Characterization of hydrocarbon and fluorocarbon microdomains formed in aqueous solution of associative polymers: A molecular probe technique

Krzysztof Szczubiałka [a], Łukasz Moczek [a], Agnieszka Goliszek [a],
Maria Nowakowska [a,*], Anton Kotzev [b], André Laschewsky [c]

[a] *Faculty of Chemistry, Jagiellonian University, 30-060 Kraków, Ingardena 3, Poland*
[b] *Université Catholique de Louvain, Department of Chemistry, Place L. Pasteur 1, B-1348 Louvain-la-Neuve, Belgium*
[c] *University of Potsdam, Department of Chemistry, Karl-Liebknecht-Str.24-25, D-14476 Potsdam-Golm, Germany*

Abstract

Fluorocarbon associative polymers of the polysoap type were studied using two fluorescent probes, 1-octanoylpyrene (OcPyH) and 1-perfluorooctanoylpyrene (OcPyF). In aqueous solution the polymers formed hydrophobic domains composed of hydrocarbon, fluorocarbon or both types of polymeric side chains, which could solubilize the probes. This resulted in the appearance of new fluorescence emission bands and changes in the fluorescence polarization of the probes. The differences in the solubilization properties of the polymers are discussed.
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1. Introduction

Hydrocarbons and fluorocarbons are strongly incompatible [1]. That is manifested as the phase separation of mixtures of liquid hydrocarbon and fluorocarbon compounds. In the case of hydrocarbon and fluorocarbon surfactants that incompatibility may lead to the formation of two kinds of the micelles, as was theoretically predicted by Mysels [2]. Shinoda further found that at least eight carbons are required for the formation of the separate fluorocarbon and hydrocarbon micelles to occur [3]. On the other hand, some studies on mixtures of hydrocarbon and fluorocarbon surfactants have shown that they are miscible, at least partially [4]. For yet another fluorocarbon/hydrocarbon systems controversial conclusions have been reached. For example, for the sodium dodecanoate–sodium perfluorooctanoate system, some groups concluded that both surfactant

mix within the micelles [3,5] while others found indications of demixing in this surfactant system [6]. It seems that the factors favoring the formation of separate fluorocarbon and hydrocarbon domains, are identical charges of the head groups and different length of the hydrocarbon and fluorocarbon chains [7].

Fluorocarbons are more hydrophobic than their hydrocarbon analogues; one CF_2 group corresponds to about 1.7 CH_2 group [8] as far as the hydrophobic effect is concerned. Other differences between fluorocarbon and hydrocarbon surfactants are that the former, as a result of greater stiffness and volume, tend to form aggregates with smaller curvature (e.g. cylindrical) and have lower surface energy [1,9].

There is a growing interest in systems where both hydrocarbon and fluorocarbon are present. A particularly interesting example of such systems are polymers which form multicompartment polymeric micelles (MCPM) [10]. The literature data on MCPM systems are, however, scarce. One such was obtained by micellar terpolymerization of acrylamide with both hydrocarbon and fluorocarbon

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* Corresponding author. Tel.: +48 12 6632250; fax: +48 12 6340515.
E-mail address: nowakows@chemia.uj.edu.pl (M. Nowakowska).

polymerizable surfactants [11]. The content of hydrocarbon and fluorocarbon chains in the polymers obtained was, however, very low (about 1 mol.%), and the authors did not compare their capability to solubilize hydrocarbon and fluorocarbon compounds. Another MCPM system was obtained by both statistical and block copolymerization of cationic ionenes with a high content of hydrocarbon and/or fluorocarbon side chains [12]. From viscometric studies, the authors found that the statistical copolymers with hydrocarbon and fluorocarbon side chains tend to associate intermolecularly to avoid unfavorable interactions between unlike hydrophobic chains and to maximize interactions of like chains. But the block copolymers with blocks composed of hydrocarbon and fluorocarbon chains tend to associate intramolecularly with the formation of distinct hydrocarbon and fluorocarbon domains. It was found that the block copolymer showed higher solubilizing power than the statistical one towards both hydrocarbon and fluorocarbon probes; the solubilizing power of the block copolymer was always significantly higher than the average of the two respective homopolymers. The authors concluded that the statistical copolymers form mixed hydrocarbon/fluorocarbon domains while the block copolymer associates forming multicompartment micelles containing separate hydrocarbon and fluorocarbon domains. This was corroborated by ^{1}H NMR and ^{19}F NMR studies [12]. Most recently, a mixed-arm star ABC terpolymer made of a hydrophilic poly(ethylene oxide) arm, a hydrophobic hydrocarbon polymer arm, and a hydrophobic perfluorinated polyether was synthesized, and the large multicompartment micelles formed in water were visualized by Cryo-TEM [13].

The polymers studied in this paper (Scheme 1) were synthesized by classical free radical polymerization using 2,2′-azobisisobutyronitrile (AIBN) as initiator (homopolymers and statistical copolymers) or a two-step reversible addition fragmentation chain transfer polymerization (RAFT) (block polymer) [14]. Previous studies on these polymers suggest that there is limited partial miscibility of the fluorocarbon and hydrocarbon microdomains. It was found from ^{19}F NMR spectra that the fluorocarbon microdomains are almost solid which may decrease their solubilization capacity. The purpose of the present paper was to study the ability of the above polymers to solubilize hydrocarbon and dual hydrocarbon/fluorocarbon compounds using fluorescence probes and to characterize the hydrophobic domains formed by these polymers. For this purpose two fluorescent probes were synthesized, the hydrocarbon one being a new variant.

2. Results and discussion

2.1. Polymers

The polymers studied were polysoaps with a "head type" geometry, i.e. the monomers ("surfmers") in these polymers are attached to the polymer backbone at the hydrophilic head group. The hydrophobic groups in the polymers are hydrocarbon chains (Hs), fluorocarbon chains (Fs), or both. In the case of the polymers containing both hydrocarbon and fluorocarbon chains, a statistical (HsF) and a block (HbF) polymers were studied (Scheme 1).

2.2. Fluorescence probes

Two 1-alkanoylpyrene probes were used in the studies which were obtained via Friedel-Crafts acylation of pyrene. OcPyH (Scheme 1) is a hydrocarbon probe which should be solubilized best in the hydrocarbon polymeric domains. This paper describes the first use of OcPyH as a fluorescent probe, but the very similar 1-heptanoylpyrene, has been applied before in studies on hydrogen bonding in microaggregates and biological membranes [15]. Because 1-heptanoylpyrene and OcPyH differ only by one CH$_2$ group in the alkyl chain, it could be anticipated that OcPyH would have very similar spectroscopic properties to those of 1-heptanoylpyrene. The probe OcPyF, although of dual hydrocarbon/fluorocarbon character, is expected to be preferentially solubilized in fluorocarbon polymeric domains due to the long fluorocarbon side group. There are only a few papers describing the use of OcPyF (Scheme 1) as a fluorescent probe in the studies of fluorinated surfactants and polymers [11,16–20].

2.3. Fluorescence studies using OcPyH

1-Acyl derivatives of pyrene are used as fluorescent probes sensitive to the polarity of the solvent and as probes for hydrogen bonding in biological systems. These compounds possess closely lying π-π* and n-π* states. In nonpolar solvents, the non-fluorescent n-π* state is the lowest singlet state, so the fluorescence quantum yield is low. Weakly interacting polar solvents (e.g. methanol) decrease the energy of the fluorescent π-π* states due to their large transition dipole moments, while strongly interacting polar solvents (e.g. trichloroacetic acid) increase the energy of the n-π* due to ground state hydrogen bonding. It was suggested that a dielectric constant larger than 10 is required to invert the sequence of both states [21]. In fact, the quantum yield of the fluorescence of 1-acylpyrenes grows in polar solvents, and the fluorescence emission band becomes red-shifted. For instance, the fluorescence emission maximum of pyrene-1-aldehyde in cyclohexane is found at about 390 nm, in ethanol at 449 nm and in water at 475 nm [21]. The broad shape of this emission band is likely due to the conjugative effect of the carbonyl group which is planar with respect to the pyrene ring [22].

1-Acylpyrene derivatives described in the literature are, e.g. pyrene-1-aldehyde [21,23–25], tris-acetylpyrene derivative of a cryptand [22,26], pyrenyl-ketone-labeled amphipathic polypeptide [27,28], and benzyl 1-pyrenoate [29]. Increasing the length of the alkyl chain attached to the