

Study of the solution and aqueous emulsion copolymerization of vinylidene chloride with methyl acrylate in the presence a poly(ethylene oxide) macromolecular RAFT agent

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ARTICLE INFO

Article history:

Received 22 July 2013

Received in revised form

24 September 2013

Accepted 7 October 2013

Available online 12 October 2013

Keywords:

RAFT polymerization

Emulsion polymerization

Vinylidene chloride

ABSTRACT

The reversible addition-fragmentation chain transfer (RAFT) copolymerization of vinylidene chloride (VDC) with methyl acrylate (MeA) was studied in the presence of poly(ethylene oxide)-based macromolecular RAFT (macroRAFT) agents of the trithiocarbonate type (PEO-TTC) in solution and in aqueous emulsion. Firstly the formation of PEO-*b*-P(VDC-*co*-MeA) diblock copolymers was performed in toluene solution at 30 °C and a good control over the polymerization with high chain-end functionality was shown. A first aqueous emulsion copolymerization of VDC with MeA was performed using one of the amphiphilic PEO-*b*-P(VDC-*co*-MeA) diblock copolymers as macromolecular stabilizer. Then, in a series of experiments the PEO-TTC macroRAFT agents were directly tested as both chain transfer agents and stabilizing agents in similar conditions (aqueous batch emulsion copolymerization of VDC with MeA at 70 °C). The influence of the nature and concentration of the initiating system and the presence or not of a buffer were studied. We demonstrated that in simple conditions, nanometric latex particles composed of amphiphilic PEO-*b*-P(VDC-*co*-MeA) diblock copolymers formed by polymerization-induced self-assembly (PISA). It can thus be concluded that PEO-TTC macroRAFT agents are valuable non-ionic macromolecular stabilizers in the emulsion copolymerization of VDC and MeA and allow the formation of core-shell diblock copolymer particles in the absence of free surfactant. However, when rather high molar masses of the hydrophobic PVDC-based block were targeted, the determined molar masses deviated from the theoretical values.

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1. Introduction

Controlled radical polymerization (CRP) processes, such as reversible addition-fragmentation chain transfer (RAFT) [1,2], have been extensively studied during the past two decades. Through these polymerization techniques, polymers with predetermined molar mass and narrow molar mass distribution, exhibiting a variety of chemical compositions, topologies, and well-maintained chain-end functionalities have been successfully prepared. The

main processes used for CRP were either bulk or solution polymerizations, but more recently environmentally friendly aqueous dispersed media, such as emulsion, miniemulsion or dispersion were applied [2–7]. The latter lead to aqueous suspensions of submicrometric polymer particles, usually stabilized by traditional low molar mass, anionic or non-ionic surfactants. More recently, the development of *ab initio* semi-continuous [8–10] or batch emulsion polymerizations under RAFT control in absence of free surfactant was achieved [5,11–24]. In this successful approach, water-soluble macromolecular RAFT agents (macroRAFT agents) are employed to act as both the stabilizer and the control agent. The method, which leads to the *in situ* creation of amphiphilic block copolymers, has been named *polymerization-induced self-assembly* (PISA) [6,25–29]. The resulting polymer latexes do not contain free

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Scheme 1. Synthetic route for the PEO-TTC-mediated RAFT copolymerization of vinylidene chloride and methyl acrylate in toluene or in aqueous emulsion.

Standard Services), using only the RI detector. The absolute number-average molar masses, M_n^{LS} , were calculated using the RALS/LALS and RI signals. The refractive index increments (dn/dc) were measured with the online RI detector as described before [32].

Dynamic light scattering (DLS). The z-average particle diameter (D_z) and the dispersity factor of highly diluted samples (Poly) were measured by dynamic light scattering (DLS) (NanoZS from Malvern Instruments) at 90° at 25 °C.

Transmission electron microscopy (TEM). The diluted samples were dropped on a carbon-coated copper grid and dried under air. The TEM images were recorded without staining using a Philips CM120 microscope operating at an accelerating voltage of 80 kV (Centre Technologique des Microstructures, Claude Bernard University, Villeurbanne, France).

2.3. Synthesis of PEOXK-TTC macroRAFT agents

PEO2K-TTC and PEO6K-TTC refer to the PEOXK-TTC hydrophilic macroRAFT agents with number-average molar masses, M_n , of 2400 and 6700 g mol⁻¹, respectively. The M_n were determined by ¹H NMR spectroscopy by integrating the signals of the methyl protons of the dodecyl alkyl chain and the methylene protons of the poly(ethylene oxide) block at 0.86 ppm and at 3.64 ppm, respectively. The PEO2K-TTC macroRAFT agent was prepared according to reference 12 and the PEO6K-TTC macroRAFT agent was prepared as described before [33] except that the molar ratio of TTCA and DCC with respect to the PEO was changed from 20 to 9.

2.4. Synthesis of PEOXK-*b*-P(VDC-co-MeA) diblock copolymers in toluene solution

In a typical experiment (Table 1, entry S4) 1.4299 g (0.21 mmol) of PEO6K-TTC was dissolved in 10.07 g of toluene in a 25 mL round-bottom flask. 0.010 g (0.03 mmol) of V70 were added and the resulting mixture was purged with nitrogen for 20 min in a cold water bath. After being deoxygenated by bubbling with nitrogen for 20 min, the monomers MeA (1.6032 g, 18.6 mmol) and VDC (3.9880 g, 41.1 mmol) were injected through the septum into the reaction mixture. The sealed round-bottom flask was immersed in a thermostated oil bath at 30 °C, and the polymerization lasted for 6.3 h. The polymer was recovered after precipitation in cold methanol. The overall monomer weight conversion was determined by gravimetric analysis.

2.5. Emulsion copolymerization of VDC with MeA in the presence of amphiphilic PEO2K-*b*-P(VDC-co-MeA) copolymer

The emulsion polymerization was initiated by a persulfate/metabisulfite redox couple according to reference [35] and conducted at 70 °C in order to reach a convenient polymerization rate. In details, in experiment E1, Table 2, 0.5660 g (0.15 mmol) of

amphiphilic copolymer S2 ($M_n^{LS} = 3700$ g mol⁻¹), 0.1974 g (0.74 mmol) of TSPP and 0.0434 g (0.23 mmol) of SMBS were dissolved in 80.09 g of distilled water. The resulting mixture was introduced into the reaction vessel and was purged with argon for 20 min at 16 °C. After deoxygenation by bubbling with nitrogen for 20 min, 1.8 mL (0.02 mol) of MeA, 6.4 mL (0.08 mol) of VDC and 4 mL of an aqueous solution of APS ([APS] = 0.07 mol L⁻¹) were introduced via the injection valve into the reactor. Then the autoclave was pressurized at 1 bar with argon and the reaction mixture was heated to 70 °C and stirred at 400 rpm. Samples were periodically withdrawn to measure the overall monomer weight conversion by gravimetric analysis, along with particle size and particle size distribution by DLS. After complete drying, for each sample the raw polymer was dissolved in THF for size exclusion chromatography analysis. After 5 h, the autoclave was depressurized, and the latex was purged with argon in order to remove the residual monomers under gentle stirring during 1 h and then stored at 4 °C.

2.6. Emulsion copolymerization of VDC with MeA in the presence of PEOXK-TTC macroRAFT agents

In experiment E2, Table 2, 0.5630 g (0.24 mmol) of PEO2K-TTC, 0.2043 g (0.77 mmol) of TSPP and 0.0453 g (0.24 mmol) of SMBS were dissolved in 80.12 g of distilled water. The resulting mixture was introduced into the reaction vessel and was purged with argon for 20 min at 16 °C. After deoxygenation by bubbling with nitrogen for 20 min, 1.8 mL (0.02 mol) of MeA, 6.4 mL (0.08 mol) of VDC and 5 mL of an aqueous solution of APS ([APS] = 0.06 mol L⁻¹) were introduced via the injection valve into the reactor. Then the autoclave was pressurized at 1 bar with argon and the reaction mixture heated to 70 °C and stirred at 400 rpm. Samples were periodically withdrawn to measure the overall monomer weight conversion by gravimetric analysis, along with particle size and particle size distribution by DLS. After complete drying, for each sample the raw polymer was dissolved in THF for size exclusion chromatography analysis. After 7.3 h, the autoclave was depressurized, and the latex was purged with argon in order to remove the residual monomers under gentle stirring during 1 h and then stored at 4 °C.

The procedure was the same for the emulsion copolymerization of VDC with MeA with ACPA as an initiator, except that the latter was directly introduced in the reaction vessel with the aqueous solution of PEOXK-TTC macroRAFT agent.

3. Results and discussion

3.1. Synthesis of PEOXK-*b*-P(VDC-co-MeA) diblock copolymers in toluene solution

A series of amphiphilic PEO-*b*-P(VDC-co-MeA) diblock copolymers was synthesized in toluene solution using PEO2K-TTC and PEO6K-TTC as macromolecular RAFT agents (Scheme 1, Table 1). It

Table 1
Synthesis of PEOXK-*b*-P(VDC-co-MeA) diblock copolymers in toluene at 30 °C with $[V70]_0/[RAFT]_0 = 0.15$.

Entry	PEOXK-TTC	Mol% MeA ^a	$[M]_{0, tot}$ (mol L ⁻¹)	$[M]_{0, tot}/[RAFT]_0$	Time (h)	Conv. (wt%)	M_n^{th} (kg mol ⁻¹)	dn/dc_{calc}^b (mL g ⁻¹)	dn/dc_{exp}^c (mL g ⁻¹)	M_n^{PSd} (kg mol ⁻¹)	M_n^{LSe} (kg mol ⁻¹)	\bar{D}^d
S1	2K	12.4	5.33	219	43.0	40.3	10.8	0.100	0.100	8.8	10.0	1.3
S2	2K	32.6	2.43	64	7.3	20.2	3.6	0.078	0.081	4.1	3.7	1.1
S3	6K	11.2	4.81	212	44.0	50.3	16.9	0.093	0.086	12.1	13.2	1.3
S4	6K	31.2	3.60	279	6.3	17.6	11.3	0.081	0.080	11.1	10.6	1.2

^a Initial mol% of MeA in the mixture of monomers.

^b dn/dc_{calc} was calculated from the wt% of MeA₀ and wt% of PEO in the polymer using equation (1).

^c dn/dc_{exp} was determined by size exclusion chromatography by injecting a solution of the copolymer ($c = 10$ mg mL⁻¹) at 4 different volumes [32].

^d Number-average molar masses, M_n^{PS} , and dispersities, \bar{D} , determined by a PS calibration curve.

^e The number-average molar masses based on static light scattering detection, M_n^{LS} , were determined using the experimental dn/dc values.

Table 2
Aqueous emulsion copolymerization of VDC with 20 mol% of MeA à 70 °C at 10% of solids content.

Entry	Macro RAFT	Initiator (mmol L ⁻¹ _{aq})	pH _i = 0	pH _f = final	Wt% macro-RAFT ^c	$n_{\text{monomers}}/n_{\text{macroRAFT}}$	[Macro RAFT] ₀ (mmol L ⁻¹ _{aq})	Time (h)	Conv. (wt%)	$M_{n,\text{th}}^d$ (kg mol ⁻¹)	M_n^{PS} (kg mol ⁻¹)	$M_n^{\text{LS,e}}$ (kg mol ⁻¹)	D_z^{DLS} (nm)/poly
<i>Use of the amphiphilic PEO2K-b-P(VDC-co-MeA) copolymer as stabilizer</i>													
E1	S2 (Table 1)	APS ^{a,b} (3.3)	7	4	6	654	2	5	99	64.9	8.9 (3.1)	29.5	516/0.13
<i>Use of PEOXK-TTC for the in situ formation of PEO-b-P(VDC-co-MeA) copolymers</i>													
E2	PEO2K-TTC	APS ^{a,b} (3.5)	7	4	6	425	3	7.3	100	42.8	12.5 (2.2)	23.9	536/0.21
E3	PEO2K-TTC	APS ^{a,b} (2.0)	8	6	5	541	2	7	92	49.5	12.5 (3.3)	n.d.	531/0.17
E4	PEO2K-TTC	APS ^a (3.5)	5	2	6	423	3	2.5	100	42.5	10.9 (2.5)	19.3	103/0.02
E5	PEO2K-TTC	ACPA (3.6)	5	2	6	417	3	8	95	37.7	13.1 (2.1)	15.8	107/0.001
E6	PEO2K-TTC	ACPA (0.7)	5	3	6	415	2	9.5	82	34.6	20.3 (1.6)	29.0	95/0.06
E7	PEO6K-TTC	ACPA (1.6)	5	2	6	1161	1	9	95	111.1	21.9 (2.6)	47.2	105/0.06

n.d. = not determined.

^a $n(\text{APS})/n(\text{SMBS}) = 1.2$.

^b In the presence of TSPP: $[\text{TSPP}]_0 = 9 \text{ mmol L}^{-1}$.

^c wt% macroRAFT agent (surfactant) with respect to monomers ($m_{\text{macroRAFT}}/m_{\text{monomers}} \times 100$).

^d $M_{n,\text{th}} = m_{\text{monomers},0}/n_{\text{PEO-TTC},0} \times \text{conv.}/100 + M_n \text{ macroRAFT}$.

^e The number-average molar masses based on static light scattering detection, M_n^{LS} , were determined using equation (1).

should be noted that in the solution copolymerization of VDC with MeA, the reactivity ratios are both equal to 1 so that the MeA fraction in the formed P(VDC-co-MeA) copolymer matches that of the initial comonomer feed [32]. The polymerizations of VDC were performed with either about 10 or 30 mol% of MeA as a comonomer in order to reduce crystallinity, to form soluble polymers and to favour better polymerization control [32]. In addition, for this range of compositions, the copolymer should remain soluble during the polymerization, and may only crystallize upon isolation or under appropriate annealing conditions. With both macroRAFT agents, a clear shift in the size exclusion chromatograms was observed accounting for the efficiency of the transfer reaction (S1 in Fig. 1). The dispersities remained below 1.3 in all cases. As expected, they were lower ($\bar{D} = 1.1$ or 1.2) when higher quantities of the acrylic comonomer were used (30 mol% of MeA) [32]. In most of the previously published works, the molar masses of PVDC-based copolymers were reported using a calibration curve based on PS standards [31,36]. However, we have recently demonstrated that such calibration is hardly suitable for PVDC-based copolymers and even less for PVDC-based amphiphilic copolymers [32]. Thanks to the use of an in-line static light scattering detector it was possible to obtain reliable values in the case of amphiphilic PAA-b-P(VDC-co-MeA) copolymers. As expected again due to difference in interaction parameters of PS and PVDC-based copolymer with THF (SEC solvent), the average molar masses of the PEOXK-b-P(VDC-co-MeA)

copolymers determined by a conventional PS calibration (M_n^{PS}) did not correspond to those determined using a static light scattering detector (M_n^{LS}) (see Table 1). The latter were however close to the theoretical values, which further confirmed the control over the copolymerization of VDC and MeA in the chosen conditions. According to our earlier study [32], the refractive index increments (dn/dc) of these amphiphilic block copolymers were calculated using the following equation (1),

$$(dn/dc)_{\text{block copo}} = (1 - \text{wt\%PEO}/100) \times (dn/dc)_{\text{P(VDC-co-MeA)}} + \text{wt\%PEO}/100 \times (dn/dc)_{\text{PEO}} \quad (1)$$

with $(dn/dc)_{\text{P(VDC-co-MeA)}} (\text{mL g}^{-1}) = -4.69 \times 10^{-4} \times (\text{wt\% MeA}_0) + 0.114$ and $(dn/dc)_{\text{PEO}} = 0.068 \text{ mL g}^{-1}$. The calculated values were close to the experimentally determined ones, which shows again the validity of this equation.

The efficiency of the transfer reaction with the formation of diblock copolymers was further confirmed even with a low amount of MeA comonomer (12 mol% for S1) by using SEC equipped with an in-line UV detector. Indeed, the trithiocarbonate functionality strongly absorbs at 309 nm [37]. Due to the molar response of the detection, we can conclude from Fig. 1 (right side) that the final copolymer was almost free of residual PEO2K-TTC macroRAFT agent

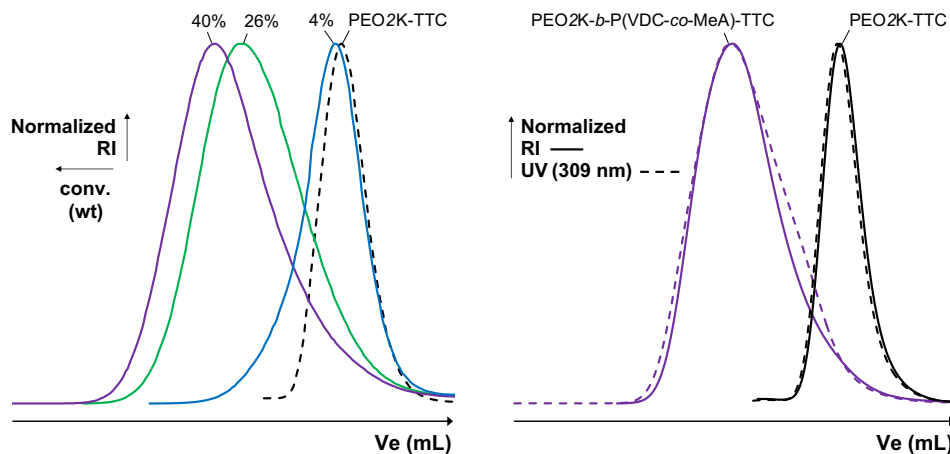


Fig. 1. Evolution with conversion of the differential refractive index response in the size exclusion chromatograms for experiment S1 (left). SEC peaks obtained with the UV detector at 309 nm (dashed line) and the differential refractive index detector (full line) for the PEO2K-TTC macroRAFT agent and the formed PEO2K-b-P(VDC-co-MeA) diblock copolymer (S1) (right).

and that the formed diblock copolymers were terminated by a trithiocarbonate function. The formed copolymers can thus act as chain transfer agents in a subsequent polymerization reaction.

3.2. Aqueous emulsion copolymerization of VDC and MeA in the presence of the amphiphilic copolymer PEO2K-*b*-P(VDC-co-MeA)

The diblock copolymer PEO2K-*b*-P(VDC-co-MeA) S2 was used as a non-ionic macromolecular surfactant in the emulsion copolymerization of VDC with MeA. It was selected because it exhibits the shortest hydrophobic block, which facilitates its direct dissolution in water (see Figure SI-1, Supporting Information) and avoids the formation of large, ill-defined aggregates. Moreover, it possesses a reactive trithiocarbonate group at the hydrophobic chain end, which may participate as a chain transfer agent in the polymerization process. This reaction would lead to the extension of the hydrophobic block and improve the anchoring of the stabilizer at the particle surface. The experiment was performed using 6 wt% of PEO2K-*b*-P(VDC-co-MeA) with respect to the monomers in *ab initio* batch conditions at 70 °C (allowing for sufficient polymerization rate) with a monomer concentration in the latex of 10 wt% and 20 mol% of MeA based on the monomers. According to a previous work by Lacroix-Desmazes et al. [35] the redox couple ammonium persulfate/sodium metabisulfite was selected as an initiator and TSPP was added to prevent severe acidification of the latex.

As reported in Table 2 entry E1, close to complete monomer conversion was reached in quite short reaction time (5 h). A homogeneous and fluid white latex was obtained, composed of large polymer particles (average diameter about 500 nm), with an amount of coagulum of about 1 wt% (with respect to $m(\text{monomers} + \text{macroRAFT})_{t=0}$). The presence of TSPP allowed the final pH to be limited at 4 instead of lower pH in the absence of this salt. Due to the high density of the PVDC-based polymers (1.77 g cm^{-3}) [30a,38] a small fraction of the particles deposited at the bottom of the flask over time, but could be redispersed upon stirring. Interestingly, the size exclusion chromatograms displayed in Fig. 2 showed a shift with monomer conversion indicating the participation of the TTC end-function in the polymerization process. Nevertheless, as expected, the polymerization did not show the features of a controlled polymerization with broad molar mass distributions ($\bar{D} = 3.1$) and asymmetric SEC traces with tailing

towards low molar masses. The high targeted degree of polymerization (here 654), the high initial initiator concentration and the existence of side reactions such as transfer to VDC [36] may explain the lack of control during the polymerization. Nevertheless, the hydrophilic PEO segments were covalently linked to the final latex particles with long hydrophobic block, preventing any possible migration during film formation.

3.3. Surfactant-free batch aqueous emulsion copolymerization of VDC and MeA in the presence of PEOXK-TTC macroRAFT agents

As mentioned in the Introduction, it was previously shown that stable latexes composed of amphiphilic diblock copolymers could be reached via a so-called PISA process, where amphiphilic block copolymers form and self-assemble in the course of the controlled radical emulsion polymerization of hydrophobic monomers in the presence of hydrophilic macromolecular initiators or RAFT agents [6]. Such process could be performed in the simplest conditions, *i.e.* in batch, *ab initio* conditions in absence of free conventional surfactants. For instance, we have successfully implemented this concept to the use of PEO-TTC macroRAFT agents in the RAFT emulsion (co)polymerization of *n*-butyl acrylate (with methyl methacrylate) and styrene with the formation of amphiphilic PEO-based diblock copolymers that self-assemble into self-stabilized nanoparticles [12,33,39]. We thus performed a series of VDC/MeA emulsion copolymerizations (with a concentration of 10 wt% of monomers containing 20 mol% of MeA) replacing the PEO2K-*b*-P(VDC-co-MeA) diblock copolymers by the PEOXK-TTC macroRAFT agents (Table 2).

Comparison of the performance of PEO2K-TTC with that of the amphiphilic copolymer PEO2K-*b*-P(VDC-co-MeA). The experiment E2 was performed with 6.0 wt% of macroRAFT agent in the same conditions as in experiment E1 (using the diblock copolymer). The final monomer conversion was again high and the colloidal stability was similar in both cases, with large particles of about 500 nm average diameter (DLS), heterogeneous in size ($\text{Poly} = 0.2$), and an amount of coagulum of 1 wt% (with respect to $m(\text{monomers} + \text{macroRAFT})_{t=0}$). Concerning the macromolecular characteristics of the formed polymers, in contrast to the former experiment with the diblock copolymer (E1), the SEC revealed a quite symmetric molar mass distribution with lower dispersities (final $\bar{D} = 2.2$) (Fig. 3). In these two experiments the mass ratio between the stabilizing polymer and the monomers was kept constant, which consequently led to an increase of the mole number of stabilizing hydrophilic chains (lower targeted degree of polymerization, here 425) in experiment E2. An additional experiment (E3) was thus performed, introducing PEO2K-TTC in a similar mole number as in experiment E1 ($2 \text{ mmol L}^{-1} \text{ aq}$), thus in smaller quantity compared to E2, *i.e.* 4.7 wt%. Regardless of the quantity of PEO2K-TTC introduced, similar particle diameters were obtained ($D_z(\text{E2}) = 536 \text{ nm}$ vs. $D_z(\text{E3}) = 531 \text{ nm}$), but the formation of more coagulum (6 wt%) was observed, indicating that with this amount of PEO2K-TTC the limit of colloidal stability was reached. Again, a shift of the SEC traces with increasing monomer conversion was observed, but dispersities were larger ($\bar{D} = 3.3$) than for a controlled system.

It can thus be concluded that PVDC-based latex particles can be stabilized by the use of PEO-TTC macroRAFT agents in very simple *ab initio* batch emulsion polymerization conditions using the PISA concept. However, due to the lack of good control over the polymer molar mass and structure, the final particles cannot be described as amphiphilic block copolymer micelles in a strict way. Nevertheless the PEO-*b*-P(VDC-co-MeA) stabilizer efficiently forms *in situ* and the final surfactant-free latexes exhibit essentially the same characteristics as those obtained in presence of preformed analogous

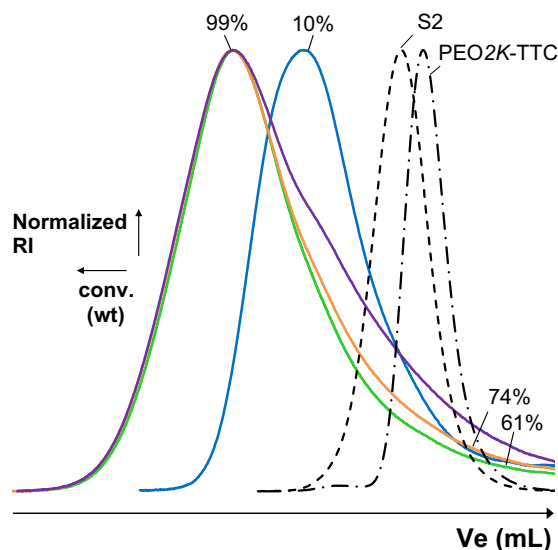


Fig. 2. Evolution of the size exclusion chromatograms for the emulsion polymerization of VDC/MeA in presence of the amphiphilic diblock copolymer S2 (expt. E1, Table 2).

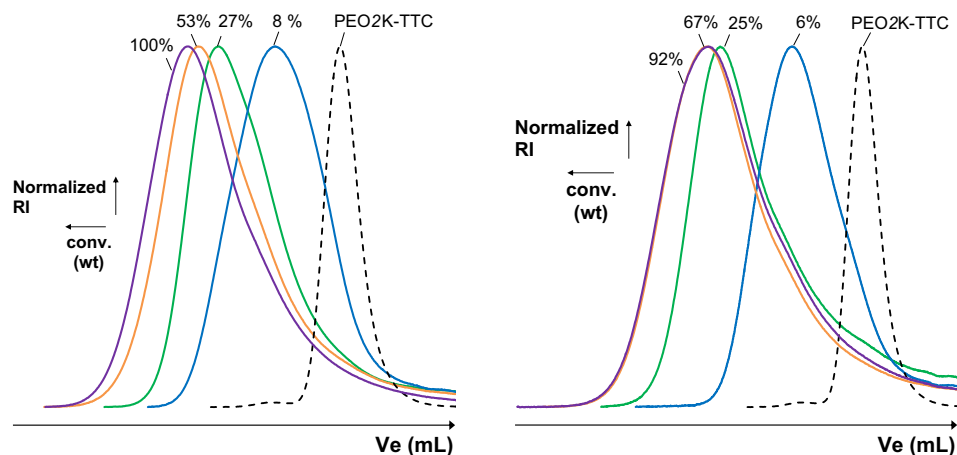


Fig. 3. Evolution of the size exclusion chromatograms for the emulsion polymerization of VDC/MeA in presence of PEO2K-TTC: expt. E2 performed with 6.0 wt% (with respect to monomers) of macroRAFT agent (left) and E3 performed with 4.7 wt% of macroRAFT agent (right) initiated by SMBS/APS.

amphiphilic block copolymers, with however much simpler experimental conditions and a reduced number of steps. It should be noted that TSPP was introduced as a buffer in these experiments, which increases considerably the ionic strength in the reaction medium and might impact the stabilization of the particles by the PEO chains [40]. We thus performed an additional experiment without TSPP (Table 2, experiment E4). In this case, significantly smaller particle diameters were obtained (average diameter of about 100 nm, no coagulum was observed) which confirmed the impact of the tetravalent ion TSPP on the particle size. Similar results were obtained with PEO6K-TTC macroRAFT agent (See Supporting Information, Table SI-1). In order to increase the pH in the latex after polymerization, the same quantity of TSPP as that used during the polymerization in experiment E2 ($[\text{TSPP}] = 9 \text{ mmol L}^{-1} \text{aq}$) was introduced at room temperature in latex E4. The pH increased to 6.7 and the particle diameter remained unchanged ($D_z = 103 \text{ nm}$), and no aggregation was observed. The same result was obtained when the TSPP-added latex was heated to 70°C during 5 h. The first experiment shows that it is possible to reduce the particle size by a factor of 5 while preserving a pH close to neutral in the final latex by simply adjusting the timing of buffer addition.

Impact of the nature and amount of the initiator. It has been discussed formerly that the use of peroxide initiators might raise problems over the polymerization control with the occurrence of side reaction especially in RAFT polymerizations [41]. Therefore the following experiments were performed with the diazo-initiator ACPA instead of SMBS/APS, in similar conditions as those reported before for the RAFT emulsion polymerization of *n*-butyl acrylate with PEOXK-TTC macroRAFTs [12,33]. TSPP was not used in these experiments and therefore the final pH decreased to 2 by the end of the reaction. Using ACPA led to similar molar mass dispersities ($\bar{D} = 2.1$) and also to a constant growth of the polymer chains with conversion (Table 2, experiment E5, see SEC traces in Fig. 4). Compared to the redox system in the absence of TSPP (experiment E4), a similar particle diameter was obtained (about 100 nm). The particle size distribution determined by DLS was very narrow ($\text{Poly} = 0.001$) but an amount of coagulum of 4.5% was calculated (with respect to $m(\text{monomers} + \text{macroRAFT})_{t=0}$).

For all the experiments, the determined absolute molar masses, M_n^{LS} , were lower than the theoretical values calculated without considering the contribution of the chains generated by the initiator and transfer reactions. In order to reduce the number of chains coming from the initiator, experiment E6 was performed with a

lower initial initiator-to-RAFT agent molar ratio of 0.3 (in comparison to experiment E5), which allows generally a better control in RAFT polymerization [2]. Again, a particle diameter in the 100 nm-range was obtained but no formation of coagulum was observed. As shown in Fig. 5, the SEC traces were narrow and shifted towards higher molar masses with increasing monomer conversion. The molar mass dispersities were significantly below (Table 2, $\bar{D} = 1.6$) those of the reference experiment E5 indicating a better control, as expected. In addition, the absolute number-average molar mass values, M_n^{LS} , increased linearly with monomer conversions and were close to the theoretical values up to about 30% conversion. A slight deviation of the molar mass from the theoretical values was observed for higher conversions mainly due to the contribution of chains generated by the initiator (Fig. 5). Based on the calculation considering the contribution of the initiator (see Supporting Information), it seems that the contribution of chains generated by transfer to VDC monomer remains negligible in our case, which might be underestimated if one considers the high transfer constant value to VDC monomer ($C_{\text{tr}} = 6.4 \times 10^{-3}$) [36].

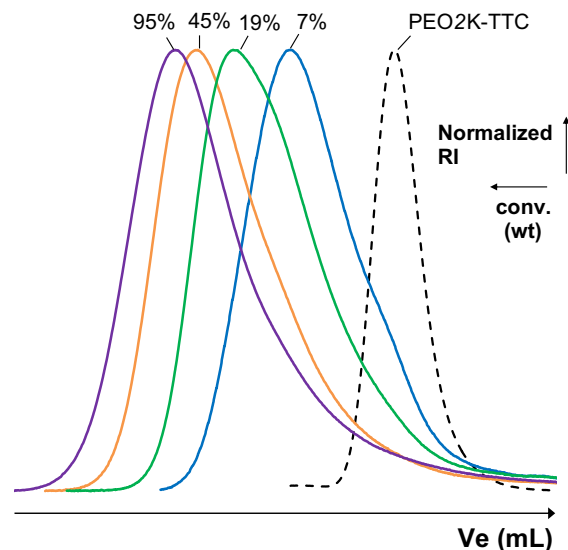


Fig. 4. Evolution of the chromatograms for the emulsion polymerization of VDC/MeA in presence of PEO2K-TTC initiated by ACPA, expt. E5.

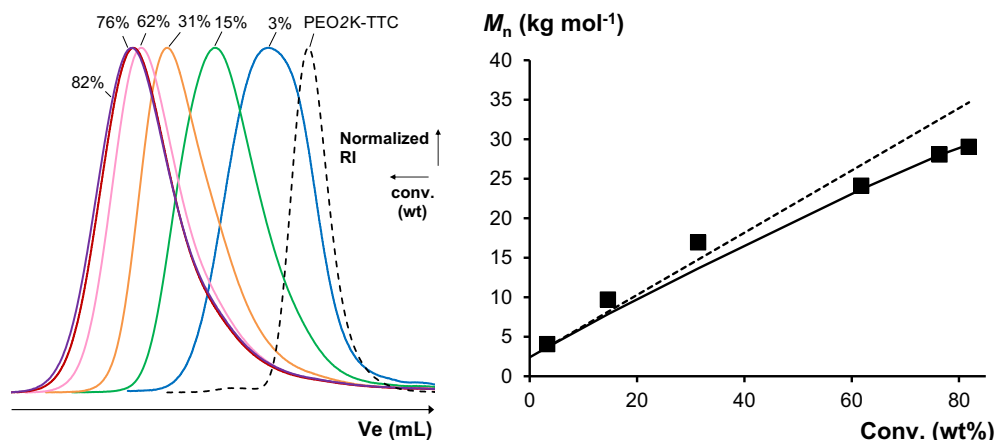


Fig. 5. Evolution of the chromatograms (left) and the M_n^{S} (square) with monomer conversion for the emulsion polymerization of VDC/MeA in presence of PEO2K-TTC performed with a molar ratio [ACPA]/[PEO-TTC] = 0.3, expt. E6. The dashed line (—) corresponds to the theoretical expected M_n vs. conversion without considering the contribution of the chains generated by the initiator. The black line corresponds to the theoretical expected M_n vs. conversion considering the initiator derived chains as described in the Supporting Information (right).

These results show that it is possible to control the emulsion copolymerization of VDC and MeA with PEO-TTC in batch *ab initio* conditions.

Impact of the PEO molar mass. As we had formerly demonstrated an impact of the PEOXK-TTC molar mass on the particle size and stability [33], a supplementary experiment was performed with the higher molar mass macroRAFT agent PEO6K-TTC (Table 2, expt. E7) at the same macroRAFT/monomers mass ratio (but consequently with a lower molar concentration of macroRAFT agent) as in the reference experiment performed with PEO2K-TTC (E5). Within 9 h of polymerization quasi complete monomer conversion was reached and again an evolution of the SEC traces with increasing monomer conversion was observed with similar molar mass dispersities ($\bar{D} = 2.6$) (see Supporting Information, Figure SI-2). The particle diameters were almost the same (105 vs. 107 nm) but the particle size distribution was slightly broader (0.06 vs. 0.001). Furthermore after one day of stirring at 70 °C, the amount of coagulum was considerably higher (14% vs. 4.5% for E5). It can thus be concluded that the use of PEO6K-TTC instead of PEO2K-TTC did not improve the particle stability. It has already been reported that the stabilization by PEO-based surfactants is more efficient in the case of a larger amount of shorter PEO chains compared to a smaller amount of longer PEO chains [42].

4. Discussion and conclusion

The copolymerization of VDC with MeA in the presence of macromolecular poly(ethylene oxide) macroRAFT agents, PEO-TTC, was studied in solution and in aqueous emulsion. In toluene solution well-defined amphiphilic PEO-*b*-P(VDC-*co*-MeA) copolymers could be obtained exhibiting the features of a RAFT-controlled polymerization. The amphiphilic PEO2K-*b*-P(VDC-*co*-MeA) diblock copolymer with a short hydrophobic block of 1.3 kg mol^{-1} was readily soluble in water and employed as a stabilizer in the *ab initio* batch emulsion copolymerization of VDC with MeA. A Stable latex was obtained at high monomer conversion with particle diameters of about 500 nm. Interestingly, it was shown that the diblock copolymer not only provided stability of the dispersions but also took part in the polymerization via a chain transfer reaction to the TTC end-group. Most of it should therefore be strongly anchored to the particles. In the next step we directly tested PEO-TTC macroRAFT agents in the same emulsion polymerization conditions. Again, stable dispersions with similar particle diameter were

reached and the efficiency of the transfer reaction was demonstrated by SEC. This approach is particularly appealing since it requires less synthesis and purification steps compared to the diblock copolymer while maintaining good stabilizing ability and the formation of PEO-*b*-P(VDC-*co*-MeA) copolymers directly in water. We therefore further investigated this method, with the aim of reaching smaller particle size and possibly a better control of the polymerization. We found that the particle size was strongly influenced by the presence of salt. Indeed, in order to keep the pH close to neutral, a TSPP buffer was added in the first experiments leading to particle diameters of about 500 nm. When the polymerizations were performed in the absence of this salt, the diameter could be reduced to 100 nm, and addition of the same quantity of buffer after the polymerization step allowed for increasing the pH to 7 without altering the particle size. Moreover, we studied the impact of the initiating system on the outcome of the emulsion polymerization. When switching from the redox couple APS/SMBS to ACPA, similar kinetics, particle sizes and polymerization control were reached. Due to transfer reactions and the relatively high amount of initiator used, the experimental molar masses of the hydrophobic block were always inferior to the theoretical values. Yet, it was possible to improve the control over the molar masses by diminishing the amount of ACPA. In these “controlled” conditions, however, longer polymerization times were required to reach high monomer conversions. Such longer reaction durations are less viable for industrial application, and the preparation of auto-stabilized PVDC-latexes without free surfactant, which is the main target of this study, can also be reached using higher amount of initiator allowing for shorter polymerization times. In conclusions, non-ionic PEO-TTC macroRAFT agents are excellent candidates to conduct the copolymerization of VDC and MeA in solution and aqueous emulsion leading to the formation of diblock copolymers dissolved in the polymerization medium (toluene) or self-assembled as core-shell nanoparticles in water. Further work will deal with the use of ionic macroRAFT agents in a similar polymerization system.

Acknowledgements

The authors thank the French Agence Nationale de la Recherche (ANR-2010-RMNP-005-02 ASAP) for financial support of this work. B.C. thanks the Institut Universitaire de France for her nomination as a senior member.

Appendix A. Supplementary information

Supplementary information related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2013.10.016>.

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