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Polyester synthesis in aqueous miniemulsion

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Abstract

Hydrophobic polyesters have been synthesized in miniemulsion in the presence of large amounts of water. The yield of the esterification and the molecular weight of the polyesters have been determined for different reaction conditions. It was found that the dispersion state has no influence on the equilibrium: the yield is the same in 100 nm particles than in very large droplets. However, an important parameter is the water concentration inside the particles, as shown by an increase in the yield with more hydrophobic monomers. Another important parameter is the structure of the alcohol monomer. Alcohol compounds bearing electron-donating groups allow to displace the equilibrium toward ester formation. It is also shown that polyester/polystyrene hybrid particles can be synthesized in a very simple way using a one pot procedure.

Keywords: Polycondensation; Polyester synthesis; Aqueous miniemulsion

1. Introduction

The synthesis and application of polymer nanoparticles dispersed in water, so-called polymer latexes, are of high interest since firstly water is a cheap, safe and environmentally friendly solvent, secondly latexes can easily be processed, e.g. for the production of films, and thirdly, one has the possibility to imprint an additional length scale into the polymer material, for instance if the particles have an internal structure.

Usually or most widely applied, polymer latexes are made by emulsion polymerization. However, here one is restricted to radical polymerization. The reason for this is the polymerization mechanism where the polymer particles are the product of a kinetically controlled growth and are built from the center to the surface, where all the monomer has to be transported by diffusion through the water phase. Because of the dictate of kinetics, even for radical copolymerization serious disadvantages such as lack of homogeneity and restrictions in the accessible composition range have to be accepted. Different polymer reactions, such as polycondensation cannot easily be carried out in heterophases using emulsion polymerization. However, the synthesis of polymer dispersions is not limited to the process of emulsion polymerization. Using other techniques, other kinds of polymerization could be applied. For instance, by suspension, precipitation or interfacial polycondensation a wide range of polymers have been synthesized [1]. Recently, it was also shown that the process of miniemulsion is excellently suited to perform a variety of reactions in dispersed media and to prepare stable polymer latex. The principle of this technique is to prepare stable monomer droplets (50–500 nm) obtained by intense shearing of a system containing a hydrophobic dispersed phase (the monomer), water, a surfactant, and a hydrophobe, a component which suppresses the mass exchange between the different oil droplets, the Ostwald ripening, by osmotic forces [2,3]. Polymerization of these stable monomeric droplets leads to particles which ideally keep their size. It has been shown that polyaddition to obtain epoxy [4] and polyurethane particles [5], but also anionic polymerization [6,7], cationic polymerization [8,9] or catalytic polymerization [10,11] could be carried out in miniemulsion.

Also, the formation of polyester is expected to be successful in miniemulsion in order to obtain stable polyester latexes, even though it is not yet reported in the literature. However, the polyester synthesis in such a process is very different from the classical direct polyesterification process as conducted in the industry. Indeed,

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polyesters are usually synthesized in bulk at relatively high temperature (180–230 °C) in order to remove water and obtain high yield and high molecular weight [12].

In principle, the synthesis of polyesters or esters in the presence of large amount of water has only been studied by few groups. Saam et al. studied the polycondensation in suspension of hydrophobic diol and diacid compounds using different sulfonate surfactants [13,14]. They defined the principles of such polycondensation and showed that polyesters of low molecular weight could be obtained in an aqueous media. The formation of a stable latex was however not reported. Although in the first article, the mechanism of polycondensation was not very clear, later, they could show that the polycondensation was as a matter of fact catalyzed by acidic compounds and they claimed that the principal driving force for this process was the free energy released in the transfer of water formed in the organic phase to the hydrophilic phase [15,16]. A kinetic study of the reactions allowed them to conclude that hydrolysis was taking place in the organic phase whereas esterification was an interfacial reaction.

More recently Manabe et al. studied the esterification of hydrophobic mono-functional compounds in aqueous suspension [17,18]. They studied the esterification kinetics with different acidic catalysts and showed that the most hydrophobic ones were also the most effective, because they could adsorb at the surface of the particle and catalyze the reaction at the interface. Indeed, compounds like the dodecylbenzenesulfonic acid (DBSA) can play the role of a surfactant as well as a catalyst of the esterification (‘CATASURF’). They also evaluated the yield of esterification and found that it increased with increasing hydrophobicity of the reactants or with decreasing temperature. For them, high esterification yields can be obtained because of the formation of hydrophobic domains in which the reaction takes place. The water which is formed by esterification, is not soluble in those domains and is expelled out of the particles (Fig. 1), even in the presence of a large amount of water as a continuous phase. Thus, compared to completely water soluble reactants, the equilibrium of the reaction is displaced to the ester formation. The authors have also studied the effect of increasing the amount of DBSA. They found that the yield decrease with increasing amount of CATASURF and they related this observation to the decrease in particle size. In their opinion, larger surface area between reactants and water would favor hydrolysis. This plausible explanation differs from the analysis concerning the localization of the reaction from Saam et al. [15].

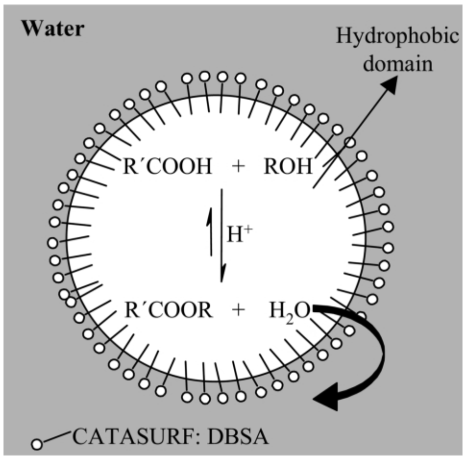


Fig. 1. Principle of the ester synthesis in aqueous medium.

As a completely different process, Kobayashi et al. reported the synthesis of polyesters in aqueous medium catalyzed with lipase [19–21]. For example, the reaction of sebacic acid and 1,8-octanediol using *Pseudomonas cepacia* lipase in water yielded the corresponding polyester in 43% with a molecular weight of 1600 g mol^{-1}. The reaction depended on the origin of lipase and the methylene length of the dicarboxylic acids and glycols.

In this article, the formation of stable polyester latexes by using the process of miniemulsion will be described. We especially want to improve the understanding of the acid-catalyzed polyesterification in dispersed aqueous medium. The conditions of stability of such dispersions have been described and the influence of several parameters on the esterification equilibrium has been studied.

2. Experimental details

2.1. Chemicals

Dodecanediol (DDD), decanediol (DD), dibutyl-2,2-propane-1,3-diol, octadecanol, tetradecanol, decanol, 3,7-dimethyl-1-octanol, 2-butyl-1-octanol, dodecanedioic acid (DDA), azelaic acid (AA), *tert*-butyl-3-adipic acid (BAA), octadecanoic acid, decanoic acid, dodecanoic acid, 2-butyloctanoic acid, pentadecanelactone, hexadecane (HD), ethyl benzene (EtΦ), sodium dodecyl sulfate (SDS), cetyltrimethyl ammonium chloride (CTAC, 25 wt% in water) and potassium persulfate (KPS) were purchased from Aldrich and used as received. Styrene (Aldrich) was freshly distilled and stored at −10 °C. Dodecylbenzenesulfonic acid (DBSA, purity 90%) as a mixture of isomers was purchased from Fluka and used without further purification. Diethyl-2,4-pentane-1,5-diol, Lutensol AT80 (C16–C18 fatty alcohol + 80 ethylene oxide units) was kindly provided by BASF.

2.2. Polyester latex preparation

As a classical recipe, 3.194 g of dodecanedioic acid (13.9 mmol), 2.806 g of dodecanediol (13.9 mmol), and 200 mg of hexadecane was added above the melting point of the monomer mixture at 95 °C to 200 mg of dodecylbenzenesulfonic acid and 24 g of water and was then stirred together for 1 h at the elevated temperature.

The miniemulsion was prepared by ultrasonicating the mixture during 120 s at 90% amplitude (Branson sonifier W450 digital) at 90 °C. The polycondensation was performed in a closed reactor at temperatures between 90 and 150 °C. Above 100 °C, the polymerization was performed in a hydrothermal reactor, in which the pressure is in principle close to the saturated vapor pressure of water. Completion was observed after 24 h (at 90 °C), as checked by SEC analysis by stabilization of the molecular weight of the polymer.

2.3. Hybrid latex preparation

As a classical recipe, a solution of 1.597 g of dodecanedioic acid (6.93 mmol), 1.403 g of dodecanediol (6.93 mmol), 3 g of styrene, and 200 mg of hexadecane was added at 70 °C to 200 mg of dodecylbenzenesulfonic acid and 24 g of water and was then stirred together for 1 h at 70 °C. The miniemulsion was prepared by ultrasonicating the mixture during 120 s at 90% amplitude (Branson sonifier W450 digital) at 70 °C. Firstly, the polycondensation was conducted at 70 °C in a closed reactor for 24 h. Compared to the initial amount of styrene, 10% in weight of polystyrene was then detected, due to thermally induced polymerization. Secondly, for radical polymerization, the temperature was increased to 72 °C and 100 mg of potassium persulfate was then added. Completion of the reaction was observed after 6 h, as checked by NMR by the absence of vinylic protons.

2.4. Analysis

The polymer molecular weights were determined by SEC analysis performed on a P1000 pump with an UV1000 detector ($l = 260$ nm) (both from Thermo Separation Products) and a RI detector (Shodex RI-71), with 5 μm 8 × 300 mm SDV columns with 10^6, 10^5, and 10^3 Å (from Polymer Standard Service) in THF with a flow rate of 1 ml min^{-1} at 30 °C. The molecular weights were calculated with a calibration relative to polystyrene standards.

The particle sizes were measured by dynamic light scattering at low concentration, using a Nicomp particle sizer (model 370, PSS Santa Barbara, CA) at a fixed scattering angle of 90°.

The liquid ^{1}H NMR spectra were recorded with a Bruker DPX400 using deuterated chloroform as solvent. As an example, the spectrum of a polymer obtained by polyesterification of dodecanediol and dodecanedioic acid in aqueous miniemulsion is shown in Fig. 2.

The esterification yield was calculated from the integration of the peaks at 4.05 and 3.6 ppm (or at 2.25 and 2.3 ppm) according to the equations:

Yield :

$$p = \frac{[\mathrm{RCOOR'}]}{[\mathrm{RCOOH}]_0} = \frac{[\mathrm{RCOOR'}]}{[\mathrm{R'OH}]_0} = \frac{I_{\mathrm{ester}}}{I_{\mathrm{ester}} + I_{\mathrm{acid}}} = \frac{I_{\mathrm{ester}}}{I_{\mathrm{ester}} + I_{\mathrm{alcohol}}}$$

(with I_{ester} corresponding to the integration of the peaks at 4.05 or 2.3 ppm, I_{acid} corresponding to the integration of the peaks at 2.25 ppm and I_{alcohol} corresponding to the integration of the peaks at 3.6 ppm). The error is ±0.5%.

The number-average degree of polymerization was determined as follows: $\overline{\mathrm{DP}_\mathrm{n}} = 1/(1 - p)$.

3. Results and discussion

3.1. Range of stability of polyester miniemulsions

Stable miniemulsions of monomer droplets and stable dispersions of polyester particles could be obtained if two requirements were respected:

1. The temperature of the miniemulsion and dispersion has to be higher than the crystallization temperature of the dispersed phase (monomers or polymer) in order to keep a long-time stability. If not, the crystallization in the droplets or particles can easily lead within hours to days to a destabilization of the miniemulsion or dispersion. In practice, in order to increase the range of temperature in which the miniemulsions and dispersions remain stable, it is possible to use a solvent for the polymer. For instance, the melting point of poly(decamethylene azealate) is close to 60 °C and below this temperature, the miniemulsion is not stable. But, by dissolving the polymer in ethyl benzene (50 wt%), the polymer dispersion remains stable at room temperature.
2. The pH of the monomer miniemulsion has to be lower than 4, otherwise acidic monomers deprotonate (for example, azealic acid: $\mathrm{p}K_{\mathrm{A1}} = 4.55$ and $\mathrm{p}K_{\mathrm{A2}} = 5.42$). If this happens, the solubility of the monomer increases strongly, leading to a fast destabilization of the miniemulsion. In practice, this is easily achieved by using an acidic surfactant which presents the dual-purpose of catalyzing the polyesterification and stabilizing the particles (CATASURF). Once the polymer is formed, the pH range in which the dispersion is stable increases. Carboxylic acid terminated polyesters are too hydrophobic to diffuse in the water phase.

A DBSA content of as low as 0.4 wt% was already sufficient to stabilize the droplets in miniemulsion and after

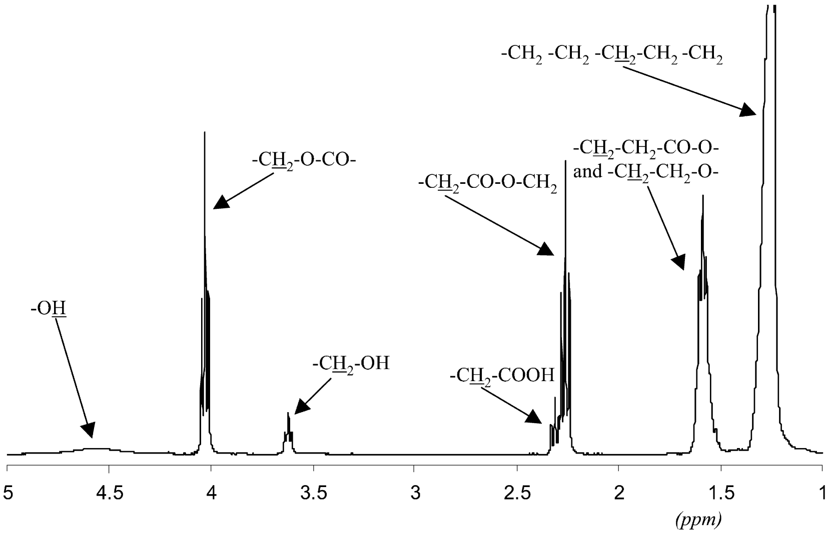


Fig. 2. ^{1}H NMR spectrum of an aliphatic polyester prepared from dodecanediol and dodecanedioic acid with peak assignments.

polymerization the polyester particles with a size of 280 nm. Although the surfactant (DBSA) is necessary to stabilize the miniemulsion, increasing its amount leads only to a slight decrease in the particle size (200 nm) (see Fig. 3).

In principle, an increase in the surfactant amount in the miniemulsion composition leads to a pronounced decrease in the particle size [22]. However, in the case of polyester miniemulsions, this is not observed. Firstly, the monomers used are fatty acids and alcohols. These compounds act as cosurfactant at the oil/water interface and lower the surface tension. Therefore, the addition of DBSA has presumably little influence on the surface tension. Secondly, the stabilization seems to require a very low amount of DBSA. In this system, the particle size is certainly controlled by other parameters like the viscosity and the hydrophobicity of the organic phase. This is in particular confirmed by replacing half of the organic phase by ethylbenzene. The viscosity of the oil phase decreases which enables a more effective miniemulsification process and the particle size after polymerization is then close to 110 nm.

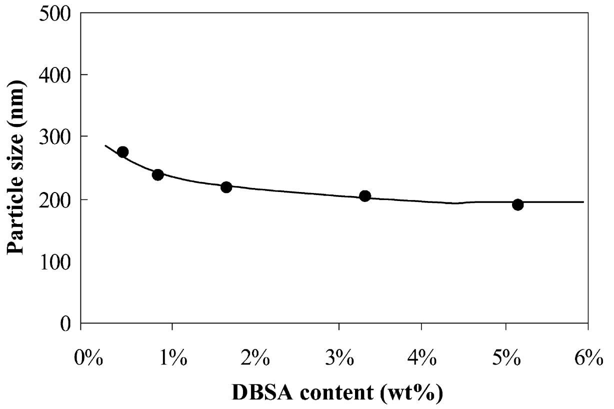


Fig. 3. Evolution of the particle size versus the weight fraction of surfactant compared to monomer. The miniemulsions were prepared and kept at 90 °C.

3.2. Polymer characterization

Our aim was to investigate the yield and molecular weight of the polyester at the equilibrium, and to find the parameters allowing to increase them. Therefore, apart from the estimation of the time required to attain the equilibrium, kinetic aspects are momentarily put aside.

3.2.1. Influence of the monomer nature

Different polyester or ester miniemulsions have been prepared starting from monomers or model compounds having different structures and hydrophobic properties. The particle size, the yield of the esterification reaction and, if possible, the molecular weight of the polyesters have been determined (Table 1). Although 24 h are sufficient to attain the equilibrium at 90 °C, the polyesters or esters formed have been characterized after 48 h of reaction.

In all cases, stable miniemulsions and after polymerization stable dispersions with particle sizes in the range of 100–400 nm were obtained. Depending on the reagents, different esterification yields and molecular weights have been obtained. In order to understand these results, Fig. 4

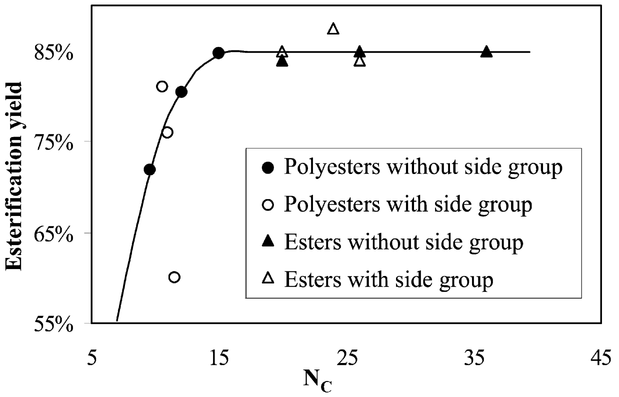
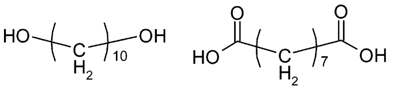
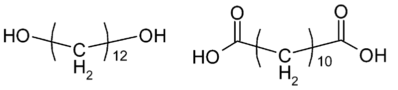
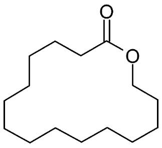
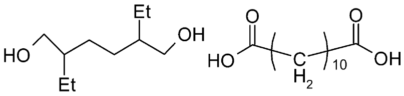
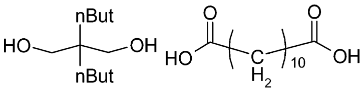
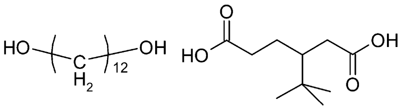
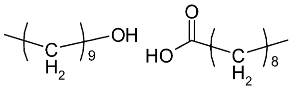
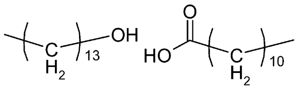
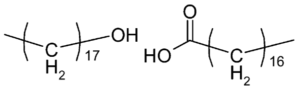
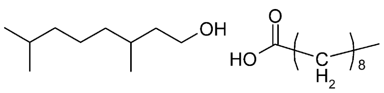
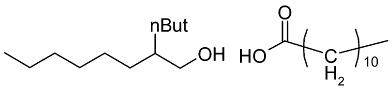
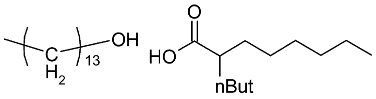


Fig. 4. Esterification yield as a function of N_C.

Table 1
Esterification reactions carried out in aqueous miniemulsion with different monomers or model compounds—experimental conditions and results

Exp. group	Ref. [a]	Reagents	N_C [b]	Results				
				Part.[c] (nm)	M_n [d]	PI[e]	Yield[f] (%)	M_n [g]
Aliphatic polyester (no side group)	A1		9.5	225	1200	1.8	74	650
	A2		12	205	1850	1.9	82	1130
	A3		15	200	[h]	[h]	85	1570
Aliphatic polyester (with side group)	A4		10.5	210	1170	2.6	81	990
	A5		11	195	910	1.7	60	500
	A6		11.5	330	1170	1.9	76	760
Aliphatic ester (no side group)	A7		20	245	[i]	[i]	84	[i]
	A8		26	135	[i]	[i]	85	[i]
	A9		36	185	[i]	[i]	85	[i]
Aliphatic ester (with side group)	A10		20	400	[i]	[i]	85	i
	A11		24	190	[i]	[i]	88	[i]
	A12		26	195	[i]	[i]	84	[i]

[a] All experiments were carried out at 90 °C, using 6 g of the esterification reagents in equimolar amounts, 0.2 g of DBSA, 0.2 g of hexadecane and 24 g of water.

[b] N_C is the theoretical average number of carbon atoms per ester bond in the product (in the case of polymer, it is calculated for the repeat unit).

[c] Particle size in nm, determined by dynamic light scattering at low concentration.

[d] Number average molecular weight in g mol^{-1}, determined by SEC versus polystyrene standards uncorrected.

[e] Polydispersity index of the polymer, determined by SEC.

[f] Esterification yield determined by ^1H NMR.

[g] Number average molecular weight in g mol^{-1}, determined by ^1H NMR.

[h] Polymer insoluble in THF.

[i] Not relevant.

shows the evolution of the yield as a function of N_C (theoretical average number of carbon atoms per ester bond in the product). This N_C value is supposed to give a fairly good appreciation of the hydrophobicity of the reactants and therefore of the particles: the higher this value is, the higher the hydrophobicity in principle also will be.

The results shown in Fig. 4 can be explained by two main effects:

1. A hydrophobic effect: by increasing the aliphatic chain of the reagents, the yield of esterification increases (experiments A1–A3 black dots on the curve). This is due to a hydrophobic effect. With increasing N_C, the water concentration in the particles decreases and the equilibrium is displaced toward the ester formation. However, this effect seems to be limited. For N_C values above 15, the esterification yield does not increase (experiments A7–A9) and we assume that the yield for the synthesis of aliphatic polyester without side group cannot exceed 85% in such conditions. At least two explanations could account for this result. Firstly, this limitation could indicate that, above 15, an increase in N_C does not result in a decrease in the concentration of water in the particles. Secondly, we could suppose that the water concentration in the particles becomes so low that hydrolysis mainly takes place at the interface. In that case, with increasing N_C, even if the water concentration in the core of the particles further decreases, this has no influence on the hydrolysis rate at the interface and on the equilibrium. This second explanation would lead to the conclusion that hydrolysis can take place both at the interface and in the core.
2. A side group effect: comparing aliphatic monomers or model compounds with different structure, interesting results could be obtained. On one hand, by changing the nature of the organic acid compounds, no effect on the esterification yield could be observed: experiments A6 and A12 fit perfectly on the curve. This result is in good agreement with a study from Vojtko [23] showing that the equilibrium constant of the esterification reaction does not depend on the organic acid structure. On the other hand, the structure of the alcohol has a great influence on the yield of the reaction. With the diethyl-2,2-pentan-1,5-diol (A4) or the butyl-2-octanol (A11), the yield is clearly higher than with alcohol compounds bearing no side group. Conversely, with the dibutyl-2,2-propane-1,3-diol (A5), the yield is comparatively much lower. These results are also perfectly in accordance with a study from Lee et al. [24]. It was shown that the equilibrium constants are sensitive to electronic effects the largest values are obtained with alcohols bearing electron donating groups. Therefore, the alcohol compounds bearing alkyl side groups (experiments A4 and A11) give higher esterification yield, whereas with the dibutyl-2,2-propane-1,3-diol (A5), the vicinity of the second alcohol group (electron withdrawing group) lowers the yield.

3.2.2. Influence of temperature and polymer dilution

The second parameter we investigated was the temperature. As for some polyesters the crystallization temperature was too high to study the esterification equilibrium at low temperature (<60 °C), a good solvent of the polymer (ethylbenzene) was used in order to decrease the melting point significantly. Moreover, as one of our goal was to synthesize hybrid polyester/polystyrene particles, it is also interesting to evaluate the influence of ethyl benzene as a model for styrene, on the esterification equilibrium. The experimental conditions of this study are summarized in Table 2. Because of the very long reaction time to attain the equilibrium (24 h at 90 °C, 100 h at 70 °C, etc.), in order to shorten the duration of this study, the following method has been applied: the temperature is increased to the highest value of the range studied and the equilibrium is characterized. The temperature is then decreased step by step and the polymer is analyzed after establishment of the equilibrium.

The evolution of the SEC traces as a function of temperature is shown in Fig. 5. An increase in the molecular weight is clearly observed when decreasing the temperature. This result cannot be explained by the thermodynamical characteristics of esterification. Indeed, the reaction is known to be slightly endothermic, and therefore, in comparable reaction conditions, an increase in the yield and of the molecular weight should be observed with increasing temperature. In the present conditions, this opposite result is probably correlated to the concentration of water in the dispersed phase. With decreasing temperature, the solubility of water in the dispersed phase decreases and the esterification equilibrium is therefore displaced toward ester formation. This result has already been observed for other polymerization systems involving water both as dispersed phase and possible reactive agent,

Table 2
Influence of temperature and dilution—experimental conditions

Experiment	Experimental conditions[a]			Part. (nm)[b]
	Monomers	Solvent	T_{re} (°C)[c]	
B1	DD/AA	–	150–60	200–250
B2	DD/AA	EtΦ[d]	90–24	150–180
B3	DDD/DDA	EtΦ[d]	98–30	110–170

[a] Unless otherwise stated, experiments were carried out using 6 g of the esterification reagents in equimolar amounts, 0.2 g of DBSA, 0.2 g of hexadecane and 24 g of water.

[b] Particle size in nm, determined by dynamic light scattering at low concentration. A slight increase is observed for long polymerization times (>500 h).

[c] Temperature range of the study.

[d] Half of the monomer amount is replaced by ethyl benzene.

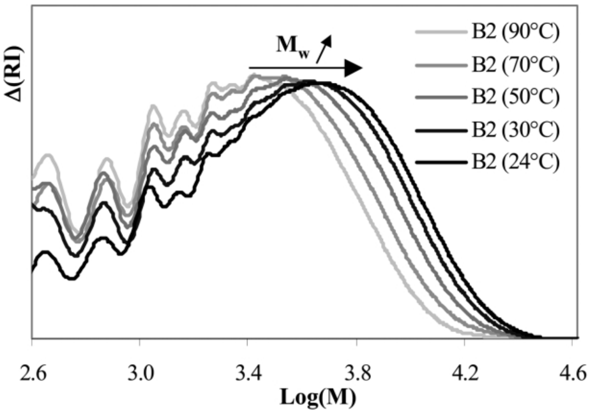


Fig. 5. Evolution of the SEC traces of the polymer obtained at different temperatures—Experiment B2.

for instance in the case of silicon [25] and polyurethane [26] synthesis.

For the three experiments, the weight-average molecular weight of the polyester at the equilibrium is reported as a function of temperature (Fig. 6).

For the three systems, the molecular weight always decreases with increasing temperature. Comparing experiments B1 and B2 at the same temperature, the effect of dilution is observed. As expected, with increasing dilution of the reactants, M_w increases. By decreasing the viscosity, the dilution favors chain end reaction (esterification) in comparison to hydrolysis which involves a chain and a small molecule (water).

In the case of the DDD/DDA polycondensation, the molecular weight can be as high as 7000 g mol^{-1} at 30 °C. Nevertheless, because of the very slow polyesterification kinetic at such temperature, the equilibrium is maybe not yet fully established even for very long reaction (> 1000 h). Therefore, the molecular weight at low temperature is probably undervalued.

3.2.3. Influence of other parameters

Experiment A2 has been reproduced varying several parameters and the results are reported Table 3.

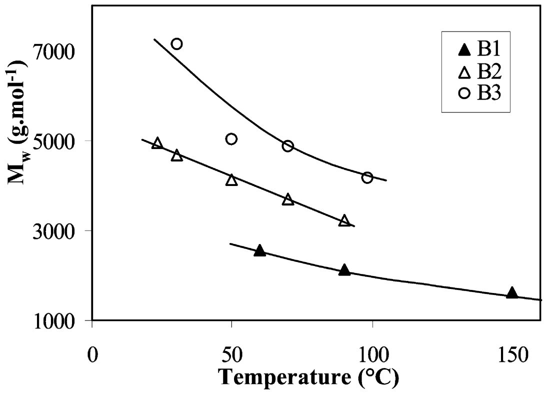


Fig. 6. Evolution of M_w as a function of temperature—Experiments B1, B2, and B3.

- As already observed, with increasing amount of DBSA, the particle size of the miniemulsion slightly decreases (experiment A2 and C1–C4). However, the molecular weight and the yield of esterification are the same for a particle size between 200 and 300 nm as well as for much larger particles like in suspension (Entry C5). This observation seems to disagree with the results obtained by Kobayashi et al. [18]. They indeed found that with increasing DBSA concentration, the esterification yield decreased and this was related to the decrease in the particle size. This is, however, not inconsistent with our results. The range of DBSA concentration are completely different in the two studies: relatively low DBSA concentration in our miniemulsion system and very high in their system which is closed to a microemulsion one. Therefore, the two studies are probably complementary.
- Increasing the amount HCl in the continuous phase (experiment C6) leads to a fast destabilization of the miniemulsion. However, no effect on the molecular weight of the polyester is observed. This result confirms that the amount of monomer dissolved in water is very low and has no influence on the equilibrium. Indeed, with increasing ionic strength the concentration of monomer in the water phase should decrease.
- DBSA has been replaced by a cationic surfactant (CTAC), a non ionic surfactant (Lutensol AT80) or another anionic surfactant (SDS), using stoichiometric amounts of HCl as catalyst. Again, there is no significant effect of the surfactant nature on the molecular weight of the polymer at the equilibrium. However, concerning the polyesterification kinetics, with the cationic surfactant, more than 400 h are necessary to reach the equilibrium, around 200 h for the non-ionic surfactant and less than 50 h for SDS. This emphasizes the catalytic effect of anionic surfactants, which make the acid more hydrophobic so as to bring it at the interface (CATASURF) or in the core of the particles (phase transfer agent).

3.3. Synthesis of hybrid particles

Using styrene as a solvent for the synthesis of polyester, hybrid polyester/polystyrene particles could be synthesized in a one pot procedure (Scheme 1).

Firstly, the polyesterification monomers, styrene and hexadecane are mixed and miniemulsified in water using DBSA as surfactant. Then, the polyester is synthesized at 70 °C during 24 h. Finally, the miniemulsion is neutralized, the temperature is further increased to 72 °C and potassium persulfate (KPS) is added in order to initiate the polymerization of styrene. The characteristics of the hybrid particles synthesized are listed in Table 4.

The presence of styrene leads to a strong decrease in the particle size (from 200 to 300 nm for pure polyester particles to 100 nm). Moreover, no flocculation is observed: the miniemulsion is perfectly stable. The characteristics of

Table 3
Influence of other parameters—experimental conditions and results

Exp.	Parameter changed		Results				
			Part.[a] (nm)	M_{n}[b]	PI[c]	Yield[d] (%)	M_{n}[e]
A2[f]			205	1850	1.9	82	1130
C1	DBSA amount	25 mg[g]	280	1950	1.9	80	1040
C2	DBSA amount	50 mg[g]	240	1930	1.8	81	1070
C3	DBSA amount	100 mg[g]	225	1830	1.9	82	1130
C4	DBSA amount	310 mg[g]	200	1800	1.8	81	1080
C5	Process (suspension)		[h]	1950	1.9	81	1070
C6	Ionic strength[i]		[h]	1840	1.9	80	1030
C7	Surfactant nature	CTAC[j]	[h]	1750	1.9	80	1010
C8	Surfactant nature	Lutensol AT80[j]	[h]	1870	1.9	80	1060
C9	Surfactant nature	SDS[j]	215	1810	1.9	80	1030

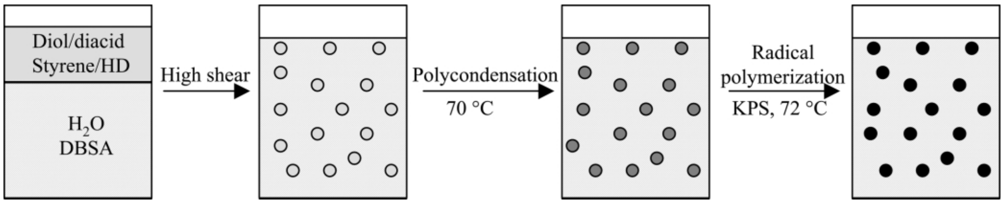
[a] Particle size in nm, determined by dynamic light scattering at low concentration.
[b] Number average molecular weight in g mol^{-1}, determined by SEC versus polystyrene standards uncorrected.
[c] Polydispersity index of the polymer, determined by SEC.
[d] Esterification yield determined by ^{1}H NMR.
[e] Number average molecular weight in g mol^{-1}, determined by ^{1}H NMR.
[f] Experiment carried out at 90 °C, using 2.806 g of DDD, 3.194 g of DDA, 0.2 g of DBSA, 0.2 g of hexadecane and 24 g of water.
[g] Total amount of DBSA.
[h] Unstable dispersion.
[i] Addition of 0.6 g HCl (1N).
[j] DBSA is replaced by the same molar amount of another surfactant and HCl.

the two polymers are close to what was expected, although the molecular weights are slightly low for the polyester. In order to limit the thermal polymerization of styrene, the polyesterification time has been limited to 24 h. However, at 70 °C, the establishment of equilibrium would require longer reaction time (around 100 h).

4. Conclusion

Even in the presence of large amount of water, the miniemulsion process allows the synthesis of hydrophobic polyesters in a very simple way and at very low temperature in order to obtain stable polyester dispersions. The influence of several parameters on the esterification yield has been studied. On the one hand, any modification of the dispersed phase such as the hydrophobicity of the components, viscosity, and the reactant nature results in different yield. With increasing hydrophobicity of the monomers or decreasing viscosity, the yield increases. On the other hand, any modification of the surrounding environment of the droplets such as the interface nature, the ionic strength and the interface area has no influence onto the equilibrium. From a thermodynamical point of view, this polycondensation presents the characteristics of a bulk or solution polymerization. Independently of the dispersion state in the range studied, the equilibrium is the same as in bulk or in solution polycondensation with an organic phase saturated with water. It is, however, very unlikely that the reactions exclusively take place in the core of the particle. To answer this question, a kinetic study related to the interface area would be necessary. In the last part, polyesterification and radical polymerization have been combined in a one pot procedure to synthesized well defined polyester/polystyrene particle in the range of 100 nm. Because of shortened reaction time, the polyester molecular weight is relatively low. This points out the necessity of finding very effective esterification catalyst which could allow the synthesis of polyester at low temperature in short reaction time.

These polyesters even though they have not a high molecular weight can be excellently used as precursor materials for further reaction, e.g. polyurethanes.



Scheme 1. Synthesis of hybrid polyester/polystyrene particles in a one pot procedure.

Table 4
Synthesis of hybrid polyester/polystyrene particles

Experiment[a]	Polyesterification monomers	Results				
		Part.[b] (nm)	Polyester		Polystyrene	
			M_w[c]	PI[d]	M_w[c]	PI[d]
D1	DDD/DDA	110	3.48	1.7	525	3.4
D2	DDD/BAA	105	1.10	1.4	155	2.2

[a] The experiments were carried out at 70 °C using 3 g of the esterification reagents in equimolar amounts, 3 g of styrene, 0.2 g of DBSA, 0.2 g of hexadecane and 24 g of water.

[b] Particle size in nm, determined by dynamic light scattering at low concentration.

[c] In kg mol^{-1}, determined by SEC versus polystyrene standards uncorrected.

[d] Polydispersity index of the polymer, determined by SEC.

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