

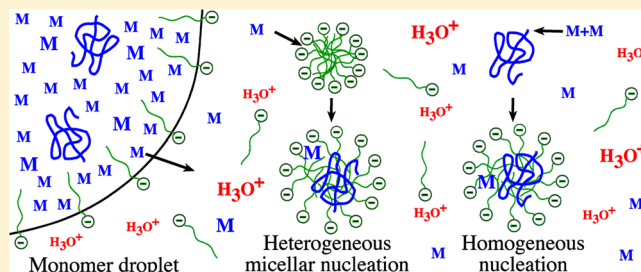
Emulsion Condensation Polymerization in Dispersed Aqueous Media. Interfacial Reactions and Nanoparticle Formation

Johanna Bailey Jönsson, Markus Müllner,[†] Lennart Piculell, and Ola J. Karlsson*

Physical Chemistry, Center for Chemistry and Chemical Engineering, Lund University, Box 124, S-22100 Lund, Sweden

Supporting Information

ABSTRACT: The polycondensation of polyesters from C_{12} monomers at 95 °C in aqueous o/w emulsions, stabilized by acidic surfactants, has been studied in detail with a range of methods during the course of the reaction, resulting in a better understanding of the underlying reaction mechanisms. Comparisons of different surfactants, and effects of added NaCl, demonstrate that the reaction site is located at the interface between the hydrophobic core of the emulsion droplets and the surrounding water and that the reaction rate is dependent on the local concentration of oxonium ions at the reaction site. The equilibrium conversion achieved at long reaction times is, however, independent of the choice of surfactant or addition of salt, and the state of thermodynamic equilibrium is discussed thoroughly. Interestingly, a fraction of numerous “nanoparticles” (droplets in the size range ≤ 100 nm) have been found to develop in addition to the original fraction of droplets in the 10 μm size range. It is suggested that these nanoparticles are formed when monomers dissolved in the aqueous phase undergo an acid-catalyzed reaction to generate water-insoluble oligomers. Once the nanoparticles are formed, the reactions in them proceed with a reaction mechanism similar to emulsion polymerization.



INTRODUCTION

Polyesters are traditionally made from polycondensation reactions carried out in organic solvents, at elevated temperature and in a majority of the cases with a catalyst present.¹ The reaction is favored by elevated temperature, which promotes removal of water in the reaction, but high temperature also results in a number of side reactions such as ring formation, oxidation, etc.¹ The reaction temperature, the reactants, and the choice of solvent all affect the outcome of the polycondensation reaction. Organic solvents are often not desired once the polyesters reach the end-user market, and the polyesters are thus separated from the organic solvent. Depending on the application, polyesters are used either as prepared or could for example be redispersed into water for formation of nanoparticles, so-called secondary emulsions, to be used in coating applications with no or low amounts of organic solvents present in the final product.²

Recent research efforts have been devoted to enable polycondensation reactions at lower temperatures, to avoid the use and ultimate separation of organic solvents, and to avoid side reactions.^{3,4} There have been trials to produce polyesters in situ, and one route has been to perform polycondensation reactions in dispersed media, i.e. o/w and w/o emulsions, miniemulsions, or microemulsions.^{5–13} In addition, enzymatic catalysis has been used in miniemulsions to form polyesters or to react carboxylic acids with linear phenyl alkanols.^{12,14,15}

A common feature of all these approaches is that the final polycondensation product is located in the organic phase,

whereas the water formed in the condensation reaction ends up in the aqueous phase. Various reactants and catalysts have been investigated where the highest conversions were achieved with hydrophobic monomers, with low water solubility, in the presence of an acidic catalyst.^{4,16} Surfactants with acidic catalytic functions have been found to be particularly useful in this context, since they stabilize the emulsions and catalyze the reaction at the same time. Manabe et al.^{17,18} made detailed studies of the formation of simple esters and the reverse ester hydrolysis in surfactant-stabilized o/w emulsions, addressing both kinetic and equilibrium aspects of the reactions. They reported that the rate of the reaction increased with increasing hydrophobic chain length of the acid surfactant but that the equilibrium conversion was the same in an o/w emulsion as in a mixture initially containing the same proportions of reactants and surfactant, but no water. On the other hand, very large proportions of the acidic surfactant (mole fractions similar to or even larger than those of the original reactants) were found to give a decreased equilibrium yield of the ester. Barrère and Landfester made a very thorough study of the formation of both simple esters and polyesters in acid surfactant-stabilized miniemulsions, establishing important kinetic and equilibrium trends.¹⁶ Of particular relevance here is that the equilibrium conversion was found to be independent of the size of the

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emulsion droplets but increased with increasing hydrophobicity of the monomers.

Although a significant amount of experimental data is now available in the scientific literature, establishing important trends, the fundamentals of polyester formation in surfactant-stabilized emulsions need to be further clarified. Both the detailed reaction mechanism(s), affecting the reaction kinetics, and the ultimate equilibrium conversion of the reaction are still poorly understood. To address these questions, we have studied polycondensation reactions in aqueous surfactant-stabilized emulsions with the monomers 1,12-dodecanediol and 1,12-dodecanedioic acid (1:1) at 95 °C. In most of the reactions we have used dodecylbenzenesulfonic acid (DBSA) as the surfactant, but we also compare with emulsions with the nonacidic sodium dodecylbenzenesulfonate (SDBS) and, furthermore, two phosphoric acid esters of ethoxylated surfactants. To locate the site of the reaction, we have carried out experiments with added NaCl at varying concentrations. The polyester formation at different stages of the reactions was studied by titration, GPC, and/or NMR, and the evolution of the emulsion droplet sizes was monitored by dynamic light scattering and conductometry. The latter experiments established, for the first time, that nanoparticles (droplets in the ≤ 100 nm size range) may form during an acid-catalyzed o/w emulsion polycondensation. Finally, the thermodynamics of the reaction equilibrium is discussed in detail, and a model for the reaction mechanisms, including the formation of the nanoparticles, is presented.

EXPERIMENTAL SECTION

Materials. 1,12-Dodecanedioic acid (DA) (99%, $T_m = 127$ – 130 °C), 1,12-dodecanediol (DO) (99%, $T_m = 79$ – 81 °C), dodecylbenzenesulfonic acid (DBSA) (90%), sodium dodecylbenzenesulfonate (SDBS) (techn. gr.), and hexadecane (HD) ($\geq 98\%$) were from Sigma-Aldrich (Mitteldorf, Germany). Two phosphoric acid esters of ethoxylated surfactants, commercially available as Disponil FEP 7030 and Disponil AEP 5300, were kindly provided by Cognis (Monheim am Rhein, Germany). For brevity, we will refer to said surfactants as FEP and AEP, respectively. Figure 1 gives the structural formulas of the surfactants.

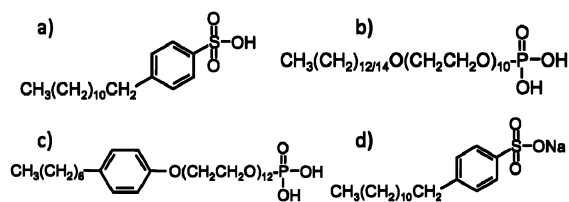


Figure 1. Structural formulas of the surfactants (a) DBSA, (b) FEP, (c) AEP, and (d) SDBS.

Deuterated chloroform (CDCl_3) (99.8%, with 0.03 v/v % tetramethylsilane (TMS)) from Dr. Glaser AG (Basel, Switzerland) was used in the NMR experiments. Ethanol (Kemetyl, Stockholm, Sweden), xylene, potassium hydroxide (KOH), and phenolphthalein (Sigma-Aldrich, Mitteldorf, Germany) were used in the titrations. For gel permeation chromatography (GPC) tetrahydrofuran (THF) ($\geq 99\%$) from VWR (Stockholm, Sweden) was used for the continuous phase. Sodium chloride p.a. was from Merck (Stockholm, Sweden). All chemicals were used as received.

Polymerization Procedure. The reactions were carried out at 95 °C either in a 250 mL glass reactor or in 25 mL parallel reactors (Carousel 12 Place Reaction Station, Radleys Discovery Technologies, Essex, UK). Reactions in the 250 mL reactor were performed by charging DO (4.7 g = 23 mmol), DA (5.3 g = 23 mmol), and HD

(0.28 g = 1.25 mmol) to the reactor together with 150 mL of distilled water. In the parallel reactors the amounts of all components were less by a factor of 1/10, but all other sample treatments were identical. Thus, in all reactions the DO and DA concentrations in the total reaction volume were 144 mmol/L, and the HD concentration was 8.1 mmol/L. The small amount of HD was added to facilitate comparison with previous miniemulsion experiments.¹⁶ The reactor was heated to 95 °C, and after 2 h of mixing to achieve homogeneity of the dispersed phase the reaction was initiated by addition of the surfactant (DBSA, SDBS, FEP, or AEP) dissolved in 10 mL of distilled water. The reactions were typically run for at least 3 h, in several cases for 24 h or longer. Samples were withdrawn and dried prior to analysis, which were carried out at room temperature unless otherwise stated. Table 1 presents an overview of all polymerization experiments and the observed conversion after 3 h measured by NMR.

Table 1. Experimental Overview (Concentrations in mmol/L) of the Investigated Reaction Mixtures and the Observed Conversion after 3 h by NMR^a

name	surfactant	salt	conv at 3 h by NMR (%)
DBSA-5	5.2 DBSA		85
FEP-5	5.2 FEP		47
FEP-8	7.7 FEP		47
FEP-17	17.4 FEP		59
AEP-5	5.0 AEP		51
AEP-8	7.5 AEP		49
AEP-17	16.9 AEP		54
SDBS-5	5.2 SDBS		14
NaCl-300	5.4 DBSA	293 NaCl	29 (at 2 h)
NaCl-150	5.3 DBSA	144 NaCl	36 (by GPC)
NaCl-8 ^b	5.2 DBSA	8.1 NaCl	70
NaCl-5 ^b	5.2 DBSA	5.2 NaCl	78
NaCl-0.5 ^b	5.2 DBSA	0.52 NaCl	73
NaCl-0.05 ^b	5.2 DBSA	0.05 NaCl	69

^aIn all experiments the DO and the DA concentrations in the total reaction volume were both 144 mmol/L and the HD concentration was 8.1 mmol/L. Experiments were carried out in a 250 mL glass reactor except where indicated. ^b25 mL parallel reactors.

Characterization of Solutions and Reaction Mixtures. Particle sizes were obtained from dynamic light scattering using a Malvern Mastersizer 2000 at room temperature. The pH of the aqueous phase was measured using a Schott CG842 pH meter with a BlueLine 23 pH gel electrode. The conductivity was measured at ambient temperature on 3 mL reactor samples diluted in 50 mL of Millipore water using a Radiometer Analytical CDM210, Switzerland. Surface tension measurements to determine the cmc for the grade of DBSA used in this study were performed at 25 °C using the pendant drop method on a drop and bubble shape tensiometer PAT-1 from SINTERFACE, Germany.

At selected times, samples for further analysis were withdrawn from the reactor with a glass pipet to a glass vial that was immediately immersed in an ice bath to stop the reaction. In order to prevent further reaction, the samples were then dried below the melting point of the monomers at 40 °C in a vacuum for 48 h.

Melting points of samples withdrawn and dried were determined using a DSC 823e (Mettler Toledo) run with a heating rate of 10 K/min. The results were evaluated using STARE SW 9.01 software (Mettler Toledo).

The conversion of the polycondensation reaction was determined by titration and/or NMR. The conversion is defined as the percentage of initial reactant (alcohol or carboxylic acid groups, depending on the method) converted during the condensation reaction. The titration of the remaining carboxylic acid was done with 1 mol/L KOH in ethanol at 30 °C with phenolphthalein as an indicator by dissolving 0.1–0.3 g of dried sample in 30 mL of xylene and 8 mL of ethanol.¹⁹ For NMR

studies the dried samples were transferred to NMR tubes and dissolved in CDCl_3 . ^1H NMR spectra were obtained using a Bruker AV-200 MHz at 25 °C. The conversion was calculated from the spectra by comparing the area of the ester peak, $\delta = 4.08$ ppm, with the sum of the ester peak area and the area of the peak of the hydrogen atoms adjacent to the alcohol end groups, $\delta = 3.53$ ppm (see Figure 2). TMS was used as an internal standard for the chemical shift.

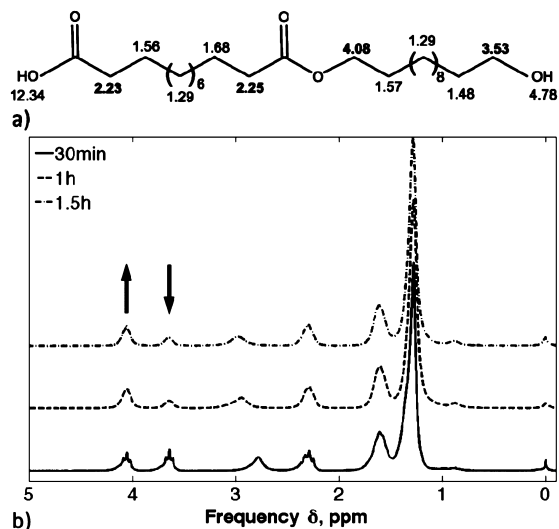


Figure 2. (a) Chemical shifts in ppm for a dimer of 1,12-dodecanedioic acid and 1,12-dodecanediol. (b) NMR spectra for DBSA-5 after 30 min (solid, bottom), 1 h (dashed, middle) and 1.5 h (dash-dotted, top). Arrows indicate the increasing ester peak (pointing up) and the decreasing peak for the alcohol end groups (pointing down).

The various methods used to determine conversion with time gave consistent values for the plateau (equilibrium) conversion for the rapidly evolving DBSA-5 system (see the Results section), whereas some systematic deviations in conversion values obtained by different methods were observed at low conversions. Each method was internally consistent, however, and the differences in conversion with time between the different systems were clearly much larger than any differences between results obtained with different methods.

Solutions for gel permeation chromatography (GPC) were prepared by dissolving approximately 2 mg of dry sample in 1 mL of tetrahydrofuran (THF), followed by filtering with a syringe filter (Acrodisc CR 13 mm syringe filter, 0.45 μm PTFE membrane, HPLC certified). In the analysis 20 μL of the solution was injected on the GPC setup and analyzed at 40 °C with 0.5 mL/min eluent flow. The GPC setup consisted of a Varian PL-gel 3 μm Mixed-E column in a Shimadzu analytical HPLC (Prominence with degasser) with a refractive index detector (RID 10A). The instrument was calibrated with an EasiVial PS-L kit (Varian) containing 12 polystyrene standards with molecular weights ranging from 162 to 38 640 g/mol.

RESULTS

Melting Transitions of Reactants and Dispersed Reaction Mixtures. For the interpretation of the other experimental data presented here it is essential to establish the state of the dispersed state (solid or liquid) during the course of the reaction. DA has a melting point of 127–130 °C, which is higher than the reaction temperature of 95 °C. DO has a melting point of 79–81 °C, and HD has a melting point of 17–19 °C.²⁰ Figure 3 shows DSC traces in the interval 25–200 °C for samples withdrawn and dried (see Experimental Section) from dispersions differing in composition and, for reacting mixtures, taken out after different reaction times. All mixtures

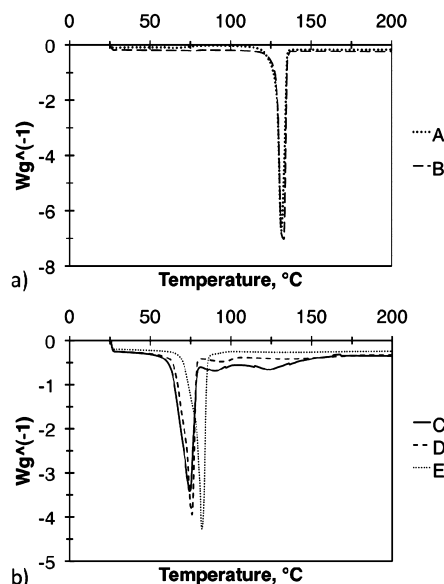


Figure 3. DSC curves showing melting transitions after drying for (a) dispersions in 5.2 mmol/L of DBSA of 144 mmol/L of DA only (dotted line) or mixed with 8.1 mmol/L of HD (dashed line) and (b) for the complete reaction mixture DBSA-5 (containing 144 mmol/L of DA, 144 mmol/L of DO, 8.1 mmol/L of HD, and 5.2 mmol/L of DBSA) 30 min (solid line), 2 h (dashed line), and 24 h (dotted line) after addition of DBSA.

were based on the “standard” reaction mixture DBSA-5 and thus contained 5.2 mmol/L of DBSA, but two of the mixtures were reference mixtures lacking DO and, for one mixture, also HD. All ingredients except DBSA were mixed and heated at 95 °C for 2 h before DBSA was added. Figure 3a compares the traces for the dispersion of DA and DBSA with that containing also HD. The dispersion of DA alone shows a peak at the reported bulk melting point of DA, and as anticipated, a small proportion of added hexadecane has an insignificant effect on the melting temperature. By contrast, the DBSA-5 mixture containing all of DA, DO, and HD (Figure 3b) formed a homogeneous melt above a temperature interval (we recall that a mixture generally does not display a sharp melting transition) initially around 75 °C, but slowly increasing during the course of the reaction. With time the dispersed phase of the reaction mixture also became more homogeneous, as can be seen from the progressive development of a smooth baseline above the main transition. With the help of conversion data presented below, we show in Figure 4 how the “melting point” (taken as the peak of the main thermal transition) increases with conversion during the course of the reaction. At low conversions the increase was slow, but above ca. 70% conversion the melting temperature increased rather sharply, reflecting the increasing melting temperature of the produced polyesters with an increasing degree of polymerization. Importantly, however, even at the final equilibrium conversion around 85% (which has been reached well before 24 h; see below), the melting temperature of the dispersed phase was still significantly below the reaction temperature of 95 °C. This analysis therefore shows that the dispersed phase was in the liquid state throughout the entire reaction.

Conversion with Time Using Different Acidic Surfactants. For practical reasons as well as for obtaining a better understanding of reaction mechanisms (see the Discussion section), it is of interest to compare the rates of conversion with

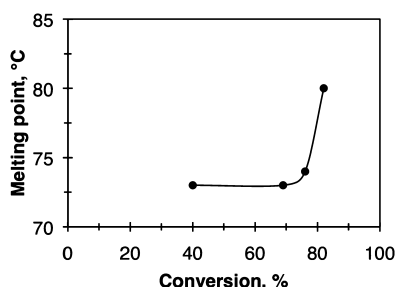


Figure 4. Increase in melting point with increased conversion for dried samples of DBSA-5 (mixture of DO, DA, HD, and DBSA). The melting points were taken as the peaks from the DSC transitions in Figure 3, and the conversion vs time was obtained from the NMR data presented in Figure 9.

different acidic surfactants. Figure 5 shows conversion over time obtained by titration for experiments using different

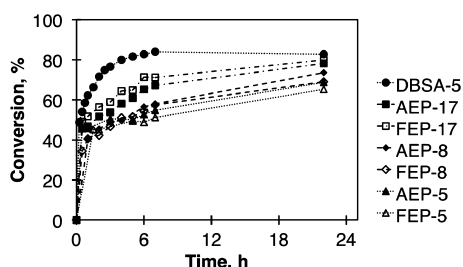


Figure 5. Conversion obtained by titration for experiments with different catalysts at 5 (dotted line), 8 (dashed line), and 17 mmol/L (dash-dotted line).

surfactants (notations are explained in Table 1). The sulfonic acid DBSA resulted in the fastest overall reaction, reaching a constant degree of conversion of around 85% in less than 6 h for the reference mixture DBSA-5. The acidic surfactants AEP and FEP also function as catalysts, giving a substantial increase in conversion over time. As shown in Figure 5 for experiments at three different surfactant concentrations, the catalytic efficiency was very similar for these two surfactants. However, even at a concentration of 17 mmol/L, the conversion at any reaction time was much lower with FEP or AEP than with 5 mmol/L of DBSA up to at least 22 h, when the experiments were terminated. In the remainder of the Results section, all presented results are obtained with 5.2 mmol/L of DBSA or, in one experiment, the sodium form (SDBS) of the same surfactant.

Analysis of Reactants and Products at Different Times. The results in Figure 5 give the overall conversion but no information on the distribution of oligomeric species that exist in the mixture at different times. The latter information is provided in Figure 6, which reproduces typical GPC curves for DBSA-5 with samples taken out of the reactor at long times, after 24, 48, or 144 h. The detector signal is given as a function of the number-average molecular weight, M_n , obtained using polystyrene standards. At long times, the reaction mixture is seen to contain a wide distribution of species, including the two monomers; the latter appear as the two overlapping peaks to the far left. Shorter oligomers can also be seen as separate peaks, but at degrees of polymerization higher than ca. 10 monomer units, the GPC column could no longer resolve individual peaks for higher oligomer generations.

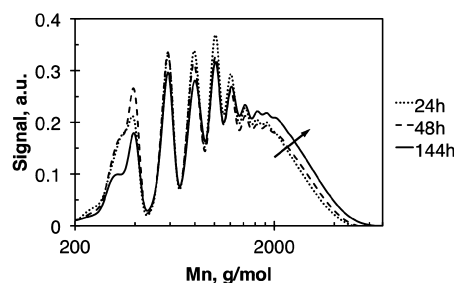


Figure 6. Normalized GPC curves for DBSA-5 samples over time. The signal at higher molecular weight increased with increasing reaction time, indicated by the arrow.

Calculations using the integrals under the normalized distributions confirmed a plateau conversion around 85% at long times. Even at very long times (above 48 h), the distribution still shifts slowly toward higher molecular weights, but the effect is too small to give a significant effect on the overall conversion; NMR results showed an increase from 84% at 48 h to 86% at 144 h.

Droplet Size Distributions at Different Times. Figure 7 shows the evolution with time of the emulsion droplet size,

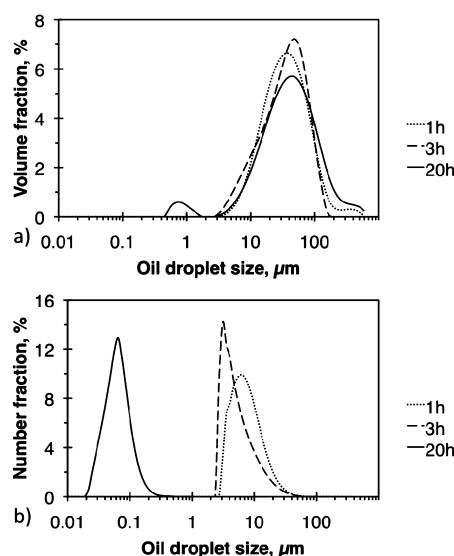


Figure 7. Droplet size distributions at room temperature after 1, 3, and 20 h of reaction based on (a) volume and (b) number for DBSA-5.

obtained from dynamic light scattering at room temperature, for the mixture DBSA-5. Interestingly, a change of the droplet size distribution was observed at long times in experiments that had reached a conversion above ca. 75%. At 20 h of reaction time the volume distribution (Figure 7a) showed that a fraction of smaller droplets had formed. In the number distribution (Figure 7b) the shift toward smaller droplet sizes is more clearly evident, and at 20 h the number distribution is in fact dominated by a distinct fraction of droplets with a diameter of 100 nm or less. In the following, we will refer to the latter droplets as “nanoparticles” to distinguish them from the large emulsion droplets.

Variation of Conductivity with Time. As we will discuss below, conductivity measurements provide complementary information on the formation of nanoparticles. Figure 8 shows the conductivity against conversion for 3 mL samples withdrawn from the reaction mixture DBSA-5 and diluted with

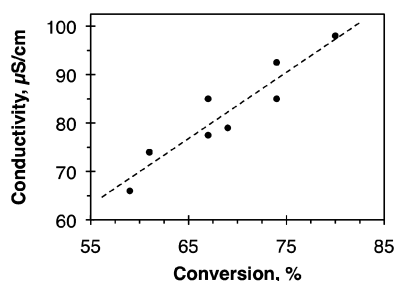


Figure 8. Conductivity as a function of conversion for DBSA-5 for diluted samples.

50 mL of Millipore water to yield a final total DBSA concentration of 0.3 mM, far below the cmc. Thus, the aqueous phase of the diluted samples contained no surfactant micelles, but only molecularly dissolved surfactant molecules. As can be seen, the conductivity increased linearly as a function of conversion during the reaction. For comparison, the conductivity measured for solutions of surfactant alone increased approximately linearly with increasing concentration up to the cmc, seen as a break point around 2 mM of DBSA, at which the conductivity was ca. 700 $\mu\text{S}/\text{cm}$. A few measurements were also made on undiluted samples from DBSA-5 reaction mixtures, giving conductivity values in the range 820–950 $\mu\text{S}/\text{cm}$.

Influence of the Surfactant Counterion or Added Salt on the Conversion. To investigate the catalyzing effect of the local concentration of oxonium ions at the surface of the emulsion droplets (see the Discussion below), we performed experiments where DBSA was replaced by SDBS or where additional salt was added to reaction mixtures containing 5 mmol/L of DBSA. Some of the resulting reactions are compared in Figure 9. In the experiment with added salt, NaCl was added at a concentration chosen to be equal to the total initial molar concentration of acid (DA and DBSA) in the mixtures. In both of the alternative experiments, the reaction proceeded significantly slower than in the DBSA-5 system. Exchanging DBSA for SDBS had the most drastic effect; even

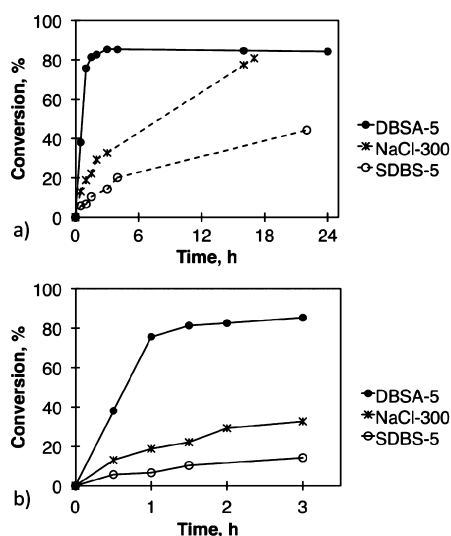


Figure 9. Conversion (from NMR) versus time for the indicated mixtures (see Table 1 for explanations). Results are shown (a) during the first 24 h and (b) zoomed in to show the first 3 h more clearly. Lines connecting the points are only guides.

after 72 h of reaction (not included in Figure 9), the conversion was only 70% and thus still lower than with DBSA. With salt added, the reaction rate also decreased significantly. After 16 h the conversion reached 78% for NaCl-300, which translates (using the Carothers equation)²¹ to a number-average of 4.5 monomer units per formed oligomer. This is to be compared with the reference experiment DBSA-5 that had reached its plateau conversion of ca. 85% (number-average of 6.7 monomer units/oligomer) well before 16 h.

The effect on conversion of lower NaCl concentrations was studied in a series of experiments where the salt concentration was varied. Figures 10a and 10b show the results after 3 and 24 h

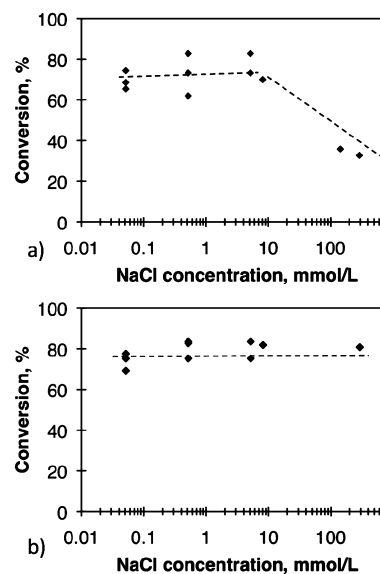


Figure 10. Conversion (from NMR) after (a) 3 h and (b) 24 h of reaction as a function of the concentration of added salt. 5.2 mmol/L DBSA was used in all experiments. Dashed lines are only guides.

h of reaction, respectively. 5.2 mmol/L DBSA was used in all experiments (see Table 1). At 3 h of reaction, NaCl concentrations below 5 mmol/L seemed not to affect the conversion significantly, whereas higher NaCl concentrations resulted in a lower conversion. After 24 h reaction time no difference in conversion was observed for the investigated concentrations of added NaCl (up to 300 mmol/L).

DISCUSSION

The Thermodynamic Equilibrium State of the Reaction. Manabe et al. carefully studied DSBA-catalyzed emulsion reactions quite analogous to ours, but producing simple esters rather than polyesters.^{17,18} Importantly, they could show that an equilibrium conversion was eventually reached in the reaction by demonstrating that the reverse ester hydrolysis, carried out starting with the ester in otherwise the same emulsion system, at long times led to the same time-independent proportions of reactants and products. They generally used very large proportions of catalytic surfactant in their reactions, but for the system with the least amount of surfactant the equilibrium state corresponded to 84% conversion to the ester, a number very similar to what we have found at long times for the emulsion process producing polyesters. Also for the condensation polymerization of polyesters in water, it seems generally appreciated that the reaction eventually reaches equilibrium, at least when efficiently

catalyzed by, for instance, acidic surfactants.^{4,22} Specifically, this means that the leveling off of the conversion at long times fundamentally is due to the attainment of a dynamic equilibrium between the (forward) condensation and (backward) hydrolysis reactions, rather than to some conceivable decrease of the (effective) forward reaction coefficient.

Since an increase of the degree of polymerization of the final product beyond the modest number-average degree of polymerization of ca. 7 found here and in previous work⁴ would be desired, it seems appropriate to consider the equilibrium situation in some detail. To that end, we prefer to base our discussion on thermodynamics (chemical potentials) rather than kinetic arguments (rate constants). Specifically, we consider the case of a simple esterification reaction (we will return to polyesters below) where a hydrophobic alcohol (A) reacts with a hydrophobic carboxylic acid (C) in a condensation reaction to produce a hydrophobic ester (E) and water (W). Our point of departure is the following fundamental relation between the chemical potentials of the reactants and products of this reaction at equilibrium:

$$\mu_A + \mu_C = \mu_E + \mu_W \quad (1)$$

By introducing the assumptions (1) the reaction occurs in a two-phase system of one organic and one aqueous phase, (2) the organic phase is an ideal mixture containing all of the components A, C, and E and, possibly, also some additional component (e.g., hexadecane), and (3) the aqueous phase is essentially pure water, we arrive at the following simple relation between the equilibrium amounts of ester, alcohol, and acid in the reaction. (For the convenience of the reader, we provide the detailed derivation as Supporting Information.)

$$\exp(-\Delta G^\circ_r/RT) = n_T n_E / n_A n_C \quad (2)$$

In eq 2, ΔG°_r is the standard free energy of the reaction (with all reactants and products in their pure states at the reaction temperature), n_i is the number of moles of component i in the organic phase, and n_T is the total number of moles of molecules in the organic phase. R and T are the ideal gas constant and the temperature of the reaction mixture, respectively.

Consequences of the Expression for Thermodynamic Equilibrium. Equation 2 may seem trivial, but it immediately leads to the following important conclusions regarding the equilibrium state of the reaction.

As long as the reaction mixture contains a phase however small, of essentially pure water, the chemical potential of water is fixed, and the concentration of any water that may enter the organic phase does not enter explicitly in the equilibrium expression. Returning again to the thorough experimental study of Manabe et al., they remarkably obtained the same equilibrium conversion in an initially neat (no added water) homogeneous mixture of reactants and surfactant as in the presence of water.¹⁷ We should note, however, that at equilibrium 8.4 mol of water had been produced for each mole of surfactant present in their mixture. (This follows from the stoichiometry of their mixture and from the 84% equilibrium conversion.) The final equilibrium state of the system was therefore presumably a surfactant-stabilized w/o microemulsion with a water/surfactant ratio ≥ 8.4 . With such a large water-to-surfactant ratio, the chemical potential of the water in the reverse micelles should be close to that of pure water, explaining the similarity of the equilibrium conversion with or without water initially present.

Any diluent (additional component) that is dissolved in the organic phase will increase the total number of moles n_T of that phase. As a consequence (neglecting for the moment possible effects of preferential interactions, which may be important), the degree of conversion to ester must decrease, according to eq 2. This is again in qualitative agreement with the results of Manabe et al. in their experiments where very large proportions (up to 200 mol % compared to the reactants) of surfactant were added. Under these conditions, the surfactant clearly dominated the organic phase of reactants, products, and surfactant in the droplets and acted as a diluent, lowering the chemical potentials of the reactants. The diluent effect is also in qualitative agreement with the finding of Barrère and Landfester—that an increasing solubility of water in the organic domain leads to a decrease in conversion.¹⁶

Importantly, we can now use eq 2 as a point of departure for discussions of how we could possibly increase the (equilibrium) degree of conversion in our systems, and the options are actually quite limited. The only way to change the value of $\Delta G^\circ_r/RT$ is to change the temperature, which is certainly one possibility. Turning to the expression on the right-hand side of eq 2, we recall that it is derived under the assumption of ideal mixing in the organic phase. By introducing a diluent that also interacts preferentially with the ester (with a sufficiently strong preference), we should indeed be able to drive the equilibrium toward higher conversion. Conversely, however, since the reactants—and especially the carboxylic acid—should be more hydrophilic than the product, we conclude that polar additives might preferentially interact with the reactants, rather than the product. In particular, more hydrophilic reactants, leading to a finite dissolution of water in the organic phase, should impede the conversion. Another assumption made in deriving eq 2 (see the Supporting Information) is that the aqueous phase is essentially pure water. Going back to the derivation, we find that lowering the chemical potential of water should also increase the yield of the reaction. This could be done by adding significant amounts of some solute that only resides in the aqueous phase. However, very large quantities of solute are generally required for a significant reduction of the water activity in the aqueous phase.

At this point we should consider possible consequences of two further differences between a real emulsion polycondensation system and the simplified system discussed above. First, the organic and aqueous phases in an emulsion system are separated by an interfacial layer, an “interphase”, that contains a mixture between the reactants, the product, and the stabilizing surfactant. However, as long as the fraction of reactants and products in the interphase is small, its presence will not significantly affect the overall equilibrium conversion. Second, the product of the polyester reaction is a mixture of oligo- and polyesters, not a simple ester as assumed above. This fact will affect the expression for the entropy of mixing in the chemical potential of the polyester, as described by the Flory–Huggins theory,²³ making the final expression of the equilibrium constant more complicated. However, it will not affect the qualitative conclusions drawn above.

Regarding the specific systems investigated in this study, we note that the proportion of reactants and products residing in the interfacial layer should always be small (most of the organic phase is contained in large droplets). Moreover, the aqueous phase should always be dilute in the sense that $\mu_W \approx \mu^\circ_W$. Even for the systems with added salt, experimental data on water vapor pressure over salt solutions show that the effect on the

activity of water from the comparatively low (less than 2 wt %) concentrations of salt used in the present study is marginal.²⁴ Since the reaction temperature was the same in all experiments, we can thus conclude the equilibrium degree of conversion should be the same in all systems studied here. The reason for the observed differences in conversion at long times is therefore a purely kinetic effect.

The Pathway of the Condensation Reaction. Above we discussed the equilibrium conversion of our system, which we found to be the same for all the investigated mixtures in our study (Table 1). In order to understand the large observed differences in the rate of conversion and the production of a population of nanoparticles under certain conditions, we must therefore consider the reaction mechanism(s), starting with the reaction pathway. Both a priori considerations and the results of our studies indicate that the dominating reaction pathway is an acid-catalyzed polycondensation, and the suggested reaction pathway is shown in Figure 11. The oxonium ion reacts with

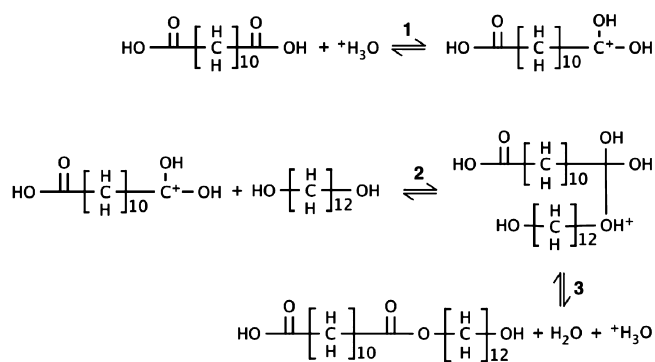


Figure 11. Reaction scheme for the acid-catalyzed condensation of 1,12-dodecanediol and 1,12-dodecanedioic acid.²⁵

the carboxylic acid and a charged complex is formed (1) that can react with the alcohol moiety (2). During the last reaction step (3) water is split off, and the oxonium ion is recovered for further reactions.

Salt and Counterion Effects: Implications for the Reaction Mechanism. As shown in Figure 5, the sulfonic acid DBSA was the most efficient catalyst, giving the fastest initial reaction rate and a plateau conversion of ca. 85% in only a few

hours. However, with NaCl added to the reaction system or when the DBSA was replaced by SDBS, the conversion rates were lowered significantly. The obvious conclusion is that the conversion occurs essentially at the interface between the organic emulsion droplets and the surrounding aqueous phase and that the rate of the reaction, occurring according to the scheme in Figure 11, is strongly dependent on the local concentration of oxonium ions in this interfacial region. From basic colloid science we know that the distribution of counterions outside a charged particle is highly nonuniform, owing to long-range electrostatic attractions.²⁶ In the salt-free systems containing DBSA, there is therefore a high local concentration of the oxonium counterions (note that the acid is strong and can be assumed to be fully dissociated) near the droplet surfaces, attracted by the high surface charge from the surfactant ions. This high concentration results in an efficient acid catalysis of the reaction, as schematically illustrated in Figure 12. The observed lower conversion with addition of salt is then due to a decrease in the local concentration of oxonium ions near the reaction site at the droplet surface. In general, added salt will, of course, increase the total concentration of counterions in the vicinity of the surface. However, for a highly charged surface a phenomenon often called counterion condensation occurs, which effectively means that the surface concentration of counterions is insensitive to the bulk concentration of added salt.²⁶ The dominating consequence of adding salt is therefore a simple ion exchange process, where the oxonium ions near the surface are partially replaced by the cations of the added salt. If there is no specific affinity of any of the ions to the surface, the interfacial ratio of oxonium to sodium ions of our system will therefore equal the global concentration ratio. This competition effect will therefore clearly grow with increasing salt concentration, which agrees exactly with the observations made. Completely replacing the oxonium counterion with sodium when replacing DBSA with SDBS has the most drastic effect; available oxonium ions are then only those resulting from the dissociation of the weakly acidic carboxylic acid groups residing at the droplet surfaces. We emphasize that the only difference between the DBSA-5 and SDBS-5 experiments is the change of the counterion; the surfactant ion is the same, and the ionic strength is the same.

The reaction mechanism proposed by us is schematically illustrated in Figure 12 and shows the organic droplets covered

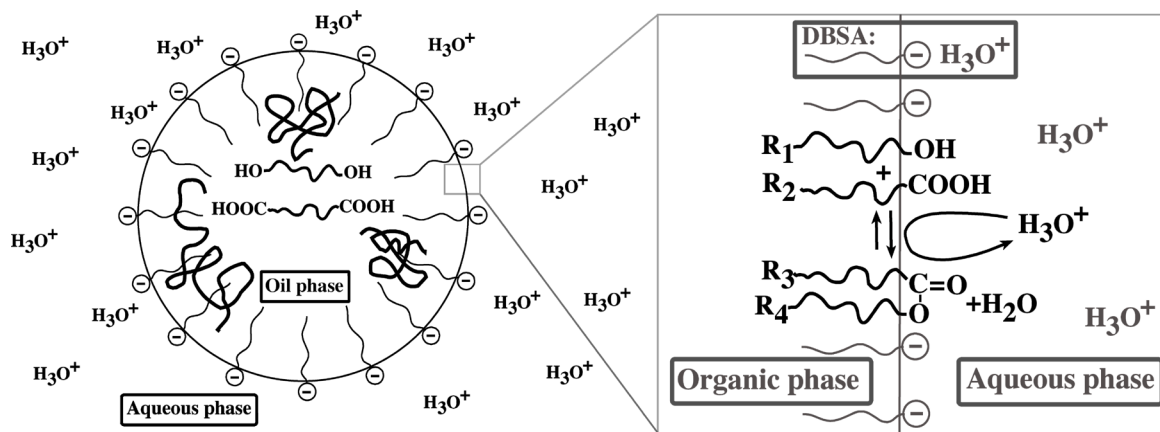


Figure 12. Schematic drawing of the interfacial reaction between DO and DA catalyzed by DBSA, with transport to and from the interior of the droplet to the interface by diffusion. The inset shows the organic/aqueous interface of the droplets. R_1 – R_4 are –OH or –OOH ends on chains of varying length. Global charge neutrality is retained.

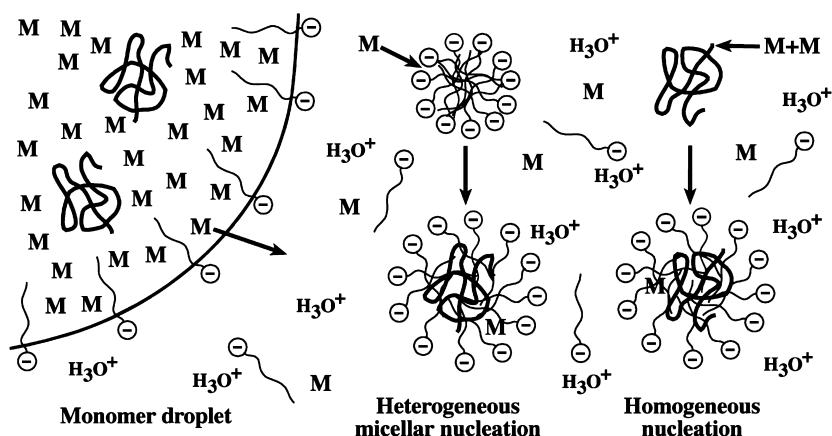


Figure 13. Mechanisms for formation of nanoparticles. Monomers diffuse from the large droplet (to the left) into the aqueous phase to either enter into micelles directly or react in solution and condense to particles onto which surfactant adsorbs. In either case, the primary particles then grow by monomer diffusion to the observed ≤ 100 nm sized range. M denotes reactants.

by DBSA and an expanded view of the interfacial area. The reaction takes place at the organic/aqueous interface. The interfacial concentration for the molecules involved is largest for the surfactants followed by DA and DO. At the interface, ester bonds can be formed by the condensation reaction, catalyzed by oxonium ions according to the reaction scheme shown in Figure 11. The interface is also the location where a majority of the hydrolysis of the ester is likely to occur, resulting in acid and alcohol end groups. Inside the droplets noncatalyzed or so-called “self-catalyzed” reactions also occur,¹ but these reactions are slow compared to the acid-catalyzed reactions in the aqueous part of the interfacial region. Furthermore, the concentration of the charged oxonium ion inside the nonpolar organic droplet is negligible. The attainment of true equilibrium of the system also requires that reactants and products mix efficiently in the droplet interior and exchange sufficiently rapidly between the droplet interior and the interfacial region. This can occur in the liquid-like droplets of our investigated system, which coalesce and break up as a result of the stirring. However, the efficiency of the mixing process, and the rate of molecular exchange between droplet interior and interfacial region, should both decrease as the droplet viscosity increases with an increasing fraction of polymeric products. We propose that this effect might explain the very slow evolution of the molecular weight distribution toward higher molecular weights at long times (several days) (see Figure 6). However, in terms of conversion this is not a large effect; we recall that the conversion was only shifted from 84% at 44 h to 86% at 144 h.

Saam et al.⁵ investigated condensation polymerization of oligomeric polydimethylsiloxanols in miniemulsion where they obtained nanometer-sized particles by running the aqueous dispersions through a Manton Gaulin homogenizer. They concluded that the reaction occurred at the polydimethylsiloxanol–water interface, and the principal driving force for that reaction to occur was the heat of condensation when the water vapor formed was driven out and condensed in the aqueous phase. Analogous explanations have been given by others where the condensation reaction is suggested to take place due to generated water being transported out of the hydrophobic droplets and into the surrounding aqueous phase.^{5,12,15,16,27} However, our analysis (see eq 2) does not give any support for the suggested interpretation which, to us, illustrates the danger in attempting to explain a reaction equilibrium in terms of

reaction mechanisms. Moreover, the current study shows that the condensation reaction occurs at the aqueous side of the interface; the production of water molecules in the droplet interior should be negligible.

Consequences of Changing the Surfactant for the Rate of Conversion. The recorded traces of conversion versus time were very similar for the two phosphoric acid surfactants AEP and FEP at all tested surfactant concentrations, but the times to reach equilibrium were much longer than with DBSA even when the former surfactant concentrations were more than 3 times (17 mmol/L) as high as the reference DBSA concentration (5 mmol/L). It remains for us to explain this difference. The hydrophobic tails of DBSA, AEP, and FEP have approximately the same length. Part of the difference could be due to the different acid functionalities of the catalytic surfactants. The pH values for solutions of only the surfactants in distilled water at concentrations of 5 mmol/L were 2.5 for DBSA but 3.1 for FEP and 3.2 for AEP. However, we suggest that an important difference is the presence of fairly long nonionic EO chains in the headgroups of AEP and FEP. These chains extend into the aqueous domain; therefore, they move the surface charges (the phosphoric end groups) and, consequently, the region of maximum concentration of oxonium ions away from the surface where the reacting hydroxyl and carboxylic acid groups are located. The high concentration of EO chains in the interfacial layer may also give rise to a steric hindrance for the reacting species to meet.

Mechanism for the Formation of Nanoparticles. The evolution of a fraction of nanoparticles (smaller droplets ≤ 100 nm) over the course of the reaction under acidic conditions (see Figure 7) strongly suggests that in addition to the interfacial reaction described above there exists a parallel mechanism for the reactants to react in the aqueous phase. Our proposed mechanism is shown in Figure 13.

The partition coefficients, i.e. $\log P$, between water and octanol for DO and DA at 25 °C are around 3,²⁸ and as discussed earlier both monomers are thus slightly soluble in the aqueous phase at the reaction temperature of 95 °C. We may assume that the diffusion of monomers into the aqueous phase is nonrestricted, and therefore the aqueous phase contains dissolved monomers at their equilibrium concentrations throughout the reaction. A comparison of the conductivities of undiluted reaction mixtures with those obtained for simple surfactant solutions (see the text in connection with Figure 8

above) indicates that surfactant micelles could also exist in the aqueous phase at the beginning of the reaction in the standard experiment; hence, such micelles are also included in Figure 13. A sufficiently high concentration of oxonium ions in the aqueous phase leads to a finite production of oligomers in water according to the reaction scheme in Figure 11. Already the dimers should have a low water solubility, and thus a nucleation of small droplets of dimers and oligomers could result, i.e., homogeneous nucleation. Monomers should partition into these droplets, and surfactant molecules should adsorb to their surface. The difference in surface-to-volume ratio between the large droplets and the small nanoparticles results in a higher consumption rate of the monomers in the nanoparticles and, therefore, a compensating net transport of monomers from the large droplets via the aqueous solution to the nanoparticles. The process of creating nanoparticles should in principle occur throughout the reaction; however, the equilibrium concentration of monomers in the aqueous phase will continuously decrease as the mole fractions of monomers decreases in the “reservoir” of large droplets. Once a surfactant-stabilized nanoparticle is formed, a continued polymerization should proceed mainly at the particle surface exactly as described for the large emulsion droplets above.

The increasing conductivity (see Figure 8) as a function of conversion implies—since no new charges are produced in the reaction—that the charge-bearing particles, on average, become smaller in the system during the course of the reaction, leading to a more rapid charge transport. In principle, a conceivable explanation for this effect would be that the total surface area of the droplets decreases with time, resulting in a net transfer of surfactant ions from the droplet surface to the aqueous phase. However, the evolution of the droplet size distribution (Figure 7) rules out this explanation; there is no change in size of the large droplets, but instead there is a growing fraction of small nanoparticles in the system. Clearly, the total area of the droplets increases with time. The creation of nanoparticles then becomes the likely mechanism to explain the increased conductivity, since it should lead to a net transport of charged surfactant molecules from the surface of the large droplets to the more rapidly diffusing nanoparticles. The fact that the conductivity increases with conversion throughout the whole reaction then supports a continuous formation of nanoparticles. It is likely that the light scattering methods used are not sensitive enough to detect the initially low numbers of nanoparticles in the presence of the high volume fractions of micrometer sized droplets, and therefore, nanoparticles are only seen at high conversions by light scattering.

The replenishing of reactants from the large droplets into the aqueous phase, and the fact that the polycondensation reaction takes place in the aqueous phase, gives rise to the large increase in the number of nanoparticles over time as shown in Figure 7b, where at the end of the reaction the particle size number distribution is dominated by the nanoparticles. However, even at long times a majority of the organic phase in the reaction system still resides in large droplets as shown in Figure 7a. Thus, the system as described here does not provide a complete route to form exclusively polyester nanoparticles, but it is nevertheless the first report on this mechanism for forming nanoparticles for this type of emulsion polycondensation reactions performed in dispersed media starting with large micrometer-sized droplets. The proposed mechanism is similar to classical radical emulsion polymerization, which also starts with large emulsion droplets and where nanometer-sized latex

particles are formed over time through micellar nucleation and homogeneous nucleation followed by monomer transport through the aqueous phase.²⁹

Results from a previous study for similar reaction systems, but using miniemulsion, indicate that if the water solubility is too high, no or very low conversion will be possible.¹⁶ The same study showed that the conversion increased with decreasing water solubility up to 15 carbons in the monomers. We have not in the current study investigated the influence of the water solubility on the nanoparticle formation, but it is reasonable to anticipate a window of water solubility of the monomers where the formation of nanoparticles is possible. With too high monomer and thus oligomer solubility in the water phase no droplets will be formed, and the amplified effect of having high concentrations of oxonium ions at the droplet surfaces will be lost. Conversely, for completely hydrophobic species with zero water solubility no reaction in the aqueous phase will occur.

CONCLUSIONS

Emulsion polycondensation reactions in aqueous dispersed media at 95 °C resulted in conversions above 80% in a system where 1,12-dodecanediol (DO) and 1,12-dodecanedioic acid (DA) droplets were emulsified in water using dodecylbenzenesulfonic acid (DBSA) as a combined emulsifier and catalytic surfactant. The conversion remained unchanged after approximately 3 h of reaction, but a slow drift in the molecular weight distribution was seen to occur even after very long times (>2 days). When the surfactant cation was changed from oxonium in DBSA to sodium in SDBS, the catalytic efficiency was dramatically decreased, resulting in much lower conversions within the same time span for the reactions. A concentration-dependent decrease in reaction rate occurred also when NaCl was added to the system. Finally, exchanging DBSA for phosphoric acid esters of ethoxylated surfactants, the latter featuring water-soluble “spacers” between the headgroup charge and the alkyl tail, resulted in lower conversions. Collectively, the observed differences in catalytic efficiency of the different surfactants in the present study showed that the dominating polymerization reaction was an oxonium-ion-catalyzed condensation occurring at the aqueous side of the droplet/water interface, where an exchange of the surfactant counterion, additional salt, or changing the architecture of the surfactant head groups all resulted in large differences in the local concentration of oxonium ions at the reaction site.

The thermodynamic equilibrium situation in the emulsion reaction is analyzed in detail, and the main factors affecting this equilibrium are identified. It is concluded that the conversion at equilibrium should be the same in all the systems investigated here, but that equilibrium was not reached within the experimental time in all experiments.

Droplets in the ≤100 nm size range were formed continuously in salt-free systems with DBSA as the surfactant. The proposed mechanism for this process is that reactants migrate from larger droplets into the aqueous phase to react there and generate water-insoluble oligomers, which nucleate and form small droplets in which the polymerization reaction then continues as in the large droplets. This reaction suggests a route toward making *in situ* polyester nanoparticles.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed derivation of eq 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail ola.karlsson@fkem1.lu.se (O.J.K.).

Present Address

[†]M.M.: Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville 3010, Victoria, Australia.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

AEP, Disponil AEP 5300; DA, 1,12-dodecanedioic acid; DBSA, dodecylbenzenesulfonic acid; DO, 1,12-dodecanediol; FEP, Disponil FEP 7030; GPC, gel permeation chromatography; HD, hexadecane; NMR, nuclear magnetic resonance; SDBS, sodium dodecylbenzenesulfonate; TMS, trimethylsilane.

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