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# Synthesis of styrene based liquid-filled polymeric nanocapsules by the use of RAFT-mediated polymerization in miniemulsion

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**Abstract**

Nanocapsules (below 100 nm) with liquid cores and molar mass controlled polystyrene shells were synthesized by an in situ miniemulsion polymerization reaction in the presence of a RAFT (reversible addition fragmentation chain transfer) agent. The formation of structured particles with the targeted core/shell morphology, i.e. liquid cores and polymeric shells, is extremely dependent on the type of RAFT agent used in conjunction with the type of initiator used. Different RAFT agents lead to different polymerization rates, thus resulting in different chain lengths as a function of time. This will influence viscosity and consequently chain mobility and can therefore cause a deviation from the desired morphology. The type of initiator used influences the surface activity of entering oligomers and is therefore also an important factor in obtaining the correct structure. Results showed that a RAFT agent that causes no rate retardation (phenyl 2-propyl phenyl dithioacetate, PPPDTA), used in conjunction with a surface active initiating species (potassium persulfate, KPS), is able to lock the locus of polymerization at the droplet/water interface. This results in entering oligomers being anchored at the droplet/water interface with consequent core/shell (nanocapsule) formation only if the RAFT agent used leads to a sufficiently rapid increase in chain length with time and thus a restriction of chain mobility of the mediated species.


*Keywords:* Nanocapsules; RAFT; Miniemulsion

## 1. Introduction

Living/controlled radical polymerization techniques have been known for more than 30 years, [1] but have only started to receive broad academic and industrial interest during the last decade. Although living/controlled radical polymerization all started with the use of iniferters (initiator-transfer agent-terminator), [1] techniques such as reversible addition fragmentation chain transfer (RAFT) polymerization, [2,3] atom transfer radical polymerization (ATRP) [4,5] and nitroxide mediated radical polymerization (NMP) [6,7] have led to a significant revitalization of the field of radical polymerization. These techniques provide the ability to control radical polymerizations (when compared to ordinary free radical polymerization chemistry) and can also impart living properties to a polymeric species, which enables immediate or delayed chain extension by addition of more monomer units.

Homogeneous media are preferred for living/controlled polymerizations. However, recent developments [8] have shown that this type of polymerizations can also be extended to heterogenous media via different routes, some of which include miniemulsions, [9–13] emulsification of RAFT end-capped oligomers, [14] RAFT agent transport [15] and ab initio emulsion polymerization [16,17]. The transition from homogeneous to heterogeneous media is most welcome from an industrial point of view, where aqueous phase polymerization is preferred. It is not only more cost effective, but an added advantage is the environmental friendly aspects of polymerization without solvents. However, although living/controlled polymerizations have been performed in aqueous systems, these

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systems have in some cases proven to be limited to specific monomers or conditions. In a heterogeneous system, the partitioning of the mediating species used in living/controlled polymerization differs invariably from that of the monomer, which makes a multiphase polymerization system far more difficult to control than a homogeneous system. It is therefore very important to tailor a method when chain growth mediating agents are used. When doing heterophase polymerization, partitioning of the mediating species between the aqueous phase and the polymerization loci has to be optimized. This problem is partially overcome by the use of predispersion or homogenization.

The focus of many research groups has shifted due to the development of living/controlled polymerization techniques that are able to control chain architecture in aqueous media. Products that depend on multiphase systems such as core/shell particles, which have many applications ranging from impact modifiers and toughening agents, [18] opacifiers, gloss enhancers for paper coatings, polymeric nanocapsules for controlled and sustained drug delivery [19,20] to encapsulation of volatile solvents or toxic substances, can now potentially be prepared with polymers of controlled chain architecture. The ability to combine such versatile techniques, i.e. complete control of encapsulating and core material with the added versatility of morphology control, is opening new horizons on the scientific front including the possibility of revolutionary applications such as adapting the molar mass of the encapsulating species to patient weight or illness in drug delivery.

For the formation of nanocapsules the establishment of the polymerization locus is very important especially when the difference in hydrophobicities of the constituting core and shell material produces undesired morphologies [21]. When the core material is a liquid, encapsulation becomes even more difficult. Previous research in our laboratories demonstrated that the desired nanocapsule morphology can be locked-in by choice of surfactant and initiating species in the in situ miniemulsion polymerization of nanocapsules with liquid cores [21]. Thus, when the correct initiating species (which will facilitate adequate immobilization at the droplet/water interface) is added to a miniemulsified oil containing monomer, core-oil and RAFT agent, the initiator radicals will anchor themselves at the interface, leading to preferential polymerization at the droplet/water interface. Unfortunately transfer is the basis of the RAFT process which will initially result in small radical species being generated. This problem must therefore be addressed by the reaction kinetics, thus, the type of RAFT agent. In addition, the choice of RAFT agent will also influence the chain lengths produced as a function of time and thereby chain mobility [22]. When all conditions are met, polymerization will occur at the droplet/water interface as a result of monomer depletion from the inside of the droplet, causing phase separation and leaving an oily core [23–26].

The use of RAFT in miniemulsion has been controversial due to the problems that have been encountered as far as stability and control are concerned. The early work by de Brouwer et al. [27] with SDS is a perfect example. Low conversions and colloidal instabilities led to a change in direction and to the use of polymeric surfactants. Butté et al. [28] and Lansalot et al. [9] were able to show that polymeric RAFT agents that exceed the critical length for water solubility were suitable for miniemulsion polymerizations using SDS. However, the degree of control that was obtained typically lead to PDIs above 1.5 and some classes of RAFT agents were unable to provide control in miniemulsion polymerization. Work in our group [29] has shown that excellent control can be obtained in miniemulsion polymerization with no loss of latex stability, using conventional RAFT agents that have not been pre-polymerized in homogeneous media, [9,14,28] and being independent of the class of RAFT agent used. The expansion of the RAFT technique into structured particles should for this reason be the logical next step for investigation.

In this study nanocapsules were synthesized by using RAFT agents to control the molar mass of the shell polymer. Styrene was used as the encapsulating monomer and isooctane as the core-oil. The influence of RAFT agents was investigated as well as the influence of different initiating species. It was found that the production of nanocapsules is controlled by the selection of initiator and RAFT agent.

Note that blank experiments without RAFT agents were not performed. The reason for this is that the experiments in this paper were based on published data, which were performed in similar monomer/oil systems but in the absence of the RAFT agents [21,30,31]. In the published data the influence of the type of initiator in the absence of the RAFT agent were already explained, thus it was not necessary to repeat the experiments as the outcome was already known.

## 2. Experimental section

### 2.1. Materials

Styrene (Sty, 99.9%) (Protea Chemicals) was washed with a 0.3 M potassium hydroxide (KOH, 85%) (ACE) solution followed by vacuum distillation to remove the inhibitor. The monomer was stored at −12 °C prior to use. Sodium dodecyl sulfate (SDS, 90%) (BDH); isooctane (99.5%), diethyl ether (99.5%) (both Merck); chloroform (99%) (Labchem); HCl (32%) (ACE); methanol (MeOH, 99.8%), *n*-hexadecane (99%) (both ACROS); potassium persulfate (KPS, 99+%), benzyl magnesium chloride (1.0 M in diethyl ether), α-methyl styrene (99%), bromobenzene (99%), $CS_2$ (99.9%), $CCl_4$ (99.9%) (all Aldrich); hexane (99%) (Saarchem); 4,4′-azobis(4-cyanovaleric acid) (75%) and *p*-toluene sulfonic acid (98.5%) (both Sigma-Aldrich), were used as received. 2.2′-Azobis(isobutyronitrile)

(AIBN, 98%) (Delta Scientific) was recrystallized from methanol. Distilled deionized (DDI) water, obtained from a Millipore Milli-Q purification system, was used.

*2.1.1. Synthesis of phenyl 2-propyl dithiobenzoate (1, CDB)*

The synthesis of cumyl dithiobenzoate was carried out according to the method of Le et al. [2] and purified by successive liquid chromatography on silica and alumina using hexane as an eluent system. The product crystallized after removal of the solvent under vacuum and storage below −10 °C. The purity was estimated by $^1$H NMR to be >95%, 25% yield based on dithiobenzoic acid.

*2.1.2. Synthesis of phenyl 2-propyl phenyl dithioacetate (2, PPPDTA)*

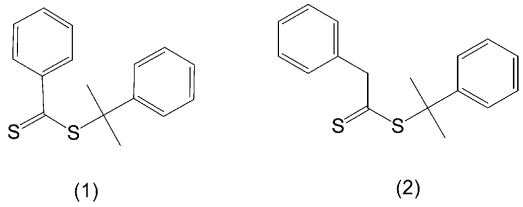
Phenyl 2-propyl phenyl dithioacetate was prepared according to the method of Quinn et al. [22] with the following modifications. Benzyl magnesium chloride was purchased and used as reagent. The Grignard agent was added to $CS_2$, in an equimolar amount, in a dropwise fashion under nitrogen while the reaction temperature was maintained below 20 °C by using an ice bath. After the addition was completed, the reaction was terminated by pouring the reactor contents into ice water and extracting the organic by-products with diethyl ether. The aqueous layer was then acidified with 32% HCl and extracted with diethyl ether. The organic layer was concentrated and a molar equivalent of α-methyl styrene was added. *p*-toluene sulfonic acid catalyst was added and the mixture was allowed to reflux in $CCl_4$ overnight. The product was then concentrated and crystallized from cold methanol. $^1$H NMR purity was estimated at 99%, 15% yield based on carbon disulfide.

All of the above RAFT agents are shown in Scheme 1.

*2.2. Preparation of nanocapsule particles*

Polystyrene/isooctane nanocapsule particles were synthesized through a miniemulsion polymerization reaction. 10.98 g (106 mmol) styrene, 1.14 g (5 mmol) hexadecane, 8.55 g (75 mmol) isooctane, 10.00 g (0.31 mol) MeOH [31] and the RAFT agent were premixed with a SDS/water solution (4 g (14 mmol) in 93 g $H_20$) for 1 h after which a miniemulsion was obtained by sonicating the mixture with a Sonics and Materials Inc. Vibracell VCX 750 ultrasonicator for 10 min at 95% amplitude. Sample volumes of up to 40 ml can be sonicated in the vessel used. Successive sonications were performed on 40 ml fractions of larger sample volumes with an average energy output per sample of 95 kJ. During this period the solution was continuously stirred in a water-cooled jacketed vessel to avoid polymerization due to heating and to facilitate homogeneous sonication. After miniemulsification the solution was transferred to a glass reactor which was suspended in a thermostatted oil bath and equipped with a condenser and nitrogen purge. Polymerization was achieved by adding initiator at 75 °C and was allowed to continue under continuous nitrogen purging. KPS has a documented influence on the pH of emulsion polymerization and for this reason systems are normally buffered against major pH changes, which could affect surfactant efficiency in the case of ionic surfactants [26]. Experimental data showed no major effect of pH on particle size or latex stability and for that reason any variation that might occur in the pH of the system is deemed to have a minimal impact on the interpretation of the data. The hydrolytic stability of dithioesters in aqueous media with time has been studied and it has been shown that degradation of the dithioester moiety is minimal on the timescale of these polymerizations [32]. The typical pH value of the studied latexes was 5.4. Samples were removed for analysis at regular intervals via a septum and the conversion was determined gravimetrically.

For formulations for the particle synthesis with different RAFT agents and initiators, refer to Table 1.




(1) (2)

Scheme 1. RAFT agents (1) phenyl 2-propyl dithiobenzoate (CDB) and (2) phenyl 2-propyl phenyl dithioacetate (PPPDTA).

## 3. Latex characterization

*3.1. Molar mass*

Molar mass distributions were measured via size-exclusion chromatography (SEC). Dried latex samples were dissolved in THF (8 mg ml$^{-1}$) and filtered through a 0.45 μm nylon filter. Analyses were carried out with a SEC system consisting of a Waters 610 Fluid Unit, Waters 410 Differential Refractometer at 30 °C, Waters 717$_{plus}$ Autosampler and Waters 600E System Controller. Two PLgel 5 μm Mixed-C columns (molar mass region 200−2×10$^6$ g mol$^{-1}$) and a pre-column (PLgel 5 μm Guard) were used and the column oven was set at 30 °C. Millennium$^{32}$ was used for data acquisition and data analysis. THF was used as solvent and the flow rate was 1.0 ml min$^{-1}$. The volume of the injected samples was 100 μl. The system was calibrated with narrow polystyrene standards ranging from 800 to 2×10$^6$ g mol$^{-1}$.

*3.2. Transmission electron microscopy (TEM)*

For TEM analysis 2 ml of the latex was added to an excess of MeOH to aid precipitation of the particles. The solution was homogenized by shaking and transferred to a copper TEM grid by pipette. The grid was left to dry at ambient temperature before analyses were performed. No

Table 1
Formulations for particle synthesis with different RAFT agents and initiators

| Exp | Initiator (mmol) | RAFT agent (mmol) | $D_n$ (nm) |
|---|---|---|---|
| 1 | 0.037[a] | 0.37[c] | 52 |
| 2 | 0.061[b] | 0.37[c] | 58 |
| 3 | 0.074[a] | 0.38[d] | 52 |

$D_n$ = number average particle diameter as determined by CHDF.
[a] KPS.
[b] AIBN.
[c] PPPDTA.
[d] CDB.

staining was applied to the dried particles. Contrast between the core and shell was the result of the combined effect of the difference of path length and material density of the constituting materials. This resulted in increased scattering of the incident $e^-$-beam from the wall material resulting in a darker region on the TEM images. Analyses were done on a JEM-200CX and 2000FX (JEOL Ltd, Tokyo, Japan) TEM. Copper grids were prepared by a deposition of a thin film of carbon for increased strength and conductivity.

### 3.3. Capillary hydrodynamic fractionation (CHDF)

Particle size was determined by capillary hydrodynamic fractionation (CHDF). Analyses were performed on a Matec Applied Sciences CHDF 1100, which was calibrated with PSty latex standards.

## 4. Results and discussion

One of the advantages of a controlled radical polymerization is that the molar mass of the polymer formed increases in a uniform manner. Unfortunately the advantage in controlling molar mass could become a disadvantage in controlling morphology. Long chains, which lock-in the morphology, are not formed rapidly with many RAFT agents. The shorter chains result in a higher degree of chain mobility and thus a loss of control of particle morphology. This loss of control means that it becomes important to use a RAFT agent that allows for rapid polymerization to chain lengths that will provide higher viscosity within the particles and in that way lock-in the morphology. This work uses two classes of RAFT agents, i.e. dithiobenzoates and phenyl dithioacetates. The kinetics that accompany the different agents have been and are still under investigation [33–35], but what is known is that dithiobenzoates lead to a large retardation in polymerization rate and for that reason the molar mass distribution of the corresponding polymer will develop more slowly than in the case of a phenyl dithioacetate, even though the target molar mass may be identical.

The second critical factor is the degree of surface activity that is present in the oligomeric radical that enters the particle. If no surface activity is present, i.e. in the case of an oil soluble initiating species such as AIBN, then there is no driving force for interfacial initiation or surface stabilization via the functional endgroup, which would have been present in the case of a water-soluble initiator such as KPS. This means that the probability that an inverted system (liquid encapsulating the polymer) is formed, which is predicted as being thermodynamically stable (for this specific monomer/oil combination) during the formation of high molar mass polymer, becomes overwhelming [30,31]. However, when initiation takes place from the water phase and if the anchoring effect occurs, entering radicals will (1) allow the reduction of the interfacial tension between the entering oligomers and the water phase, (2) facilitate the presence of the mediated species at the droplet/water interface and (3) if the RAFT agent used induces little or no retardation, rapid polymerization can occur at the interface, which will result in an increase in viscosity. Polymerization will therefore take place mainly at the interface hence leading to the desired nanocapsule morphology.

### 4.1. Influence of the type of initiator

As a starting point a RAFT agent that causes no retardation (PPPDTA) was used together with KPS as initiating species. KPS was chosen for its interfacial effects in combination with SDS as surfactant.

SEC traces for the above system can be seen in Fig. 1 and clearly indicate the living nature of the system, which can be seen by the steady increase in molar mass as a function of conversion. Note the very small peak (displayed in insert) that can be attributed to secondary nucleation and which will be explained in more detail later [29]. The predicted number average molar mass was calculated according to De Brouwer et al. [36]

$$\bar{M}_n = M_{RAFT} + \frac{x[M]_0 M_M}{[RAFT]_0 + 2f[I]_0(1 - e^{-k_d t})} \quad (1)$$

and this, as well as the experimentally acquired $\bar{M}_n$ and polydispersity data, can be seen plotted against the fractional conversion in Fig. 2. In Eq. (1) $M_{RAFT}$ is the molar mass of the RAFT agent, $x$ is the fractional conversion, $M_M$ is the molar mass of a single monomer unit and $[M]_0$, $[RAFT]_0$ and $[I]_0$ are the initial concentration of the monomer, RAFT agent and initiator. $k_d$ is the

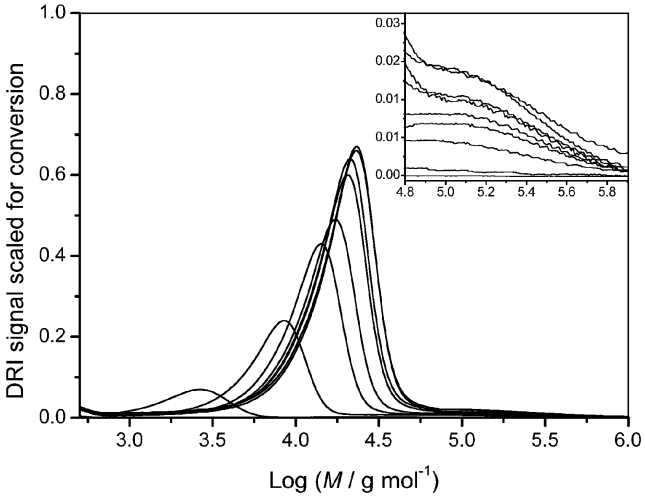



Fig. 1. SEC traces showing the living/controlled nature of particles synthesized with PPPDTA (0.37 mmol) and KPS (0.037 mmol) as initiating species at 75 °C (exp 1, Table 1). In the inlay the presence of a small amount of polymer formed due to secondary particle nucleation can be seen.

dissociation rate constant of the initiator at the reaction temperature, $f$ is an efficiency factor and $t$ is the time in seconds.

The experimental $\bar{M}_n$ values correspond well with the theoretically calculated $\bar{M}_n$ values. This is a strong indication of the controlled nature of the system and is strengthened by the low polydispersity index values obtained. The small secondary nucleation peak was not taken into account when the polydispersity and $\bar{M}_n$ values were calculated. The polymer (contributing to this) in this peak was formed by a different mechanism in this compartmentalized system, [37] thus justifying this decision. When the secondary nucleation peak is disregarded, excellent correlation with predicted values is obtained, which shows us that the percentage of the polymer mass contained within this peak is negligible.

Fig. 3 shows a TEM image obtained from the synthesized nanocapsule particles. The image shows nanocapsules clumped together thus causing overlapped shapes. Some of the obtained particles show deformed structures. This is quite normal when considering the low molar mass values obtained for the synthesized particles together with the fact that no crosslinkers were added. The particles will therefore easily deform if no further strengthening is performed and can thus lead to visually flattened or deformed particles. Fig. 4 shows a high magnification image of the synthesized particles. Fig. 5 shows a close-up of individual particles along with a scale bar indicating the particle size. Although the predominant particle morphology is core/shell (i.e. nanocapsules), Fig. 6 shows the existence of a population of solid spherical particles. These particles are most likely caused by secondary nucleation in the aqueous phase (note that three particle nucleation mechanisms can occur for heterophase polymerizations namely micellar nucleation, homogeneous nucleation and heterogeneous nucleation), [38] which will result in the formation of particles that do not contain core material. Due to the fact that virtually no RAFT agent is present in the aqueous phase, or for that matter the free micelles, polymerization will continue under ordinary free radical conditions thus leading to uncontrolled polymerization and hence high molar mass. This is confirmed in the SEC traces (Fig. 1). Up to now the confirmation of secondary nucleation has been rather difficult in RAFT mediated miniemulsion polymerization. This was because droplets nucleated were usually homogeneous, thus leading to solid spherical particles and therefore making it impossible to differentiate between controlled particles and particles produced under ordinary free radical conditions.

For initiator comparison the same RAFT agent (PPPDTA) was used but with the oil soluble initiator (AIBN) as initiating species. SEC traces for the miniemulsion polymerization can be seen in Fig. 7. As with the KPS, it can be seen that the polymer grows in a controlled fashion. The inlay is again a magnification of the secondary nucleation part which was not taken into consideration

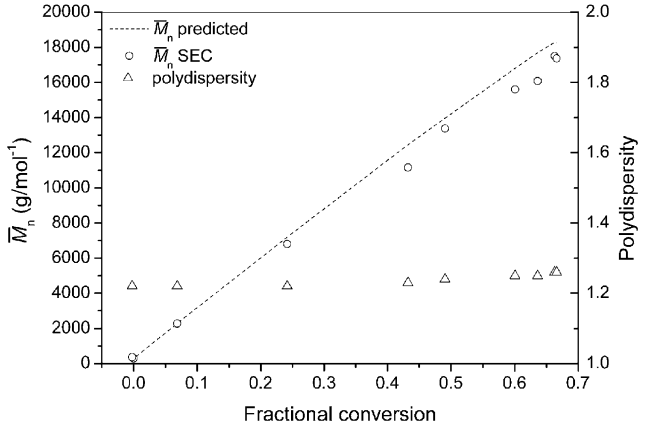



Fig. 2. Predicted $\bar{M}_n$, experimental $\bar{M}_n$ (SEC) and polydispersity values versus the fractional conversion for the miniemulsion polymerization of PSty/isooctane nanocapsules in the presence of PPPDTA and KPS.

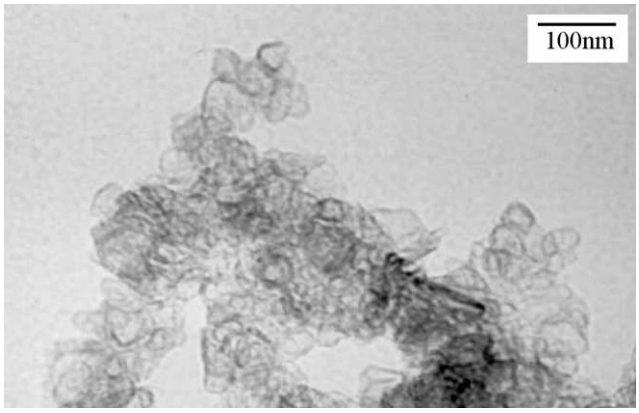



Fig. 3. TEM image of Psty/isooctane nanocapsules synthesized in the presence of PPPDTA (0.37 mmol) and KPS (0.037 mmol) under controlled conditions.

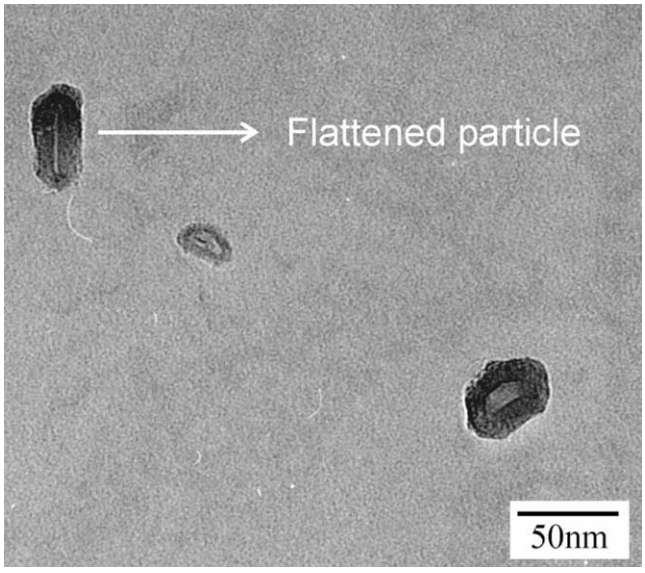



Fig. 4. Higher magnification of nanocapsule particles synthesized in the presence of PPPDTA (0.37 mmol) and KPS (0.037 mmol). In the top-left corner a flattened nanocapsule can be seen.

when $\bar{M}_n$ and polydispersity index values were calculated. Fig. 8 shows theoretical $\bar{M}_n$ values, SEC $\bar{M}_n$ values and polydispersity index values versus fractional conversion for the system and confirms that the criteria for living polymerization are met. A slight discrepancy between the theoretical and experimental $\bar{M}_n$ values is observed at high fractional conversion. This is caused by tailing of the MMD towards lower molar mass, the cause of which is not exactly known. The phenomenon is accompanied by a decrease in polymerization rate (Fig. 9). It therefore seems that some side reaction is leading to the formation of dead chains, and simultaneously slowing down the polymerization.

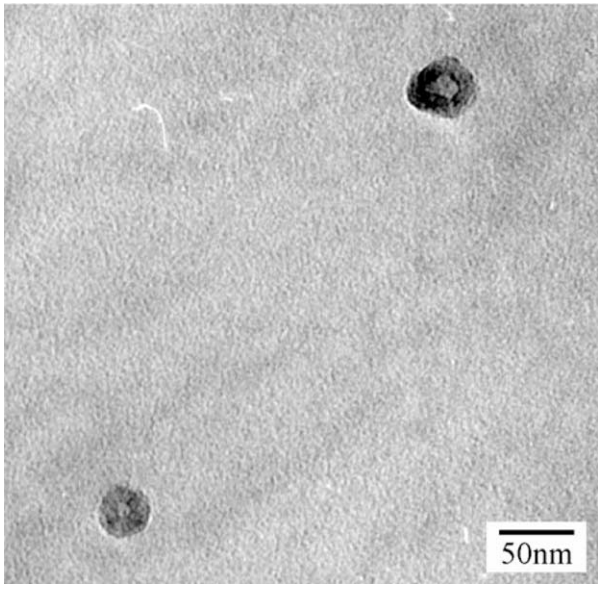



Fig. 5. High magnification TEM image of individual nanocapsule particles synthesized in the presence of PPPDTA (0.37 mmol) and KPS (0.037 mmol).

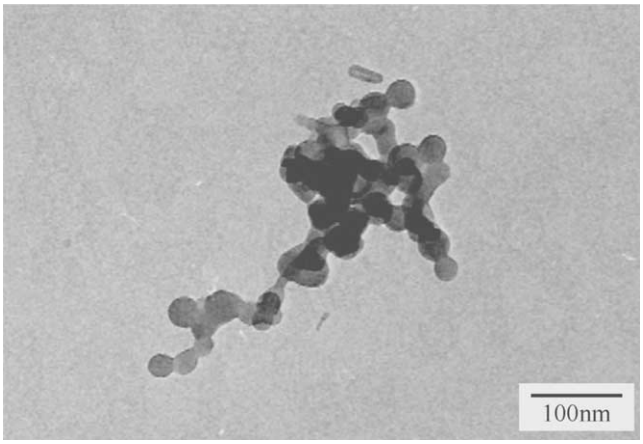



Fig. 6. TEM image of particles synthesized in the presence of PPPDTA (0.37 mmol) and KPS (0.037 mmol) showing the presence of solid particles that were caused by secondary nucleation. Note the flattened nanocapsule at the top of the image.

Fig. 10 shows the TEM image of the obtained particles. All synthesized particles show solid structures and thus no nanocapsule morphology (liquid core and polymer shell). In this instance the anchoring effect will not be present as a result of the fact that AIBN does not possess any ionic groups that will interact with the surfactant molecules stabilizing the droplet surface. Thus, although AIBN has some degree of water phase initiation [39] the entering radicals will not be able to anchor themselves at the water/droplet interface and therefore polymerization, due to mediated species, will not preferentially take place at the droplet/water interface. Further propagation and transfer will all take place inside the droplet without any necessity

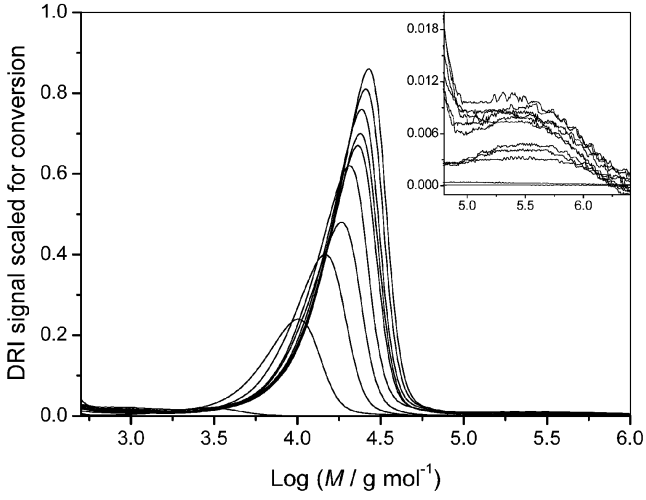



Fig. 7. SEC traces showing the living/controlled nature of particles synthesized with PPPDTA (0.37 mmol) and AIBN (0.061 mmol) as initiating species at 75 °C (exp 2, Table 1). In the inlay the presence of a small amount of polymer formed due to secondary particle nucleation can be seen.

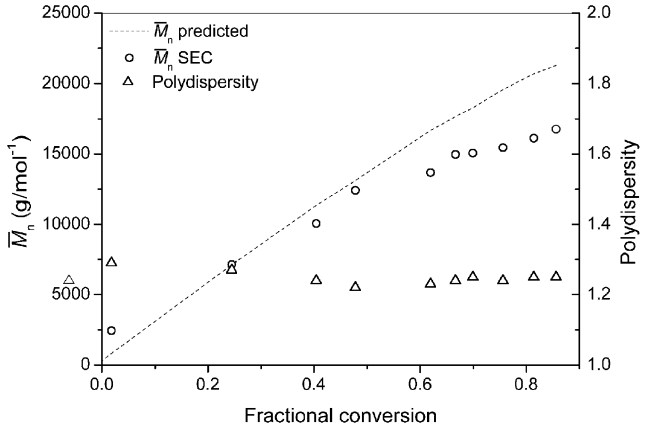



Fig. 8. Predicted $\bar{M}_n$, experimental $\bar{M}_n$ (SEC) and polydispersity values versus the fractional conversion for the miniemulsion polymerization of PSty/isooctane in the presence of PPPDTA (0.37 mmol) and AIBN (0.061 mmol) at 75 °C.

for the more hydrophobic oligomers to migrate to the interfacial layer to form the desired nanocapsule morphology. Controlled polymerization will therefore take place in the entire volume of the droplet and not only at the water/droplet boundary thus causing solid particles. Polymer encapsulation is limited due to the polarity difference between the polystyrene and water and will therefore rather result in an inverse morphology due to the lack of kinetic influences, which causes thermodynamics to dominate.

From the above it is therefore quite obvious that the type of initiator used will play a crucial role in establishing nanocapsule morphology.

### 4.2. Influence of the type of RAFT agent used

In the last instance the type of RAFT agent used will be compared. For this experiment a RAFT agent that induces

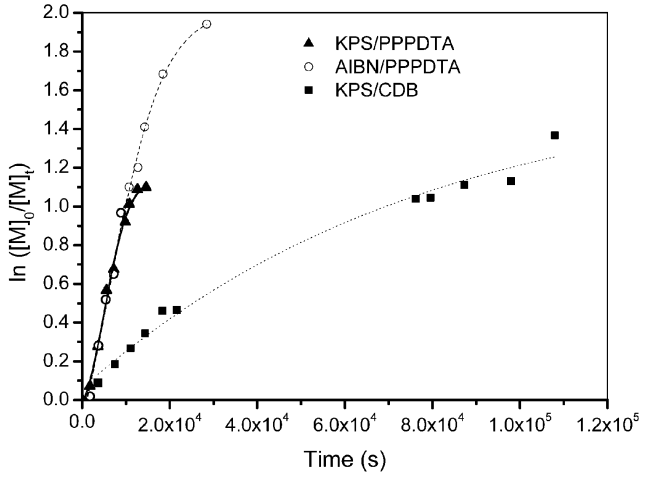



Fig. 9. First order kinetic plots for reactions done with PPPDTA (0.37 mmol) and CDB (0.38 mmol) using KPS (0.037 mmol) and AIBN (0.061 mmol) as initiating species at 75 °C.

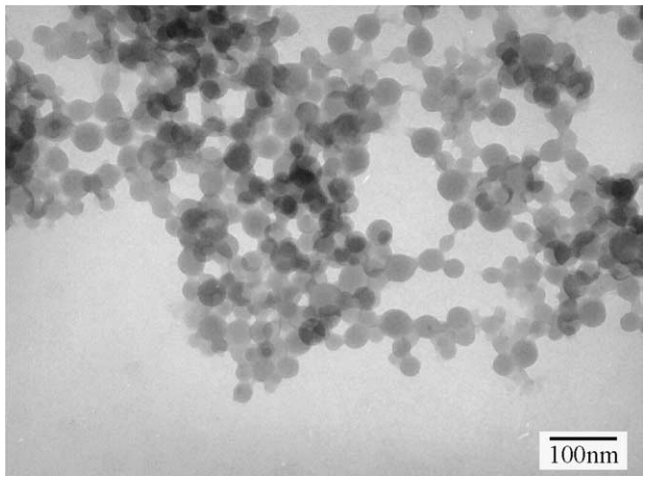



Fig. 10. TEM image of solid particles synthesized under controlled conditions in the presence of PPPDTA (0.37 mmol) and AIBN (0.061 mmol).

larger retardation in polymerization rate was chosen, namely CDB. Styrene polymerizations mediated by CDB are much slower than those mediated by PPPDTA under identical experimental conditions (see Fig. 9 for a first order kinetic comparison between the different RAFT agents used). KPS was used as initiating species, which will facilitate the presence of mediated species at the oil/water interface. In Fig. 11 the SEC curves for the miniemulsion polymerization reaction with CDB as RAFT agent and KPS as initiating species can be seen. Again it is quite obvious that controlled polymerization could be achieved as is confirmed from the plots in Fig. 12. Here the $\bar{M}_n$ values obtained from SEC follow the theoretically predicted $\bar{M}_n$ values and the polydispersity values are acceptable. A slight deviation is again observed at high fractional conversion and this can also be attributed to low molar mass tailing. Although it would be expected that the usage of KPS as

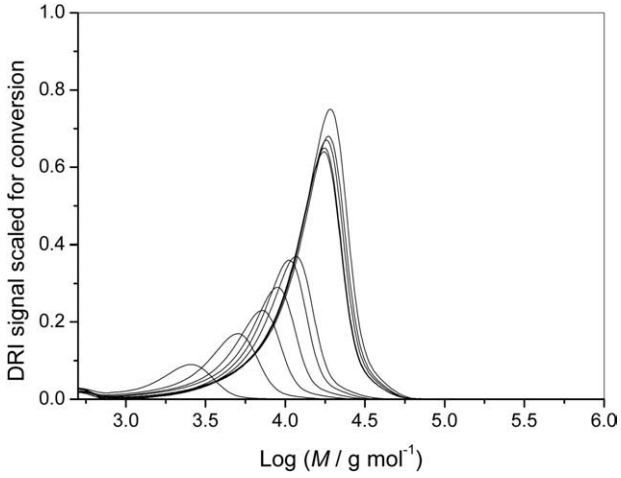



Fig. 11. SEC traces showing the living/controlled nature of particles synthesized with CDB (0.38 mmol) and KPS (0.074 mmol) as initiating species at 75 °C (exp 3, Table 1).

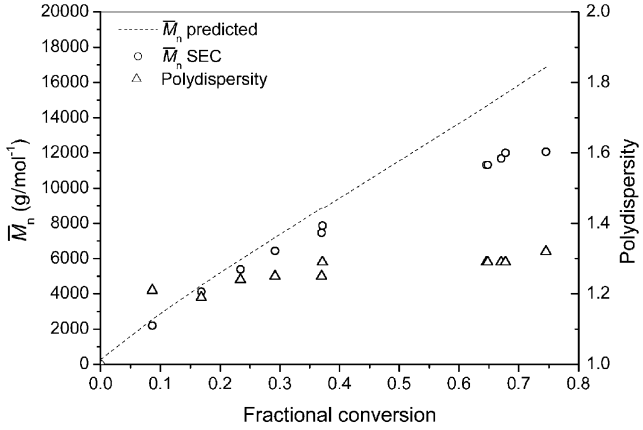



Fig. 12. Predicted $\bar{M}_n$, experimental $\bar{M}_n$ (SEC) and polydispersity values versus the fractional conversion for the miniemulsion polymerization of PSty/isooctane in the presence of CDB (0.38 mmol) and KPS (0.074 mmol) at 75 °C.

initiating species would increase the chances of nanocapsule formation, Fig. 13 showing TEM images of the obtained particles, proves the opposite. Keep in mind that CDB induces a much larger rate retardation than PPPDTA. On the entry of radical species into a droplet, multiple RAFT mediated transfers will take place prior to the next radical entry event. As the initial RAFT leaving groups do not have an ionic character the majority of chains will not have ionic end-groups. Thus, even though KPS will provide some surface anchoring of the entering oligomers, polymerization at the droplet interface, caused by radicals produced by mediating species, is rather slow when using dithiobenzoates, which will cause a slow increase in viscosity as a function of time. There is now no driving force for the formation of an interfacial polymer layer. The slow formation of chains will allow diffusion due to the low viscosity of the polymerization locus and hence the thermodynamically preferred morphology, which in this case is inverse core/shell (solid core and oily shell), to dominate, thus causing solid particles. This clearly differs from the case of PPPDTA where the rapid formation of polymer at the particle/water interface does not allow the thermodynamically predicted morphology to establish, thus leading to an oil droplet encapsulated by polymer, i.e. nanocapsule morphology.

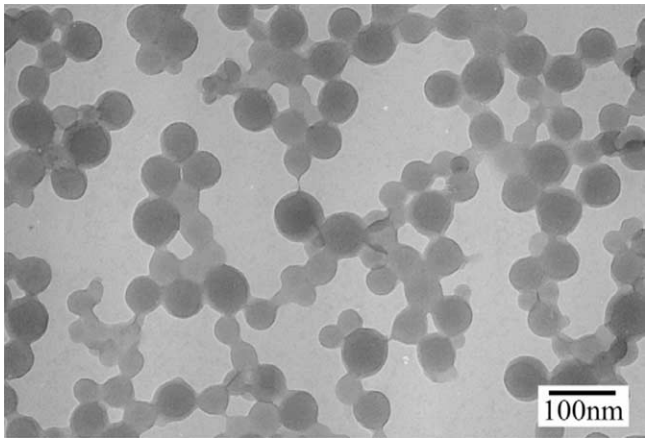



Fig. 13. TEM image of solid particles synthesized under controlled conditions in the presence of CDB (0.38 mmol) and KPS (0.074 mmol).

## 5. Conclusions

Chain architecture and morphology of structured particles can be controlled by using living/controlled polymerization techniques in conjunction with surface active initiating species. In this study, nanocapsule particles consisting of an isooctane core and polystyrene shell could be synthesized with additional control of the molar mass of the shell polymer. The formation of particles with the desired morphology is made possible by controlling the kinetics of the reaction, i.e. polymerization kinetics, as well as surface effects, i.e. anchoring of the entering oligomeric species. To study these effects two different RAFT agents were used to study the consequence of chain growth rate, which is inherent in the nature of the agent used. An agent that induces no retardation as well as an agent that induces large retardation in polymerization rate, phenyl 2-propyl phenyl dithioacetate (PPPDTA) and phenyl 2-propyl dithiobenzoate (CDB) respectively, were used in conjunction with two initiators, KPS and AIBN, solely chosen for their difference in surface activities. When the non rate retarding agent (PPPDTA) was used in conjunction with KPS, the entering radicals could be anchored at the droplet/water interface. This, together with the fact that the use of PPPDTA as a transfer agent leads to a rapid increase in chain lengths and a decrease in chain mobility, resulted in the polymerization loci being locked at the droplet/water interface, causing the formation of nanocapsule particles. When AIBN was used, on the other hand, no surface activity was present, allowing entering radicals to transfer into the droplet without being anchored at the surface. Even though a non rate retarding RAFT agent was used, there is no thermodynamic driving force for the hydrophobic oligomers to migrate to the droplet/water interface, which consequently results in polymerization across the total volume of the droplet, hence resulting in solid particles. Finally, a RAFT agent with larger rate retardation (CDB) was used in conjunction with a surface active initiating species, KPS. In this case entering oligomers could be anchored at the droplet/water interface. However, due to the slow polymerization, no rapid increase in chain length took place and consequently no related increase in viscosity and decrease in chain mobility. Diffusion of transferred species (non-charged) into the droplet can therefore take place, causing polymerization over the entire volume element of the droplet and leading to the formation of solid particles.

Due to the scope of the present project we limited the study to styrene polymerization. From the results reported

here it can be concluded that systems with so-called hybrid behavior are expected to be particularly suitable for the formation of nanocapsules. An example of such a system is the polymerization of methyl methacrylate (MMA) mediated by PPPDTA [40].

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