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Polymerization of *N*,*N*-Didodecyl-*N*-methyl-*N*-(2-(methacryloyloxy)ethyl)ammonium Chloride, an Inverse Micelle Forming Detergent

G. Voortmans, A. Verbeeck, C. Jackers, and F. C. De Schryver*

The Department of Chemistry, K. U. Leuven Celestijnenlaan, 200F B-3030 Heverlee, Belgium.

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ABSTRACT: In this paper the first results obtained on the polymerization of *N*,*N*-didodecyl-*N*-methyl-*N*-(2-(methacryloyloxy)ethyl)ammonium chloride, an inverse micelle forming detergent, are presented. A full characterization of the monomeric reverse micellar system is presented, from use of the fluorescence probe technique. The critical micelle concentration (cmc) of the monomer was determined to be 10^{-4} M. Fluorescence quenching and viscosity measurements were used to determined the aggregation number and dynamic character of the monomeric aggregates. The same experiments were carried out for the polymeric aggregates, and the results are compared with those of the monomeric aggregates. This comparison shows that the polymeric aggregates form inverse micellar systems. It is further proved that the dynamic character of the reverse micellar system is lowered upon polymerization. Gel permeation chromatography (GPC) analysis indicates that the polymerization of the monomer leads to high molecular weight polymers with a degree of polymerization several times larger than the aggregation number of the initial reverse micellar system.

Introduction

The polymerization of monomers in the presence of detergents is well established in both aqueous and nonaqueous media.[1] Recently a strong interest has developed in the polymerization of some surfactant aggregates.[2–9] This is undoubtedly caused by the potential use of these systems, which could be further enhanced when stabilized by polymerization. Polymerization could combine the beneficial properties of stable polymer particles with the specific properties of micelles, microemulsions, and vesicles.[4] Considerable work has been done in the field of polymerization of vesicles, monolayers, and multilayers.[2–7] In contrast only a few reports exists on the polymerization of aqueous micellar systems.[8,9] The polymerization of a reverse micellar system has not yet been reported. This paper presents the first results obtained on the polymerization of a reverse micellar system of *N*,*N*-didodecyl-*N*-methyl-*N*-(2-(methacryloyloxy)ethyl)ammonium chloride (I) in toluene.

Characteristics of the Monomer I

To determine in which cases the monomer can form reverse micellar structures, we tested a series of apolar solvents to evaluate the solubility of the monomer. In addition the amount of water soluble in these systems has also been investigated. If the monomer is soluble in the apolar solvent and can also solubilize water, one can then conclude that reverse micellar structures are formed.[10a] The results are presented in Table I. As benzene and toluene are solvents in which the monomer is soluble and in which it can also solubilize water, one can conclude that in these solvents the monomer forms reverse micellar structures.

Table I
Monomer Solubility and Water Solubility in Various Solvents

solvent	monomer solubility	R^a
benzene	*b*	$0 \rightarrow 4$
toluene	*b*	$0 \rightarrow 4$
cyclohexane	*c*	$0 \rightarrow 2$
hexane	*d*	

[a] $R = [H_2O]/[\text{monomer}]$. [b] Very soluble. [c] Soluble. [d] Insoluble.

An important characteristic of the monomer is its cmc. The meaning of this term in a reverse micellar system is somewhat different from that of aqueous micellar system.[10b] Eicke et al. proposed that in apolar media the surfactant AOT upon aggregation first forms linear aggregates, which then undergo a transformation to cyclic ones.[11] This last phenomenon is then called the cmc. It was found that the model of Eicke was also valid for ammonium surfactants.[10a] The cmc can be determined by monitoring the absorbance and/or fluorescence of a probe as a function of the logarithm of the surfactant concentration. From these properties, presented in Figures 1 and 2, it can be seen that there is aggregation of the monomer that leads to an increase in the absorbance of the probe (Figure 1). As the probe is already fully solubilized by the small linear aggregates, there is no second inflection in absorbance that would be caused by cyclization, so that one cannot determine the cmc from absorbance measurements. The cmc can however be determined by monitoring the fluorescence decay of the same probe as a function of the logarithm of the surfactant concentration. In Figure 2 the contribution of the long decay time of the probe is plotted as a function of the logarithm of the

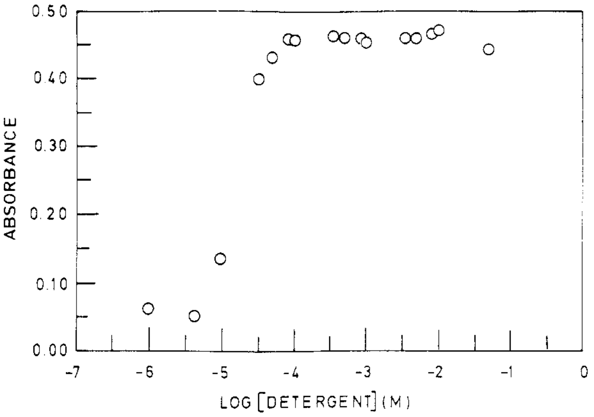

Figure 1. Absorbance of sodium pyrenesulfonate added to the monomeric system, as a function of the logarithm of the detergent concentration.

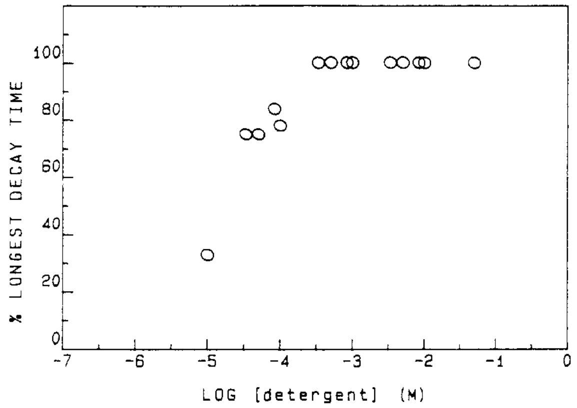

Figure 2. Contribution of the longest decay time of the fluorescence of sodium pyrenesulfonate added to the monomeric system, as a function of the logarithm of the detergent concentration.

surfactant concentration. At low surfactant concentration the fluorescence decay of the probe is two-exponential; on increasing the concentration the fluorescence decay of the probe becomes one-exponential. This behavior has been explained by assuming that there are two possible associations of the probe with the linear aggregates, which causes a two-exponential decay. On the other hand, after cyclization of the aggregate there is only one possible association of the probe with the cyclic aggregates, resulting in a single-exponential fluorescence decay of the probe after the cmc. On this basis the cmc of the monomer can be determined as to be about 10^{-4} M, which is a reasonable value and comparable to other ammonium surfactants were the polymerizable group is substituted by an alkyl group.[10]

Finally the aggregation number and the dynamic character of the reverse micellar system were determined by using fluorescence quenching and viscosity measurements.

Fluorescence Quenching. For determination of the average aggregation number (N_{agg}) and the rate constant of exchange (k_e) via dimer formation,[12-14] a given concentration of a fluorescence probe, which is insoluble in the apolar phase and can be localized at the interphase of the reverse micellar aggregate, is added. In addition to this, different concentrations of quencher, also localized at the interphase and insoluble in the apolar phase, are added. Furthermore, the quencher concentration must be low enough so that only one probe or quencher can be exchanged, the decay time of the probe must be sufficiently long to detect the slow dynamic processes, and the rate of quenching in the aggregate must be larger than the rate of exchange. Under these conditions one can analyze the fluorescence decay of the probe as pointed out by Verbeeck and De Schryver.[15] The probe/quencher system pyrenesulfonic acid/potassium iodide meets these conditions and was used to determine N_{agg} and k_e. The results are presented in Table II.

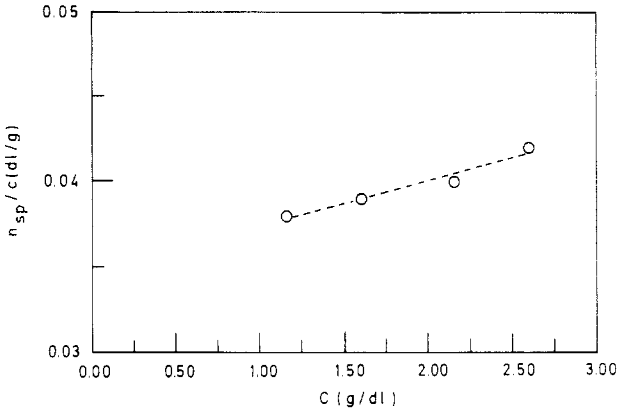

Figure 3. Ratio of the specific viscosity over the detergent concentration as a function of the detergent concentration.

Table II
Aggregation Number and k_e Determined for the Monomeric Reverse Micellar System in Toluene from Fluorescence Quenching (fq) and Viscosity Measurements (v)

R	N_{agg}	k_e, s^{-1}	method
1			fq
1	19.1		v
2	28.2	2.0×10^8	fq
2	26.2		v
2.5	33.0	2.3×10^8	fq
2.5	30.3		v

Viscosity Measurements. According to the method described by Day et al. the N_{agg} of the reverse micellar system can be determined by using viscosity measurements:[16]

$$n_{sp} = 2.5\Phi + 14.1\Phi^2 \qquad (1)$$

where Φ is the volume fraction of the dispersed phase and is determined by measuring the specific viscosity and applying eq 1. A plot of the volume fraction of the dispersed phase as a function of R (R = $[H_2O]/[\text{surfactant}]$) allows the determination of the necessary parameters to compute the aggregation number according to the method described by Day et al.[16]

The results are also reported in Table II. A comparison of the aggregation numbers determined from fluorescence quenching and viscosity measurements shows very good agreement.

In addition to the aggregation number, the Huggins' hydrodynamic interaction parameter (k_h) of the system can be determined from a plot of n_{sp}/c as a function of the detergent concentration (c), according to

$$n_{sp}/c = [n] + k_h[n]^2c \qquad (2)$$

where $[n]$ = intrinsic viscosity, k_h = Huggins' hydrodynamic interaction parameter, and c = concentration in g/100 mL. As this parameter is a measure for the frequency of doublet formation by the aggregates,[17] it can also be regarded as a measure for the dynamic character of the system. The curve is presented in Figure 3, and the slope k_h was determined to be equal to 2.2.

Characterization of the Polymer

Molecular Weight. The molecular weight of the polymer was determined by GPC. The molecular weight as a function of the average number of initiators per mi-

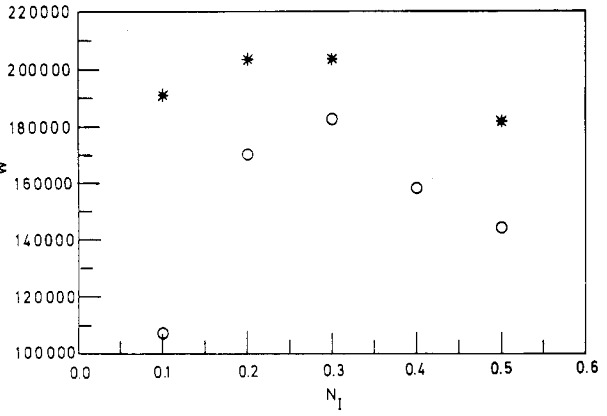

Figure 4. Molecular weight (weight average) of the polymer as a function of mean number of initiators per micelle at constant R value (R = 1) for a polymerization in toluene (○) and benzene (*).

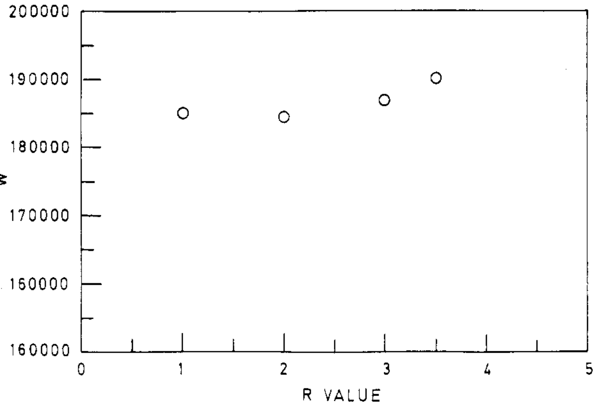

Figure 5. Molecular weight (weight average) of the polymer as a function of the R value at constant mean number of initiators per micelle (n_I = 0.3). The solvent for polymerization was toluene.

celle is plotted in Figure 4 for polymerization (under identical conditions) in benzene and toluene. From these plots it is clear that at low initiator concentrations transfer to solvent is very important as there is a drastic decrease of the molecular weight in toluene, while this is substantially less in benzene. This is to be expected as the transfer constant for benzene is 4 times smaller than that of toluene.

The effect of the amount of water added to the system was also examined and is presented in Figure 5. The molecular weight increases slightly with increasing amounts of water. This is at first surprising as one has to decrease the overall initiator concentration to keep the average number of initiators per micelle constant. This would lead to a decrease in molecular weight, as in Figure 4 the molecular weight decreases in the range n_I = 0.3–0.1 due to transfer to solvent. If it is assumed that all the initiator is located at the interphase of the reverse micelles, which is a reasonable assumption as the initiator is not soluble in toluene but is soluble in water, an increase of the R value at constant surfactant concentration increases the size of the aggregate, and thus more monomers will be in the vicinity of the created radical. Under these conditions the propagation can better compete with the transfer to the solvent. A further consequence of the location of the initiator is that the initiation rate remains constant in an aggregate upon increasing the initiator concentration as long as this concentration does not exceed the concentration at which the chance of having two initiators in one aggregate is no longer negligible. Under these circumstances the initiation rate is independent of the initiator concentration but does depend upon the concentration of micelles with an initiator. This is a function of the aggregation number of the reverse micellar aggregate and the surfactant concentration. Keeping the surfactant concentration constant and increasing the water concentration, one increases the aggregation number so that there are less reverse micelles. This in turn means that the concentration of reverse micelles with initiator decreases with R and the initiation rate decreases. These two phenomena would explain the slight increase of the molecular weight with the R value.

Table III
Polymer Solubility and Water Solubility in Various Solvents

solvent	polymer solubility	R^d
toluene	*b*	0 → 4
benzene	*b*	0 → 4
hexane	*c*	
cyclohexane	*c*	

[a] $R = [H_2O]/[\text{monomer}]$. [b] Soluble. [c] Insoluble.

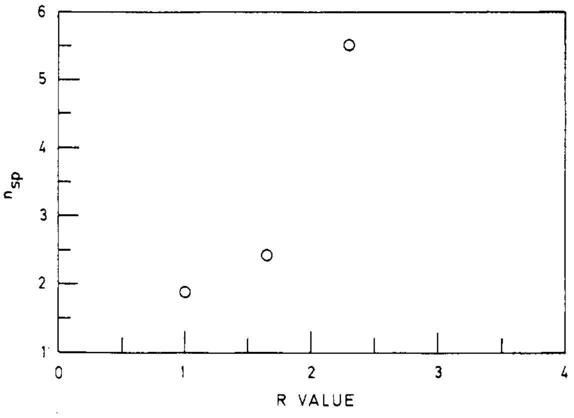

Figure 6. Specific viscosity of the polymerized system as a function of the concentration of polymer.

Solubility Characteristics of the Polymer. As in the case of the monomer, the solubility of the polymer in various solvents and the amount of water that could be solubilized in the system were determined, and the results are presented in Table III. Table III shows that the solubility characteristics of the polymer are analogous to that of the monomer (Table I). The polymer can solubilize water until R = 4, above which the solutions became opaque, but a phase separation for solutions with $R > 3$ occurred. This phase separation vanishes upon heating but returns after cooling to room temperature. Furthermore, upon dilution at R constant this phase separation also vanished. This suggest that at higher R values the polymer chains become physically cross-linked either by the water pools that they have to stabilize or by the interaction of the dodecyl side chains.

Viscosity Behavior of the Polymer. From measurements of the specific viscosity (n_{sp}) as a function of the concentration of the polymer the Huggins' hydrodynamic interaction parameter can be determined according to eq 2 and is found to be equal to 1, which is about 2 times smaller than for the monomer. Since this parameter is a measure of the dynamic character of the system, it can be concluded that polymerization of a reverse micellar system leads to a decrease of the dynamic character of the system. An attempt to determine the aggregation number of the polymerized aggregates by measuring the specific viscosity as function of R value as for the monomer failed. The specific viscosity increases asymptotically, so that it was not possible to use this method to determine the aggre-

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gation number (Figure 6). This drastic increase of the specific viscosity is probably caused by interchain interaction leading to the phase separation mentioned in the previous paragraph.

Conclusion

From these results it can be concluded that polymerization of the reverse micellar system does not proceed intramicellarly but rather by a mechanism analogous to that described for water-soluble monomers solubilized in a reverse micellar system. Viscosity measurements show that polymerization leads to a stabilization of the inverse micellar system. Further addition of water after polymerization leads to a drastic increase in the viscosity finally resulting in gelation.

Experimental Section

Synthesis of Monomer I. Monomer I was synthesized by coupling *N*-didodecyl-*N*-methyl-*N*-(2-hydroxyethyl)ammonium chloride with methacryloyl chloride by using general methods. *N*-Didodecyl-*N*-methyl-*N*-(2-hydroxyethyl)ammonium chloride was synthesized as described elsewhere.[18]

Polymerization. Monomer I was photopolymerized by using 4,4′-azobis(4-cyanovaleric acid) as the initiator. A typical sample contained the desired amounts of initiator and water and 0.05 M of monomer solubilized in either toluene or benzene. The samples were then degassed with nitrogen for 0.5 h and then illuminated with 350-nm lamps for 4 h.

Fluorescence decay curves of degassed solutions were determined by using a single-photon counting apparatus coupled to a PDP 11/23 computer. Several statistical criteria were used[19] to judge the goodness of the fit. A Perkin-Elmer Lamda 5 UV–vis spectrophotometer was used for the UV absorption measurements.

Viscosity measurements were performed by using an Ubbelohde viscosimeter.

GPC chromatograms were taken on a Perkin-Elmer Series 10 liquid chromatograph by using styragel columns of 10^5, 10^4, 10^3, and 10^2 Å. The flow rate was 5 mL/min. An IR detector locked at 5.7 μm was used to detected the polymer. Chloroform with 10^{-3} M tetrabutylammonium bromide was used as the solvent since this is a polar solvent, which inhibits the formation of aggregates. The salt was added to avoid the polymer remaining on the column. Polystyrene standards with molecular weight of 10^5, 10^4, and 3600 were used for the calibration.

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Registry No. I, 114199-09-6; I (homopolymer), 114199-10-9.

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Glyceryl Polyphosphazenes: Synthesis, Properties, and Hydrolysis

Harry R. Allcock* and Sukky Kwon

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received September 9, 1987*

ABSTRACT: Methylene-, isopropylidene-, and methoxymethylene-protected glyceryl units have been linked to cyclic and high polymeric phosphazenes. The structures and physical properties of these protected glyceryl-substituted phosphazenes were investigated by ^{31}P NMR, ^{1}H NMR, and IR spectroscopy and thermal analysis. Hydrolytic deprotection reactions in acidic media yielded the water-soluble cyclic trimeric and high polymeric glycerylphosphazenes. Cross-linking of the protected high polymers was accomplished by γ irradiation. The deprotected polymer cross-linked in the presence of adipoyl chloride or hexamethylene diisocyanate to yield systems that absorbed water to form hydrogels. Slow hydrolysis of poly(diglycerophosphazene) occurred in neutral aqueous media at 37 °C to yield glycerol, phosphoric acid, and ammonia.

Introduction

Water-soluble synthetic polymers are of interest as models for biological macromolecules and for their possible uses in biomedicine. Prominent among the biomedical uses are applications that involve the formation of hydrogels that can be utilized as membranes, structural materials, or matrices for the immobilization of bioactive agents.[1–3]

Particular interest has been shown in polymers that bear hydroxyl units in the side-group structure. Such units provide sites for cross-linking or binding to bioactive agents, for example, via treatment with cyanogen bromide.

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