Synthesis of Monoalkyl End-Capped Poly(2-methyl-2-oxazoline) and Its Micelle Formation in Aqueous Solution

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ABSTRACT: Novel monoalkyl end-capped poly(2-methyl-2-oxazoline) (POXZ-C_{12} and POXZ-C_{18}), with molecular weights varying from 5500 to 8500, were synthesized by the use of the "initiator method". The micellar behavior of these polymers in water was investigated by the fluorescence technique. Critical micelle concentrations are in the range of 0.007−0.4 g L^{-1} and are dependent on the hydrophilic/lipophilic balance. An aggregation number of 11 was determined for POXZ-C_{12}. The structural properties of the aggregates have also been investigated by viscometry. Intrinsic viscosities of these polymers have been compared to the ones of poly(2-methyl-2-oxazoline) (POXZ). The POXZ-C_{12} aggregates show similar compactness as POXZ precursor chains, whereas POXZ-C_{18} aggregates are more expanded. Addition of β-cyclodextrin (CD) has dissociated the aggregates, and the intrinsic viscosities of the CD end-capped chains have become comparable to the ones of POXZ precursor chains.

Introduction

Polymeric micelles derived from amphiphilic polymers in aqueous solution are of great interest due to their potential application in detergency, dispersion stabilization, foaming, emulsification, lubrication, separation technologies, drug delivery systems, and protection of microorganisms against mechanical damages in bioreactors.[1−7] Most amphiphilic polymers are block or graft copolymers based on poly(ethylene oxide) used as the hydrophilic moiety, and the hydrophobic moiety was made of poly(propylene oxide), polyesters, polystyrene, poly(amino acids), or polyalkanes.[8−12] Other amphiphilic copolymers can be made from poly(*N*-acylethylenimine) or poly(2-substituted-2-oxazoline). Indeed, cationic polymerization of 2-oxazolines provides a convenient, versatile method for producing linear poly(*N*-acylethylenimine) which become hydrophilic or hydrophobic by changing the nature of the acyl group.[13−16] The living character of the polymerization provides easy access to block copolymers by the sequential addition of different monomers. By utilizing these characteristics, some amphiphilic copolymers have been prepared.[17,18] Diblock copolymers were synthesized based on poly(2-ethyl-2-oxazoline) as the hydrophilic block and poly(L-lactide) or poly(ϵ-caprolactone) as the hydrophobic block.[19,20] Other diblock copolymers were synthesized based on poly(2-methyl-2-oxazoline) (POXZ).[21−23] This hydrophilic polymer contains an amide function in its unit (also present in proteins) which justifies its use in biomimetic polymer systems because it constitutes a pseudopeptide chain. Another interest in POXZ is that it shows comparable properties as poly(ethylene oxide), particularly its nontoxicity and its good biocompatibility,[24−27] and no immuno-response has been reported even in complex biological matrices.[26] Consequently, poly(2-methyl-2-oxazoline) is widely studied for biomedical applications such as drug-delivery systems and for the construction of artificial membranes.[28] Previously, we have reported the synthesis and the micellar structures of a diblock copolymer in selective solvents: the poly(isobutylvinyl ether-*b*-2-methyl-2-oxazoline).[29,30]

Another way to prepare an amphiphilic polymer is to modify an hydrophilic polymer with functional end groups by the use of functional initiators and/or terminating agents.[24,31−33] In this work, the method used to introduce functional end groups is the "initiator method". Poly(2-methyl-2-oxazoline) is employed as the hybrophilic polymer backbone, and a hydrophobic group is introduced at the initiation stage of polymerization of the monomer.

In this paper, the synthesis of the poly(2-methyl-2-oxazoline) having a hydrophobic group at one end (POXZ-C_n) is described in the first part. The alkyl end group (C_{12} or C_{18}) is structurally incorporated in the chain by the use of specific alkyl iodide initiator. The micellar characteristics of these POXZ-C_n polymers were investigated by fluorescence technique for cmc and aggregation number determination. The properties in aqueous solution of these amphiphilic polymers were investigated by viscometry.

Experimental Section

Materials. The monomer 2-methyl-2-oxazoline (Aldrich, Milwaukee, WI, purity 99%) was dried overnight over calcium hydride and purified by distillation under a nitrogen atmosphere. Acetonitrile (SDS, Peypin, France) was distilled over calcium hydride before use. Iodomethane (purity 99%), 1-iodododecane (purity 98%), and 1-iodooctadecane (purity 95%) were purchased from Aldrich and used as received. Methanolic KOH was prepared from methanol (SDS) and pellets of KOH used as purchased. Pyrene, *N*-dodecylpyridinium chloride (DPC), used in the fluorescence studies, and β-cyclodextrin were purchased from Aldrich.

Synthesis of Alkyl End-Capped Poly(2-methyl-2-oxazoline). The monomer 2-methyl-2-oxazoline has been polymerized in dry acetonitrile under dry nitrogen. Different alkyl iodides were used as initiator: iodomethane, 1-iodododecane, or 1-iodooctadecane. A typical procedure whith iodomethane as initiator is given as follows. To 30 mL of dried acetonitrile, 10 mL (1.18×10^{-1} mol) of 2-methyl-2-oxazoline was introduced and 0.12 mL (1.93×10^{-3} mol) of iodomethane was added. After stirring during 18 h, at 80 °C, the polymerization was stopped by pouring methanolic KOH into the

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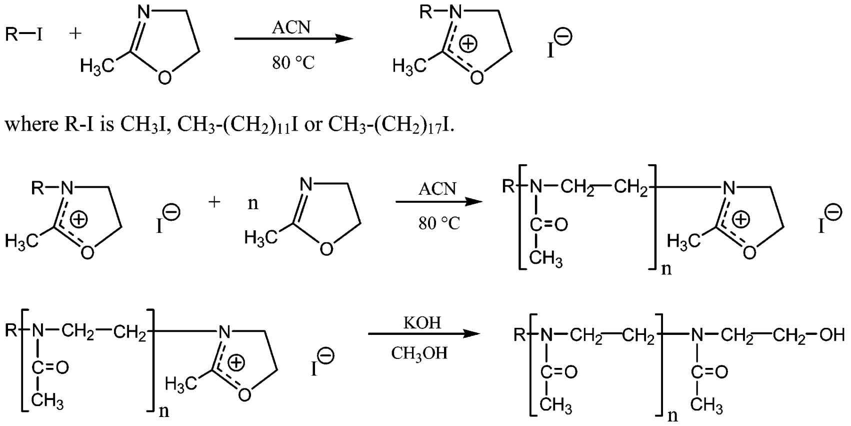
Scheme 1



where R-I is CH_3I, CH_3-$(CH_2)_{11}I$ or CH_3-$(CH_2)_{17}I$.

reaction mixture. The polymer was purified by precipitation in diethyl ether and then dried under vacuum. The other polymers with hydrophobic group were prepared similarly using 1-iodododecane or 1-iodooctadecane as initiator.

Kinetic Study. In the case of 1-iodooctadecane a kinetic study was carried out. Several POXZ-C_{18} polymers were synthesized with the same conditions (concentrations, temperature, solvent, etc.) in the same way as described above, but with reaction times varying from 1 to 48 h.

Analytical Techniques. The polymers were characterized by ^1H NMR and ^{13}C NMR on a Brüker Avance 300 spectrometer, in deuterated chloroform or deuterated water. Size exclusion chromatography (SEC) was performed on a chromatograph equipped with a pump P 100 (Spectra-Physics, Fremont, CA), a Rheodyne injector, and a set of two columns PL-aquagel OH-30 and OH-40 (Polymer Laboratories, Shropshire, UK). Two detectors were connected in series at the end of the columns: a differential refractometer RI 71 (Shodex, Japan) and a MiniDawn light scattering detector (Wyatt Technology, Santa Barbara, CA). The MiniDawn instrument (LS) uses a polarized semiconductor diode laser ($\lambda = 690$ nm) and measures the scattered light at three angles (45°, 90°, and 135°). The chromatographic analysis of polymers was done in aqueous 0.1 mol L^{-1} $LiNO_3$ solution after calibration of columns with a set of poly(ethylene oxide) (PEO) standards with a range of molecular weights from 200 to 645 000. The polymer solutions were prepared at concentration 10 mg mL^{-1}.

Fluorescence Measurements. Fluorescence spectra were measured, at 23 °C, on a SLM Aminco 8100 spectrometer. Pyrene was used as a fluorescent probe. A pyrene stock solution was prepared in dichloromethane at a concentration 6×10^{-4} mol L^{-1}. A first polymer solution was prepared by dissolving 0.2 g of polymer in deionized and filtered water (20 mL). The dilution of this first solution provides other polymer solutions of concentrations ranging from 0.2 to 10^{-5} wt %. To get sample solutions, a known amount of pyrene stock solution was added to each of a series of empty flasks, and dichloromethane was evaporated. The amount was chosen to give a pyrene concentration in the final solution of 6×10^{-7} mol L^{-1}. 3 mL of polymer solution was then added to the flask. After stirring the sample solutions 48 h at room temperature, the fluorescence spectra were recorded from 360 to 410 nm using slit openings of 0.5 mm, and the excitation wavelength was set at 336 nm. The emission intensities measured at 373 nm (I_1) and 384 nm (I_3), the first and third vibronic peaks in the fluorescence emission spectrum of pyrene, were used to calculate the ratio I_1/I_3.[34] In a second step, the decrease of the pyrene's fluorescence intensity as a function of the concentration of an added fluorescence quencher was measured. The used quencher was *N*-dodecylpyridinium chloride (DPC). An aqueous DPC stock solution was prepared at a concentration 5×10^{-2} mol L^{-1}. A polymer solution was prepared at a concentration 5 times larger than the critical micelle concentration (cmc). The sample solutions, containing pyrene and polymer, were prepared as previously. Directly into the cell, DPC stock solution and sample solution were introduced in varying amounts in order to increase the concentration of quencher. The pyrene concentration was sufficiently low that excimer formation could be neglected. The data were analyzed using the equation[35]

$$\ln\left(\frac{I_0}{I}\right) = \frac{[Q]}{[M]} \tag{1}$$

where I_0 and I are the fluorescence intensities in the absence and in the presence of quencher, respectively; [Q] and [M] are the molar concentration of quencher and micelles, respectively. When plotting $\ln(I_0/I)$ vs [Q], a straight line of slope 1/[M] is expected, and the aggregation number is determined by the following relationship:

$$N = \frac{C_{\text{alkyl}} - C_{\text{free alkyl}}}{[M]} \tag{2}$$

where C_{alkyl} is the overall concentration of alkyl group and $C_{\text{free alkyl}}$ is the concentration of free alkyl group which is approximated as the cmc.

Viscometry. The viscometric measurements were done by means of an Ubbelohde suspended level viscometer at 25 ± 0.1 °C. All the polymer solutions were prepared by weight in ultrapure water and filtered with 0.45 μm filters (Minisart RC 15, Sartorius, Hannover, Germany). The initial polymer concentration was close to 20 g L^{-1}, and the successive dilutions of polymer solution were directly done into the viscometer. The reduced viscosity η_{red} of the polymer was calculated from the formula

$$\eta_{\text{red}} = \frac{\eta - \eta_0}{\eta_0 C_{\text{p}}} \tag{3}$$

where η and η_0 are the viscosities of the polymer solutions and the solvent, respectively, and C_{p} is the polymer concentration expressed in g L^{-1}. The intrinsic viscosity [η] was determined by extrapolation of the reduced viscosity at zero concentration.

Results and Discussion

Synthesis and Characterization of POXZ-C_n.

Since its discovery, the mechanism of the cationic (or electrophilic) polymerization of 2-methyl-2-oxazoline has been studied in great detail.[16,36–39] The polymerization of 2-methyl-2-oxazoline is a clean reaction, which is not disturbed by chain transfer and termination. When iodomethane is used as initiator and acetonitrile as solvent, the propagating species have a structure of oxazolinium salt with iodide being a strongly nucleophilic counterion. The cationic polymerization proceeds via ring-opening isomerization, as shown in Scheme 1. The rate-determining step is the nucleophilic attack of monomer on oxazolinium iodide. The oxazolinium living

Table 1. Polymerization of 2-Methyl-2-oxazoline and Characteristics of Polymer POXZ-C$_n$

polymer	initiator	$[M]_0/[I]_0$ feed ratio	time (h)	yield (%)	M_n	$M_n{}^c$	DP^c	$M_w/M_n{}^d$
POXZ	CH_3I	90	18	95	7900^a			1.1
POXZ-C$_{12}$	$CH_3-(CH_2)_{11}I$	58	18	95	5500^b	5200	61	1.1
POXZ-C$_{18-1}$	$CH_3-(CH_2)_{17}I$	30	3	98	3200^b	3100	36	1.2
POXZ-C$_{18-2}$	$CH_3-(CH_2)_{17}I$	60	18	97	5400^b	4700	55	1.2
POXZ-C$_{18-3}$	$CH_3-(CH_2)_{17}I$	117	48	87	8500^b	8200	96	1.2

^{a} Estimated by SEC and light scattering detector. ^{b} From ^{1}H NMR. ^{c} From ^{13}C NMR. ^{d} From SEC-RI chromatogram.

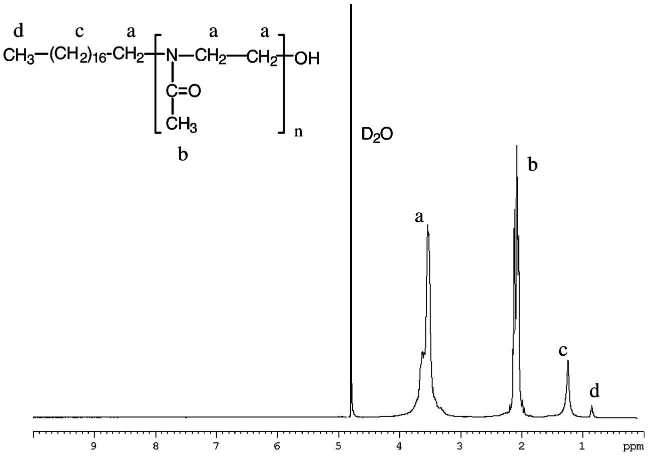


Figure 1. ^{1}H NMR spectrum of POXZ-C$_{18-1}$.

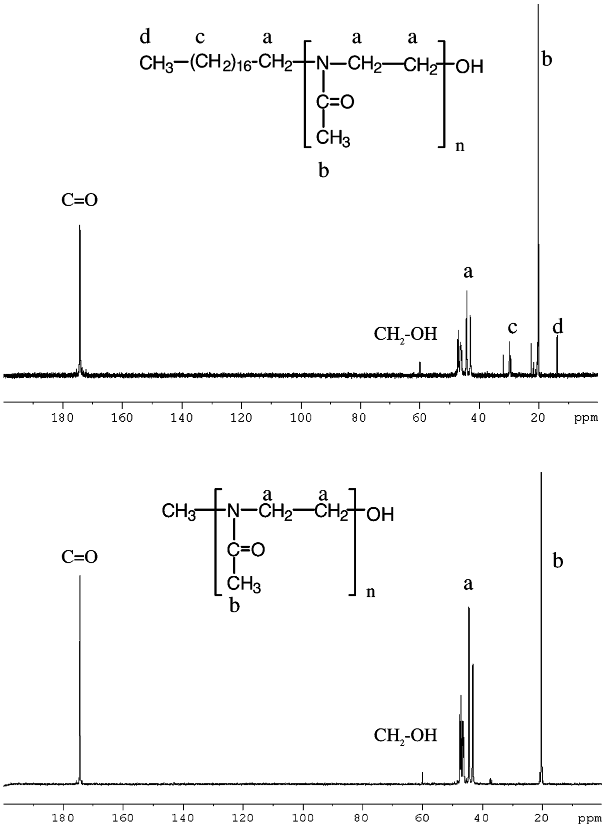


Figure 2. ^{13}C NMR spectra of POXZ-C$_{18-1}$ and POXZ.

end groups are terminated by methanolic KOH to introduce hydroxyl groups at the chain end.[20] The conditions of synthesis are reported in Table 1. Yields have been calculated after precipitation of polymers in diethyl ether. Each polymer was characterized by ^{1}H NMR, ^{13}C NMR, and SEC. A typical ^{1}H NMR spectrum of POXZ-C$_{18}$ polymer is shown in Figure 1, where characteristic peaks have been assigned. Molecular weights were determined from the peak integration ratios of methyl protons in POXZ repeating unit at 2.01 ppm and methyl protons of C$_{18}$ at 0.77 ppm. The ^{13}C NMR spectra of POXZ and POXZ-C$_n$ in Figure 2, as a representative example, show the characteristic resonance peaks of methylene linked to the hydroxyl group at the chain end. Quantitative ^{13}C NMR allowed the molecular weight determinations from peak integration ratio at 13.9 and 20.2 ppm for POXZ-C$_n$. A good agreement is obtained between the molecular weight calculated by ^{1}H NMR (for example, 5500 for POXZ-C$_{12}$) and ^{13}C NMR (5200 for POXZ-C$_{12}$). In the case of POXZ, the NMR molecular weight determinations could not be done since the terminal methyl group could not be isolated on the spectra. Instead of that, it has been analyzed by size exclusion chromatography in aqueous solvent. A first determination, based on PEO calibration curve and using a refractometric detector, gives M_n = 3500 and M_w = 4800 g mol^{-1} in the same range as the ones determined by NMR. Absolute molecular weights were also measured by a light-scattering detector (LS): M_n = 7900 and M_w = 8300 (M_w/M_n = 1.1). The molecular weights calculated from light-scattering detector are twice as high as those determined from PEO calibration curve. This discrepancy cannot be attributed to the presence of small amount of large molecular weight aggregates which could increase the scattered intensities because the refractometric and light scattering peaks are well superimposed. In fact, the POXZ chains seem to be more compact than PEO chains in aqueous solvent. POXZ-C$_n$ have also been analyzed by SEC. As it will been shown later, these polymers associate into micellar structures in aqueous solvents. However, the micellar aggregates are adsorbed in the prefilters, and the observed elution peaks reflect the unassociated polymers. Figure 3 shows the SEC chromatograms (RI) of the three POXZ-C$_{18}$ samples. It can be noticed that the distributions are quite narrow (M_w/M_n = 1.1−1.2), and the small peaks observed at high elution volume are due to presence of salts in aqueous eluent. POXZ-C$_n$ molecular weights have not been determined by chromatography because the concentrations of free chains are not known precisely. The polydispersity indexes M_w/M_n reported in Table 1 are between 1.1 and 1.2, giving as narrow molecular weight distributions as for POXZ. According to the molecular weights estimated from ^{1}H NMR, the degrees of polymerization were calculated and reported in Table 1. The values are in good agreement with the initial feed ratio of monomer/initiator, at complete conversion, which indicates that all the initiator was consumed during the polymerization.

In the case of polymerization using an initiator such as 1-iodooctadecane, a brief kinetic study was carried out. Among numerous kinetic studies previously achieved on polymerization of 2-substituted-2-oxazolines,[36,39−41] few have been made on the monomer 2-methyl-2-

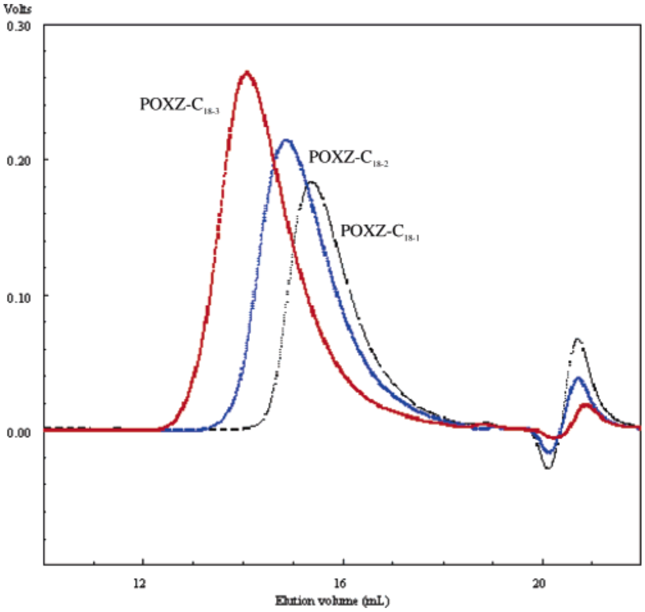


Figure 3. SEC-RI chromatograms of three POXZ-C_{18}.

oxazoline using CH_3I as initiator in acetonitrile[36] or in *N*,*N*-dimethylacetamide[39] or on the monomer 2-ethyl-2-oxazoline with iodobutane as initiator in chlorobenzene.[40] Reactions were run in a spectrometer, and ^1H NMR spectra were collected at programmed intervals as the polymerization proceeded to determine the concentration of each component.[36,40] The authors showed that early propagation stage was different than subsequent steps and identified rate constants for initiation (k_i), early propagation step (k_{p1}), and subsequent propagation stage (k_{pn}). In this work, only the rate constant of the subsequent propagation stage has been determined. Assuming that the initiator was consumed in a relatively early stage of polymerization as it is the case for iodomethane,[36] the rate of polymerization is given by eq 4:

$$-\frac{d[M]}{dt} = k_p[M][P^+] = k_p[M][RI]_0 \qquad (4)$$

where [M], $[P^+]$, and $[RI]_0$ are the concentration of monomer, propagating macromolecular chain, and initiator, respectively. An integration of eq 4 leads to

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_p[RI]_0 t \qquad (5)$$

The ratio $[M]_0/[M]$ has been evaluated from the yield. The kinetic plot of $\ln([M]_0/[M])$ vs reaction time (Figure 4) revealed a linear relationship which demonstrated first-order kinetics and suggested a living polymerization mechanism. From the slope of the linear plot, a polymerization rate constant of 13.3×10^{-4} L mol^{-1} s^{-1} was determined, assuming that each molecule of alkyl iodide initiated a macromolecular chain. The value obtained has the same order as previously reported rates[36] in the same solvent but at a lower temperature. The number-average molecular weight was plotted against conversion (Figure 5). A straight line can be drawn through these data points, implying that the molecular weight increases linearly with conversion and that chain transfer reactions are absent from the polymerization system. However, further investigations would be required to state that the system is a perfect living system.

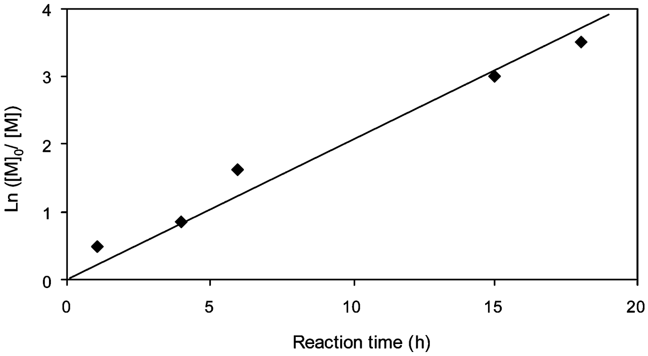


Figure 4. Kinetic plot of $\ln([M]_0/[M])$ vs reaction time for POXZ-C_{18}.

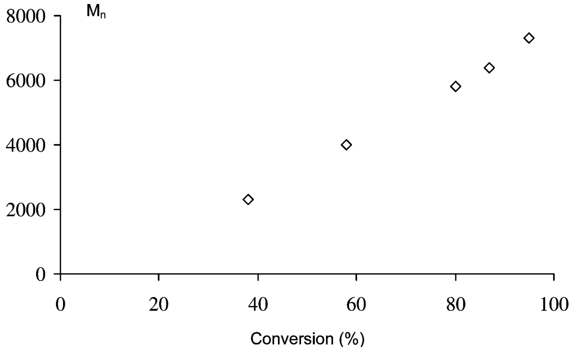


Figure 5. Plot of M_n calculated from ^1H NMR vs conversion for POXZ-C_{18}.

Fluorescence Measurements. The amphiphilic nature of the polymer consisting of hydrophilic POXZ and hydrophobic alkyl group at one end provides an opportunity to form aggregates or micelles in water. Information about micellization phenomena of the POXZ-C_n in dilute aqueous solution was obtained from steady-state fluorescence probe studies. A well-known method[34,35] is to use pyrene as a fluorescent probe since its solubility in water is very low, and it is preferably solubilized into hydrophobic microdomains like the micellar cores. In the first set of experiments, the variation of I_1/I_3 intensity ratios of the first and third vibronic peaks in the fluorescence emission spectrum of pyrene vs polymer concentration was used to follow the association process and to determine the critical micelle concentration (cmc) of polymer, by analogy with the cmc of surfactants.[34,42,43] The I_1/I_3 ratio is an index of the polarity of the pyrene microenvironment. In the presence of hydrophobic domains, I_1/I_3 decreases from 1.8 to 1.9 (aqueous environment) to 1.45 when the pyrene is located mainly in the micellar aggregates. A preliminary experiment was carried out with POXZ in order to check that the ratio I_1/I_3 remains constant at 1.9 whatever the polymer concentration. Figure 6 displays the variation of I_1/I_3 ratio vs polymer concentration for the different POXZ-C_{18}. When the polymer concentration increases, a gradual decrease of I_1/I_3 over a range of polymer concentrations of more than 1 decade is observed, revealing the formation of polydisperse hydrophobic aggregates.[43] The cmc is determined as the first fall of I_1/I_3 when pyrene starts to be included in micelles,[44] as shown by the intersection of the two lines in Figure 6. The results are reported in Table 2. When the molecular weight of POXZ-C_{18} increases, the cmc value is shifted toward a higher polymer concentration,

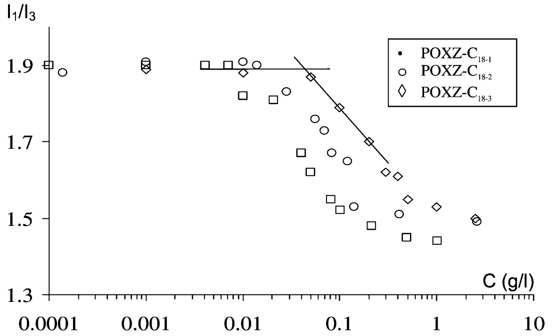


Figure 6. Variation of I_1/I_3 ratio vs polymer concentration for three POXZ-C_{18} samples (at 23 °C).

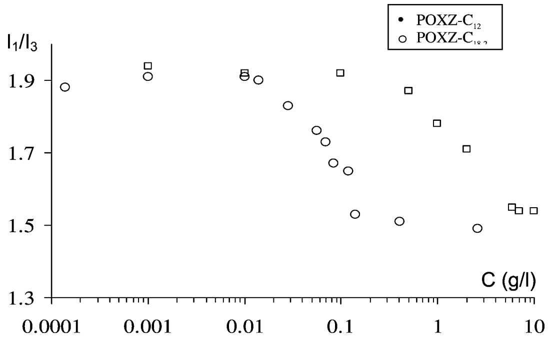


Figure 7. Variation of I_1/I_3 ratio vs polymer concentration for POXZ-C_{12} and POXZ-C_{18-2} (at 23 °C).

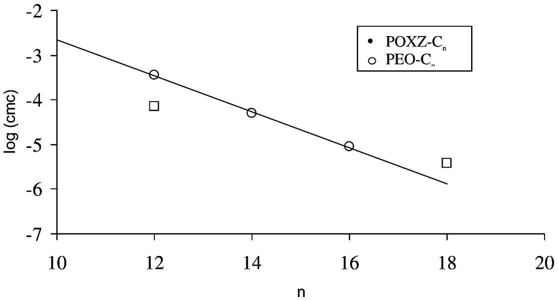


Figure 8. Plot of the logarithm of (cmc) vs alkyl chain length (n) for POXZ-C_n and PEO-C_n.[48]

Table 2. Critical Micelle Concentration (cmc) and Aggregation Number (N_{agg}) of Polymers at 23 °C

polymer	cmc (g L^{-1})	cmc (mol L^{-1})	N_{agg}
POXZ-C_{12}	0.4	7.3×10^{-5}	11
POXZ-C_{18-1}	0.007	2.2×10^{-6}	
POXZ-C_{18-2}	0.02	3.7×10^{-6}	6
POXZ-C_{18-3}	0.05	5.9×10^{-6}	6

which is in good agreement with the higher hydrophilicity of the polymer backbone. The comparison of POXZ-C_{18} with POXZ-C_{12} of identical hydrophilic backbone length is shown in Figure 7. As expected, the decrease of I_1/I_3 ratio occurs at a higher polymer concentration when the alkyl chain length is lower. Similar behaviors have been observed for alkyl end-capped poly(ethylene oxide)s[45] and hydrophobically modified polyacrylates[46] (smooth transitions, influence of alkyl chain length). A more specific comparison can be done with monoalkyl-terminated PEO[47,48] which are similar systems based on PEO instead of POXZ. The cmc (in mol L^{-1} units) of the two systems have been compared on the same graph (Figure 8). The values are in good qualitative agreement. However, the relative increase of cmc from POXZ-C_{18} to POXZ-C_{12} is 20, an order of magnitude lower than the relative increase observed for the corresponding PEO-C_n systems (250). This may be related to the difference of the polymerization indexes in the two systems (around 40 for the PEO-C_n, around 60 for the POXZ-C_n).

In the second set of experiments, aggregation numbers of the hydrophobic microdomains were determined from the decrease of the probe's fluorescence as a function of the concentration of an added fluorescence quencher.[35,43,49] The quencher used was *N*-dodecylpyridinium chloride (DPC). The aggregation numbers, determined from the results of static quenching experiments, are $N_{agg} = 11$ and $N_{agg} = 6$ (Table 2) chain ends per micelle for POXZ-C_{12} and POXZ-C_{18}, respectively, assuming all the DPC quenchers to be solved within the micelles. The aggregation numbers are quite lower than the ones determined for dialkyl-terminated poly(ethylene oxide): N_{agg} were in the range 20−60,[43,49] depending on the method used for the determinations and on the polymer characteristics (M_w and alkyl chain length). In the case of monoalkyl-terminated PEO, N_{agg} has been shown to vary linearly with the alkyl chain length from 16 (C_{11}) to 35 (C_{17}) at 20 °C.[47] Moreover, theoretical models for amphiphilic diblocks copolymers also predict an increase of N_{agg} with the length of the hydrophobic chain.[50]

In the case of POXZ-C_{12}, the aggregation number (11) is lower than the reported value for PEO-C_{11} (16).[47] This behavior can be again attributed to the larger hydrophilicity of the chains, the polymerization index of POXZ-C_{12} being 60 compared to 40 for PEO-C_{11}. The decrease of the aggregation numbers from POXZ-C_{12} to POXZ-C_{18} is contrary to the expected tendency. The low values determined for POXZ-C_{18} can be related to an experimental problem. Several conditions must be fulfilled to valid the fluorescence quenching method. One of them requires that the quenching rate constant must be very large compared to the inverse of the pyrene fluorescence lifetime. It implies that the pyrene and the quencher are close to each other. This should not be the case if the micellar aggregates were large or nonspherical. As will be seen below, the large intrinsic viscosity of POXZ-C_{18-2} also suggests that the C_{18} aggregates are expanded.

Viscosity of Polymers in Aqueous Solutions. To investigate the behavior of the polymer solutions, the intrinsic viscosity [η] was measured for each polymer. The results are reported in Table 3. In water, the intrinsic viscosity of POXZ-C_{12} is close to the one of POXZ, whereas the intrinsic viscosity of POXZ-C_{18} is twice. According to the fluorescence measurements, the concentrations used for viscosity measurements (concentrations 7−20 g L^{-1}) are larger than the cmc; [η] measured for POXZ-C_{12} and POXZ-C_{18} characterize then the aggregates.

To compare intrinsic viscosities of the alkyl end group polymers (POXZ-C_n) to the one of the precursor POXZ (same molecular weight but without alkyl termination), POXZ of molecular weights ranging from 1.7×10^3 to 1.1×10^4 have been synthesized. The molecular weights were determined by SEC and light scattering detector. Intrinsic viscosity measurements allowed to determine the Mark−Houwink coefficients K and a characterizing the molecular weight dependence of [η]: $[\eta] = KM_n^a$. At 25 °C, $K = 2.5 \times 10^{-4}$ and $a = 0.7$, showing that water is a good solvent for POXZ (Figure 9). Using this

Table 3. Intrinsic Viscosity of Polymers

	in water		in water + CD		
polymer	$[\eta]$ (L g^{-1})	$[\eta]_{prec}{}^{a}$ (L g^{-1})	$[\eta]_{mix}$ (L g^{-1})	$[\eta]_{POXZ}{}^{b}$ (L g^{-1})	$[\eta]_{POXZ-C_n/CD}{}^{c}$ (L g^{-1})
POXZ	0.013	0.013	0.0077	0.011	
POXZ- C_{12}	0.011	0.010	0.0071		0.0095
POXZ-C_{18-2}	0.026	0.010	0.0053		0.0071

[a] $[\eta]_{prec}$ calculated from Mark–Houwink relationship with M_n^{SEC-LS} for POXZ and M_n ^{1}H NMR for POXZ-C_n. [b] $[\eta]_{POXZ}$ calculated from eq 8. [c] $[\eta]_{POXZ-C_n/CD}$ calculated from eq 10.

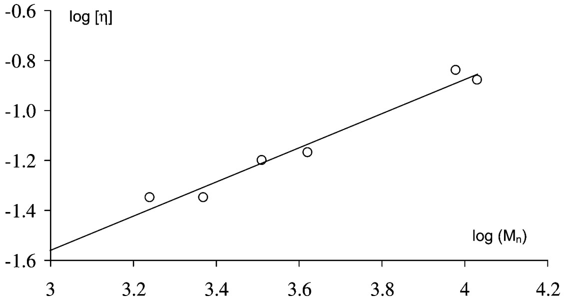


Figure 9. Plot of the Mark–Houwink relationship for POXZ.

relationship, $[\eta]_{prec}$ have been calculated for the POXZ-C_n, and the values are reported in Table 3. For POXZ-C_{12}, $[\eta]$ is about the same as the one of its precursor, whereas for POXZ-C_{18-2} it is almost 3 times larger. Studies on alkyl-terminated PEO (at both ends) report that intrinsic viscosities are comparable to the one of the precursors,[51] as observed with POXZ-C_{12}. The ratio of the hydrodynamic volume of the micelle (V_h) to the one of the precursor ($V_{h_{prec}}$) should vary as

$$\frac{V_h}{V_{h_{prec}}} = N_{agg}\frac{[\eta]}{[\eta]_{prec}} \tag{6}$$

where N_{agg} is the aggregation number. Given the numerical values of Tables 2 and 3, the hydrodynamic volume ratio is 11 for POXZ-C_{12} and 16 for POXZ-C_{18-2}. Moreover, the aggregation number of POXZ-C_{18} being certainly underestimated (see above), this ratio should be even higher. The micellar aggregates are thus more expanded (compared to the precursor) in the case of POXZ-C_{18-2} than for POXZ-C_{12}.

An alternative method used, to compare the structural properties of the aggregates to the ones of isolated chains, was to add β-cyclodextrin (CD) (Figure 10) to the polymer solutions, in excess compared to the alkyl groups (molar ratio β-CD/alkyl of 3/1). Indeed, cyclodextrins are known to incorporate suitable guest molecules into their hydrophobic cavity and are used for reducing the viscosity of aqueous amphiphilic polymer solution.[52–54] The complexation of hydrophobic groups inside the hydrophobic cavity of β-CD should induce the dissociation of aggregates (Figure 11). The intrinsic viscosities of the mixtures $[\eta]_{mix}$ have been reported in Table 3. For a mixture of noninteracting species, $[\eta]_{mix}$ should be related to the intrinsic viscosities of the two solutes by the following equation:

$$[\eta]_{mix} = w_1[\eta]_{POXZ} + w_2[\eta]_{CD} \tag{7}$$

where w_1 and w_2 are the weight fraction of the two components and $[\eta]_{POXZ}$ and $[\eta]_{CD}$ are their intrinsic viscosities. Cyclodextrins are small and compact molecules whose intrinsic viscosity can be neglected compared to the one of the polymer. Then

$$[\eta]_{POXZ} = \frac{[\eta]_{mix}}{w_1} \tag{8}$$

with $w_1 = M_{POXZ}/(M_{POXZ} + 3M_{CD})$. This calculation has been done for the POXZ mixtures because no interaction is expected between POXZ and CD. The result, reported in Table 3, shows almost the same intrinsic viscosity for POXZ in the CD mixture as in pure water. This confirms the assumption of noninteracting species. For POXZ-C_{12} and POXZ-C_{18}, the same assumption cannot be hold because CD are known to interact specifically with alkyl groups by formation of inclusion complexes. Assuming a total dissociation of the hydrophobic microdomains by addition of CD in excess, the solutions can thus be considered as a mixture of the two following noninteracting species: the complexes POXZ-C_n/CD and the excess of CD. $[\eta]_{mix}$ can thus be written

$$[\eta]_{mix} = w_1'[\eta]_{POXZ-C_n/CD} + w_2'[\eta]_{CD} \tag{9}$$

$[\eta]_{POXZ-C_n/CD}$ is the intrinsic viscosity of the chain end-capped with CD. w_1' and w_2' are the weight fraction of the complex and free CD in solution. $[\eta]_{CD}$ is again neglected and

$$[\eta]_{POXZ-C_n/CD} = \frac{[\eta]_{mix}}{w_1'} \tag{10}$$

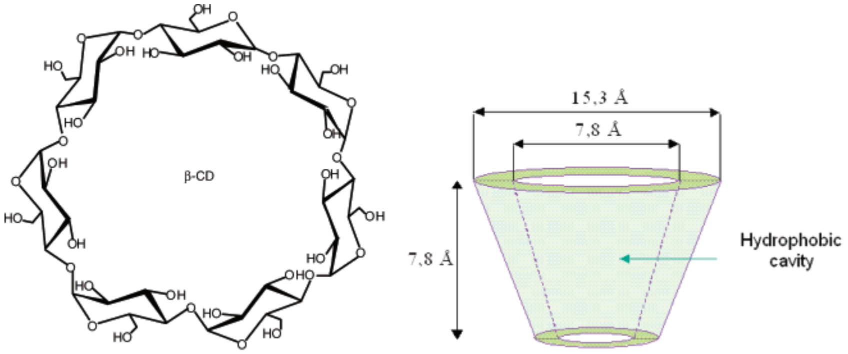


Figure 10. β-Cyclodextrin formula.

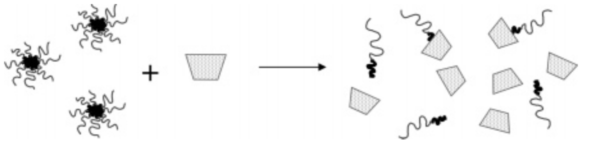


Figure 11. Dissociation of micellar aggregates by addition of β-cyclodextrin.

where $w_1' = (M_{\mathrm{POXZ-C}_n\mathrm{/CD}} + M_{\mathrm{CD}})/(M_{\mathrm{POXZ-C}_n} + 3M_{\mathrm{CD}})$. It is also assumed that only 1/1 complexes are formed between alkyl and CD. The intrinsic viscosities of the complexes have been calculated using eq 9, and the results are reported in Table 3. These are relatively close to the ones of the precursor polymers. This shows that β-cyclodextrin dissociated the micellar structures, and the resulting CD-complexed polymers have compactnesses very close to the precursors' ones. The addition of CD to aqueous solutions of POXZ-C_n is then a good method to completely dissociate the aggregates.

Conclusion

Amphiphilic polymers were synthesized with poly(2-methyl-2-oxazoline) as a hydrophilic backbone and a hydrophobic alkyl group at one end. The polymers were prepared by cationic polymerization of 2-methyl-2-oxazoline using alkyl iodide such as 1-iodododecane or 1-iodooctadecane as initiator. Their molecular weights were over the range from 3.2×10^3 to 8.5×10^3. The micelle formation of polymers in aqueous solution was investigated by fluorescence measurements. These amphiphilic polymers formed micellar aggregates in water solution. Critical micelle concentrations were in the range of 0.007−0.4 g L^{-1} and were dependent on the hydrophilic/lipophilic balance. These results are in good quantitative agreement with the cmc determined for monoalkyl end-capped poly(ethylene oxide). Aggregation numbers have been determined by static quenching experiments. The value 11 for POXZ-C_{12} is lower than the ones determined for monoalkyl end-capped PEO due to higher hydrophilicity of the chains. The compactness of the aggregates have been studied by intrinsic viscosity measurements and compared to the ones of the precursor chains. A clear difference in the structural properties of POXZ-C_{12} and POXZ-C_{18} aggregates has been evidenced as their relative intrinsic viscosities (compared to the precursor chain) are 1 and 2.6 for POXZ-C_{12} and POXZ-C_{18-2}, respectively. Addition of β-cyclodextrin (CD) which makes inclusion complexes with the alkyl end groups induces the dissociation of the aggregates. Intrinsic viscosities of the complexes POXZ-C_n/CD have been estimated from the intrinsic viscosity measurements of mixtures POXZ-C_n containing β-cyclodextrin (CD) in excess. The intrinsic viscosities of the CD decorated chains are shown to be comparable to the ones of their precursor POXZ chains.

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