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SHORT COMMUNICATION

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Highly hydrophobically modified polyelectrolytes: Field variables to control emulsion type

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Abstract Highly hydrophobically modified (with *n*-dodecylamide chain) linear poly(acrylic acid)s (HHMPAAH) and poly(sodium acrylate)s (HHMPAANa) with various degrees of grafting (τ) were synthesized and used as emulsifiers of the *n*-dodecane/water system. The type of emulsion, oil in water (O/W) or water in oil (W/O), was investigated as a function of the polymer chemical structure (τ, salt or acid form of the copolymer) and aqueous phase electrolyte concentration ($NaNO_3$). Increasing τ and/or salt concentration was found to favor the formation of inverse emulsions. Direct liquid–liquid dispersions are more likely to form with poly(sodium acrylate)s than with poly(acrylic acid)s. Hence, field variables such as τ, pH and ionic strength are relevant parameters to control emulsion type. Moreover, a balanced polyelectrolyte neither soluble in oil nor in water was synthesized for the first time. With this original emulsifier, the dispersion type was found to change from O/W to W/O with polymer salting out. The work provides convenient model system for fundamental studies of polymer conformation at liquid–liquid interfaces.

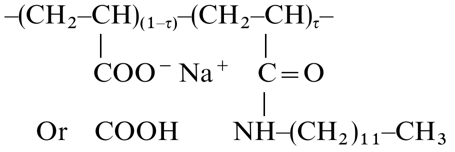
Key words Emulsion type – amphiphilic polymer – polyelectrolyte – polymeric surfactant – balanced copolymers

Introduction

Whether a liquid–liquid dispersion formed after mixing oil, water and an emulsifier will be oil or water continuous is a central problem. Basically, the dispersed systems are either oil in water (O/W) or water in oil (W/O) although much more complex morphologies such as multiple macroemulsions or bicontinuous microemulsions can be obtained as well under specific conditions. Contrary to microemulsions, macroemulsions are thermodynamically unstable systems which means that they must end as a coalesced system [1–3]. Consequently, the two kinds of dispersions are apparently very different and it would not be surprising if macroemulsion type could not be controlled in the same way as microemulsion phase inversion. However, the existence of a strong correlation between microemulsions phase behavior and macroemulsions stability was reported several times in the literature [4–8]. Furthermore, it was recently suggested from theoretical considerations that both dispersion types were dependent on the same physical parameters and, in particular, the spontaneous radius of curvature of the surfactant [9]. Consequently, the parameters (or field variables) [10] controlling microemulsions phase behavior can certainly be used to tune macroemulsion type. For instance, in the case of ionic surfactants, field parameters [10] include salt activity [11], type of counterions [12, 13], pH and, to a lesser extent, temperature. The recipes for the preparation of microemulsions with both ionics and nonionics were summarized in a recent paper [14]. Most of the above conclusions were essentially drawn from contributions dealing with surfactant small molecules. To the best of our knowledge, systematic studies of macroemulsion type emulsified with amphiphilic polyelectrolytes are totally lacking. Our previous studies [15, 16] on the stability and rheological behaviors of *n*-dodecane in water macroemulsions were restricted to polyelectrolytes of relatively low hydrophobicity so that only oil in water emulsions could be obtained even at high salt concentrations. In this paper, we have extended our investigations to the case of highly hydrophobically modified poly(acrylic acid)s (HHMPAAH) and poly(sodium acrylate)s (HHMPAANa). We report preliminary results that show how emulsion type can be monitored by changing copolymer structure (degree of grafting) and also by means of external parameters such as electrolyte concentration or pH. This is the first time that a well-balanced amphiphilic polyelectrolyte was synthesized. With this polymer, both stable O/W and W/O emulsions can form upon changing salt concentration.

Experimental

Poly(acrylic acid) precursor polymer in concentrated aqueous solution (50% w/w) was provided by Polysciences. The average molecular weight, $M = 50\,000$ g/mol, given by the supplier was found to be in agreement with our size exclusion chromatography measurements. The syntheses were carried out with using *n*-dodecylamine (supplied by Fluka). The chemical structures of the highly hydrophobically modified poly(acrylic acid)s (HHMPAAH) and poly(sodium acrylate)s (HHMPAANa) are given by



$$\begin{array}{lll} & -(\mathrm{CH_2{-}CH})_{(1-\tau)} & -(\mathrm{CH_2{-}CH})_{\tau}- \\ & | & | \\ & \mathrm{COO^-\,Na^+} & \mathrm{C{=}O} \\ & & | \\ \mathrm{Or} & \mathrm{COOH} & \mathrm{NH{-}(CH_2)_{11}{-}CH_3} \end{array}$$

τ, the degree of grafting, is given in mol%. Modified poly(acrylic acid)s and poly(sodium acrylate)s are, respectively, noted τH and τNa. Characterizations of modified polymers are presented below but details of the grafting reactions will be presented in separate papers. However, it is important to notice that the chemically grafted alkyl chains are probably randomly distributed along the polymer backbone since we have used a synthesis procedure close to that used in the case of low hydrophobically modified poly(sodium acrylate)s [17]. Both the 30H and 40H hydrophobically modified poly(acrylic acid)s were directly obtained by acidification of the corresponding poly(sodium acrylate)s. The degree of grafting was determined by ^{13}C NMR spectroscopy, elemental analysis and carboxylate groups titration. Aqueous solutions were prepared with double-distilled deionized water with a Milli-*Q* system (Millipore); *n*-dodecane supplied by Prolabo was used as oil without purification. Polymer concentration in emulsions is equal to 0.5% (w/v). 0.05 g of polymeric emulsifier were dissolved in the appropriate amount of water (or oil) by gently stirring the solution for 24 h. The volume fraction of *n*-dodecane in emulsions, ϕ, was adjusted by adding to the polymer solution the required amount of *n*-dodecane (respectively, water). An emulsion with $\phi = 0.7$ is noted W3D7 (30% v/v water, 70% v/v oil). The two phases were left in contact at rest for 24 h. Oil and aqueous phases were mixed up for 5 min at 24 000 rpm (ambient temperature) using a rotor–stator type of disperser (Heidolph DIAX 600). Total volume of emulsions is 10 ml. Electrolyte is sodium nitrate ($NaNO_3$). The type of emulsions was determined by conductivity measurements and dilution tests.

Results and discussion

Characterization of copolymers

Modified copolymers with various degrees of grafting were synthesized: five poly(sodium acrylate)s, 20Na, 30Na, 40Na, 60Na, 80Na and two poly(acrylic acid)s, 30H and 40H. As shown in Table 1, the three methods used to determine the grafting degree are in good agreement. With elemental analysis, the degree of grafting was calculated either from the carbon and sodium atoms content or from the nitrogen and sodium atoms content. Both values agree well with each other. Solvent conditions are also reported in Table 1. The values in brackets correspond to the mol% of dodecylamine introduced into the reactor to perform the syntheses. Results clearly indicate that the hydrophobic chains were grafted with a yield of about 100%. The purification and hence the characterization of the 80Na copolymer could not be suitably completed. However, as shown further, it is clear from the emulsion-type diagram, that the 80Na copolymer is, as expected, the most hydrophobic poly(sodium acrylate) of the series. Finally, less than 70 ppm of sodium atoms were detected by elemental analysis for both the 30H and 40H copolymers indicating quantitative transformation of carboxylate groups into carboxylic acid groups.

Macroemulsion type

For each copolymer a large number of emulsions was prepared at various oil volume fractions and sodium

Table 1 Characterization of copolymers

	Elemental analysis		^{13}C NMR	COONa titration
	C and Na	N and Na		
20Na (21%)	23	23	19 D_2O	21 H_2O
30Na (32%)	32	33	33 D_2O/MeOD 80/20	33 H_2O/MeOH 80/20
40Na (42%)	40	41	41 D_2O/MeOD 70/30	45 H_2O/MeOH 70/30
60Na (62%)	64	65	60 C_6D_6/MeOD 80/20	60 H_2O/MeOH 70/30

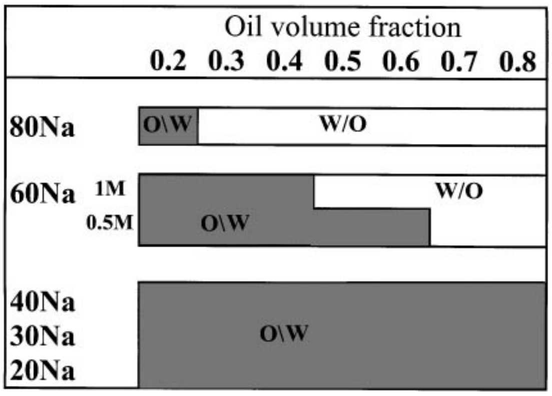


Fig. 1 Emulsion type diagram. With the 20Na, 30Na, 40Na and 80Na copolymers, the type of emulsions remains unchanged over a broad range of salt ($NaNO_3$) concentrations: 10^{-3}, 0.1, 0.5 and 1 M; In the case of the well-balanced amphiphilic polyelectrolyte, 60Na, the emulsion type changes from O/W to W/O between 0.5 and 1 M. (More details are given in Fig. 2)

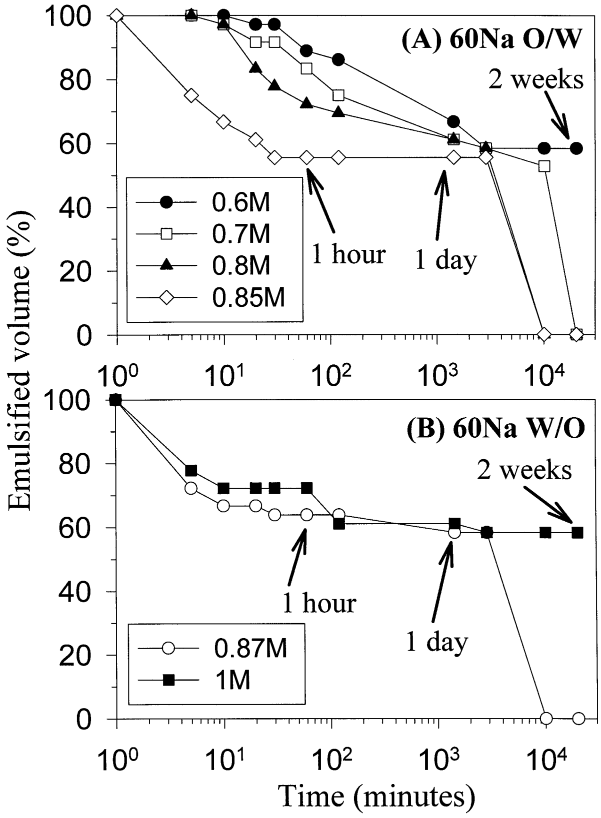


Fig. 2 Stability behavior of W5D5 emulsions at various salt ($NaNO_3$) concentrations (indicated above) around the inversion point (copolymers were first dissolved in water): (A) Stability of direct emulsions decreases with increasing salt activity; (B) Stability of inverse emulsions increases with increasing salt concentration

nitrate concentrations. As shown in Fig. 1, copolymers with τ up to 40 mol% lead exclusively to the formation of O/W emulsions regardless of oil volume fraction. Simply, W/O emulsions cannot be obtained with these too hydrophilic copolymers. The situation appears to be quite different with the 80Na copolymer since W/O liquid–liquid dispersions are mostly formed even at both low ϕ and $NaNO_3$ concentration. An original intermediate behavior is found with the well-balanced 60Na polyelectrolyte. At salt concentration up to 0.5 M, emulsions are water and oil continuous, respectively, for $\phi \leq 0.6$ and ≥ 0.7. A larger W/O domain is observed upon increasing electrolyte concentration to 1 M. For example, at oil volume fractions of 0.5 and 0.6, direct emulsions are formed at $NaNO_3$ 0.5 M whereas inverse dispersions are obtained at 1 M. More precisely, Fig. 2 displays stability behavior of W5D5 emulsions at electrolyte concentrations close to the inversion point. The stability of the dispersion samples was assessed by measuring volumes of emulsions (within an error of 5%) remaining at different times of observation. Due to breakdown mechanisms, the emulsified volume is only a fraction of the total volume. Clearly, increasing salt concentration from 0.6 to 0.85 M causes the destabilization of W5D5 direct emulsion samples (Fig. 2A). At concentration of 0.8 and 0.85 M, total coalescence was achieved within one week. Complete phase separation of emulsions into two phases occurs two weeks after sample preparation at a concentration of 0.7 M while at lower salt concentration, 0.6 M, the emulsified volume is still around 60%. Further increase in $NaNO_3$ concentration (0.87 M) leads to the formation of inverse emulsions which phase separate within one week (Fig. 2B). At 1 M, W/O emulsions become more stable and an emulsified volume close to 60% is again measured two weeks after sample emulsification. Figure 3 illustrates the effect on the emulsion type of changing the sodium carboxylate groups into

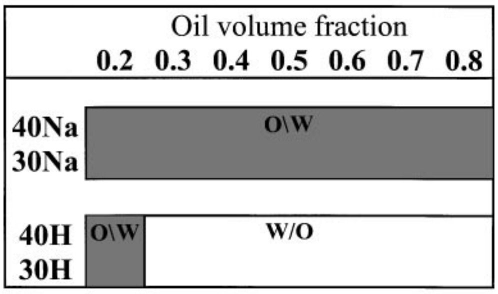


Fig. 3 Effect of changing the carboxylate groups into carboxylic acid groups on emulsion type. Sodium nitrate concentration is 10^{-3} M. Copolymers were first dissolved in oil

carboxylic acid groups at constant salt concentration (10^{-3} M). In contrast with the 30Na and 40Na hydrophobically modified poly(sodium acrylate)s which yield exclusively direct emulsions, the corresponding poly(acrylic acid)s provide inverse emulsions over a broad range of oil volume fractions hence suggesting pH as a parameter to control emulsion type.

To summarize, the degree of grafting (copolymer structure), pH and ionic strength are suitable variables to change the hydrophile–lipophile properties of the system and hence, to tune the type of emulsion. The copolymer with $\tau = 60$ mol% exhibits the properties of a well-balanced amphiphilic polyelectrolyte. With this new type of polymer, both stable O/W and W/O emulsions are able to form upon changing salt activity. To complete this work, it is certainly worth finding other field parameters (length of hydrophobic chain is an example) to create a HL balance scale for polymers. Moreover, this work provides convenient macroscopic model systems for studies of the conformation of the copolymers at liquid–liquid interfaces since, as suggested from recent theoretical considerations, the effect of any parameters that are able to modify the HL properties of the system (temperature, oil chain length, type or size of both hydrophilic and hydrophobic moieties of surfactant, electrolyte and cosurfactant type and concentration) are all reflected in the change of the monolayer spontaneous curvature which in turn determine whether the dispersion formed will be water or oil continuous [9].

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