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Polymerization in Nanostructured Media: Applications to the Synthesis of Associative Polymers

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Summary: Some recent developments obtained by free radical polymerization in nanostructured media are presented. The characteristic features of the confined media like the large overall interfacial area and the particular microenvironment are taken advantage to yield novel materials with interesting properties. The examples considered here include the synthesis of i) thermosensitive polyampholytes by polymerization in bicontinuous microemulsions, ii) ionomers by polymerization in inverse microemulsions and iii) multicompartment polymeric micelles by means of an aqueous micellar polymerization process. The characteristics inherent to each of these syntheses are discussed.

Introduction

Over the past years, we have become interested in free-radical polymerization reactions in nanostructured media, like micelles or microemulsions, with the aim of preparing functionalized water-soluble polymers carrying hydrophobic groups and/or ionic sites. Some characteristics features of these processes are the very large overall interfacial area (due to the small size of the droplets) and the particular microenvironment (like for example the difference in polarity between the bulk and the micellar phase). These characteristics can be capitalized upon to modulate the nature, number and size of the sites distributed along the hydrophilic backbone. It is thus possible to prepare polymers with widely different properties susceptible to be used in a number of applications.

Below, we describe some recent advances obtained in our group by means of three different processes of polymerization reactions in confined media.

I. Synthesis of stimuli-responsive polyampholytes by microemulsion polymerization

In the past years, there has been considerable interest in the use of materials that are stimuli-responsive, i.e. whose properties can be varied by tuning external parameters such as

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temperature,[1] pH,[2] ionic strength,[3] or shear rate.[4] In this respect poly(*N*-isopropylacrylamide) (PNIPAM) which exhibits a well-defined lower critical solution temperature (LCST) in water around 32°C is one of the most studied temperature-responsive polymers.[5-8] Also of particular interest are materials which respond to several stimuli either simultaneously or independently (e.g. pH, ionic strength and temperature). These materials can be obtained for example by copolymerization of NIPAM with an ionic monomer[9, 10] or by grafting PNIPAM side chains on an ionized polymeric backbone.[11] However, a major problem encountered in the study of copolymers prepared by free radical polymerization concerns the heterogeneity in composition of the full conversion samples. In general, the inhomogeneities are due to differences in the reactivity ratios of the monomers that produce a drift in the copolymer composition as the reaction proceeds. Over the last years, we have addressed extensively this problem; in particular, we have shown that polymerization reactions carried out in nanostructured media like micelles or microemulsions, together with an appropriate choice of the components, allows the synthesis of samples with a controlled architecture and well defined characteristics.[12-14]

In the present study, we have applied a free radical microemulsion polymerization process to the synthesis of NIPAM-based polyampholytes, the latter containing both negative and positive charged units on the same polymer chain. The three monomers investigated were the following: *N*-isopropylacrylamide (NIPAM, neutral), sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS, anionic) and 2-acrylamido-2-propanetrimethylammonium chloride (APTAC, cationic). The choice of these monomers was guided by the fact that they bear almost an identical polymerizable function, which should favor the formation of samples homogeneous in composition.

Let us recall that microemulsions are oil-water systems stabilized by an appropriate mixture of surfactants. They are thermodynamically stable and optically transparent due to the low size of the domains. They can be globular or bicontinuous (sponge-like structure).[15] Our recent studies have shown that free radical polymerization of various types of water-soluble monomers leads in all cases to an inverse microlatex, the latter consisting of polymer droplets swollen by water and dispersed in the organic continuous phase.[16]

1. Formulation and polymerization

In the past, we have devoted much effort to find an optimum formulation for monomer-containing microemulsions, so that it is compatible with an economical process, since the formation of a microemulsions requires more surfactant than a conventional emulsion. Our approach was based on the cohesive energy ratio concept which assumes a perfect chemical match between the partial solubility parameters of oil (δ_O) and surfactant lipophilic tail (δ_L), and of water and hydrophilic head.[16-19] Under these conditions, one gets the following relationship:

$$HLB_0 = 20\ \delta_L^2 / (K + \delta_L^2) \qquad (1)$$

where HLB_0 is the optimum HLB (Hydrophile-Lipophile Balance) of the surfactant when $\delta_L^2 = \delta_O^2$ and K is a constant estimated at 210 for a W/O (water-in-oil) emulsion. It is thus possible to calculate the required HLB for a given oil. This criterion led us to select the following experimental conditions for the microemulsion based on NIPAM/NaAMPS/APTAC monomer feed (20/60/20):

- Oil: Isopar M ($\delta_O = 7.79\ (cal/cm^3)^{1/2}$)
- Aqueous phase / oil weight ratio = 1
- Monomer / water weight ratio in the aqueous phase = 0.78
- Surfactants: mixture of sorbitan sesquioleate (Montane 83, HLB = 3.7) and of polyoxyethylene sorbitan hexaoleate with 50 ethylene oxide residues (HLB = 11.4). The solubility parameters of the lipophilic tails of these surfactants are equal (same oleate tail, $\delta_L = 7.87\ (cal/cm^3)^{1/2}$) indicating complete miscibility. This value is very close to that of the paraffinic oil.

Figure 1 represents the percentage of surfactants required for the formation of the microemulsion containing the NIPAM/NaAMPS/APTAC monomer mixture as a function of the HLB number. The curve delineates the transition between a turbid emulsion and an optically transparent microemulsion. It can be seen that microemulsions are found in a HLB domain ranging between around 10.6 and 11.3. The curve exhibits a minimum, S_{min} for an optimum HLB value, HLB_{opt}. Note also the quite low surfactant concentration needed for the formation of clear systems ($S_{min} \approx 7$ wt%) in spite of the large proportion of monomers incorporated.

The HLB values are higher than those classically used in inverse emulsion polymerization (HLB ≈ 4-6), and are indicative of microemulsions with a bicontinuous structure, as shown by previous studies performed on other systems.[16, 18] The formation of microemulsions with a bicontinuous structure can be ascribed to the presence of monomers in large proportions in the systems, which affects the HLB and the interfacial properties. The role of the monomers was thoroughly investigated by our group for other monomer pairs.[18, 20, 21] It was found that the water-soluble monomer usually acts as a cosurfactant, leading to a considerable extent of the microemulsion domain in the phase diagram. For example, the cosurfactant role of NaAMPS was confirmed by surface tension experiments.[20] A direct consequence of this effect is an enhancement of the flexibility and fluidity of the interface, which favors the formation of a bicontinuous structure.

The high HLBopt values observed are also partly due to the electrolyte character of the charged monomers.[16, 21] Addition of a salting-out type electrolyte like those studied here (NaAMPS, APTAC) leads to an optimum HLB value larger than what would be obtained in the absence of salt. The salting-out effect provokes a decrease in the solubility of the ethoxylated surfactants in water. It is therefore necessary to shift the HLB to higher values in order to counterbalance the solubility decrease, for an optimum microemulsification.

The optimal conditions defined in the formulation of the polymerizable microemulsions are those needed to promote a clear and stable microlatex. The free radical polymerization was initiated with a redox initiator (cumene hydroperoxide / sodium metabisulfite) at 20°C. The size of the dispersed particles in the final system was determined by quasi-elastic light scattering experiments and was found equal to d = 85nm.

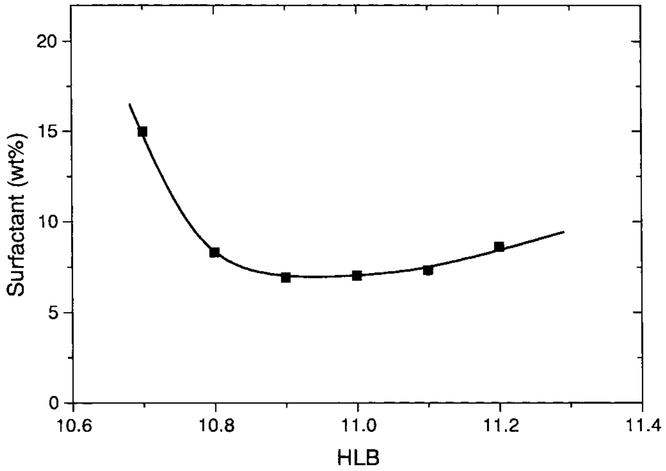

Figure 1. Percentage of surfactants required for the formation of a microemulsion versus HLB for a NIPAM/NaAMPS/APTAC 20/60/20 monomer feed.

2. Copolymer characteristics

The weight average molecular weight of the terpolymer was determined by light scattering As expected for polymerization reactions in heterogeneous media, its value is high and of the order of 5×10^6.

As the solution properties of copolymers are very sensitive to the heterogeneity in composition, it was important to evaluate the latter parameter for the system investigated here. This determination is particularly relevant for polyampholytes since previous experimental and theorical studies have shown that their conformations and properties were directly related to their monomer sequence distribution.[22-24] We have then followed the evolution of the terpolymer composition with conversion; the degree of conversion was determined gravimetrically and the composition was obtained by elemental analysis. The average terpolymer composition-conversion data are reported in Figure 2. It can be seen that the terpolymer composition values determined at various degrees of conversion are close to those of the monomer feed (dotted lines), within the experimental errors of the elemental analysis. This is strongly in favor of terpolymers homogeneous in composition.

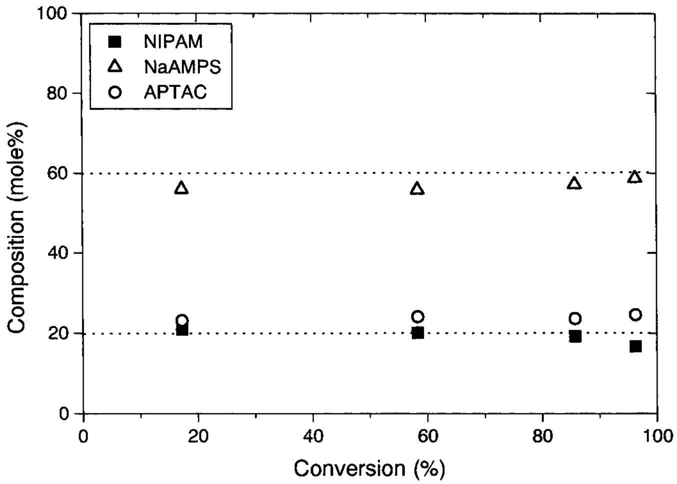

Figure 2. Terpolymer composition versus conversion for a NIPAM/NaAMPS/APTAC system (experimental data points) with a monomer feed composition of 20/60/20 (dotted lines).

This result has to be compared to the data obtained by S. Neyret et al. for an ampholytic terpolymer, also prepared by microemulsion polymerization but based on monomers with different polymerizable groups (Figure 5 of ref. [25]). A significant drift in composition was observed, in striking contrast with the present data, confirming that the choice of monomers is of prior importance in terpolymerization reactions, regardless of the type of process used.

II. Synthesis of ionomers with a controlled microstructured by inverse microemulsion polymerization

The same process as that described in section I, can be used to prepare ionomers, which are hydrophobic polymers containing a few ionic sites capable to associate in organic solvents to form ion-pairs, multiplets, etc...[26] However in this case, the two monomers are microphase segregated and not located in the same water domains as before. The starting system is an inverse globular microemulsion stabilized by AOT (Aerosol OT, sodium bis-2-ethylhexyl-sulfosuccinate). This surfactant is known to form water-pools when dispersed in an organic medium and the polymerization of water-soluble monomers, e.g. acrylamide, in the water-pools has been the subject of several studies.[19, 21, 27-29] In the present case, the ionic monomer, sodium acrylate (NaA), is encapsulated within the water droplets whereas the hydrophobic monomer, methylmethacrylate (MMA) is solubilized in the organic continuous phase (toluene) together with the initiator (AIBN, azo-bis-isobutyronitrile) (see Figure 3 and ref. [30]). Note the small amount of ionic monomer used in the overall monomer feed (~1-2 mol%). This particular process is expected to lead to multiblock ionomers, i.e. copolymers containing a few ionic blocks along the hydrophobic backbone: indeed, when a growing radical formed in the continuous phase encounters a droplet, it should add all of the ionic NaA molecules located in the water-pool, forming a small ionic block whose length corresponds as a first approximation to the number of ionic units in the droplet, N_H. Let us mention that hydrophobically modified water-soluble polymers with a multiblock structure were successfully prepared by using the "mirror" image of this process (i.e. an aqueous micellar medium, see for example [14] and references therein) but to our knowledge this is the first example described in the literature for the synthesis of ionomers with a multiblock structure. An attractive feature of the process is that, for a given hydrophobe / ionic monomer ratio, it is possible to tune the length of the ionic block of the ionomer by adjusting the initial number of ionic monomers per water-droplet (N_H). It follows that copolymers of same composition but different microstructure can be prepared this way.

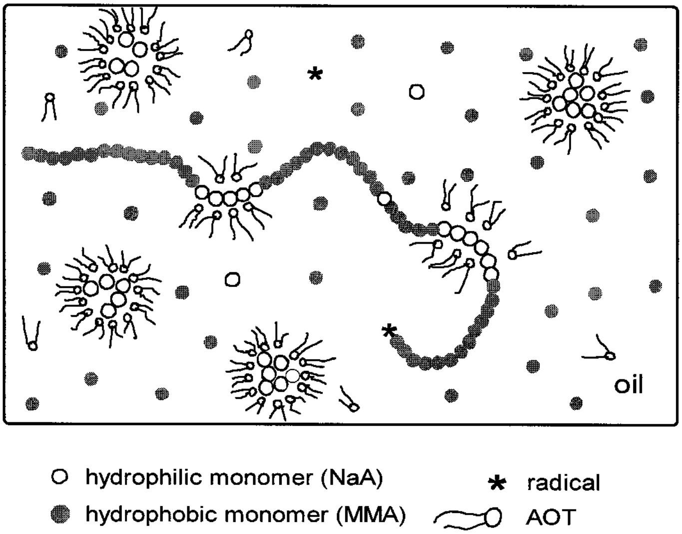

Figure 3. Schematic representation of the copolymerization process in inverse microemulsion.

We have investigated a possible effect of the microstructure of ionomers on their macroscopic properties in the solid state by Differential Scanning Calorimetry (DSC). In this respect, a series of PMMA-based ionomers with different N_H ($1 < N_H < 4$) and a weight-average molecular weight of about 40 000 was prepared. The ionomers were obtained in their Na-salt form and converted thereafter in Ca-salts. In Figure 4 are reported the values of the glass transition temperature, Tg, for a series of PMMA-based ionomers versus ion content. Several observations can be made:

i) Na ionomers: Tg increases with increasing ion-content. ii) Ca ionomers: Tg is always higher than that of the corresponding Na ionomer. iii) for a fixed ion-content, the Tg of the Ca ionomers depends on their microstructure: the longer the ionic blocks, the lower the Tg value. i) represents general properties observed for ionomers,[26] ii) was found for various ionomer systems.[26, 30, 31] As for the third point, we can conclude that the micellar polymerization technique allows the synthesis of Ca ionomers with a glass transition temperature adjustable through the ionomer

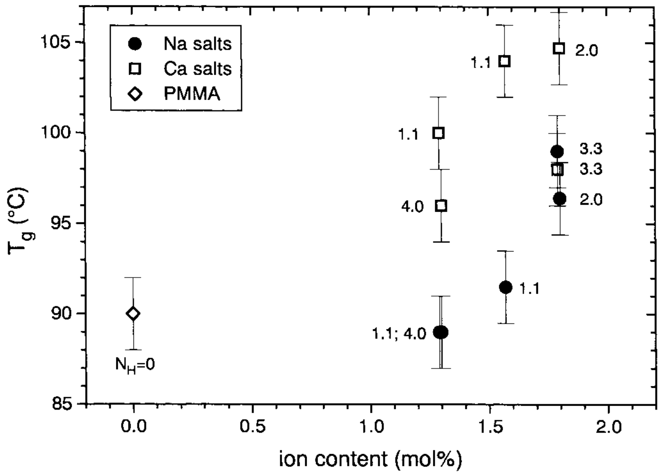

Figure 4. Glass transition temperature versus ion content for PMMA-based ionomers. (data points labels refer to the value of N_H)

microstructure. This microstructure effect can be explained by the divalent nature of the Ca ions. In the case of an ionomer with isolated ionic units and carrying only one anionic charge per unit, the ionic sites must find an inter- or intra molecular counterpart, when neutralized with Ca^{++} ions. This leads to an increased crosslinking and consequently to a higher Tg. On the contrary, a blocky distribution of the ionic groups opens the possibility for the Ca ion to neutralize the charge within the same ionic block and fewer crosslinks with other chains may be formed, resulting in a lower Tg. As for Na ionomers, such an effect of the microstructure is not observed nor expected as Na^+ is monovalent.

Although these results are preliminary, they demonstrate the feasibility of an inverse micellar copolymerization process for the synthesis of multiblock ionomers. Further work on systems containing higher ionic contents and longer ionic blocks should allow one to obtain ionomers with enhanced microstructure effects.

III. Synthesis of multicompartment polymeric micelles by micellar polymerization

The third example described in this paper concerns polymerization reactions carried out in direct micellar systems, i.e. systems where the continuous phase is water instead of an organic solvent (as in sections I and II). The motivation of these studies was the synthesis of water-soluble polymers which associate in water via hydrophobic interactions. These associating polymers consist generally of a water-soluble polymer containing a very small percentage of hydrophobic units (1-3 mol%). In aqueous solution, the hydrophobic groups associate to build up a transitory three-dimensional network that induces a strong increase in viscosity and this particular behavior is of great technological interest in a large number of applications.[32] Also the inter- or intramolecular interactions which take place lead to the formation of hydrophobic microdomains and this characteristic can be used for the encapsulation of hydrophobic compounds. The cartoon represented in Figure 5 resembles that shown in Figure 3 for the synthesis of ionomers, except that the water-soluble monomer (acrylamide, AM) is now dissolved in the aqueous continuous phase and the hydrophobe(s) is not encapsulated within micelles but is itself an amphiphilic monomer, i.e. a surfactant with a polymerizable group

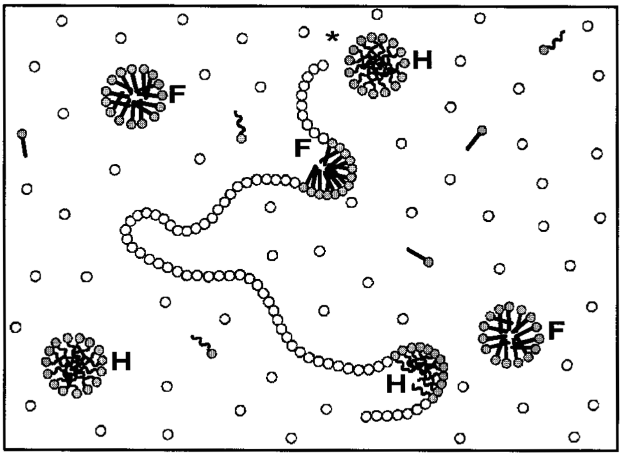

Figure 5. Schematic representation of the micellar copolymerization process of a water-soluble monomer (O) with hydrocarbon (H) and fluorocarbon (F) polymerizable surfactants.

(surfmer). The mechanism of polymerization is similar to that described in section II but the length of the hydrophobic blocks is longer than the length of the ionic blocks of ionomers since it corresponds roughly to the aggregation number of the surfmer. The structure of these copolymers was investigated by our group in detail,[33] they have a polysoap-like structure essentially controlled by intramolecular interactions and similar to a string of beads where the beads are the covalently linked hydrophobic microdomains randomly distributed along the hydrophilic string.

Recently, we have extended this process to the formation of multicompartment polymeric micelles (MCPM).[34] The idea, based on a concept developed by H. Ringsdorf,[35, 36] was to graft on the same hydrophilic backbone, hydrophobic microdomains of different nature and strongly incompatible (for example hydrocarbons and fluorocarbons (see Figure 5)). Such systems could be of great interest for drug delivery since one expects these domains to selectively solubilize fluorocarbon (F) and hydrocarbon (H) hydrophobic compounds and to release them selectively. The synthesis of MCPM was achieved by aqueous radical terpolymerization of acrylamide with both hydrocarbon (H) and fluorocarbon (F) surfmers in the micellar state. The selected H- and F-surfmers are:

$$CH_2{=}CHCON(C_2H_5)CH_2CH_2\overset{\oplus}{N}(CH_3)_2CH_2COOC_{16}H_{33}\ ,\quad Br^{\ominus}\ /\ Cl^{\ominus}$$

and $$CH_2{=}CHCONHCH_2CH_2\overset{\oplus}{N}(CH_3)_2CH_2COOCH_2CH_2C_8H_{17}\ ,\quad Br^{\ominus}$$

In order to maintain the solubility of the final terpolymer in water, the amount of surfmers in the monomer feed was restricted to 1-2 mol%. More details on the procedure can be found in ref. [34].

Surface tension experiments confirmed the existence of two types of demixed micelles in water prior to polymerization. An example is given in Figure 6. The single break points observed in the surface tension curves of the aqueous solutions of the pure H and F surfmers reflect the onset of the critical micellar concentration (cmc). The two break points in the surface tension curve of the H-F equimolar mixture can be interpreted as two cmc values related to two distinct types of micelles.

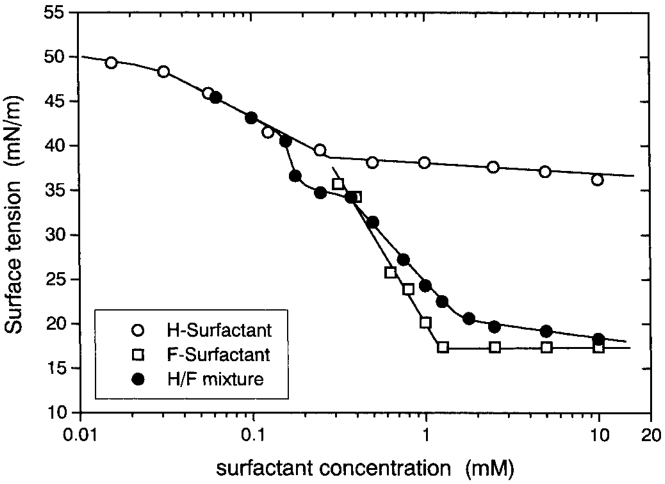

Figure 6. Surface tension versus surfactactant concentration for aqueous solutions of pure H-surfmer, pure F-surfmer and the equimolar H/F mixture.

Information on the microstructure of the terpolymers formed after polymerization could be obtained from fluorescence experiments using pyrene as a probe. The fluorescence emission spectra of some compounds and in particular the ratio of the first to the third emission peaks (I_1/I_3) of this probe are very sensitive to the microenvironment and the polarity of the medium; the lower the value, the greater the hydrophobicity of the medium. In Figure 7 is reported the I_1/I_3 ratio of free pyrene versus polymer concentration for aqueous solutions of copolymers and terpolymers of acrylamide containing the hydrocarbon and/or the fluorocarbon surfmers. High values of the I_1/I_3 ratio are observed for homopolyacrylamide (PAM) solutions, as expected for a water-soluble polymer. The behavior of the AM / F-surfmer copolymer is found to be quite similar to that of the unmodified PAM. This shows that pyrene has no or small interactions with the fluorocarbon domains. This result is typical of phobic interactions in pyrene-fluorocarbon systems.

On the other hand, the I_1/I_3 ratio decreases sharply for all copolymer and terpolymer samples that contain similar amounts of hydrocarbon side chains (≈ 0.4 mol %). This process starts already at polymer concentrations (≈ 0.02 mol%) which correspond to surfmer concentrations

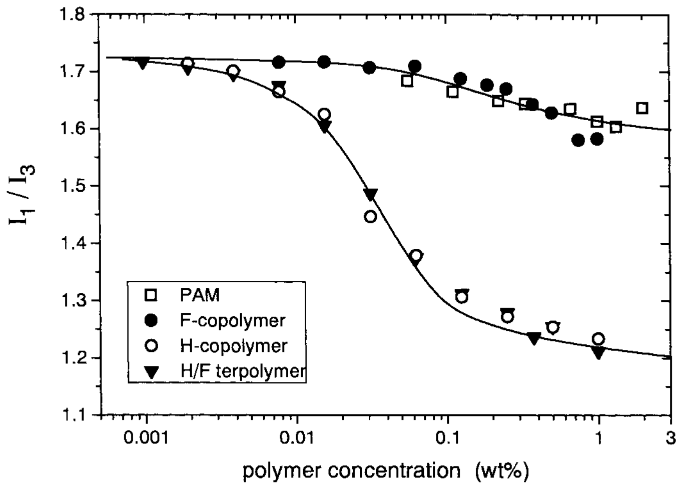

Figure 7. I_1/I_3 pyrene fluorescence ratio versus polymer concentration for various samples in aqueous solution.

about one order of magnitude lower than the cmc, suggesting the presence of long hydrophobic sequences in the polymers. The similar curves obtained for both H-copolymers and H/F-terpolymers are therefore strongly in favor of well-segregated F- and H-microdomains along the hydrophilic backbone with the string of beads-like structure schematically drawn in Figure 5.

Conclusion

The few examples reported here give an illustration of the various possibilities offered by polymerization reactions in nanostructured media. Here, we have restricted ourselves to the synthesis of functionalized polymers capable to associate in organic solvents via their ionic sites (case of ionomers) or in aqueous solution via their hydrophobic groups (case of thermosensitive polyampholytes or multicompartment polymeric micelles) but it is clear that the unlimited imagination of chemists can lead to discovery of many other polymers whose novel structures can be used to make materials with new properties.

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