

Dispersion Polymerization of Methyl Acrylate in Nonpolar Solvent Stabilized by Block Copolymers Formed In situ via the RAFT Process

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ABSTRACT The free-radical dispersion polymerization of methyl acrylate (MA) in isododecane was carried out in the presence of a poly(2-ethylhexyl acrylate) macromolecular RAFT (reversible addition–fragmentation chain transfer) agent bearing a trithiocarbonate reactive group in the middle of the chain (P2EHA-TTC). The presence of the trithiocarbonate function was crucial for the synthesis of monodisperse colloidal poly(methyl acrylate) (PMA) particles stabilized by the P2EHA segments. The hydrodynamic diameters ranged from 100 to 300 nm, using particularly low amounts of the macro(RAFT agent) (1–6 wt % vs. MA) in dispersion polymerizations carried out at 20 wt % solids content. As shown by 2D liquid chromatography, P2EHA-*b*-PMA or P2EHA-*b*-PMA-*b*-P2EHA block copolymers formed in situ at the early stage of the dispersion polymerization due to the reversible transfer process and played the role of particle stabilizer. The glass-transition temperature of the derived polymer films was not affected by the low amount of the chosen macromolecular stabilizer and the mechanical properties were mainly those of PMA, which makes the technique very attractive for coating applications.

KEYWORDS: dispersion polymerization • nonpolar solvent • reactive stabilizer • block copolymer • controlled radical polymerization • poly(2-ethylhexyl acrylate)

INTRODUCTION

The production of monodisperse nano- to micrometer-sized particles is of great importance for industrial applications such as coatings, paints, adhesives, inks or cosmetics (1–3). Among the different methods developed to synthesize polymer particles, free-radical dispersion polymerization (4) is an efficient route to obtain monodisperse, stable particles in the 0.1 to ~10 μm range. The particularity of this process lies in the homogeneous initial state of the system, i.e., all components (initiator, monomer, stabilizer) are fully soluble in the polymerization medium (polar or nonpolar organic solvent), whereas the formed polymer is nonsoluble. The oligoradicals generated by initiation and

propagation precipitate when they reach a critical length, which leads to the formation of particle nuclei in the so-called nucleation period (5). Particles are stabilized during growth and storage by soluble polymer chains, via a steric stabilization mechanism.

The most popular stabilizers, in polar solvents, are poly(*N*-vinylpyrrolidone) and poly(vinyl alcohol) but their efficiency is quite low and a large amount, between 5 and 30 wt % based on the monomer, is usually required to synthesize particles with diameters above 1 μm (6–9). Indeed, the stabilizer is incorporated at the particle surface by irreversible transfer reactions, which create amphiphilic species upon reinitiation. Reactive macromolecular stabilizers such as poly(ethylene oxide)- or poly(dimethyl siloxane)-based macroinitiators or macro(chain transfer agents) were proposed in order to increase their efficiency. However, less than 30 wt % reactive polymer was actually incorporated and participated in the stabilization of large particles (diameter >1 μm) (10–12). This phenomenon was due to either the low value of the macroinitiator dissociation rate constant (10, 11) or to the high efficiency of the irreversible transfer reaction producing insoluble blocks too short to favor a good anchorage to the particles (12). In contrast, macromonomers exhibited better stabilizing properties in comparison with the corresponding nonreactive homopolymers (13–23). However, incorporation of the stabilizing macromonomer de-

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depends on the reactivity ratios with the comonomer, which may lead to slow consumption and hence induce a lack of efficiency during the nucleation period. Up to now, the most efficient stabilizers for dispersion polymerization were amphiphilic diblock copolymers that adsorb onto the particles by their solvophobic block and provide stabilization by their solvophilic one. A decrease in the stabilizer concentration was then possible, while preserving particle stability. For example, low fractions of diblock copolymers (between 0.5 and 4 wt % with respect to monomer) were used for the stabilization of polymer microspheres synthesized by dispersion polymerization in alcoholic media (24–26). Nevertheless, such stabilizers require a preliminary two-step synthesis and do not provide a covalent link to the particles.

Recently, there has been a real interest in the in situ synthesis of diblock copolymers, simultaneously to the particle formation (27–30). For that purpose, reversible addition–fragmentation chain transfer (RAFT) (31–33) appeared to be a very promising method as it allows the synthesis of a wide variety of macromolecular chain transfer agents (also called macro(RAFT agents)). Thanks to the high reactivity of the dithioester or trithiocarbonate group involved in the transfer reaction and to the reversibility of the latter, one can expect (i) a complete conversion of the macro(RAFT agent) into an amphiphilic block copolymer at the very beginning of the dispersion polymerization, and (ii) the formation of potentially long, well-anchored solvophobic blocks. Using this strategy, D'Agosto et al. (28) used 30 wt % poly(*N*-acryloylmorpholine) macro(RAFT agent) for the synthesis of 300 nm poly(*n*-butyl acrylate) hairy particles by dispersion polymerization in an ethanol/water mixture. The macromolecular chain transfer agent was end-functionalized by a carbohydrate derivative in order to form functional latex particles for biological applications (28). In that particular work, however, control over the radical polymerization was not achieved. Nevertheless, the idea of combining an efficient stabilization with the formation of well-defined polymers can be a realistic goal, when the experimental conditions are selected on purpose, i.e., with a sufficiently high concentration of macro(RAFT agent). In recent reports (29, 30), this led to small particles of approximately 50 nm in diameter, exclusively composed of well-defined amphiphilic block copolymers.

In the present work, we focused our attention on the synthesis of large poly(methyl acrylate) particles dispersed in isododecane with a view to develop specific formulations in the field of cosmetics. The purpose was to use a low concentration of a living poly(2-ethylhexyl acrylate) macromolecular RAFT agent (P2EHA-TTC), functionalized with a trithiocarbonate group, as a highly efficient stabilizer for the free-radical dispersion polymerization of methyl acrylate (MA) in a nonpolar solvent. The main goal was the efficient incorporation of the macro(RAFT agent) at the particle surface, via in situ formation of an amphiphilic block copolymer with long PMA insoluble block and not particularly the good control over the radical polymerization of MA.

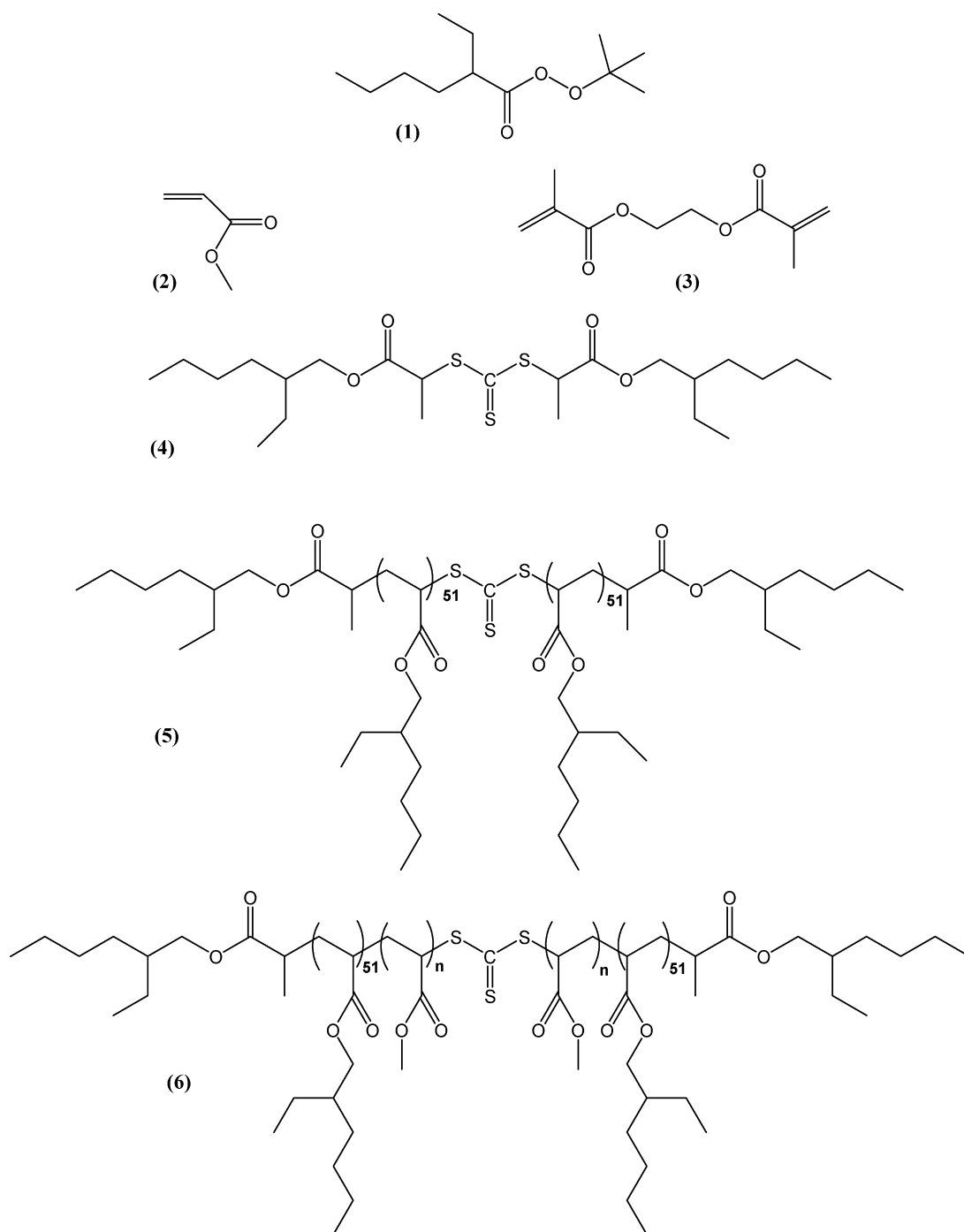
RESULTS AND DISCUSSION

The dispersion polymerization of methyl acrylate was performed at 20 wt % solids, in isododecane, at 80 °C, in the presence of a soluble poly(2-ethylhexylacrylate) macro(RAFT agent) (P2EHA-TTC). The latter was synthesized by RAFT-mediated polymerization of 2-ethylhexyl acrylate using *S,S'*-bis[1-(2-ethylhexyloxy)carbonyl]ethyl] trithiocarbonate as a reversible chain transfer agent (Scheme 1) (29). This method allowed a well-defined, living P2EHA to be synthesized, with an average degree of polymerization of 102 (= 2 × 51) and a trithiocarbonate group in the middle of the chain (see Scheme 1 and Experimental Section) as a reactive site for further chain extension.

The P2EHA-TTC indeed proved in the past to be an efficient macromolecular chain transfer agent for the synthesis of P2EHA-*b*-PMA-*b*-P2EHA triblock copolymers via the RAFT method, either in solution or in dispersion polymerizations (29). In the present work, the chain extension process was performed during the dispersion polymerization of MA, to lead to the in situ formation of an amphiphilic block copolymer (ideally the P2EHA-*b*-PMA-*b*-PA2EH triblock copolymer as shown in Scheme 1, structure 6) besides the formation of PMA homopolymer. The P2EHA blocks are fully soluble in isododecane, whereas the PMA block should precipitate and strongly adsorb onto the PMA particles. Consequently the particles would become sterically stabilized by the P2EHA segments. The stabilizing efficiency was then investigated using various amounts of P2EHA-TTC (Table 1, experiments 1, 2, and 4). The colloidal characteristics of the recovered polymer dispersions were measured by dynamic light scattering (DLS) (Table 2).

As depicted in Figure 1, high monomer conversions were reached within 6 h using low amounts of P2EHA-TTC stabilizer (from 1.5 to 6 wt % based on MA). Actually the conversion rate was particularly high but the polymerization started only after an induction period, which was longer when the concentration of the macro(RAFT agent) was increased. This phenomenon might be ascribed to a delayed nucleation, explained by the time required for the in situ formation of amphiphilic block copolymers with well-suited stabilizing properties. The latter may exhibit different micellization or adsorption properties when the macro(RAFT agent) concentration and hence the solvophobic block length was changed. The limited conversion of 80% observed with 1.5 wt % P2EHA-TTC (experiment 1) is an apparent value explained by the partial destabilization of the dispersion and the formation of a small fraction of coagulum, which led to non representative sample for gravimetry. In a general manner, however, the use of the reactive P2EHA-TTC chains enabled us to synthesize stable PMA particles exhibiting narrow particle size distribution (Figure 2, dispersity factor $\sigma < 0.10$), with *z*-average diameters ranging from 100 to 300 nm. Most interestingly, those characteristics were achieved with low amounts of stabilizer (1.5–6 wt % vs MA) (Figure 2). One experiment was carried out in the presence of ethylene glycol dimethacrylate (EGDMA) as a cross-linker in order to preserve the morphology of the particles and allow scanning electron microscopy to be performed (see experi-

Scheme 1. Chemical Structure of (1) T21S Initiator, (2) Methyl Acrylate Monomer (MA), (3) Ethylene Glycol Dimethacrylate (EGDMA) Cross-Linker, (4) *S,S'*-Bis[1-(2-ethylhexyloxy)ethyl] Trithiocarbonate RAFT Agent, (5) Poly(2-ethylhexyl acrylate)-trithiocarbonate (P2EHA-TTC), and (6) Poly(2-ethylhexyl acrylate)-*b*-poly(methyl acrylate)-*b*-poly(2-ethylhexyl acrylate) (P2EHA-*b*-PMA-*b*-PA2EH)



ment **3** in Tables 1 and 2). The cross-linker was added only after 1 h 10 min (5% MA conversion, see Figure 1), so as not to interfere with the nucleation mechanism (8). Subsequent rate of MA dispersion polymerization was not disturbed by the presence of EGDMA cross-linker (see experiments **2** and **3** in Figure 1). Monodisperse particles were also recovered (Figures 2 and 3) and similar colloidal characteristics of the PMA dispersions were obtained, whether the cross-linker was added or not (experiments **2** and **3** in Figure 2).

The importance of the living character of the P2EHA-TTC chains containing the trithiocarbonate group on the stabilizing efficiency was highlighted by the results of experiment **5** reported in Tables 1 and 2. Indeed, for that experiment, a nonfunctionalized P2EHA was used as a stabilizer for the dispersion polymerization of MA and a precipitate was observed at 50% conversion. The homopolymer itself has no tendency to adsorb onto the particle surface. Consequently, only a chain transfer reaction would convert it into a grafted amphiphilic structure able to adsorb onto the

Table 1. Experimental Conditions for the Free-Radical Dispersion Polymerization of Methyl Acrylate (MA) in Isododecane, at 80°C, Initiated by T21S and Stabilized with P2EHA

expt	nature of the stabilizer ^a	wt % P2EHA ^b	mol % EGDMA ^c	[MA] ₀ (mol L ⁻¹)	[P2EHA] ₀ (mol L ⁻¹)	[T21S] ₀ (mol L ⁻¹)
1	P2EHA-TTC	1.5	0	2.0	1.3×10^{-4}	1.3×10^{-3}
2	P2EHA-TTC	3.0	0	2.0	2.7×10^{-4}	1.5×10^{-3}
3	P2EHA-TTC	2.9	1.0 ^d	2.0	2.7×10^{-4}	1.6×10^{-3}
4	P2EHA-TTC	6.1	0	2.0	5.4×10^{-4}	1.2×10^{-3}
5	P2EHA nonfunctionalized	6.1	0	2.0	5.0×10^{-4}	1.3×10^{-3}

^a See experimental part for the synthesis of the P2EHA-TTC reactive macro(RAFT) agent and the P2EHA nonfunctionalized chains. ^b Weight percent of P2EHA-TTC stabilizer versus MA monomer. ^c Mole percent of ethylene glycol dimethacrylate (EGDMA) cross-linker versus MA monomer. ^d Addition of EGDMA cross-linker at 1 h and 10 min, MA conversion = 5%.

Table 2. Results of the Free-Radical Dispersion Polymerization of Methyl Acrylate in Isododecane: Monomer Conversion and Colloidal Characteristics of the Particles^a

expt	polym. time (h)	conversion (%)	solids (wt %) ^b	D_z (nm)	N_p (L ⁻¹) ^c	N_{P2EHA} (chains) ^d	A (nm ²) ^e
1	4	77	17.1	320	4.0×10^{16}	2000	80
2	6	94	21.3	210	1.4×10^{17}	1170	60
3 ^f	6	91	20.4	210	1.4×10^{17}	1110	60
4	6	97	22.6	120	8.3×10^{17}	390	55
5	1.5	50	12	n/a	precipitate	precipitate	n/a

^a See Table 1 for the experimental polymerization conditions. ^b Final solids content = $100 \times (m_{MA} \times \text{monomer conversion} + m_{P2EHA})/m_{\text{total}}$. ^c N_p = number of particles per liter of latex (see eq 1 in the experimental part). ^d Number of P2EHA-TTC stabilizer chains per particle (see eq 2 in the experimental part). ^e A is the surface area occupied by a P2EHA block (see eq 3 in the experimental part). ^f Presence of EGDMA as a cross-linker.

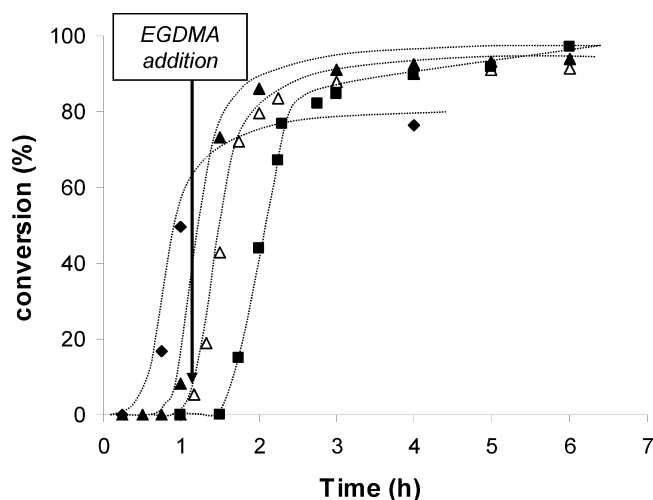


FIGURE 1. Monomer conversion vs time for the dispersion polymerization of MA in isododecane at 80 °C, with various wt % P2EHA-TTC stabilizer vs MA. See Table 1 for experimental conditions of experiment 1 (◆, 1.5 wt %), experiment 2 (▲, 3 wt %), experiment 3 (△, 3 wt % + 1 mol % EGDMA vs MA), and experiment 4 (■, 6 wt %).

particle surface and provide steric stabilization (34–36). Nevertheless, due to the low efficiency of this kind of transfer reaction, such systems require a large amount of soluble homopolymer, (up to 30 wt %) to obtain a stable dispersion (6–9). The results of experiment 5 indeed show that in our case the amount of soluble, nonfunctionalized PA2EH was not high enough to provide a sufficiently large concentration of amphiphilic chains, whereas the same amount of the functionalized polymer led to stable particles (experiment 4). In other terms the presence of a trithiocarbonate function on the PA2EH is mandatory for the stability of the system described in this paper.

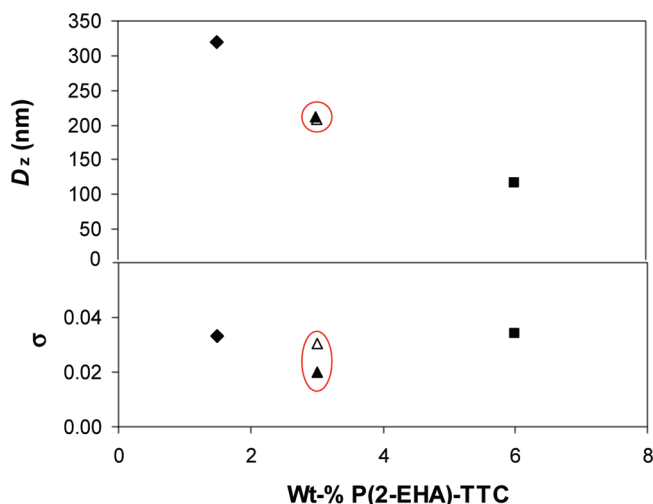


FIGURE 2. Evolution of z -average diameter (D_z) and particle size dispersity factor (σ) of the PMA particles dispersed in isododecane as a function of the amount of P2EHA-TTC stabilizer (wt % vs MA). See Table 1 for experimental conditions of experiment 1 (◆, 1.5 wt %), experiment 2 (▲, 3 wt %), experiment 3 (△, 3 wt % + 1 mol % EGDMA vs MA), and experiment 4 (■, 6 wt %).

The polymer chains of the final dispersion from experiment 4 were first analyzed by size exclusion chromatography (SEC) as displayed in Figure 4. The molar mass distribution was very broad but the absence of control over the polymerization within the particles was expected owing to the choice of the initial macro(RAFT) agent concentration. Indeed, as reported in Table 1, the experimental conditions were chosen to target monodisperse particles with diameter above 100 nm using a low amount of stabilizer. Consequently, the concentration of the P2EHA-TTC macro(RAFT) agent was low in comparison with the initiator concentration and in parallel the target chain length (calculated from the molar ratio of monomer over macro(RAFT) agent) was

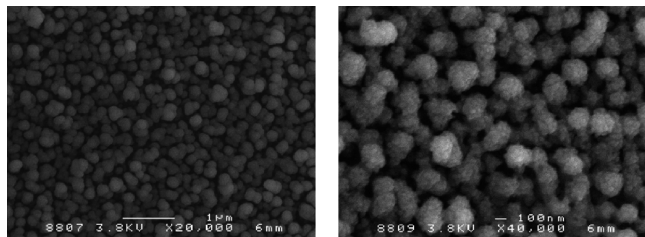


FIGURE 3. Cryo-SEM pictures of the polyacrylate particles of experiment 3 (2.9 wt % P2EHA-TTC and 1 mol % EGDMA cross-linker vs MA). Scale bar 1 μm (left) and 100 nm (right).

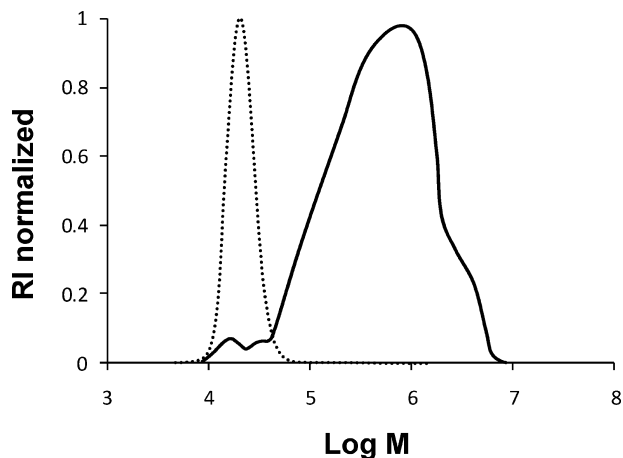


FIGURE 4. Size exclusion chromatograms of the P2EHA-TTC macro(RAFT agent) (dashed line) and of the polymer from the dispersion stabilized by 6 wt % P2EHA-TTC (plain line) (experiment 4 in Table 1, intermediate sample at 77% conversion).

particularly high, i.e., above 4000 at the minimum. Nevertheless, Figure 4 shows a quasi-complete shift of the SEC chromatogram suggesting an almost complete consumption of the P2EHA-TTC precursor toward block copolymer chains. Those should ideally exhibit a triblock structure (i.e., P2EHA-*b*-PMA-*b*-PA2EH, Scheme 1), but one cannot exclude the formation of P2EHA-*b*-PMA diblock copolymer chains in our noncontrolled conditions.

Liquid adsorption chromatography (LAC) provides precise information on the chemical composition of the polymer chains and the analysis results of experiment 4 is shown in Figure 5. The disappearance of P2EHA-TTC with conversion was confirmed together with the formation of copolymer chains. Those were most likely the expected P2EHA-*b*-PMA or P2EHA-*b*-PMA-*b*-P2EHA block copolymers which formed very early in the dispersion polymerization process, before 15% monomer conversion. This result explains the superior stabilizing efficiency of the highly reactive P2EHA-TTC in comparison with the nonfunctionalized P2EHA homopolymer. It also explains the successful synthesis of monodisperse PMA particles with low amount of stabilizer (<6 wt %) and the decrease in the particle size with the increase in the stabilizer concentration (Figure 2), as usually observed with preformed diblock copolymers (24). Figure 5 also illustrates the simultaneous formation of noncontrolled PMA homopolymer, grown without any transfer reaction to the P2EHA-TTC RAFT agent. The amount of PMA homopolymer is expected to increase when the initial PA2EH-TTC amount is decreased.

The two-dimensional liquid chromatography (2D LAC-SEC) analysis of experiment 4, shown in Figure 6, confirmed that the particles were mostly composed of both block copolymer (either P2EHA-*b*-PMA-*b*-P2EHA or P2EHA-*b*-PMA; peak 2) and PMA homopolymer (peak 1). It also highlighted that the molar mass distribution of these polymers was particularly broad. This agrees with the lack of control over chain growth, as assumed from the chosen experimental conditions. As detailed in the Figure 6 caption, the copolymer chains (peak 2) exhibited high M_n value, i.e. long PMA block, which is a key point for efficient anchoring to the particles. The number of P2EHA stabilizer chains per particle (N_{P2EHA}) was calculated assuming that all chains were involved in particle stabilization (see eq 2 in the experimental part and values reported in Table 2). We observed a decrease in the number of stabilizer chains per particle with the increase in the P2EHA-TTC concentration, the values of N_{P2EHA} ranging from 390 to 2000. The surface area occupied by one P2EHA stabilizer segment (A) was between 55 and 80 nm^2 (Table 2), which is particularly high in comparison for instance with the surface area stabilized by well-defined diblock copolymers for dispersion polymerization of styrene in alcoholic media ($A = 7\text{--}17 \text{ nm}^2$, see ref 24).

We noticed that the cross-linker did not interfere with the dispersion polymerization of MA as all the features of the particles dispersed in isododecane were the same in the presence or in the absence of EGDMA (experiments 2 and 3 in Table 2). A comparison of the particle diameters measured by DLS in different solvents enabled us to assess the efficiency of the cross-linking agent. The results displayed in Figure 7 highlight the disappearance of the non-cross-linked particles in dichloromethane, a good solvent for both P2EHA and PMA polymers, whereas an obvious swelling of the cross-linked particles was noticed in dichloromethane. The main population of the non-cross-linked particles dissolved in dichloromethane corresponds to individual chains, with diameter centered at 17 nm (Figure 7b). The small fraction of aggregates of average sizes 80 nm and 1.4 μm were presumably microgels coming from irreversible intermolecular chain transfer reactions to polymer followed by termination by combination (34, 35). DLS analysis being more sensitive to large objects, the intensity of these microgels is not correlated to their weight fraction (Figure 7b). On the other hand, the cross-linked particles exhibited only one population in dichloromethane with an increase in the particle diameter from 210 to 1080 nm (see Figure 7c,d). This result indicates a good linkage of all chains to the particle network, including the P2EHA stabilizing segments.

The films formed upon drying the PMA dispersions stabilized with 3–6 wt % P2EHA-TTC were characterized by dynamic mechanical analysis (DMA) (Figure 8). They exhibited only one glass-transition temperature ($T_g \approx 30 \text{ }^\circ\text{C}$) showing that the mechanical properties of the films were mainly driven by the PMA polymer. Indeed, the values for each polymer reported in ref 37 and measured by differential scanning calorimetry are the following: $T_{g, \text{PMA}} = 12 \text{ }^\circ\text{C}$, $T_{g, \text{P2EHA}} = -50 \text{ }^\circ\text{C}$. This result reveals the interest of

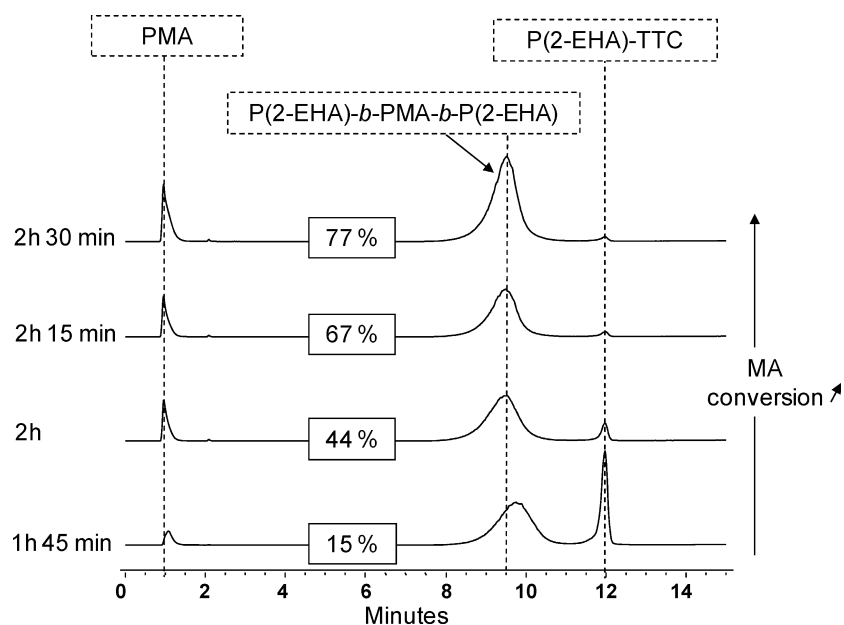


FIGURE 5. Liquid adsorption chromatograms of the polymer dispersion stabilized by 6 wt % P2EHA-TTC (experiment 4 in Table 1): evolution versus time and MA conversion.

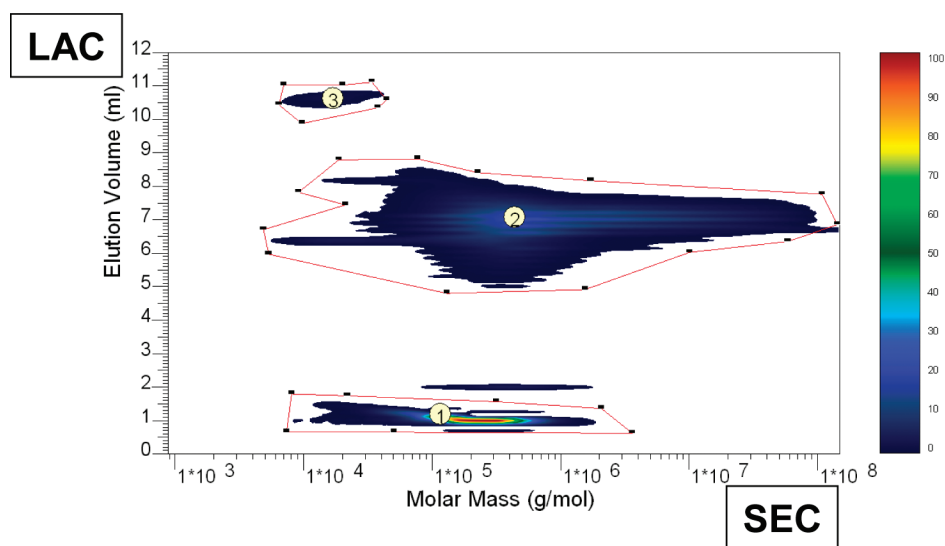


FIGURE 6. 2D LAC-SEC chromatogram of the PMA dispersion stabilized by 6 wt % P2EHA-TTC (experiment 4 in Table 1, intermediate sample at 77% conversion). Peak 1: PMA, 33 vol%, $M_n = 137\,900\text{ g mol}^{-1}$, $M_w/M_n = 1.8$. Peak 2: block copolymer, 65 vol%, $M_n = 250\,100\text{ g mol}^{-1}$, $M_w/M_n = 15$. Peak 3: P2EHA, 1 vol%, $M_n = 14\,900\text{ g mol}^{-1}$, $M_w/M_n = 1.2$.

using the minimum amount of P2EHA stabilizer, hence limiting the sticky character provided by the soft P2EHA polymer.

In a general way, the use of a highly reactive, reversible, macromolecular chain transfer agent acting as a stabilizer precursor to form the amphiphilic stabilizing species in situ for the synthesis of polymeric particles via polymerization in dispersed media meets the coating industry needs. Indeed, this strategy can be applied either to emulsion (38, 39) or dispersion polymerizations (28–30) (present work) targeting aqueous or solvent-based coatings. The decrease in the amount of stabilizer, the absence of molecular surfactant, and the covalent attachment of the stabilizer to the particles might fulfill the environmental and technical requirements.

EXPERIMENTAL SECTION

Materials. Methyl acrylate (MA, Aldrich, 99%) and 2-ethylhexyl acrylate (2-EHA, Fluka, 98%) were distilled under reduced pressure before use. *tert*-Butyl peroxy-2-ethylhexanoate (commercial name: Trigonox 21S (T21S); Akzo Nobel, 97%), ethylene glycol dimethacrylate (EGDMA, Aldrich, 98%), and isododecane (a mixture of branched C12 isoparaffins provided by Innovene) were used as supplied.

Synthesis of the RAFT Agent. *S,S'*-Bis[1-(2-ethylhexyloxy-carbonyl)ethyl] trithiocarbonate was synthesized according to the procedure previously described (29).

Synthesis of the Poly(2-ethylhexyl acrylate) macro(RAFT agent): P2EHA-TTC. For the synthesis of the P2EHA-TTC macro(RAFT agent), a mixture of 2-EHA (30 g, 0.16 mol), T21S (0.034 g, 1.6×10^{-4} mol), and *S,S'*-bis[1-(2-ethylhexyloxy-carbonyl)ethyl] trithiocarbonate (0.72 g, 1.5×10^{-5} mol) was prepared and oxygen was removed from the medium by a thirty-minutes nitrogen bubbling step. The reaction was then

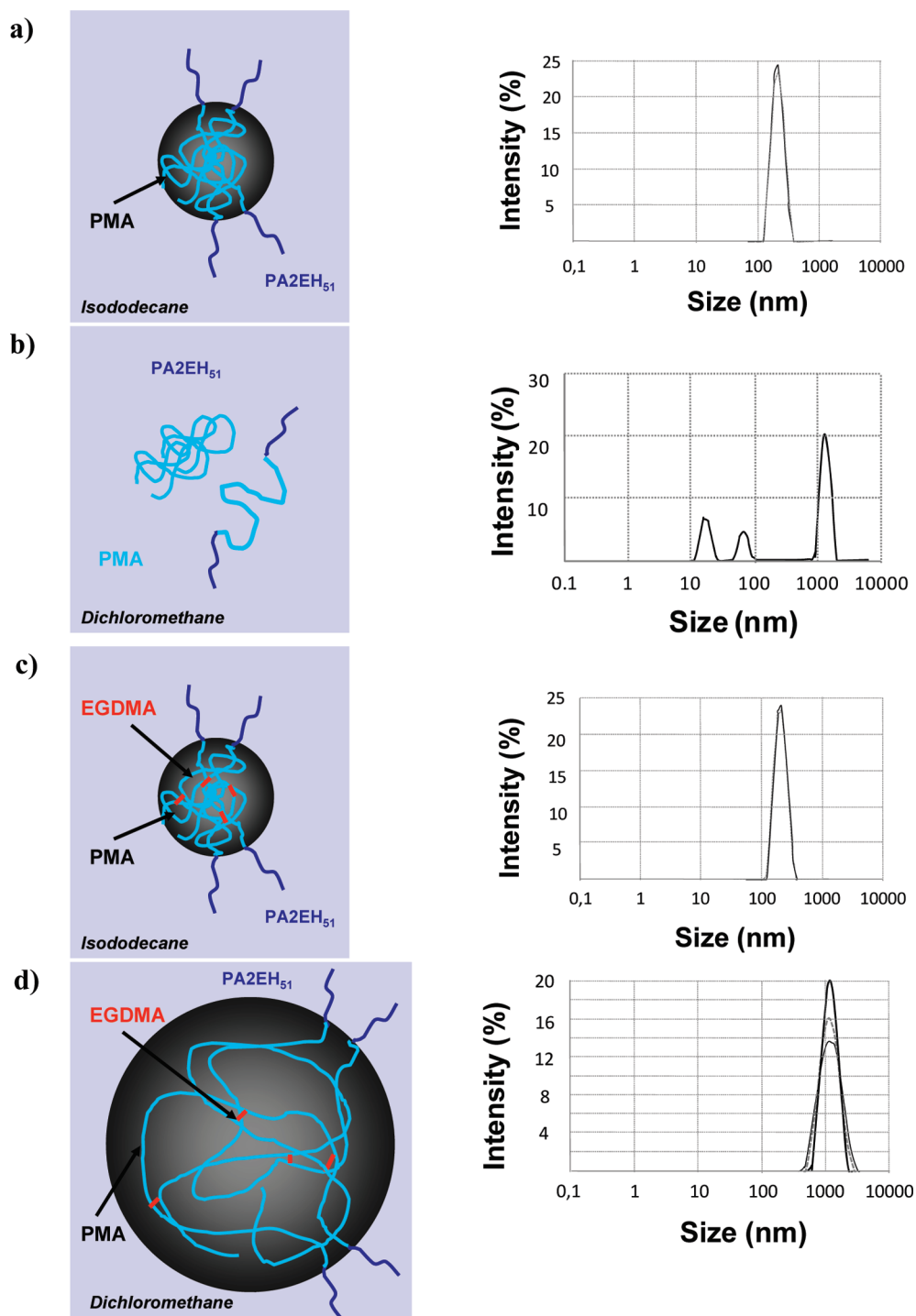


FIGURE 7. Particle size distribution of the polyacrylate particles measured by DLS: (a) experiment 2 in isododecane, $D_z = 210$ nm, $\sigma = 0.03$; (b) experiment 2 in dichloromethane; (c) experiment 3 (presence of the EGDMA cross-linker) in isododecane, $D_z = 210$ nm, $\sigma = 0.02$; (d) experiment 3 (presence of the EGDMA cross-linker) in dichloromethane; $D_z = 1080$ nm, $\sigma = 0.11$.

carried out at 60 °C under nitrogen flow for 6 h. The recovered P2EHA-TTC was diluted in dichloromethane, precipitated at low temperature in methanol and dried under vacuum. The macromolecular characteristics of the P2EHA-TTC macromolecular chain transfer agent were the following: $M_n = 19\,200$ g mol⁻¹, number-average degree of polymerization (DP_n) = 102 (51 for each segment, as the triethiocarbonate group is located in the middle of the chain), and $M_w/M_n = 1.08$.

Synthesis of the Nonfunctionalized Poly(2-ethylhexyl acrylate): P2EHA. A nonreactive poly(2-ethylhexyl acrylate) was synthesized according to the following procedure: a well-defined

poly(2-ethylhexyl acrylate) was synthesized via RAFT polymerization using a dithiobenzoate-based RAFT agent as previously described (29). The ω -terminal dithiobenzoate group was removed by heating the deoxygenated polymer solution (30 wt % polymer in toluene) at 80 °C during 2.5 h in the presence of a large excess of T21S initiator (T21S over P2EHA molar ratio = 20) (40). The nonfunctionalized P2EHA was recovered by precipitation into cold methanol and filtration. The absence of the reactive dithiobenzoate end-group was proved by the disappearance of the characteristic peaks observed in the proton NMR spectrum of P2EHA (see ref 29). The macromolecular

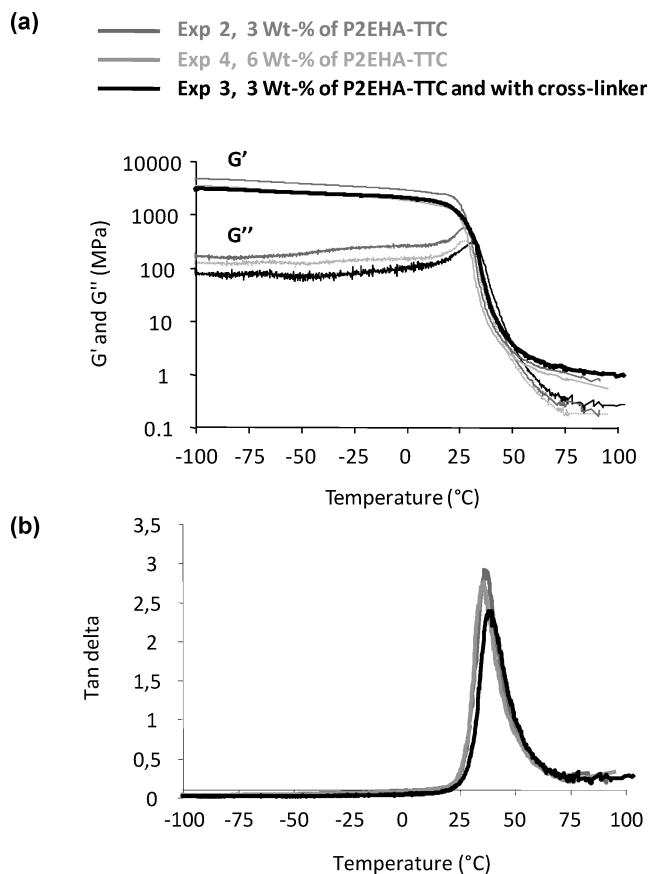


FIGURE 8. Evolution of (a) storage modulus (G'), loss modulus (G'') and (b) $\tan\delta (= G''/G')$ versus temperature (at a constant frequency of 1 Hz) for the films formed from the final dispersion (experiments 2–4 in Table 1).

features of the nonfunctionalized P2EHA were the following: $M_n = 21\,160\text{ g mol}^{-1}$, $DP_n = 113$, $M_w/M_n = 1.16$.

Dispersion Polymerization of Methyl Acrylate in Isododecane. For the experiment 2 (Table 1), a mixture containing the initiator T21S (0.034 g , $1.6 \times 10^{-4}\text{ mol}$), the P2EHA-TTC macro(RAFT agent) (0.54 g , $2.8 \times 10^{-5}\text{ mol}$), the monomer MA (17.8 g , 0.21 mol), and isododecane (63.2 g , 84.9 mL) was prepared and stirred until the P2EHA-TTC macro(RAFT agent) was properly dissolved. The homogeneous mixture was poured into a round-bottom flask sealed with a rubber septum and degassed by nitrogen bubbling for 30 min. The reactor was immersed into an oil bath thermostatted at $80\text{ }^\circ\text{C}$ and the polymerization proceeded under stirring at 250 rpm using a magnetic bar. The conversion of methyl acrylate was determined by gravimetry, from aliquots withdrawn at regular time intervals. The experimental conditions are reported in Table 1 (experiments 1–5). For the dispersion polymerization in the presence of a cross-linker (experiment 3 in Table 1), EGDMA (0.40 g , $2.0 \times 10^{-3}\text{ mol}$, 1 mol % vs MA) was added to the reaction medium 1 h 10 min after the time zero of the reaction, when the medium became cloudy.

Characterizations. Size Exclusion Chromatography (SEC). The number-average molar mass (M_n), the weight-average molar mass (M_w) and the molar mass distribution (polydispersity index = M_w/M_n) were determined by size exclusion chromatography (SEC) using tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL min^{-1} . The polymer chains forming the particles were analyzed with a SEC apparatus equipped with a Viscotek VE 5200 automatic injector, two columns thermostatted at $40\text{ }^\circ\text{C}$ (PSS SDV, linear M, $8\text{ mm} \times 300\text{ mm}$; bead diameter: $5\text{ }\mu\text{m}$) and a differential refractive index detector (LDC Analytical refractoMonitor IV). The average molar masses were

derived from a calibration curve based on polystyrene standards from Polymer Standards Service (separation limits: $260\text{ to }2 \times 10^6\text{ g mol}^{-1}$). The macromolecular features of both the non-functionalized P2EHA and the P2EHA-TTC homopolymers were accurately measured using a Triple Detector Array (TDA, model 302 from Viscotek) equipped with a two angle Light Scattering (LS) detector (LALS, $\theta = 7^\circ$, RALS, $\theta = 90^\circ$, laser $\lambda = 670\text{ nm}$), a refractive index detector and two Polymer Laboratories Mixed C columns ($5\text{ }\mu\text{m}$) thermostatted at $40\text{ }^\circ\text{C}$. The average molar masses were calculated from the LS signal with the OmniSec software, using the average refractive index increment (dn/dc) measured with the online refractometer (dn/dc for P2EHA in THF at $40\text{ }^\circ\text{C}$ is 0.072).

Liquid Adsorption Chromatography (LAC). This technique was used to qualitatively analyze the chemical composition of the chains present in a dispersion polymerization sample. The sample (1 mg of dried polymer dissolved in 1 mL THF) was injected into PLRP-S columns ($150 \times 4.6\text{ mm}$, $5\text{ }\mu\text{m}$, Polymer Laboratories) and separated with a linear gradient in 10 min from 100% acetonitrile to 100% THF as a mobile phase, at a flow rate of 1 mL min^{-1} . The LAC apparatus is equipped with an evaporative light scattering detector (ELSD).

Two-Dimensional Liquid Chromatography (2D LAC-SEC). Samples were also analyzed by two-dimensional liquid chromatography (2D LAC-SEC) using LAC as the first dimension and SEC as the second dimension. For the LAC dimension, the same columns as described above were used and a linear gradient in 200 min from 0 to 70% of THF in acetonitrile was used as a mobile phase, at a flow rate of 0.05 mL min^{-1} . For the second dimension (SEC), PLgel HTS-C, column size $150\text{ mm} \times 7.5\text{ mm}$, particle size $5\text{ }\mu\text{m}$ were used. The flow rate of THF was in this case 1.5 mL/min and a calibration curve based on PMMA standards was used (molar mass ranging from $500\text{ to }2\,000\,000\text{ g/mol}$).

Dynamic Light Scattering (DLS). The z -average particle diameter (D_z) and the dispersity factor (σ) of the diluted organic dispersions were measured by dynamic light scattering (DLS) using a Zetasizer Nano S90 from Malvern (90° angle, 4 mW He-Ne laser at 633 nm). The particle size distribution is generally considered as narrow when σ is below 0.10. For calculation, the refractive index of isododecane was $n = 1.421$ and the viscosity was $\eta = 1.4\text{ cPs}$.

The number of particles per liter of latex of latex (N_p) was calculated using

$$N_p = 6\tau / (\rho\pi D_z^3) \quad (1)$$

with τ the polymer content ($\text{g L}_{\text{latex}}^{-1}$), D_z the z -average particle diameter expressed in cm, ρ the density of poly(methyl acrylate) ($\rho = 1.16\text{ g cm}^{-3}$) (37). For the calculation of N_p , the thickness of the hairy P2EHA layer was considered as negligible in comparison with the particle diameter ($100\text{ nm} < D_z < 300\text{ nm}$) as the length of a fully stretched P2EHA chain reaches a maximum value of 12 nm ($0.25\text{ nm} \times 51\text{ } DP_n$).

The average number of macromolecular stabilizer chains per particle (N_{P2EHA}) was estimated from the following equation:

$$N_{P2EHA} = ([P2EHA-TTC]_0 \times N_A) / N_p \quad (2)$$

with N_A the Avogadro's number and $[P2EHA-TTC]_0$ the molar concentration of P2EHA-TTC chains. The surface area occupied by a P2EHA block (A) was calculated with

$$A = [4\pi(D_z/2)^2] / 2N_{P2EHA} \quad (3)$$

Scanning Electron Cryo-microscopy (CryoSEM). CryoSEM was used to visualize the cross-linked poly(methyl acrylate) particle. The analyses were performed on a JEOL 6300F in-the-lens field emission SEM. To preserve the particle morphology, we froze the samples according to the "sandwich method": a drop of the isododecane diluted dispersion (solid content above

0.5 wt %) was deposited onto a carbon grid, which was then sandwiched between two silicon lamellae (10 mm diameter, 1 mm thickness). This sandwich was then frozen in pasty nitrogen (a mixture of liquid and solid nitrogen) prepared under reduced pressure. Temperature of the mixture was $-210\text{ }^{\circ}\text{C}$. Once the sample was frozen, the sandwich was opened in liquid nitrogen ($-196\text{ }^{\circ}\text{C}$). The silicium lamella, on which the carbon grid remained, was then introduced into the preparation room, which was maintained for 30 min at $-80\text{ }^{\circ}\text{C}$ under secondary vacuum in order to sublime the solvent and the frost from air that might have formed during the transfer. After sublimation, the temperature of the sample was leveled down to $-180\text{ }^{\circ}\text{C}$ under a secondary vacuum. Platinum (amount equivalent to 15 nm) was then sputtered on the specimen surface. Finally, the specimen was then transferred into the microscope room for observation at $-180\text{ }^{\circ}\text{C}$ and 3.8 kV.

Dynamic Mechanical Analysis (DMA). The dynamic mechanical measurements were conducted on a DMA 2980 instrument (TA Instruments) in tensile mode. All analyses were conducted on rectangular samples ($10 \times 5\text{ mm}$, $350\text{--}400\text{ }\mu\text{m}$ thickness) dried for 10 days under 50% relative humidity atmosphere. Rigidity of the films (storage modulus E') as well as mechanical damping ($\tan\delta$) were quantified by DMA (at room temperature, i.e., $23\text{ }^{\circ}\text{C}$) at a frequency ranging from 1 to 20 Hz. Each sample was tested 5 times. The glass-transition temperature areas were determined by DMA at a frequency of 1 Hz and by heating the sample from $-110\text{ }^{\circ}\text{C}$ to $+150\text{ }^{\circ}\text{C}$ with an increment of $3\text{ }^{\circ}\text{C}/\text{min}$. Each sample was tested 3 times.

CONCLUSIONS

This study highlighted the interest of using a poly(2-ethylhexyl acrylate) macromolecular RAFT agent to produce stable, monodisperse poly(methyl acrylate) particles by dispersion polymerization in a nonpolar solvent. The trithio-carbonate group of P2EHA-TTC allowed a stabilizing block copolymer to be formed in situ via the RAFT process at the early stage of the polymerization. Liquid adsorption chromatography coupled with size exclusion chromatography (2D-LC) showed the complete consumption of the macro(RAFT agent) and revealed that the particles were composed of both block copolymer and PMA homopolymer. As a consequence, stable poly(methyl acrylate) dispersions with particle diameter in the $100\text{--}300\text{ nm}$ range were obtained at 20 wt % solids content. A very low amount of P2EHA-TTC homopolymer (1.5–6 wt % vs MA) was required to stabilize the particles and the films formed by coating were little affected by the nature of the stabilizer as a result. The proposed strategy of using a reactive homopolymer instead of a preformed diblock copolymer stabilizer presents thus a great interest for scale up as it allows the number of synthetic and purification steps to be reduced, while reaching a very high stabilizing efficiency and a good anchorage to the particle surface. In addition, the RAFT method can be extended to a variety of monomers, which opens the way to particles with functional shell for instance.

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