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Poly(*N*-isopropylacrylamide) Microgels at the Oil–Water Interface: Interfacial Properties as a Function of Temperature

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Highly monodisperse poly(N-isopropylacrylamide), PNiPAM, microgels were prepared by the conventional radical polymerization of NiPAM in the presence of dimethylamino ethyl methacrylate (DMAEMA) monomers at various concentrations. The effect of DMAEMA on the polymerization of PNiPAM microgels was examined at constant initiator (V50) and cross-linker (MBA) concentrations. The presence of DMAEMA in the synthesis batch allows for the preparation of PNiPAM microgels with controlled size and a narrow size distribution. The oil(dodecane)/water interfacial properties of the model PNiPAM microgels were then investigated. The pendant drop technique was used to measure the interfacial tensions as a function of temperature. Over the whole range of temperature (20-45 $^{\circ}$ C), the interfacial tension remains low (on the order of 17 mN/m) and goes through a minimum (12 mN/m) at a temperature of about 34 °C, which well matches the volume phase transition temperature (VPTT) of PNiPAM microgels. Below the VPTT, the decrease in the interfacial tension with temperature is likely to be due to the adsorption of dense layers because of the decrease of the excluded volume interactions. Above the VPTT, we suggest that the increase in the interfacial tension with temperature comes from the adsorption of loosely packed PNiPAM microgels. We also studied the effect of temperature on the stability of emulsions. Dodecane in water emulsions, which form at ambient temperature, are destabilized as the temperature exceeds the VPTT. In light of the interfacial tension results, we suggest that emulsion destabilization arises from the adsorption of aggregates above the VPTT and not from an important desorption of microgels. Aggregate adsorption would bring a sufficiently high number of dodecane molecules into contact with water to induce coalescence without changing the interfacial tension very much.

I. Introduction

Nanogels/microgels, synthesized either by conventional or controlled radical polymerization,¹ have received considerable interest for applications in a diverse range of areas including materials science,^{2,3} drug delivery,⁴ biosensors,⁵ and targeted therapies⁶ because of their unique physical and chemical properties. Nanogels/microgels are defined as gel particles of any shape with an equivalent diameter of approximately 0.01 to 100 μ m, exhibiting network structures that swell in a suitable solvent.⁷ Several authors have focused on the development of responsive microgels whose properties can be tuned in response to an environmental stimulus such as pH, temperature, or light. In this class of stimuli-responsive polymers used in microgel synthesis, the most-studied temperature-responsive polymer is poly(N-isopropylacrylamide), PNiPAM, which possesses a lower critical solubility temperature (LCST) roughly equal to 32 °C.⁸ For NiPAM microgels, the responsiveness appears as a volume

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collapse referred to a volume phase transition temperature (VPTT).

Very recently, several groups have prepared stimuli-responsive microgels that can be used as a novel emulsifier to form smart responsive interfaces.^{9–15} Indeed, responsive gel particles represent a new class of emulsifiers and stabilizers for oil-in-water emulsions and foams. The destabilization of interfaces, stabilized by gel particles instead of surfactants, in response to an environmental stimulus is a promising way in many fields in which destroying interfaces (liquid/liquid or liquid/gas) is required, such as for water treatment or oil recovery.¹⁶ Last, in contrast to surfactants, the use of stimuli-responsive gel particles leads to heterogeneous media, which makes it easy to recycle.

Ngai et al. first reported the preparation of stable octanol-inwater emulsions with poly(*N*-isopropylacrylamide-*co*-methacrylic acid) microgels as solid-stabilized particles.^{9,10} They observed that NiPAM-MAA microgels stabilize octanol-in-water emulsions at high pH and at temperatures below the VPTT of the microgels. However, the destabilization of the emulsions was carried out either by decreasing the pH or increasing the temperature. Ngai et al. explained that both at high temperature and/or at low pH, NiPAM-MAA microgels become hydrophobic and move into the oil phase.

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Table 1. Formulations Used in the Microgel Synthesis and the Corresponding Hydrodynamic Diameters, D_h, and Swelling Ratio of the Microgels

| entry | $\begin{array}{c} \text{NiPAM} \\ (\text{mol} \times 10^3) \end{array}$ | $\frac{\text{MBA}}{(\text{mol} \times 10^3)}$ | DMAEMA (mol %) | initiator V50 (mol \times 10 ³) | hydrodynamic diameter (nm) (polydispersity) ^a | | |
|------------------|---|---|-------------------|---|--|--|--------------------------------|
| | | | | | 25 °C | 40 °C | swelling ratio ^b |
| 1 | 8.83 | 0.35 | 0 | 0.27 | 758 (0.084) | 318 (0.028) | 13.5 |
| 2 | 8.71 | 0.35 | 0.5 | 0.27 | 446 (0.015) | 198 (0.016) | 11.4 |
| 3 | 8.75 | 0.35 | 0.7 | 0.27 | 402 (0.011) | 168 (0.006) | 13.7 |
| 4 | 8.71 | 0.35 | 1 | 0.27 | 302 (0.030) | 140 (0.082) | 10.0 |
| 5 | 8.68 | 0.35 | 1.25 | 0.27 | 238 (0.011) | 110 (0.024) | 10.2 |
| 6 | 8.83 | 0.35 | 1.5 | 0.27 | 222 (0.020) | 94 (0.028) | 13.2 |
| 7 | 8.48 | 0.35 | 3 | 0.27 | 125 (0146) | 45 (0.085) | 11.4 |
| ^a Det | ermined by dyna | mic light scatterir | or (DLS) Polydis | persity factors were dete | ermined from cumulant ana | lysis ^b The swelling ratio wa | as calculated |

^{*a*} Determined by dynamic light scattering (DLS). Polydispersity factors were determined from cumulant analysis. ^{*b*} The swelling ratio was calculated between 25 and 40 °C.

The destabilization of the oil-in-water emulsions thus occurs by the formation of holes at the interface because of the possible desorption of the microgel particles. A similar hypothesis (i.e., a reduction of the surface coverage by gel particles) was also proposed by Kawaguchi et al. for purified NiPAM microgels.11 Nevertheless, in the case of Ngai's work, the preparation of the emulsions was conducted with a synthesis batch that contains not only microgels but also unreacted monomers and small oligomers or copolymers that can stabilize oil-in-water emulsions as reported by Brugger et al.¹³ Brugger et al. studied in detail both the stabilization and destabilization of oil-in-water emulsions using similar dual stimuli-responsive microgels.^{13,14} They found that (i) only a few methacrylic acid monomers were introduced into the NiPAM-based microgels,¹³ (ii) purified microgels can hardly stabilize oil-in-water emulsions,¹³ and (iii) above the VPTT of the NiPAM-MAA microgels, aggregates of microgels form at pH 3, inducing a destabilization of the emulsions whereas at pH 9 no aggregates are observed and consequently emulsions are stable.¹⁴ However, in a more recent paper,¹⁵ the authors report the formation of well-ordered interfacial layers of gel particles at pH 3 using a cryo-SEM technique, whereas clusters of microgels are found for pH 9. Surprisingly, these clusters of microgels seem to stabilize oil-in-water emulsions.

In the present work, we also report on the properties of temperature-responsive microgels (PNiPAM) at the oil(dodecane)/ water interface. The article is organized as follows. First, we describe the synthesis and characterization (size, size distribution, swelling, and VPTT) of the PNiPAM microgels. One of our goals with respect to synthesis issues was to produce easy-to-purify microgels with controlled size and low polydispersity factors. Second, we focus our attention on the interfacial tension properties of the model PNiPAM microgels as a function of temperature. To the best of our knowledge, detailed interfacial tension measurements at oil/water interfaces covered with microgels, in particular, PNiPAM, have not yet been reported. Third, by investigating the stability of emulsions using the PNiPAM microgels as emulsifiers, we find that the temperature is indeed an efficient trigger to destabilize dodecane in water (direct) emulsions. We then discussed possible mechanisms by which destabilization occurs in light of the interfacial tension data.

II. Experimental Part

II.1. Materials. *N*-Isopropylacrylamide (NiPAM), methylene bisacrylamide (MBA), 2,2'-azobis (2-amidinopropane hydrochloride) (V50), and *n*-dodecane oil were purchased from Sigma-Aldrich and used as received. Dimethylamino ethyl methacrylate (DMAEMA) was purchased from Acros Organics and purified by passing it through an Al₂O₃-activated basic columm (Acros Organics). All samples were prepared using ultrapure deionized water (Milli-Q, Millipore, France).

II.2. Synthesis of the Microgels. All NiPAM-based microgels were prepared by surfactant-free precipitation polymerization. In a typical synthesis, polymerization was carried out in a jacketed round-bottomed flask equipped with a condenser, a thermometer, and a nitrogen inlet and outlet. The pH of the Milli-Q water was adjusted to 4 using 0.01 M HCl solution. The monomers, NiPAM and DMAEMA, and the cross linker, MBA, were dissolved in degassed water. A monomer aqueous solution was mechanically stirred at 300 rpm under nitrogen for 45 min to remove dissolved oxygen. After complete dissolution, the reaction mixture was heated up to 70 °C. At this time, the initiator, V50, which was separately dissolved in degassed water, was injected into the monomer solution. The proportions of reagents used in the various microgel syntheses are given in Table 1. All syntheses were carried out under a nitrogen atmosphere and constant stirring for 4 h. The reaction mixture was then cooled to room temperature. Microgels were cleaned by several centrifugation and redispersion cycles using Milli-Q water. After five centrifugation/redispersion cycles, the air-supernatant interfacial tension was 69 mN/m, which is very close to the water surface tension, therefore ensuring high-quality purification of the microgels. Then, the microgels were freeze dried.

II.3. Characterization of the Microgels. ¹H NMR and ¹³C NMR analyses were performed in D₂O solution at 25 °C using an Avance 300 Bruker spectrometer. Dynamic light scattering (DLS) was performed on an ALV goniometer (ALV/CGS-3) with a HeNe laser operated at a wavelength of $\lambda = 633$ nm, in combination with an ALV/LSE-5003 correlator. The time correlation function of the electric field resulting from scattered light is measured, which is a decaying function. This function was analyzed with a Laplace inversion program. In the limit of zero scattering angle, the decay time, Γ , is related to the diffusion coefficient, D, as $\Gamma = Dq^2$. For translational diffusion, the hydrodynamic radius, $R_{\rm h}$, can be calculated using the Stokes–Einstein equation $(R_{\rm h} = k_{\rm B}T/[6\pi\eta D])$, where $k_{\rm B}$ is the Boltzmann constant, \hat{T} is the absolute temperature, and η is the solvent viscosity. Prior to DLS measurements, all samples were prepared with ultrapure water (Milli-Q, Millipore, France), equilibrated overnight at room temperature, and filtered through Teflon filters of 0.8 μ m pore size. To study the variation of microgel size as a function of temperature, the samples were kept at rest within the apparatus at each temperature for 15 min prior to measurements. The results are given as intensity-averaged hydrodynamic diameters (mean diameters based on the intensity of scattered light).

II.4. Interfacial Tension Measurements. Oil-water interfacial tensions were measured using the pendant drop method (ITC Concept, Tracker). The shape of the drops was fitted to the Laplace equation in order to determine the interfacial tension. Dodecane oil with a purity of >99% was used as received, and the microgel aqueous solutions were prepared using doubly-distilled deionized water (Milli-Q system from Millipore). Using our setup, a value of about 50 \pm 1 mN/m was measured for the interfacial tension between dodecane and water at 20 °C, in agreement with the literature.¹⁷ This indicates that the dodecane oil and water are free from any surface-active impurities. Our analysis of the interfacial tension with temperature takes into account the temperature

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dependence of the density of both dodecane oil and water. The temperature of both the syringe used to form the drop and the dodecane cell was varied from 25 to 50 °C by circulating water in a double-envelope system. Microgel solutions were prepared by dissolving the freeze-dried microgels into doubly-distilled deionized water (Milli-Q system from Millipore) under magnetic stirring for 48 h at room temperature. Unless otherwise stated, the concentration of microgels is $C_{\rm M} = 1\%$, where $C_{\rm M}$ is the concentration of microgels given in weight of microgel/weight of solution. Two different processes were used to measure the interfacial tension. In the case of the single drop method, only one drop is formed at ambient temperature and the interfacial tensions are measured by progressively increasing the temperature up to about 40 °C. For the fresh drop method, the interfacial tension is measured by forming a new drop at each temperature. For both methods, the oil and aqueous phases were equilibrated for about 30 min at each temperature prior to measurements. The variation of the interfacial tension with time at a given temperature was thoroughly investigated (not presented here). The results typically showed that a duration of less than 5 min was required to reach a tension variation on the order of 0.1 mN/m over a period of 100 min, which corresponds to a rate of loss of 10^{-3} mN/(m·min). This criterion was actually used to determine the interfacial tension values.

II.5. Emulsion Preparation. The preparation of the dodecane in water emulsions (direct emulsions) can be described as it follows. First, we prepared 3 mL of a microgel solution at a concentration of $C_{\rm M}$ % (as mentioned above, $C_{\rm M}$ % is the concentration of microgel given in weight of microgel/weight of solution) by stirring the appropriate amount of microgel in water for 24 h at room temperature. An equal volume of dodecane (3 mL) was added to the aqueous phase so that the volume fractions of both phases are 0.5. The two phases were left at rest for 12 h at the required temperature prior to emulsification. All samples were prepared using an IKA T25 digital ultra turrax at 26 000 rpm for 2 min. Emulsion stability with time was qualitatively determined by a visual inspection of the samples with the naked eye.

II.6. Characterization of Emulsions. Optical microscopy (Leica DM IRE2 equipped with a CoolSNAP camera and a Linkam heating plate) was also extensively used, especially to study the stability of emulsion droplets with temperature. Basically, two methods were used to investigate emulsion stability. In the case of the fresh emulsion method, emulsification and emulsion stability were studied at the same temperature. In the case of the single emulsion method, emulsification was performed at ambient temperature. The stability of the emulsion was further examined, for instance, by taking pictures of the emulsion samples at given temperatures within the 20-45 °C range using optical microscopy. Before pictures were taken, the samples were left about 15 min at each investigated temperatures using the Linkam heating plate.

III. Probing the Presence of DMAEMA Monomers in NiPAM-Based Microgels

III.1. Synthesis and Characterization of NiPAM-Based Microgels. It is well known that multiresponsive microgels can be prepared by copolymerizing *N*-isopropylacrylamide (NiPAM) and pH-sensitive monomers such as acrylic acid,¹⁸ methacrylic acid,¹⁹ and more recently dimethylaminoethylmethacrylate (DMAEMA).²⁰ Herein, NiPAM-based microgels were synthesized either in the presence or absence of DMAEMA at constant initiator and cross-linker concentrations by conventional radical cross-linking polymerization (surfactant-free precipitation polymerization) in water without surfactant using methylene bisacrylamide (MBA) as a cross linker and a cationic initiator (V50) as already reported by



Figure 1. Evolution of the hydrodynamic diameters of poly(*N*-isopropylacrylamide) microgels as a function of the DMAEMA monomer amount introduced into the microgel formulation at 25 °C (\bullet) and 40 °C (\blacksquare). For all systems, the concentration of microgel solution is 0.002 wt %. The lines are guides for the eye.

Zha et al.²⁰⁻²² NiPAM-based microgels were purified by several centrifugation/redispersion cycles until the surface tension of the supernatant of the microgel dispersion reached the water surface tension. To probe the presence of the DMAEMA monomer units in the NiPAM-based microgels, the microgel dispersions and supernatant solutions were characterized by ¹H NMR and ¹³C NMR using D₂O as the solvent (Figures S1-S3 in Supporting Information). First, the ¹H NMR spectra of NiPAM-based microgels prepared with and without DMAEMA monomers are strictly identical (Figure S1 in Supporting Information). Furthermore, the ¹³C NMR spectra of all of the synthesized microgels exhibit only PNiPAM carbon peaks. As a matter of fact, the carbonyl region exhibits a single carbonyl peak corresponding to the carbon of the NiPAM carbonyl group (Figure S2 in Supporting Information). However, in contrast to previous studies, 20,22 the $^{13}\mathrm{C}$ NMR spectrum of the supernatant solution (Figure S3 in Supporting Information) shows the presence of DMAEMA monomers. Thus, NMR studies show that no DMAEMA monomer units are incorporated into the microgel, irrespective of the DMAEMA monomer concentration used to perform the microgel synthesis. One possible explanation is the difference in the reactivity ratios between (meth)acrylate and (meth)acrylamide moieties.

The NiPAM-based microgels were then characterized by dynamic light scattering (DLS) and UV-vis spectroscopy. For each microgel synthesis, we determined the size of the microgel, the temperature dependence of the hydrodynamic diameter, the temperature range of the volume phase transition temperature, and the swelling ratio using light scattering. The results of the experiments are presented in Table 1. Figure 1 shows the hydrodynamic diameters as a function of the amount of DMAEMA introduced into the microgel formulation at 25 and 40 °C (i.e., below and above the volume phase transition temperature of the NiPAM microgels). We observe that the hydrodynamic diameters, $D_{\rm h}$, of the microgels decrease with an increasing amount of DMAEMA in the microgel formulation from 0 to 3 mol %, in qualitative agreement with published work. The decrease in the size of PNiPAM microgels with the DMAEMA content during microgel formulation is likely to be induced by the so-called surfactant effect.20 Indeed, oligomers consisting of NiPAM and DMAEMA comonomers behave as efficient surfactants, which

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Figure 2. Variation of the hydrodynamic diameter, D_h , of microgels synthesized in the presence of various DMAEMA contents, used in the microgel formulation, as a function of the temperature: (\bullet) 0, (\blacksquare) 0.5, (\blacktriangle) 0.72, (\triangledown) 1, (\bigcirc) 1.25, (\square) 1.5, and (\triangle) 3%. For all systems, the concentration of the microgel solution is 0.002 wt %. The error was estimated to be less than 10%.

adsorb during the early stage of the polymerization process on the growing microgel and stabilize the formed microgels. The temperature dependence of the hydrodynamic diameter of NiPAM microgels is shown in Figure 2. The VPTT was found to be around 33 °C (\pm 2 °C) and slightly dependent on the concentration of DMAEMA monomer present in the microgel synthesis. The swelling ratio of the microgels determined within the 25 and 40 °C temperature ranges are reported in the last column of Table 1. The swelling ratio of the microgels is nearly constant and hence independent of the DMAEMA monomer introduced into the formulation of the microgel, indicating that all prepared microgels have an identical internal structure. Highly monodisperse microgel particles are formed with narrow size distributions at either low or high temperature with very low polydispersity factors (Figure S4 in Supporting Information and Table 1). The high monodispersity of microgels was also corroborated by the visual appearance of the microgel dispersions. The color observed in all microgel dispersions is due to the diffraction from ordered colloidal arrays with a lattice spacing on the order of the wavelength of visible light according to the Bragg diffraction law (Figure S5 in Supporting Information).²³

III.2. Interfacial Tension Measurements. As a complement to NMR and DLS investigations, n-dodecane-water interfacial tensions were determined for NiPAM-based microgel solutions using the fresh drop method (Experimental Part). As shown in Figure 3, the interfacial tension of *n*-dodecane against solutions of microgels synthesized in the presence or absence of DMAEMA monomers (entries 1 and 5 in Table 1 corresponding to synthesized microgels with 0 and 1.25 mol % DMAEMA, respectively) was measured as a function of temperature. To probe the possible presence of DMAEMA units within the microgel structure, the pH of the samples was adjusted to 2 so that the DMAEMA units were positively charged. Under this condition, we expect to amplify the differences in the interfacial tension between the two microgel solutions. In both microgel solutions, the number concentrations of gel particles are analogous. Over the whole temperature range (24-36 °C), the values of the interfacial tension of both microgels are superimposed. The similarity of the curves again gives a strong indication that the presence of DMAE-MA units within the microgels is unlikely. The general trend in the interfacial tension curves will be discussed in section IV.



Figure 3. Variation of the interfacial tension (dodecane/water) with temperature for microgels synthesized in the absence (\blacksquare , entry 1 in Table 1) and in the presence of DMAEMA (O, entry 5 in Table 1). The concentrations of microgel solutions, which are respectively equal to 1 and 0.062%, have been adjusted so that the total number of particles in the solution is the same for both samples. Data were acquired using the fresh drop method at pH 2.



Figure 4. Stability behavior as a function of temperature of *n*-dodecane in water emulsions stabilized with NiPAM microgels (entry 1 in Table 1) at pH 9. The particle concentration is 1% w/v. Pictures were taken using an optical microscope at temperatures indicated above. The scale bar is 20 μ m.

III.3. Emulsion Stability. The stability of *n*-dodecane droplets dispersed in a microgel aqueous phase (direct emulsions) was studied under various physicochemical conditions. Most experiments were conducted at pH 9, although some selected samples were also studied under acidic conditions (pH 2). Figure 4 shows

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Figure 5. Stability of direct emulsions (*n*-dodecane droplets dispersed in a microgel aqueous solution) under various conditions of pH and temperature as indicated above for microgels synthesized in the absence of DMAEMA (entry 1 in Table 1). Pictures were taken 3 days after sample preparation. The top series shows sideview pictures; the bottom series shows top-view pictures.

pictures of emulsions stabilized with the microgel at pH 9 synthesized in the absence of DMAEMA. They were taken at various temperatures upon heating the sample from 20 to 45 °C. In that case, note that *n*-dodecane and water were emulsified at T = 20 °C to produce the direct emulsions (single-emulsion method), the stability of which was further observed at higher temperatures. As seen from the pictures (Figure 4), polydisperse droplets with an average size on the order of a few micrometers form at 20 °C, as typically observed for (macro)emulsions. Upon increasing the temperature, coalescence clearly occurs at temperatures close to the VPTT, as shown by the formation of large deformed interfaces. We point out that similar results were obtained using the microgels synthesized in the presence of DMAEMA.

Pictures of fresh emulsion samples, prepared by emulsifying oil and water, were also taken at pH 2 and 9 at temperatures of 20 and 45 °C for microgels synthesized in the absence (Figure 5) and the presence (Figure S6 in Supporting Information) of DMAEMA monomers. The method is referred to as the fresh emulsion method (Experimental Part). The results clearly show that stable direct emulsions can be prepared at 20 °C irrespective of pH (with a visible syneresis effect). At pH 2 or 9, a white dispersion of *n*-dodecane in water can actually be produced at 45 °C with stirring. However, the breaking of the emulsion sample is almost completely achieved within a few minutes. Consequently, the stability behavior of emulsions under various physicochemical conditions does not point to the presence of DMAEMA within the purified microgels (Figure 4 and Figure S6 in Supporting Information).

As a conclusion to section III, we show that the synthesized microgels are essentially free of DMAEMA monomer units. If DMAEMA monomer units were present within the microgels, then their amounts would be below the onset of detection of ¹H NMR and ¹³C NMR spectroscopy (Supporting Information). Also, the interfacial properties of the dodecane/water interfaces as probed by interfacial tension measurements and emulsion stability experiments are not sensitive to parameters specific to DMAEMA units such as pH and can be interpreted by the sole presence of NiPAM monomer. In other words, the presence of DMAEMA monomers in the synthesis batch is important to controlling both the size and polydispersity of the microgels. However, on the basis of the above-described experiments, the purified microgel particles do not contain DMAEMA units. The



Figure 6. Variation of the interfacial tension (*n*-dodecane/water) with temperature for the NiPAM microgels synthesized in the absence of DMAEMA (entry 1 in Table 1). Data were acquired for microgel solutions at pH 9 and $C_{\rm M} = 1$ wt % using the fresh-drop method (\bigcirc) and the single-drop method (\square).

weak polydispersity of the synthesized microgels can be explained by the presence of small charged oligomers containing DMAE-MA monomers, which behave as surfactants and therefore colloidally stabilize the growing microgels in an earlier stage of the nucleation step. This surfactant effect is consistent with the fact that we obtain smaller and monodisperse microgels upon increasing the number of DMAEMA monomers.²⁴ Hence, in what follows, we report on studies dealing with the properties of NiPAM microgels (i.e., free of DMAEMA) adsorbed at *n*-dodecane/water interfaces.

IV. NiPAM Microgels at Dodecane Oil/Water Interfaces as a Function of Temperature

This section deals with the properties of NiPAM microgels because it was shown that purified microgels do not contain DMAEMA monomers. We present interfacial tension measurements of microgel solutions as a function of temperature as well as results of emulsion stability as a function of temperature for the microgel solutions. In what follows, the pH of the samples was adjusted to 9 to carry out the interfacial measurements because the emulsion stability was studied in detail at that pH. As detailed in the Experimental Part, two different methods (fresh and single drop) were chosen to measure the variation of the interfacial tension with temperature as shown in Figure 6. Figure 6 shows that, for the single and fresh-drop methods, the interfacial tensions measured at a concentration of 1% are 12-20 mN/m below that of the pure *n*-dodecane/water interface (around 50) mN/m at ambient temperature). The values, which are rather low, are of the same order of magnitude as those recently measured by Richtering et al.¹⁴ for NiPAM-MAA microgels at the *n*-heptane/ water interface. More surprisingly, as shown in Figures 3 and 6, the interfacial tension versus temperature curves exhibit two distinct regimes that expand on both sides of a minimum temperature of about 33-34 °C: (i) a decrease in the interfacial tension as the temperature increases from room temperature up to about 33-34 °C and (ii) an increase in the interfacial tension above 33–34 °C. Clearly, the variation of the interfacial tension with temperature exhibits a minimum that corresponds well to the bulk phase transition temperature of the NiPAM microgels solutions (33-34 °C, which is also the LCST of the NiPAM polymer

⁽²⁴⁾ Pelton, R. Adv. Colloid Interface Sci. 2000, 85, 1-33.

chains) (Figure 2).^{24,25} The differences in the interfacial tension between the minimum and the maxima (on both sides of the VPTT) are actually small (on the order of 4 mN/m at most, Figures 3 and 6). However, we point out that the measured difference is reproducible and hence effective. To the best of our knowledge, the presence of a minimum near the VPTT of the microgel in the variation curve of the interfacial tension with temperature has never been reported in the literature.

The decrease in the interfacial tension below the LCST has been reported for PNiPAM linear chains.²⁶⁻²⁹ This behavior was essentially attributed to two combined phenomena: $^{29-31}$ (i) the formation of more compact layers and (ii) the increase in the number of adsorbed PNiPAM chains. Indeed, a larger number of PNiPAM units adsorb in a more coiled conformation because of the decrease of the excluded volume interactions as the temperature increases. Similarly, for microgels, the decrease in the interfacial tension below the VPTT may also be due to an increase in the number of adsorbed particles and/or the formation of more compact layers. Indeed, the PNiPAM microgel particles are to some extent compressible and are likely to deform into flat lenses as already observed at interfaces.^{32–35} Such conformational rearrangements allow the system to minimize its interfacial energy by optimizing the number of NiPAM monomers in contact with interfaces. It should also be noted that Dufresnes et al.³² found that the elastic modulus of the microgel particles increases with temperature, causing it to form flat layers more slowly. Therefore, there is probably a delicate balance between the gain in interfacial energy and the loss in mechanical energy as the temperature is raised.

We now turn to the increase in the interfacial tension above the VPTT. In our series of microgels, the interfacial tensions remain surprisingly low, on the order of 12–15 mN/m within the 33– 40 °C temperature range. To some extent, this feature is puzzling because the thermodynamic solvent conditions of the NiPAM monomers in water are rather different below and above the VPTT (Figure 2 and Table 1).⁸ As a consequence, the microgel particles, which adsorb at temperatures lower and higher than the VPTT, are a priori different objects. According to the data presented in Figure 6, this does not strongly change the formation of the proximal zone formed by the adsorbed NiPAM monomers in the vicinity of the interface, which is known to set the interfacial tension. Because the interfacial tensions are of same order of magnitude (about 14 mN/m) on both sides of the VPTT as well as in the VPTT region, we come to the conclusion that the slight differences measured in the interfacial tension values within the VPTT region of temperatures are likely to be due to subtle structural organizations of the NiPAM microgels at the interface as the temperature is changed. This also suggests that an important desorption of the microgel particles as the temperature increases above the VPTT is not realistic. It is worth mentioning that the above discussion adequately describes the results obtained for both the single- and fresh-drop methods of interfacial

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tension versus temperature measurements. In both cases, with respect to the measured values of the interfacial tension at 25 and 40 °C, the overall concentration of NiPAM monomer units adsorbed at the interface is similar. Consequently, the preadsorbed microgel particles at 20 °C (single drop method) remain anchored at the interface with increasing temperature. Similarly, in the case of the fresh drop method, the adsorption of microgels under bad solvent conditions indeed occurs up to 40 °C. Also, as seen in Figure 6, the two curves differ by their values of the interfacial tension measured within the 28–40 °C temperature window. As mentioned previously, the observed differences are slight but reproducible. An attempt to comment on this feature is given below.

Nontrivial effects of the thermal history have already been observed by Zhang et al.²⁶ as well as Monteux et al.³⁶ for PNiPAM linear chains at the air-water interface. In that case, the PNiPAM units were found to be trapped at the interface when continuously heated from 20 to 40 °C as deduced from very high values of the interfacial storage and loss moduli measured above the LCST. On the contrary, when a fresh interface was formed at each temperature, the interfacial moduli dropped above the LCST because of the adsorption of disconnected aggregates at the interface. Moreover, aggregates of PNiPAM chains at soft surfaces have been reported by Jean et al.³⁰ They mentioned that these hydrophobic aggregates are able to destabilize thin-liquid films. In ref 36, entanglements of PNiPAM chains preadsorbed at the interface would be at the origin of the trapped PNiPAM chains at elevated temperatures. Though we also deal with NiPAM monomers in our study, it sounds less straightforward to use similar arguments to explain that the interfacial tensions obtained by the single drop method are lower than those obtained for the fresh drop method. As a matter of fact, the trapping of preadsorbed microgel particles at interfaces caused by the formation of entanglements is unlikely. The idea that aggregates could form at the oil/water interface is to some extent a more interesting comment on our results. This feature should be considered in our discussion because the microgel aqueous phases are turbid above the VPTT. As a consequence and to comment first on the freshdrop data, we suggest that the increase in the interfacial tension above the VPTT would be due to some kind of a heterogeneous packing of microgels, which adsorb at interfaces as particles under bad solvent conditions. In other words, the NiPAM microgels can adsorb as single particles or aggregates, which could form either in situ at the interface or in the bulk aqueous phase. Under these complex adsorption conditions, heterogeneities at the interface leading to the formation of holes (i.e., oil molecules in contact with water molecules as at the bare oil/water interface) can be reasonably considered. Such heterogeneities are more and more likely to occur with an elevation of temperature, which leads to the observation of higher interfacial tension. Similar arguments can be used to give a tentative explanation of the data associated with the single-drop method. However, in this case, the microgel particles, which are already present at the interface as the drop is formed at 20 °C, could slightly improve the pavement of the NiPAM units adsorbed at the interface. We suggest that this phenomenon could be at the origin of the slight differences observed in the interfacial tension within the 28-40 °C temperature window or could be due to the fact that the minimum in the interfacial tension is shifted to a slightly higher temperature ($T \approx$ 34 °C) in the case of the single drop experiment as compared to that of the fresh drop ($T \approx 31$ °C). As shown in Figure 6, the

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Figure 7. Formation of a microgel tablet at the *n*-dodecane/water interface as a function of time ($C_{\rm M} = 1$ wt %, T = 45 °C, and pH 9): A microgel aqueous solution (bottom phase) in contact with *n*-dodecane (top phase) prepared at ambient temperature and pH 9 is heated to 45 °C and left at that temperature. The solution becomes immediately turbid (t = 0) and evolves with time to progressively form a tablet with a well-defined shape at the *n*-dodecane/water interface. About 30 min was required to obtain the cylinder tablet, which is anchored at the interface mainly on the water side. (Top) Side view and (bottom) top view.

values of the interfacial tension measured at 40 °C with both techniques are similar for both methods. Therefore, the increase in the interfacial tension arising from hole formation is at least partially compensated for by the adsorption of microgel particles having higher NiPAM monomer unit densities as the temperature increases.

Although we cannot give direct evidence of the presence of such microgel aggregates at the drop surface, we observed a surprising phenomenon occurring with samples consisting of separated phases of *n*-dodecane and a 1% concentrated microgel aqueous solution (Figure 7). The two phases were prepared at 20 °C, heated to above the VPTT at 45 °C, and left in contact at that temperature. We observed the progressive formation of a macroscopic precipitate that grows at the oil/water interface as a function of time while the aqueous phase becomes clearer. After a duration of about 30 min, the time evolution of the phenomenon seems to end, at least to the naked eye. It is also worth mentioning that cycling the temperature between 20 and 45 °C leads to the reversible formation of the precipitate. As shown in Figure 7, the precipitate looks like a white cylindrical tablet located at the oil/ water interface, preferentially in water. Such a tablet forms similarly at the surface of aqueous microgel solutions (not shown). In our opinion, the precipitate microgel phase nucleates at the oil/water interface and grows until forming a macroscopic third phase at the plane interface. Such a phenomenon is in agreement with the formation of heterogeneous microgel loose layers at the surface of the pendant drop used in the interfacial tension measurements and hence with the observation of increasing interfacial tension as the temperature is raised to above the VPTT.

We now comment on the stability of *n*-dodecane in water (direct) emulsions with temperature. As described above, emulsions are unstable under both preparation conditions (i.e., when a fresh emulsion is prepared at given temperatures above the VPTT (Figure 5) or when an emulsion, prepared at 20 °C, is progressively heated to a temperature above the VPTT (Figure 4)). The interpretation of our interfacial data strongly suggests that an important desorption of the microgels particles cannot explain the destabilization of the emulsion samples obtained either by the single or the fresh methods of preparation. However, the formation of both unprotected contacts between oil and water (holes)

and heterogeneous hydrophobic microgel aggregates (nucleation of a precipitate) is likely to induce the breaking of the water film separating droplets and hence emulsion droplet coalescence. As shown by Monteux et al., aggregate loose layers are not efficient to stabilize air/water interfaces.³⁷ Also, we suggest that hydrophobic particle aggregates act as dewetting agents for thin-liquid aqueous films, as mentioned, for instance, by Jean and co-workers.²⁹ As a matter of fact, hydrophobic particles are commonly used in antifoaming applications, and it is known that the wetting properties of the particles play a very important role.³⁸

V. Conclusions

PNiPAM microgels were prepared by the surfactant-free radical precipitation polymerization of NiPAM at constant concentrations of the initiator (V50) and cross linker (MBA). A series of syntheses were carried out either in the absence or presence of DMAEMA monomers at various concentrations (up to 3 mol %). No DMAEMA residues are incorporated within the purified microgel particles. For instance, ¹H NMR and ¹³C NMR spectra of microgel solutions do not exhibit any peaks corresponding to DMAEMA units. In addition, the variation of the hydrodynamic diameter of the microgels (which ranges about from 200 to 800 nm at 25 °C) was studied by dynamic light scattering as a function of temperature. Because all microgels show a marked decrease in size at a temperature of about 32 °C irrespective of the DMAEMA concentration (from 0 to 3 mol %) in the synthesis batch, the presence of DMAEMA units in the microgel is again unlikely. The size transition occurring at around 32 °C (VPTT) also matches well with that of PNiPAM polymer chains (LCST). These results were also confirmed by interfacial measurements and emulsion stability behavior. Altogether, these observations show that our synthesis approach provides an interesting route to the production of pure PNiPAM microgels. Indeed, we showed that the size of the microgel particles can be finely controlled by the DMAEMA concentration (in which the size decreases with DMAEMA concentration). The use of DMAEMA monomers in the synthesis also leads to a narrow particle size distribution as shown by DLS and UV-vis spectroscopy experiments. The various NiPAM microgels synthesized in this work can thus be considered to be well-characterized model systems, which gave us the opportunity to investigate their interfacial properties thoroughly. Tensiometry was the main technique used to probe the adsorbed microgels at the *n*-dodecane/water interface. To summarize the results, we consider here that the fresh-drop and singledrop methods lead essentially to similar conclusions. The variation of the interfacial tension (in the range of 12-17 mN/m) as a function of temperature (20-40 °C) presents a minimum value of about 12–13 mN/m at 31 °C $\,<\,T_{\rm min}\,<\,$ 34 °C (close to the LCST of NiPAM chains and the VPTT of the microgels). The curve is more or less symmetric with respect to that temperature. To the best of our knowledge, these features were not yet reported in the literature. The decrease in the interfacial tension by elevating the temperature up to T_{\min} was attributed to the formation of more compact adsorbed layers and/or an increase in the number of adsorbed microgels, which can arise from a decrease in the excluded volume interactions (but without microgel aggregation or precipitation). The increase in the interfacial tension above $T_{\rm min}$ is likely to be due to the packing of particles at the interface, which becomes increasingly heterogeneous as the temperature is raised. In this regime, the microgels adsorb from bad bulk solvent

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conditions by forming loosely packed aggregates/precipitate at the oil/water interface. This assumption is supported by the formation of a macroscopic cylinder precipitate (with a diameter on the order of centimeters and a thickness on the order of millimeters) at the interface of separated phases of oil and water for temperatures above T_{min} . Finally, the interfacial data were used to give a tentative explanation of emulsion destabilization with temperature. We suggest that the droplet coalescence observed in the vicinity of the VPTT arises mainly from the presence of unprotected contacts between oil and water coming from the formation of ill-packed particle aggregates at the interface. Simultaneously, film breaking can also be due to the dewetting effect attributed to the presence of hydrophobic particle aggregates. Consequently, the destabilization of an emulsion with temperature arises from subtle rearrangements of the microgels at the interface and not from important particle desorption. The latter scenario is indeed not realistic because the interfacial tension values remain low and are the same order of magnitude over the 20-40 °C temperature range.

Supporting Information Available: ¹H NMR and ¹³C NMR spectra of microgels. Size distribution of microgels determined by light scattering. Pictures of purified microgels and colloidal crystals. Pictures of emulsions prepared in the presence of DMAEMA monomers. This material is available free of charge via the Internet at http://pubs.acs.org.