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SHORT COMMUNICATION

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# Highly hydrophobically modified polyelectrolytes stabilizing macroemulsions: relationship between copolymer structure and emulsion type

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**Abstract** The types of emulsions, oil (*n*-dodecane) in water (O/W) or water in oil (W/O), stabilized with highly hydrophobically grafted linear poly(sodium acrylate)s, were investigated as a function of polymer chemical architecture. Consequently, a large number of macroemulsifiers, covering a wide range of hydrophobicity, were synthesized by changing the degree of grafting ($\tau$), length ($n$) and type (single- versus twin-tailed) of the hydrophobic moiety. Monovalent salt ($NaNO_3$) concentration was used as a probe to adjust and hence to estimate the hydrophile-lipophile balance (HLB) of each copolymer. $\tau$, $n$, type of graft and electrolyte concentration were identified as field parameters to control emulsion type. In general, decreasing either $\tau$ or $n$ was found to favor the formation of direct emulsions. Inverse dispersions were preferentially formed with twin-tailed rather than single-tailed copolymers. Moreover, the types of emulsions stabilized with well-balanced polyelectrolytes can be flipped from O/W to W/O with increasing salt concentration. Finally, following the Davies concept, a HLB scale for polymers was created from a comparison with surfactants of nearly identical chemical structure.

**Key words** Emulsion type – amphiphilic polymer – polyelectrolyte – polymeric surfactant – balanced copolymers – HLB scale

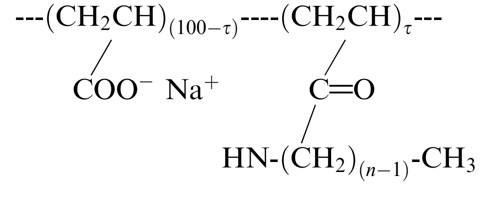
## Introduction

It is of great practical importance to control macroemulsion properties considering the large number of industrial application of macroemulsions [1]. Among others, emulsion type is a determining factor. Although oil-in-water (O/W) or water-in-oil (W/O) dispersed systems are most often formed upon mixing oil, water and emulsifier(s) under specific conditions, more complex structures, such as multiple emulsions, can also be obtained [2]. Several approaches can be used to determine whether an emulsion will be oil- or water-continuous: the empirical Bancroft rule [3], the conditions of validity of which were recently discussed in a paper by Ruckenstein [4], hydrophile-lipophile balance (HLB) concepts [5–8], the Shinoda phase-inversion temperature [9] and oriented wedge theory [10, 11], further discussed by Hildebrand [12] and revisited by Kabalnov and Wennerström [13]. These strongly interrelated concepts are most often used to explain experimental observations on liquid-liquid dispersions stabilized by surfactants since they still constitute by far the most important class of emulsifiers. In contrast, the type of emulsion containing polymers was not investigated in detail although it has long been understood that it was dependent on the structure of surfactant macromolecules [14–17]. The stability and rheological behavior of *n*-dodecane in water macroemulsions containing various hydrophobically modified poly(sodium acrylate)s were previously examined as a function of copolymer structure and concentration [18, 19]. As our studies were restricted to copolymers of relatively low hydrophobicity, only O/W dispersions could be obtained even at high ionic strength. More recently, the emulsifying ability of a modified poly(sodium acrylate) having well-balanced HL properties was reported [20]. In particular, we demonstrated that adding a salt could be an on-off switch to tune the type of emulsion containing this balanced polyelectrolyte. In this paper, we continue to explore the role played by salt concentration and copolymer structure on *n*-dodecane/water emulsions. Hence, a large number of amphiphilic macrosurfactants covering a broad range of hydrophobicity were synthesized by changing the degree of grafting, length and type of the hydrophobic moiety. Salt concentration, used as a tool to control emulsion type, provides an estimate of the HLB of the polymeric surfactants in the *n*-dodecane/water system. Finally, results were compared with those obtained with emulsions stabilized by surfactants of similar chemical structure (*n*-alkyl carboxylates) in order to build a HLB scale for this series of polymers within the framework of Davies group contribution [6–8].

## Experimental

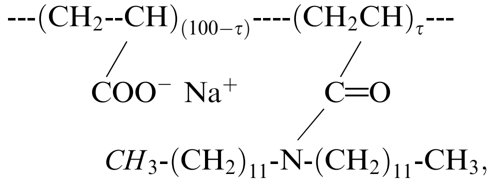
Poly (acrylic acid) precursor polymer (average molecular weight, $M = 50\,000$ g/mol) in concentrated aqueous solution (50% w/w) was supplied by Polysciences. The grafting reactions were carried out using *n*-octylamine, *n*-dodecylamine, *n*-tetradecylamine (Fluka) and di-*n*-dodecylamine without further purification. The chemical structures of the single- and twin-tailed highly hydrophobically modified poly(sodium acrylate)s are given by

single tail



$$\text{---}(CH_2CH)_{(100-\tau)}\text{----}(CH_2CH)_{\tau}\text{---}$$
$$/ \qquad\qquad\qquad /$$
$$COO^-\ Na^+ \qquad\qquad C{=}O$$
$$/$$
$$HN\text{-}(CH_2)_{(n-1)}\text{-}CH_3$$

twin tail



$$\text{---}(CH_2\text{--}CH)_{(100-\tau)}\text{----}(CH_2CH)_{\tau}\text{---}$$
$$/ \qquad\qquad\qquad /$$
$$COO^-\ Na^+ \qquad\qquad C{=}O$$
$$/$$
$$CH_3\text{-}(CH_2)_{11}\text{-}N\text{-}(CH_2)_{11}\text{-}CH_3,$$

respectively, with $\tau$, the degree of grafting (mol %) and $n$, the number of carbon atoms of monoalkyl grafts (C$n$). Single- and twin-tailed copolymers are hence denoted $\tau$C$n$ and $\tau$ (2C12) respectively. The grafting reactions will be detailed in separate papers but the copolymer characterization is briefly described later. The degree of grafting was determined by $^{13}$C NMR spectroscopy, elemental analysis and carboxylate group titration. Aqueous solutions were prepared with double-distilled deionized water with a Milli-Q system (Millipore); *n*-dodecane supplied by Prolabo was used as the oil without purification. The chemical structures of the surfactants, capric or decanoic (assay >98%, $m = 9$), lauric or dodecanoic (assay >99%, $m = 11$), myristic or tetradecanoic (assay >99%, $m = 13$) and palmitic or hexadecanoic (assay >97%, $m = 15$) acid sodium salts (Fluka) are given by $CH_3{-}(CH_2)_{(m-1)}{-}COONa$. Their respective names are C9, C11, C13 and C15 (number of hydrophobic carbon atoms). Polymer or surfactant concentrations in emulsions were 0.5% (w/v) and the oil volume fraction, $\phi$, was kept constant at 50%. 0.05 g emulsifier was first dissolved in 5 ml sodium nitrate ($NaNO_3$, analytical reagent, Prolabo) aqueous solution by gently stirring the solution for 24 h. The electrolyte concentration was taken as a parameter to control emulsion type. Then, 5 ml (3.75 g) *n*-dodecane was added to the aqueous polymer solution and the two phases were left in contact at rest for 24 h. The oil and aqueous phases were finally mixed for 5 min at 24 000 rpm (ambient temperature) using a rotor-stator-type disperser (Heidolph DIAX 600). The type of emulsion was determined by conductivity measurements and dilution tests.

## Results and discussion

### Copolymer characterization

Six single-tailed (70C8, 40C12, 50C12, 60C12, 80C12 and 50C14) and three twin-tailed [20(2C12), 35(2C12) and 50(2C12)] copolymers were synthesized. As discussed in our previous paper, the degree of grafting of 80C12 could not be determined (80 mol% is the expected degree of grafting assuming that the hydrophobic chains are grafted with a yield of 100%). However, as shown later, an emulsion type diagram clearly demonstrates that this copolymer is, as expected, one of the most hydrophobic of the series. The characterization results (Table 1) show that the three methods used to estimate the degree of grafting are in good agreement. With elemental analysis, $\tau$ was calculated either from the carbon and sodium atom or from the nitrogen and sodium atom content. Both values agree well with each other. Solvent conditions are also reported in Table 1. Suitable solvent mixtures to perform $^{13}$C NMR spectroscopy analysis were not found with the twin-tailed modified polyelectrolytes.

### Relationship between emulsion type, degree of grafting and copolymer graft structure

The effect of changing $\tau$ was discussed in our first paper on balanced polyelectrolytes. As a consequence, we have preferentially focused here on the length of the monoalkyl hydrophobic chain ($n$) and on the type of graft.

**Table 1** Characterization of copolymers

| | Elemental analysis | | $^{13}$C NMR | COONa titration |
|---|---|---|---|---|
| | C and Na | N and Na | | |
| 70C8 | 69 | 69 | 67<br>MeOD | 69<br>$H_2O$ |
| 40C12 | 40 | 41 | 41<br>$D_2O$/MeOD<br>70/30 | 45<br>$H_2O$/MeOH<br>70/30 |
| 50C12 | 54 | 54 | 50<br>$D_2O$/MeOD<br>70/30 | 56<br>$H_2O$/MeOH<br>70/30 |
| 60C12 | 64 | 65 | 60<br>$C_6D_6$/MeOD<br>80/20 | 60<br>$H_2O$/MeOH<br>70/30 |
| 50C14 | 53 | 54 | 55<br>$D_2O$/MeOD<br>70/30 | 55<br>$H_2O$/MeOH<br>70/30 |
| 20(2C12) | 22 | 23 | – | 25<br>$H_2O$ |
| 35(2C12) | 34 | 35 | – | 37<br>$H_2O$ |
| 50(2C12) | 48 | 48 | – | 53<br>$H_2O$ |

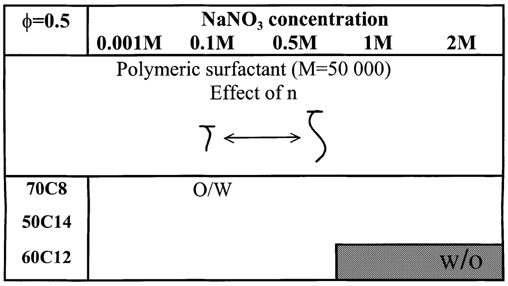


**Fig. 1** Emulsion type diagram of *n*-dodecane/water emulsions ($\phi = 0.5$) stabilized with single-tailed copolymers: effect of changing length (*n*) of the hydrophobic moiety. Salt is used as a probe to estimate the hydrophile-lipophile (HL) properties of the various copolymers

### *Effect of n (Fig. 1)*

60C12 is a balanced copolymer since it allows the formation of W/O macroemulsions at sufficiently high salt concentration. In contrast, when using shorter grafts ($n = 8$ instead of $n = 12$), a too hydrophilic macrosurfactant was obtained even at a rather high degree of grafting (70%) thereby illustrating again [18, 19] the $\tau$ and $n$ duality that exists to tune the HL properties of these amphiphilic copolymers. Also, when comparing the types of emulsions stabilized by the 50C14 and 60C12 copolymers, it appears that the loss of hydrophobicity obtained by decreasing $\tau$ from 60 to 50% could not be compensated for by increasing $n$ from 12 to 14.

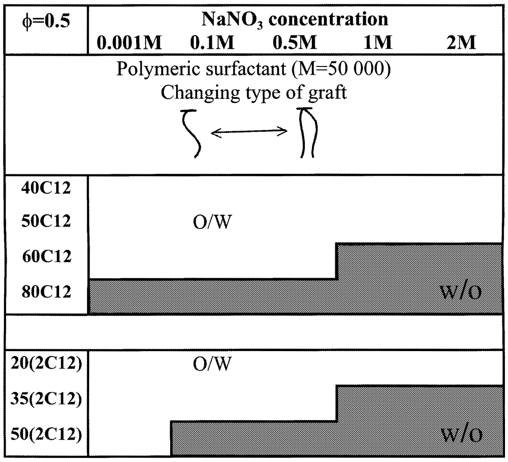


**Fig. 2** Emulsion type diagram of *n*-dodecane/water emulsions ($\phi = 0.5$) stabilized with modified copolymers: effect of changing the length and type of the graft (single- versus twin-tailed). Salt is used as a tool to estimate the copolymer HL properties

### *Single- versus twin-tailed copolymers (Fig. 2)*

With the twin-tailed 50(2C12) copolymer, emulsions are water- and oil-continuous at salt concentrations of $10^{-3}$ and 0.1 M respectively. Consequently, adding a salt provides a tool to control emulsion type with 50(2C12) contrasting with the corresponding single-tailed copolymer with the same degree of grafting (50C12), in agreement with previous studies on surfactants [21, 22]. Furthermore, by comparing the types of emulsion formed with 40C12 and 20(2C12), 60C12 and 35(2C12) and finally 80C12 and 50(2C12), we come to the conclusion that single-tailed $\tau_1$C12 and twin-tailed $\tau_2$(2C12) modified polyelectrolytes give emulsions of the same type providing their degree of grafting ratio is approximately $2 (\tau_1/\tau_2 = 2)$.

## Emulsion type and surfactant structure

The type of emulsion stabilized with single-tailed surfactants of various hydrophobicities was investigated as a function of salt concentration (Fig. 3). Basically, water-in-*n*-dodecane dispersions are obtained with C13 and C15 hydrophobic *n*-alkyl carboxylates while water-continuous emulsions are formed with C9 over the entire range of salt concentrations investigated. In between, the C11 surface-active agent appears to be more balanced than the others as shown from the question mark region where, depending on the sample, either oil- or water-dispersed emulsions were obtained. The poor reproducibility regarding the emulsion type arises from the fact that this particular domain of salt concentration corresponds to the emulsion-breaking region. Hence, C11 is

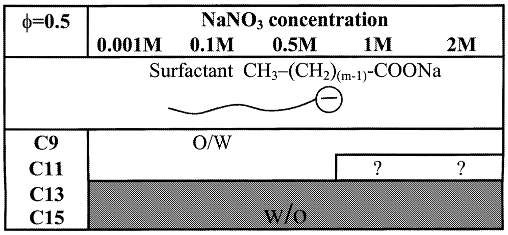


**Fig. 3** The effect on emulsion type of changing the hydrophobic tail length of *n*-alkyl carboxylate surfactants. The *question mark* domain corresponds to the emulsion-breaking region where emulsion type was found to be uncertain. *C9*, *C11*, *C13* and *C15* stand for $m = 9, 11, 13$ and 15 in the above surfactant chemical structure

one of the most balanced surfactants of the series together with C12, which is unfortunately not commercially available.

## HLB scale for copolymers

We have used the HLB concept suggested by Davies [6–8] who introduced a scheme to assign HLB group numbers to chemical groups comprising a surfactant. As pointed out several times in the literature, the HLB scale does not take into account of the effects of temperature and the nature of the oil on emulsion type and stability. It is therefore important to remember that our experiments were all carried out at room temperature (ionic emulsifiers are not very sensitive to temperature fluctuations) using exclusively *n*-dodecane as the oil. Salt is used as a probe to estimate the HLB of both copolymers and surfactants in a given system (*n*-dodecane/water at ambient temperature) exactly in the same way as Shinoda's phase-inversion temperature for nonionics. The Davies equation is:

$$\begin{aligned}\mathrm{HLB}_{\mathrm{Davies}} &= 7 + \Sigma(\text{hydrophilic group numbers}) \\ &\quad + \Sigma(\text{hydrophobic group numbers}) \\ &= 7 + \Sigma \qquad (1)\end{aligned}$$

HLB group numbers of interest are 19.1 for COONa and −0.475 for CH, $CH_2$ and $CH_3$. To the best of our knowledge, HLB numbers of the HN—C=O and N—C=O amide groups are not reported in the literature. Surfactant $\mathrm{HLB}_{\mathrm{Davies}}$ values are listed in Table 2. For the copolymers, it is first convenient to give the $\sum$ value of the poly(sodium acrylate), $\sum(\tau = 0\%) = 18.15$, obtained by summing the contribution of each chemical group comprising the repeat unit of the homopolymer. In the same way, the $\sum(\tau = 100\%)$ values corresponding to the poly(*n*-alkyl acrylamide)s and poly(di-*n*-dodecyl acrylamide) homopolymers are given by:

**Table 2** $\mathrm{HLB}_{\mathrm{Davies}}$ values for copolymers and surfactants. Values corresponding to surfactants or polymeric emulsifiers (only those actually synthesized) that lead preferentially to the formation of oil-in-water and water-in-oil emulsions appear in white and black rectangles respectively. Grey rectangles display HLB values of the most balanced emulsifiers

Surfactants

| C9 | C11 | C13 | C15 |
|---|---|---|---|
| 21.8 | 20.9 | 19.9 | 18.9 |

Single-tailed copolymers

| τ | **40** | **50** | **60** | **70** | **80** |
|---|---|---|---|---|---|
| C8 | 24.5 | 24.1 | 23.6 | 22.7 | 21 |
| C12 | 23.2 | 22.2 | 20.7 | 18.3 | 13.4 |
| C14 | 22.6 | 21.3 | 19.3 | 16.1 | 9.6 |

Twin-tailed

| τ | **20** | **30** | **35** | **40** | **50** |
|---|---|---|---|---|---|
| 2C12 | 23 | 21.4 | 20.5 | 19.4 | 16.5 |

$$\begin{aligned}\Sigma(\tau = 100\%) &= -0.475(2 + \text{number of carbon atoms of grafts}) \\ &\quad + \mathrm{HLB}_{\mathrm{Amide}} \qquad (2)\end{aligned}$$

We assume that the HLB numbers of both the secondary and tertiary amide groups are the same ($\mathrm{HLB}_{\mathrm{Amide}}$). Copolymer and surfactant $\mathrm{HLB}_{\mathrm{Davies}}$ values can be readily compared using the following equation to calculate the HLB of the modified polyelectrolytes for each polar head group, COONa.

$$\mathrm{HLB}_{\mathrm{Davies}} = 7 + [18.5(100 - \tau) + \tau\Sigma(\tau = 100\%)]/(100 - \tau) \qquad (3)$$

$\mathrm{HLB}_{\mathrm{Amide}}$ is required to use the above equation. Since emulsion type diagrams (Figs. 2 and 3) show that the HL properties of the 60C12 copolymer and C11 surfactant are close, $\mathrm{HLB}_{\mathrm{Amide}}$ was used as an adjusting parameter to fit their $\mathrm{HLB}_{\mathrm{Davies}}$ values. A good correlation, $\mathrm{HLB}_{\mathrm{Davies}}(60C12) = 20.7$ and $\mathrm{HLB}_{\mathrm{Davies}}(C11) = 20.9$, was found when using a reasonable value of 3.7 for $\mathrm{HLB}_{\mathrm{Amide}}$ (ester HLB number = 2.4 [7]). Finally, by using Eqs. (2) and (3) simultaneously, a HLB scale was built for this series of hydrophobically modified copolymers (Table 2). For each copolymer and surfactant, good agreement is observed between the HLB values and the type of emulsion. With small grafts (C8), it is clear that very high grafting degrees ($\tau > 80\%$) are required to form W/O emulsions (hence the copolymer looks much more like an ionomer than a polyelectrolyte since a few charges remain on the polymer backbone). In contrast, with longer grafts (C18), calculations (not presented in Table 2) show that a balanced copolymer could be obtained with $\tau \cong 40\%$ ($HLB_{Davies} = 20.6$). The only non-water soluble C18 copolymer we have synthesized so far has a degree of grafting of 20%. Its HLB value (23.4) is in agreement with our experimental observations since this copolymer only produces O/W emulsions even at a salt concentration of 2 M.

## Concluding remarks

Our work has revealed the existence of balanced copolymers and advantage was taken of having macroemulsifiers covering a broad range of hydrophobicity to build a HLB scale for polymers. Emulsion type was used as a criterion to estimate the HL properties of the copolymers and a comparison was made with surfactants of nearly identical chemical structure. In turn, the scale can be used as a predicting tool to tune emulsion type with this series of polyelectrolytes. It is important to point out that the construction of an accurate HLB scale for polymers is far outside the scope of this paper and we discuss here the limit of our approach. $HLB_{Davies}$ values are calculated from a summation of the structural factors which contribute individually to the overall HLB of the emulsifier. Consequently, the HLB number of a particular chemical group is constant regardless of its position in the (macro) molecule. Hence, the concept is not valid a priori for copolymers. At first sight, this is in contrast with our results since the HL properties of surfactants, single-tailed copolymers and twin-tailed copolymers were all found to be adequately described by the Davies HLB concept. However, the correspondence between the surfactant and single-tailed copolymer scale rests on the value of the amide group HLB number (3.7) used as a fitting parameter. Clearly, if the HLB number of the amide group is actually different from 3.7, a more elaborate approach than the Davies concept is required to suitably compare the HL properties of copolymers and surfactants. On the other hand, if 3.7 is a reasonable value, the dependence of HLB numbers upon the relative position of each chemical group along the polymer chain is of lesser importance (or errors cancel exactly!) in contrast to accepted ideas. It might also have been interesting to use an ester instead of an amide link to validate or invalidate the HLB approach since the ester HLB number is known to be 2.4. Hydrolysis of ester groups should not affect the reliability of such a study since only short-term measurements (type of emulsion) are required to compare the HL properties of the various emulsifiers. Now, let us examine the single-tailed copolymer series. The comparison of their HL properties is valid whatever the value of the amide HLB number. Since experimental results on emulsion type are in agreement with $HLB_{Davies}$ values of each copolymer, it thus appears that changing the degree of grafting and/or the length of the grafts does not significantly modify the HLB numbers of chemical groups comprising the polyelectrolytes. The same idea holds for the twin-tailed copolymers when compared among themselves. In the same manner, an appropriate comparison of single- and twin-tailed emulsifiers requires the knowledge of HLB numbers for both $HN{-}C{=}O$ and $N{-}C{=}O$ groups. Our assumption was to assign a unique HLB number, $HLB_{Amide}$, to both groups. Again, if the two values are actually close, it can be concluded that HLB numbers are not very sensitive to graft structure since the Davies concept was found to provide a convenient tool to compare the HL properties of single- and twin-tailed copolymers when using a unique $HLB_{Amide}$ value.

Besides the HLB concept, the macroemulsion type was recently found to be completely determined by the value and sign of the surfactant spontaneous curvature, $H_0$ [13]. For polymers, the meaning of spontaneous curvature is not as obvious as with surfactants. However, we suggest that our experimental data could provide valuable information regarding polymer conformation at the liquid-liquid interface by fitting copolymer $H_0$ values to those of surfactants of comparable HL properties. As a first approximation, copolymer spontaneous curvatures could be calculated from the sum of the $H_0$s corresponding to the hydrophilic and hydrophobic (single- and twin-tailed) repeat units weighted by the degree of grafting.

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