the hydrophobic units in copolymer cannot act as efficiently as they do in polyoxyethylene monoalkylether ($C_{16}OE_{15}OH$: $\gamma_{cmc} = 40$ mN/m) [11]. These results allow to assume that an increase in the number of hydrophobic unit of the main chain (copolymers) induces only an interaction between the apolar parts, which reduces the cmc value, but disfavors the adsorption at the interface.

Both parameters γ_{cmc} and T_{cp} are correlated, as shown on the linear curves of Fig. 8. For the homo and copoly mers studied, whose hydrophobic part is located on the main chain, the measurement of T_{cp} allows the determination of either γ_{cmc} or γ at 1% concentration. Moreover, it is likely that cmc < 40 mN/m cannot be reached with these polymers.

Surface tensions of homo and copolythiiranes with PEO-alkyl side chains

In order to improve more efficiently the hydrophobic character of the structures we designed new architectures in which large alkyl groups like lauryl, stearyl and cetyl groups were placed at the end of the PEO side chains. This type of structure is rarely described in literature. The synthesis strategy was always the same: synthesis of the macromonomers from the commercial polyoxyethylene monoalkylether and polymerization of these macromonomers. Unfortunately, only **PE20/16** and **CPE7/10/12** were water soluble.

The adsorption of these polymers is probably different than the methyl side chain studied before. Indeed two different hydrophobic parts are concerned in adsorption, surrounding the polyethylenoxide group: the apolar part constituted by the main chains and the first atoms of the side chains: $-(CH_2-CH-(CH_2-S-Z)-S)$ and the alkyl group of the side chain.

Surface tensions are plotted versus log C% in Fig. 9 together with the visible absorption spectrum of an aqueous solution of dithizone in the presence of copolymer **CPE7/10/12;** the results are collected in Table 2. Both studied structures give relatively low surface tensions and have cmc lower than the corresponding Brij® [11]. Although a plateau, corresponding to the interface saturation, is not plainly observed with these structures, an increase of the dye absorption is obvious near 6×10^{-3}% which indicates the presence of aggregated structures. At a concentration of 0.01% the homopolymer **PE20/16** gives a lower value of γ than the corresponding Brij® 58 ($\gamma = 41.1$ mN/m) and also lower than polymer **PE16** which has nearly the same number of EO units but no alkyl side chain. The alkyl terminal side groups seem to act efficiently in decreasing the surface tension, laying more easily at the interface. On the contrary, the copolymer structure exhibits a higher value than the corresponding Brij® [11] ($\gamma = 33.4$ mN/m) probably on account of its excess of hydrophilic OE.

Interfacial tension of homo and copolythiiranes with PEO-methyl side chains

The interfacial tensions at the water/xylene interface in the presence of some of polymers were also studied. Figures 10 and 11 represent the variation of γ versus log C% for polymers **PA3**, **PE7**, **PE16** and the copolymer **CPE16**. A decrease of the hydrophilic character obtained by a decrease of the length of the PEO side chains or by a decrease of the ratio of the PEO side chain, leads to lower γ values. But with very low ratios of PEO side chains, high values of γ are obtained. The plot of γ versus the ratio of EO units at $C = 0.01\%$ is represented in Fig. 12 where the results obtained from nonhydrosoluble copolymers **CPE7** are added. The better surface properties are observed for a 45–50% OE content which corresponds to polymers **PA3** and **CPE16 88/12**. Similar performances were pointed out with polysiloxane-grafted-PEO [7] or with polymethacrylate-grafted-PEO [12].

Microemulsions were prepared with 1% concentration of **PA3** or **CPE16 88/12** 40% xylene and 50% water. The value of the interfacial tension of the copolymer was $3 \times 10^{-2} \pm 10^{-2}$ mN/m and it was stable for several months. These observations are characteristic of a microemulsified system. The observed opalescence of the aqueous phase confirms the presence of L1-type microemulsion [13].

Interfacial tension of homopolythiiranes with PEO-alkyl side chains

The variation of γ versus log C% is represented in Fig. 13 for polymers **PE10/18** and **PE10/12** at the water/oil

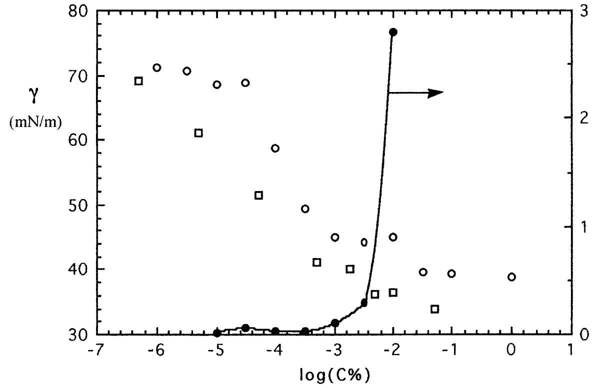

Fig. 9 Variation of tension surface with concentration for PE20/16 (□) and CPE7/10/12 (○) and variation of absorbance (●) at 455 nm with concentration of aqueous solutions of CPE7/10/12 in contact with dithizone

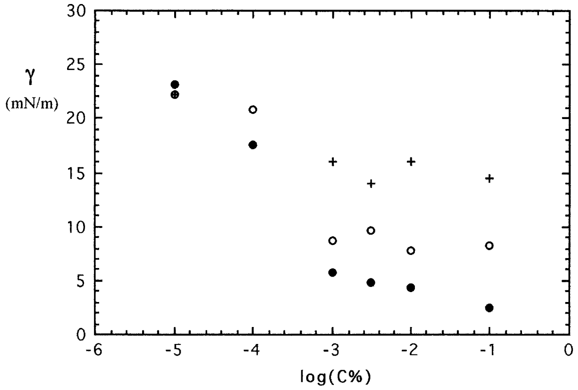

Fig. 10 Variation of water/xylene surface tension with concentration for PA3 (●), PE7 (○) and PE16 (+)

Table 2 Polymers data: molecular weight, oxyethylene weight percentage, cloud point temperature at $C = 1\%$, critical micellar concentration, surface tension at C = cmc and $C = 0.01\%$ (at 20 °C)

Compound; (M_W)	$\%_W$ OE	T_{cp} 1% [°C]	cmc [$\%_W$]	γ_{cmc} [mN/m]	γ 0.01% [mN/m]
CPE7/10/12; $(127\,000)^{LS}$	38	30	2×10^{-3}	40	40–45
PE20/16; $(29\,700)^{PS-SEC}$	69	—	1.4×10^{-3}	36	36

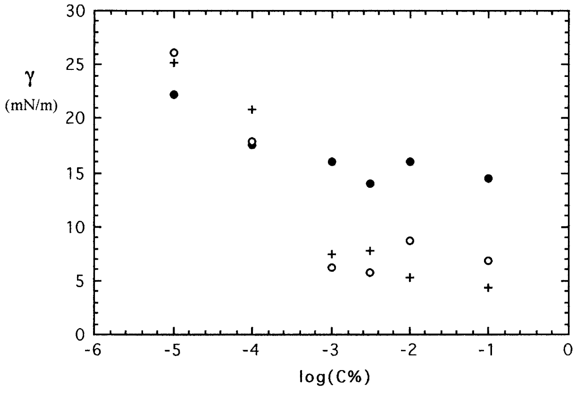

Fig. 11 Variation of water/xylene surface tension with concentration for PE16 (●), CPE16 75/25 (○) and CPE16 88/12 (+)

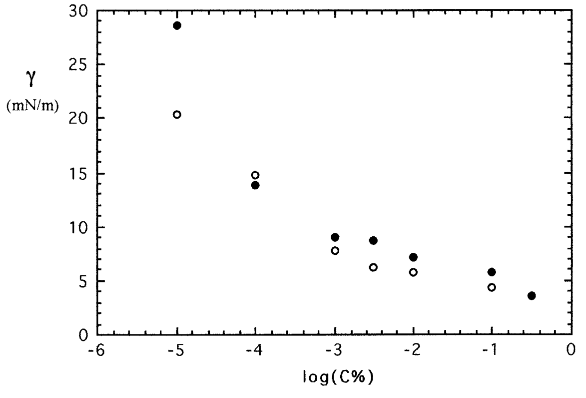

Fig. 13 Variation of water/xylene surface tension with concentration for PE10/18 (●) and PE10/12 (○)

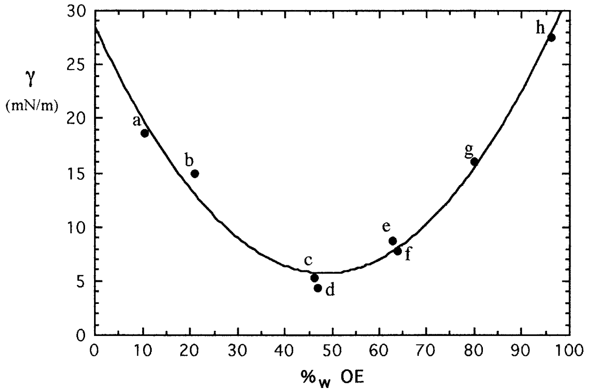

Fig. 12 Dependence of water/xylene surface tension at $C = 0.01\%$ with oxyethylene weight percentage in polymer for CPE7 97/3 (a), CPE7 93/7 (b), CPE16 88/12 (c), PA3 (d), CPE16 75/25 (e), PE7 (f), PE16 (g) and polyoxyethylene monomethylether 750 (h)

interface at $C = 0.01\%$. These structures give better results than the corresponding Brij® studied in the same conditions, as is reported below.

$C_{10}OE_{12}$–OH: $\gamma = 13.1$ mN/m; **PE10/12**: $\gamma = 5.8$ mN/m,
$C_{10}OE1_8$–OH: $\gamma = 10.9$ mN/m; **PE10/18**: $\gamma = 7.2$ mN/m,
$C_{20}OE_{16}$–OH: $\gamma = 5.8$ mN/m; **PE20/16**: $\gamma = 2.3$ mN/m.

The interfacial tensions are also lower than those obtained by Lucas [14] with side chain PEO–PPO polymethacrylate.

Conclusion

Comb-like polythiiranes with PEO side chains are amphiphiles and act as surfactants. The decrease in surface tension of homopolymers is optimized with **PE3** (3OE). Copolymers of methylthiirane are more hydrophobic and less surface active, probably because of the conformation in aqueous solution which prevents the hydrophobic group from reaching the air–water surface. For these two polymer families, the side chain length is the determinant parameter concerning their surface activity.

POE alkyl side chains polythiirane are better surfactants probably because their hydrophobic group are less attracted by the hydrophobic main chain, and therefore, more easily located at the air–water surface.

For all the polymers studied, a threshold concentration exists, which corresponds to the possible solubilization of hydrophobic molecules like dithizone. It is very low, near $10^{-3}\%$ w/w, and correlated with the threshold of the aggregation of the polymer in the bulk phase, as the cmc for a classical surfactant. The corresponding surface tension γ_{cmc} is correlated linearly with the cloud point temperature. This allows to predict γ_{cmc} knowing T_{cp} and viceversa. Interfacial tensions of homo and copolymers at water–xylene interfaces are correlated with the PEO side chain ratio. The maximum decrease is observed at 5–50% PEO. Interfacial tensions as low as 5 mN/m at 0.01% concentration and L1-type microemulsion at 1% concentration were obtained, which may be of main interest in applications.

Besides their interesting performances, these macromolecules could be considered like environmental polymeric surfactants on account of the possible degradation of the polythiirane main chain by oxidation demonstrated in other works [15, 16].

Colloid & Polymer Science, Vol. 276, No. 4 (1998)

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