Anionic Polymerization of ϵ-Caprolactam in Miniemulsion: Synthesis and Characterization of Polyamide-6 Nanoparticles

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ABSTRACT: For the first time, polyamide-6 nanoparticles were successfully obtained by anionic polymerization of ϵ-caprolactam in heterophase using the miniemulsion process. It is shown that stability of the monomeric miniemulsion was obtained by dispersing either molten ϵ-caprolactam or ϵ-caprolactam dissolved in a polar solvent. During polymerization only the latter miniemulsion stays stable, and nanometer aggregates of polyamide-6 were formed by precipitation polymerization inside the miniemulsion. The syntheses were carried out with different continuous phases, amounts of surfactant, an initiator, and the monomer. The success of the polymerization and the influence of these parameters on the particle size, morphology, and the molecular weight of polyamide-6 were studied using DLS, viscosimetry, TEM, and FT-IR spectroscopy.

Introduction

Polyamide-6 (PA6), also known as nylon-6, is a versatile material that combines excellent properties and competitive price, making it the most used type of polyamide worldwide. PA6 is either synthesized via anionic polymerization, which can be carried out at rather low temperature of 150 °C in the presence of an activator, or via a hydrolytic reaction at much higher temperature of 250 °C under pressure. During the anionic polymerization, an activator is usually added to the ϵ-caprolactam to speed up the activation step, and therefore the anionic polymerization is much faster than the hydrolytic reaction. The properties of PA6 made via anionic polymerization are affected by the irregularities in the polymer chain because of the side reactions, like Claisen-type condensations, that are occurring during the polymerization of ϵ-caprolactam. These side reactions are strongly favored by the weak heat exchange with the surrounding medium during a typical bulk polymerization.[1] Ricco et al. studied the influence of fast activators on the chain regularity and the polymorphism of the synthesized PA6.[2] It was concluded that cyclohexylcarbamoylcaprolactam was a particularly suitable fast activator, leading to a polymer free of irregularities in quasi-isothermal conditions. The same group used this activator in suspension polymerization using polyisobutylene as continuous phase. Here micron-sized particles, with average diameter from 53 to 479 μm, were obtained.[3]

It is of great interest to synthesize this polymer as nanometer-sized stable particles in a heterophase polymerization in order to allow a more effective heat exchange during the synthesis and to have a material which can be easily processed as stable dispersion.

It has been shown that also non-radical polymerizations can be carried out in heterogeneous phase. In fact, this also benefits from the traditional advantages of heterophase polymerization, e.g., the good heat exchange with the surrounding media and the low viscosity of the product, and gives access to micro- or nano-sized polymer particles with a narrow polydispersity index and/or with high functionalities. Among these unconventional heterophase polymerizations, one finds the polyadditions,[4] the polycondensations,[5,6] and the ionic polymerizations.[7−17]

Miniemulsion, suspension, and dispersion polymerizations are particularly suitable processes among the heterophase systems to perform polycondensation and polyaddition due to the nonmicellar nucleation process. In the dispersion polymerization process, the particles are formed during the polymerization; in the case of miniemulsion and suspension polymerization, the droplets themselves are the locus of reaction and become particles. Whereas the suspension and dispersion polymerization processes can only lead to micron-sized particles, the miniemulsion process allows one to produce stable particles in the nanometer size range, typically resulting in particles with a diameter of between 50 and 500 nm.[18] Moreover, the miniemulsion technique provides a complete control on the particle size since the size keeps constant during the polymerization since coalescence and Ostwald ripening are effectively avoided.

In the case of performing nonradical polymerization in miniemulsion, several papers have been recently reported in the literature. Miniemulsion droplets consisting of a mixture of epoxides and diamines, dithiols, or bisphenols in water were polymerized to obtain epoxy particles.[4] High molecular weight hydrophobic polyurethanes could be prepared in direct miniemulsion, dispersing the diisocyanate and the diol in water in the presence of an organo-tin catalyst.[5] Finally, it was shown that polyester particles could be obtained in a polycondensation reaction in miniemulsion, reacting a hydrophobic diol and a diacid dispersed in the presence of water.[6]

As another class of unconventional heterophase polymerizations, ionic polymerizations are described for the production of well-defined polymer particles. In fact, ionic polymerizations lead often to good control of the polymer architecture with a narrow polydispersity in molecular weight. There is a cornucopia of documents about the ionic polymerization of cyclosiloxanes in

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Table 1. Composition, Yield, and Hydrodynamic Diameters of the Miniemulsions of ϵ-Caprolactam

sample	polar solvent	ratio CL/polar solvent [w/w]	dispersed phase [%]	P(E/B-EO)[a] [wt %]	yield [%]	diam[b] [nm]
		variation of the amount of surfactant				
1	DMSO	1/2	20	4	93	347
2	DMSO	1/2	20	5	94	226
3	DMSO	1/2	20	7	95	174
4	DMSO	1/2	20	10	94	154
		variation of the polar solvent in the droplets				
5	dimethylacetamide	1/2	20	5	93	349
		variation of the amount of initiator: 3.3 mg instead of 5 mg				
6	DMSO	1/2	20	5	89	234
		variation of the ratio CL/DMSO				
7	DMSO	3/5	20	5	91	312
		variation of the dispersed phase content				
8	DMSO	1/2	30	4	90	641
		variation of the continuous phase (here: decalin)				
9	DMSO	1/2	20	5	91	922
		using of an additional osmotic pressure agent (here: acetamide)				
10	DMSO	1/2	20	5	94	235

[a] Compared to the dispersed phase. [b] Diameter determined by dynamic light scattering.

aqueous miniemulsion and also in emulsion.[7] The same processes were used to anionically polymerize alkylcyanoacrylates,[8] episulfides,[9] *N*-carboxy-α-amino acids,[10] methylidene malonates,[11] and glycidyl ethers.[12] Lanthanide triflate-mediated cationic polymerizations were used to polymerize *p*-alkoxystyrene in emulsion.[13] Recent contributions dealt with the water-resistant ytterbium triflate, $Yb(OTf)_3$, which mediated successfully the cationic emulsion polymerization of *p*-methoxystyrene in aqueous media in conjunction with one hydrogen chloride−vinyl monomer as the initiator.[13d]

In all ionic polymerization processes in heterophase described above, water was used as continuous phase, with most of the time using the reactive counterion of an inisurf (both initiator and surfactant) to initiate the polymerization. However, these processes are limited to very reactive monomers and/or give quite low molecular weight products.

There are only a few investigations about heterophase anionic polymerization of less reactive monomers initiated by strong bases, e.g., sodium and potassium hydride. Because of the use of the strong bases, the water is not suitable for such polymerizations. Thus, efficient anionic polymerizations initiated by strong bases are theoretically restricted to the dispersion process, the direct heterophase systems with a polar aprotic continuous phase, and the inverse systems with an apolar aprotic continuous phase. Some studies of anionic polymerization were made in dispersion.[14] They reported living conditions and narrow molecular weight. High molecular weight polyoxymethylene was prepared via cationic polymerization of trioxane catalyzed by $BF_3{\cdot}O(C_2H_5)_2$ in suspension.[15] 2-Pyrrolidone,[16] oxiranes,[17] and ϵ-caprolactam[3] were polymerized in suspension processes using strong bases, leading to polymer microparticles. THF was the continuous phase and the initiator KH for the oxirane polymerization. Polyisobutylene oil and NaH were respectively the continuous phase and the initiator for the ϵ-caprolactam polymerization.

As shown by the polyaddition and polycondensation experiments in miniemulsion, the miniemulsion process provides the possibility to synthesize submicron particles of functional polymers even by nonradical polymerization. Some anionic polymerizations in heterogeneous media have shown their usefulness to prepare functional latex with an initiation via strong bases, too. In this paper, we want to show that polymerizations initiated via strong bases can be done using the miniemulsion technique. Thus, we studied the anionic polymerization of ϵ-caprolactam (CL) in an organic solvent in order to obtain functional polyamide-6 nanoparticles in miniemulsion.

Experimental Part

Chemicals. The monomer ϵ-caprolactam was purchased from Aldrich (99+%) and then recrystallized twice in cyclohexane and vacuum-dried over P_2O_5. The activator *N*-acetylcaprolactam (ABCR, 99%) was used as received. The initiator of the polymerization NaH was purchased from Merck-Schuchardt (60% in suspension), washed with dried perfluoroether, and dried. Dimethyl sulfoxide (DMSO) from Merck was dried under CaH_2 for 15 h and then distilled under reduced pressure. Dimethylacetamide was shaken with BaO for 1 week, refluxed with BaO for 1 h, and then fractionally distilled under reduced pressure. Then the dimethylacetamide was dried under CaH_2 for 15 h and then distilled again under reduced pressure. The block copolymer emulsifier poly[(butylene-*co*-ethylene)-*b*-(ethylene oxide)], P(B/E-*b*-EO), consisting of a poly(butylene-*co*-ethylene) block ($M_w = 3700$ g mol^{-1}) and a poly(ethylene oxide) block ($M_w = 3600$ g mol^{-1}) was synthesized starting from Kraton liquid (Shell), which was dissolved in toluene, by adding ethylene oxide under the typical conditions of anionic polymerization.[19] P(B/E-*b*-EO) was vacuum-dried prior to use. P(B/E-*b*-EO) was chosen as the surfactant because of its strong ability to stabilize inverse emulsions and its inertness related to the NaH and the sodium caprolactamate. The hydrophobic apolar isoparaffinic hydrocarbon Isopar M was a gift by Exxon Chemical. Isopar M and decalin were refluxed with CaH_2 for 15 h and then distilled from the CaH_2 under vacuum. Formic acid from Merck-Schuchardt (99%) was refluxed with boric anhydride for 3 days, distilled under vacuum, and then used for UV analysis. CaH_2 and BaO were purchased from Aldrich and used as received.

Synthesis of PA6 Particles. A typical miniemulsion polymerization procedure occurred in the following way: 0.5 g of the monomer, 1 g of DMSO, and 5 mg of NaH (polar phase) were mixed at room temperature to create the sodium caprolactamate in DMSO. For some experiments as shown in Table 1, 100 mg of acetamide was added to the polar phase to use it as an additional osmotic pressure agent. The mixture was then added to a solution of a controlled amount of surfactant in 7.5 g of the continuous phase (usually Isopar M as apolar phase).

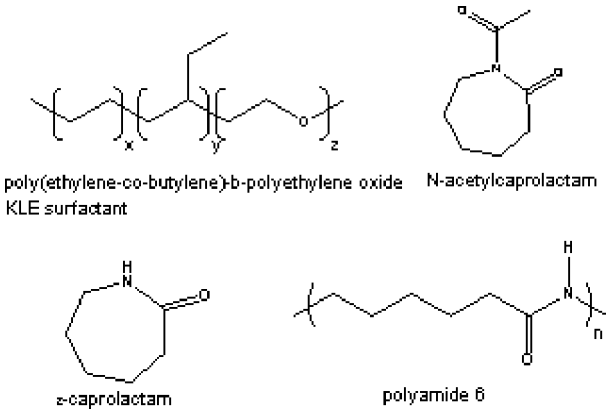

Figure 1. Chemical formula of the surfactant, activator, monomer, and polymer.

After stirring 1 h for preemulsification, the miniemulsion was prepared by ultrasonicating the mixture for 225 s, with 10 s pulse on and 5 s pulse off cycles, at 65% amplitude (Branson sonifier W450 Digital, tip size 6.5 mm) under argon at 0 °C with ice cooling in order to prevent polymerization. Then 0.05 mL of *N*-acetylcaprolactam was added to the mixture, and ultrasonication was performed for 20 s at the same amplitude as before. The miniemulsion was subsequently transferred in an oil bath at 150 °C to allow the polymerization to occur. The chemical formula are summarized in Figure 1. The overall synthesis procedure is shown in Figure 2. Completion of reaction was observed after 25 min as checked by ^{1}H NMR measurements of the monomer. The PA6 solid used for the polymer characterization was obtained by drying the miniemulsion for 96 h at 40 °C under vacuum. The monomer and oligomer were then extracted from the crude polymer with water. Finally, we washed the solid with hexane, dried the solid again, and weighed the resulting polymer to calculate the yield of polymerization. FT-IR (KBr): 3300 (vs, NH), 2933 (s, CH_2), 2860 (m, CH_2), 1642 (vs, amide I), 1541 (s, amide II), 1371 (w, CH_2), 1261 (w, CH_2), 1200 (w, CH_2), 1120 (w, CC).

Analytical Methods. The particle sizes were measured by photocorrelation spectroscopy using a Nicomp particle sizer (model 370, PSS, Santa Barbara, CA) at a fixed scattering angle of 90°. The data were processed using the cumulants method.

Electron microscopy was performed with a Phillips 400T TEM operating at 80 kV. The miniemulsions were diluted in cyclohexane and then applied to a 400 mesh carbon-coated copper grid and left to dry. No further contrasting was applied.

The FT-IR measurements were performed to check for the vanishing of the lactam bond and the creation of polyamide bonds with KBr pellets in a FTIR 113v Bruker spectrophotometer equipped with a DTGS detector using 100 signal-averaged scans at a resolution of 2 cm^{-1}. The solid used for the IR measurements was obtained by drying the miniemulsion for 96 h at 40 °C under vacuum, then washing the solid with water and hexane, and drying the solid again.

Viscometry measurements were performed using an AVS 350 Schott Geräte rheometer to evaluate the mass-weighted molecular mass on a polymer solution of 0.05 g dL^{-1} in H_2SO_4 (95−97% from Merck) at 20 °C.

UV analyses were carried out with a Perkin-Elmer UV/vis spectrometer Lambda 16. PA6 solutions in anhydrous formic acid of 0.5% (w/w) were analyzed, searching for optimum density maxima at 270−280 nm. The measurements were done between 250 and 400 nm.

Results and Discussion

Miniemulsion of Molten and Dissolved ϵ-Caprolactam. ϵ-Caprolactam is a hydrophilic monomer with a high solubility in water of 5200 g L^{-1} at 25 °C and a melting point of 69 °C.[20] Because of the high water solubility, direct miniemulsions are not possible, but inverse miniemulsions of ϵ-caprolactam in a hydrophobic medium should be obtained, either by melting the ϵ-caprolactam and dispersing it at higher temperature or by dissolving the ϵ-caprolactam and dispersing it at room temperature.

It was found that a stable (at least for a time scale of observation of several hours) miniemulsion of molten ϵ-caprolactam as droplets in the paraffinic oil Isopar M as continuous can be obtained at temperatures above 70 °C by using as low as 5 wt % related to the monomer of the block copolymer P(B/E-*b*-EO). However, for the following polymerization, temperatures of 150 °C are required. At these high temperatures, the miniemulsion

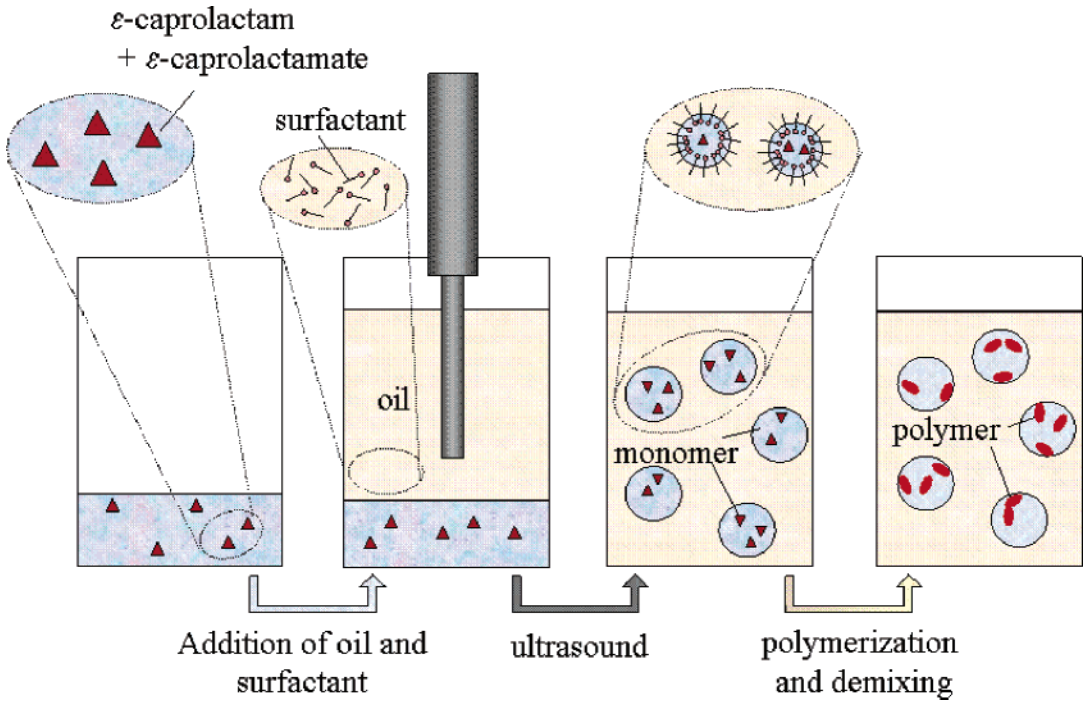

Figure 2. Process for the synthesis of PA6 nanoparticles in miniemulsion.

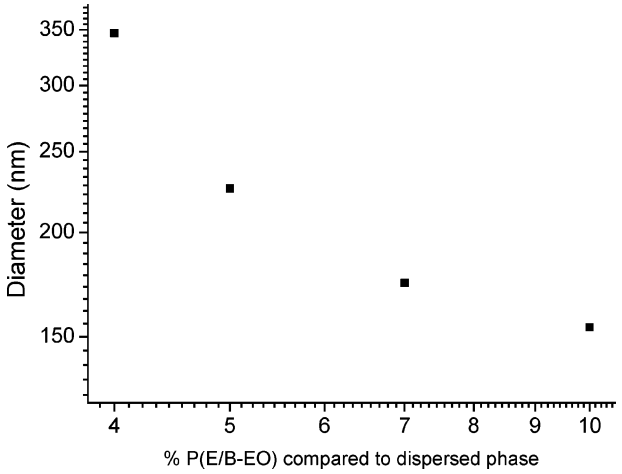

Figure 3. Dependence of the hydrodynamic diameter of the miniemulsion droplets on the amount of surfactant.

with molten ϵ-caprolactam droplets is extremely unstable, and during polymerization more than 90% of coagulum was obtained. Such instabilities can be assigned to a coalescence of the droplets due to the increased solubility of ϵ-caprolactam in the continuous phase at 150 °C. Using different osmotic pressure agents like low molecular weight PEO, 1-methyl-2-pyrrolidinone, acetamide, or dimethylacetamide in the polar phase did also not lead to a higher stability of the miniemulsions at the high polymerization temperature.

To overcome the stability problem, the droplets should also contain components which are much more polar and show a lower solubility in paraffinic oil at higher temperature than ϵ-caprolactam does. Therefore, the polar phase was constituted of ϵ-caprolactam dissolved in the polar solvent DMSO in a ratio 1:2. The salt sodium caprolactamate, which is produced by adding a small amount of NaH prior to emulsification, is used as initiator and osmotic pressure agent at the same time. Both the salt and the DMSO are more polar and show a lower solubility in the paraffinic oil at higher temperatures than the ϵ-caprolactam does, and thus it is expected to show a better stability against diffusion processes. A summary of the results is given in Table 1.

A stable miniemulsion was obtained at room temperature in Isopar M by using as low as 4 wt % of the P(E/B-EO) block copolymer stabilizer compared to the dispersed phase. Then the activator *N*-acetylcaprolactam was added to the mixture and distributed by ultrasonication homogeneously in all the droplets. The miniemulsion was subsequently successfully polymerized at 150 °C obtaining a stable dispersion with particles of about 350 nm. The particles grow a little bit (e.g., from 198 to 226 nm for sample 2) during the heating at 150 °C because of the enhancement of the Ostwald ripening while increasing the temperature. As expected, by increasing the amount of the surfactant P(E/B-EO) in further experiments, a decrease of the particle size was observed (see Table 1, samples 1−4). At 10 wt % of P(E/B-EO), particles of 150 nm were obtained. Please note that these hydrodynamic diameters are the diameter of the droplets DMSO + PA6 after polymerization dispersed in the continuous phase. The classical miniemulsions give a linear dependence of the logarithm of the hydrodynamic diameter on the amount of surfactant.[18] Figure 3 shows that a nonlinear dependence on the amount of surfactant is observed which might be due to the Ostwald ripening instabilities at high temperature.

Using the solvent dimethylacetamide (sample 5) instead of DMSO to dissolve the CL salt, at the same surfactant concentration of 5%, particles with a higher diameter were obtained than in the case of DMSO. As expected, decreasing the amount of initiator does not affect significantly the droplet size (sample 6). Increasing the ratio ϵ-caprolactam/DMSO (w/w) in the miniemulsion droplets from 1/2 to 3/5 with the same amount of surfactant relative to the dispersed phase of 5% leads to an increase of the hydrodynamic diameter in sample 7 from 226 to 312 nm. Sample 8 shows that increasing the ratio dispersed phase/continuous phase (w/w) give much bigger droplets (641 nm) for the same ratio of surfactant. The results show clearly that the droplet sizes are very sensitive to the amount of surfactant and to the ratio of the dispersed phase to continuous phase.

As a different continuous phase, decalin was used to allow creating stable particles with higher diameter of about 920 nm (sample 9). Polyisobutylene oil and silicon oil were found not to be suitable as continuous phase to provide stable miniemulsion of dispersed ϵ-caprolactam in DMSO.

Using acetamide as additional osmotic pressure agent in the sample 10 led to the same particle size, indicating that acetamide does not lead to a more efficient osmotic pressure inside the droplets. Acetamide was chosen because it is polar, has a high boiling point (222 °C at atmospheric pressure), and is inert toward all the reagents used in the process.

Morphology of the Polymer Particles. The morphology of the particles can be analyzed using TEM. After drying the dispersion and letting the DMSO evaporate, the TEM shows the PA6 particles. The precipitated particles are not spherical but ellipsoidal like and can have an average length (determined from TEM) of 27 ± 2.5 nm ($\sigma = 9.26$) and an average width of 14 ± 1.5 nm ($\sigma = 5.58$) (see TEM in Figure 4). The average aspect ratio was determined to be 1.93. Interestingly, it seem that the hydrodynamic radius does not have an influence on the geometrical radius of the PA6. This size corresponds nicely to the size which is determined by DLS after dialysis of the dispersion with hexane and Isopar M in order to get rid of the DMSO in the droplets. After dialysis, a particle diameter of 30 nm was detected which can be attributed to the pure polyamide particles.

These special morphologies are due to the demixing between the solvent DMSO and the PA6 during polymerization. Because the PA6 is not soluble in DMSO, the system can be considered as a precipitation polymerization in the miniemulsion droplets.

Molecular Weight of Poly-ϵ-caprolactam in Miniemulsion. Since PA6 is only insoluble in the most common solvents, typical means like GPC cannot be used for the determination of the molecular weight, but the molecular weight has to be measured by viscosimetry, dissolving the polymer in sulfuric acid. Results are given in Table 2. The molecular weight was calculated using the following equation:

$$[\eta] = 0.51 \times 10^{-3} M_v^{0.74}$$

where $[\eta]$ is the intrinsic viscosity in dL g^{-1}.

In fact, we obtained relatively high molecular weight polyamide-6 of about 35 000 g mol^{-1}. We obtained an

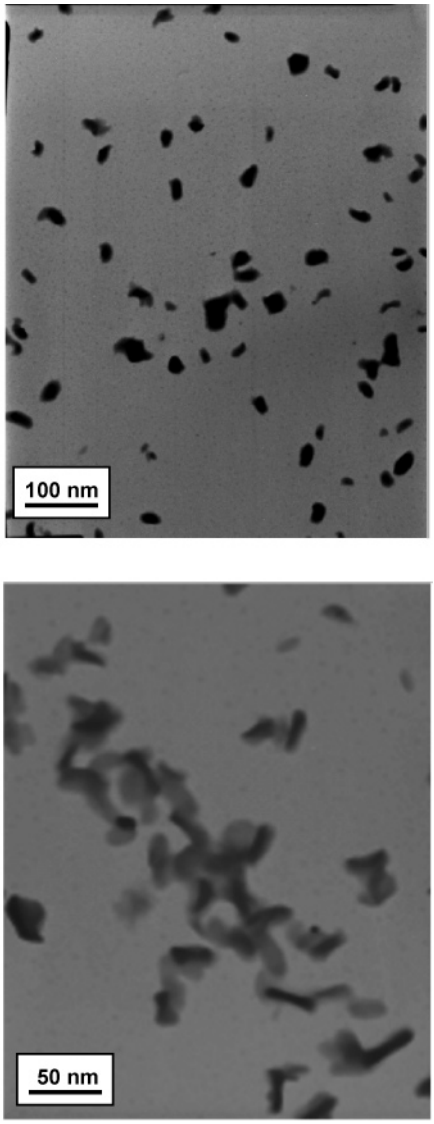

Figure 4. TEM micrographs of PA particles (sample 2).

Table 2. Influence of the Composition of the Miniemulsions on the Polyamide-6 Intrinsic Viscosities and Molecular Weights

sample	$[\eta]$ [dL g^{-1}]	M_v [g mol^{-1}]	sample	$[\eta]$ [dL g^{-1}]	M_v [g mol^{-1}]
1	1.16	34 400	5	1.15	34 000
2	1.19	35 600	6	1.30	40 100
3	1.18	35 200	7	1.17	34 800
4	1.18	35 200	8	1.15	34 000

even higher molecular weight in decreasing the amount of initiator in the polar phase with the sample 6. Unfortunately, the yield of polymerization for sample 6 is only 89% compared to the 94% (see Table 1) observed for the other samples. The nonpolymer part is known[2] to be a mixture of nonreacted monomer, oligomers, and low molecular weight side products including the cycles. The molecular weight observed for sample 6 is less than the theoretical expected ones,[2,3] which might be due to the fact that some of the NaH became inactive or that the polymer precipitation limits the chain length.

As expected, there is no significant enhancement in the molecular weight in increasing or decreasing the amount of surfactant. The bigger molecular weight (sample 6) was obtained for "average values" of surfactant content. This is maybe due to the fact that for the lower content of surfactant the droplets are less stable and that the −OH-terminated PEO part of the surfactant could react with the initiator. That means if the content of surfactant increases, the side reaction occurs more probably.

Table 3. Maximum UV Absorbance Observed for the PA6 Prepared by Miniemulsion and in Bulk

sample	absorbance max at 270−280 nm	sample	absorbance max at 270−280 nm
1	0.026	6	0.035
2	0.024	7	0.055
3	0.030	8	0.049
4	0.027	bulk	0.092
5	0.034		

In most of the studies done on ionic heterophase polymerization (emulsion, miniemulsion), an inisurf was the initiator, and thus the polymerization kinetics was governed by interfacial physiochemical parameters like the adsorption of the inisurf at the interface for instance. When using a Lewis acid surfactant catalyst for the polymerization of *p*-methoxystyrene, the initiation is located at the interface, and it was shown that it was quite difficult to obtain high molecular weight polymer. In such cases, oligomers with a molecular weight of only 1100−1400 g mol^{-1} were prepared, which is due to the difficulty for the growing oligomer to diffuse inside the droplets and because of the presence of termination or even deactivation of the catalyst.[13e] In the case polymerizing PA6 in the miniemulsion system, the in situ prepared polar initiator sodium caprolactamate is homogeneously dispersed inside the droplets, and therefore a higher molecular weight is obtained.

The structure of our PA6 chains was checked by UV measurements given in Table 3. In fact, the peak of absorbance between 270 and 280 nm is usually considered as proportional as the amount of structural irregularities in the PA6 chains due to side reactions and cross-linking.[1] The results show that PA6 obtained in miniemulsion has at least 2 times less irregularities as the sample we polymerized in bulk (see Figure 5).

Conclusion

It was shown that nanoparticles of polyamide-6 could be synthesized using the inverse miniemulsion technique. Even though stable molten ϵ-caprolactam droplets could be created at low temperatures, these droplets show a limited stability at the reaction temperature of 150 °C. Therefore, the monomer ϵ-caprolactam, the

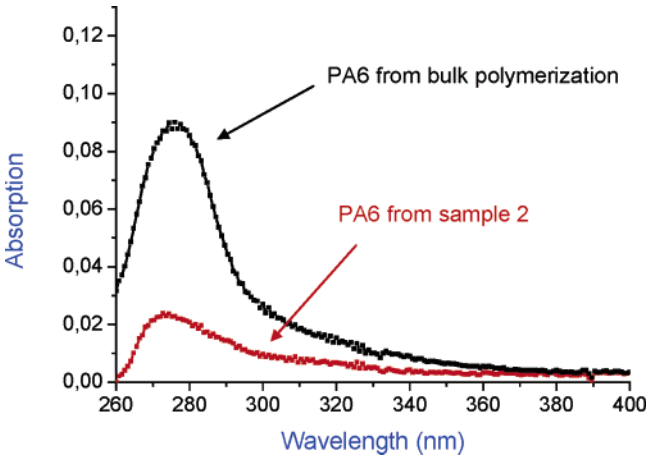

Figure 5. UV spectra of sample 2 and of a reference sample prepared in bulk polymerization.

initiator NaH, and the classical activator *N*-acetylcaprolactam were dissolved in DMSO in order to build the polar phase, which was stable after dispersing in the inexpensive isoparaffinic continuous phase also at 150 °C. During the polymerization, a demixing of the DMSO and the polymer occurred, and the polymer precipitated inside the DMSO droplets, leading to anisotropic nonspherical nanoparticles as revealed by TEM. The polyamide-6 exhibited a relatively high molecular weight of 35 000−40 000 g mol^{-1} as determined by viscosimetry measurements. The absence of structural defects, which could lead to less good mechanical properties of the polymer, could also be shown. These particles could be used as high-performance anisotropic reinforcement fillers for plastic blends.

We strongly believe that our strategy, which employs polar solvents such as DMSO for the polymerization, can be also applied to prepare polymer particle of other polar monomers that are normally slightly soluble in the apolar phase. This would also allow one to polymerize water-sensitive polar monomer or any kind of polar monomers with a water-sensitive initiating system.

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