Synthesis of Well-Defined Polyacrylate Particle Dispersions in Organic Medium Using Simultaneous RAFT Polymerization and Self-Assembly of Block Copolymers. A Strong Influence of the Selected Thiocarbonylthio Chain Transfer Agent

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ABSTRACT: The RAFT-mediated nonaqueous dispersion polymerization of methyl acrylate in isododecane, a nonsolvent for poly(methyl acrylate), was carried out using two soluble poly(2-ethylhexyl acrylate) macromolecular RAFT agents, containing either a dithiobenzoate reactive function or a trithiocarbonate one. The method produced stable colloidal particles, with hydrodynamic diameters below 100 nm. Using poly(2-ethylhexyl acrylate) with a dithiobenzoate end group, strong rate retardation and poor control over the polymer chains were observed. In contrast, when the trithiocarbonate-functionalized poly(2-ethylhexyl acrylate) was used, the formation of monodisperse micellar aggregates of well-defined self-assembled block copolymers was obtained with fast polymerization rates, irrespective of the RAFT agent concentration. Such differences were explained by the dispersed state of the system rather than by the intrinsic reactivity of the soluble macromolecular RAFT agent.

Introduction

Three main techniques of controlled free-radical polymerization (CRP)[1,2] have emerged over the past 15 years, namely nitroxide-mediated polymerization[3] (NMP), atom transfer radical polymerization[4,5] (ATRP), and reversible addition−fragmentation chain transfer (RAFT).[6−8] One of the most important achievements of those methods is the ability to produce block copolymers and complex architectures, while keeping all the advantages of free-radical polymerization, in terms of experimental conditions and process implementation. For instance, many groups used CRP to control (co)polymer architectures in aqueous dispersed systems.[9−13] In the case of CRP in dispersed media, there is an interest in the process itself not only for its specific advantages (high polymerization rate, low viscosity even at high solids content, reduced amount of organic volatile compounds in the case of aqueous systems) but also for its ability to synthesize particles with various morphologies.

In comparison with emulsion and miniemulsion polymerizations, only a few attempts have been devoted to the application of CRP to dispersion polymerization. Classical free-radical dispersion polymerization is a technique used to obtain large, highly uniform particles. In that process, the monomer is fully soluble in the continuous phase. As the polymerization proceeds, the monomer is converted into insoluble polymer, and phase separation occurs to form stable particles in the presence of a steric stabilizer.[14] Control over the dispersion polymerization of styrene or methyl methacrylate was achieved by NMP, ATRP, or RAFT either in alcane, in alcoholic media, or in supercritical carbon dioxide, although in most cases simultaneous control of polymer chains and particle size distribution was difficult to achieve.[15−24]

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Another aspect of dispersion polymerization is the synthesis of diblock copolymers in a solvent that is good for the first block and bad for the second block. In such a situation, self-assembly of the copolymers during the second polymerization step leads to the in-situ formation of diblock copolymer micelles. This was a method first developed for anionic polymerization by Quirk and co-workers in 1991.[25] A very recent work published by Wang et al.[26] follows this principle and provides several examples of polybutadiene-*b*-polystyrene block copolymer nanoparticles of various shapes and morphologies produced by anionic polymerization in hexane. The main advantage of their process relies on the ability of producing such nanoparticles in large volume reactors for industrial applications, which might not be straightforward with the most usual approach consisting in the self-assembly of preformed diblock copolymers. A similar approach was presented by Zheng et al.[27] using controlled free-radical polymerization via RAFT. In that case they took advantage of the living character of the polymerization to introduce a small percentage of a divinylic monomer in the second polymerization step to produce polystyrene-*b*-poly(4-vinylpyridine-*co*-divinylbenzene) core-cross-linked micelles directly in the dispersion polymerization medium, cyclohexane.

In the work presented here we were interested in the formation of acrylic block copolymer micelles in an organic solvent. For an industrial application of the final dispersion, the direct formation of such nanoparticles in the selective solvent appeared to be the most appropriate process. For that purpose, instead of anionic polymerization, we applied controlled free-radical polymerization. We studied the RAFT-mediated dispersion polymerization of methyl acrylate (MA) in isododecane using poly(2-ethylhexyl acrylate) (P(2-EHA)) as a soluble macromolecular reversible chain transfer agent.[28] Our aim was to design well-defined P(2-EHA)-*b*-PMA block copolymer micelles in a concentrated dispersion, to be further used directly in the

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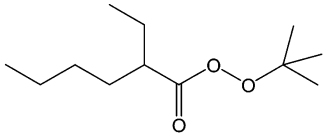
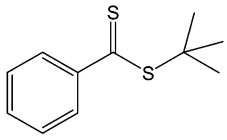
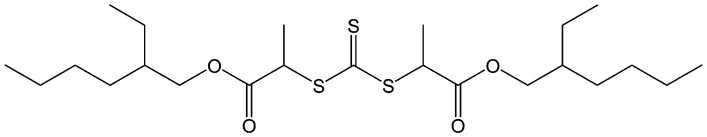
Scheme 1. Chemical Structure of the Radical Initiator (T21S), of the Molecular RAFT Agents (DTB, TTC), and of the Macromolecular (P(2-EHA)-DTB and P(2-EHA)-TTC) RAFT Agents



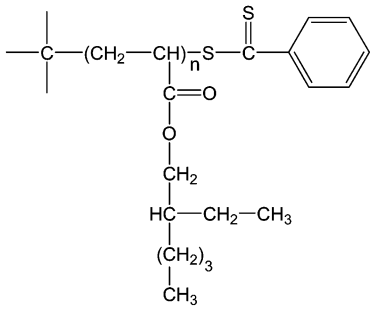
T21S (*tert*-butyl peroxy-2-ethylhexanoate)



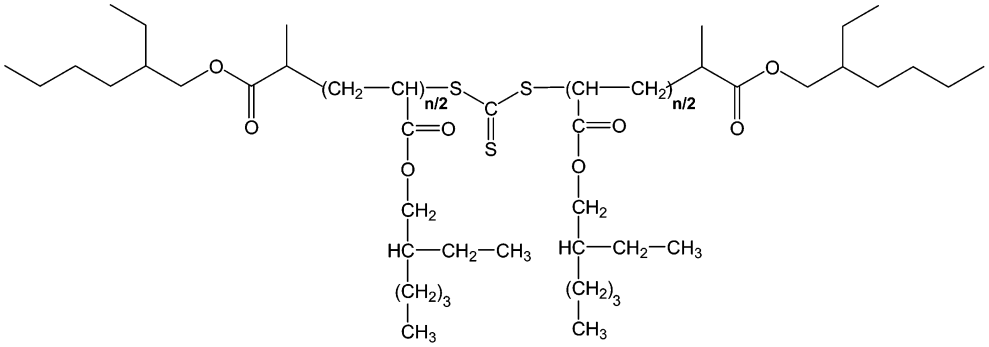
DTB (*tert*-butyl dithiobenzoate)



TTC (S,S'-bis[1-(2-ethylhexyloxycarbonyl)ethyl] trithiocarbonate)



P(2-EHA)-DTB



P(2-EHA)-TTC

isododecane medium. This prompted us to investigate the RAFT mechanism in such a heterogeneous system. In particular, we examined the influence of the concentration of the macro(RAFT agent) and the nature of its thiocarbonylthio exchangeable group on the control over the copolymer characteristics and over the colloidal properties of the formed particles. To demonstrate the impact of the thiocarbonylthio group, two different RAFT agents were selected to prepare the living poly(2-ethylhexyl acrylate) precursor, namely, *tert*-butyl dithiobenzoate (DTB) and *S*,*S*′-bis[1-(2-ethylhexyloxycarbonyl)ethyl] trithiocarbonate (TTC) (see Schemes 1 and 2). To the best of our knowledge, such a study has never been reported in the past. The conclusions are of interest for the direct synthesis of block copolymer micelle dispersions via controlled free-radical polymerization and should be a step toward more complex morphologies.

Experimental Part

Materials. Methyl acrylate (MA, Aldrich, 99%) was distilled under reduced pressure before use. *tert*-Butyl mercaptan (Aldrich, 99%), *S*-(thiobenzoyl)thioglycolic acid (Aldrich, 99%), carbon disulfide (Acros, 99.9%), nonhydrated sodium sulfur (Acros, extra pure quality), methyltributylammonium chloride (Aldrich, 75 wt % in water), tetrabutylammonium hydrogen sulfate (Aldrich, 97%), 2-bromopropionyl bromide (Aldrich, 97%), 2-ethyl-1-hexanol (Aldrich, 99.6%), *tert*-butyl peroxy-2-ethylhexanoate (commercial name: Trigonox 21S (T21S); Akzonobel, 97%), isododecane (which is in the present study a mixture of branched C12 isoparaffins provided by Innovene), and 2-ethylhexyl acrylate (2-EHA, Fluka, 98%) were used as supplied.

Synthesis of *tert*-Butyl Dithiobenzoate (DTB). The *tert*-butyl dithiobenzoate RAFT agent was prepared as previously described in the literature.[29] *S*-(Thiobenzoyl)thioglycolic acid (10.6 g, 0.05 mol) was dissolved in a dilute alkaline solution containing 2 equiv of NaOH (4.0 g, 0.1 mol in 400 mL of H_2O). *tert*-Butyl mercaptan (4.95 g, 0.055 mol) was added to the mixture at room temperature under stirring. The mixture was stirred for a period of 15 h, and afterward, *tert*-butyl dithiobenzoate was extracted with diethyl ether (1 × 600 mL, 1 × 300 mL). The organic phase was washed with 0.1 M NaOH solutions (3 × 300 mL) and water (3 × 300 mL), then dried over $MgSO_4$, and filtered, and solvent was evaporated. The final product was left overnight under vacuum (0.01 mmHg, 40 °C) in order to remove the residual *tert*-butyl mercaptan (bp = 63 °C). The yield of the dark pink oil *tert*-butyl dithiobenzoate (DTB) was 90 wt %. ^{1}H NMR ($CDCl_3$; 200 MHz) δ (ppm): 1.69 (s, 9H), 7.34 (2d, 2H), 7.47 (t, 1H), 7.87 (d, 2H). ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ (ppm): 28.17, 52.08, 126.55, 128.01, 131.61, 147.05, 230.14. ^{1}H and ^{13}C NMR did not reveal the presence of extra peaks, which indicates the absence of impurities that could be accurately quantified.

Synthesis of *S*,*S*′-Bis[1-(2-ethylhexyloxycarbonyl)ethyl] Trithiocarbonate (TTC). An aqueous solution of disodium trithiocarbonate was first prepared as follows. Carbon disulfide (6.6 g, 0.087 mol) was slowly added to a mixture of nonahydrated sodium sulfur (0.083 mol), methyltributylammonium chloride (0.42 g, 1.8 mmol), and water (28 mL). After stirring for one night at ambient temperature, a red aqueous solution was recovered and stored at 4 °C. Separately, 2-bromopropionyl bromide (15 mL, 0.143 mol) in anhydrous diethyl ether (50 mL) was added dropwise under stirring to a cooled solution containing 2-ethyl-1-hexanol (21 mL, 0.136 mol) and

Scheme 2. RAFT Mechanism Involved in the Synthesis of Poly(2-ethylhexyl acrylate) (A) and in the Dispersion Polymerizations of Methyl Acrylate (B) Using the P(2-EHA)-DTB and the P(2-EHA)-TTC Macro(RAFT agent)s

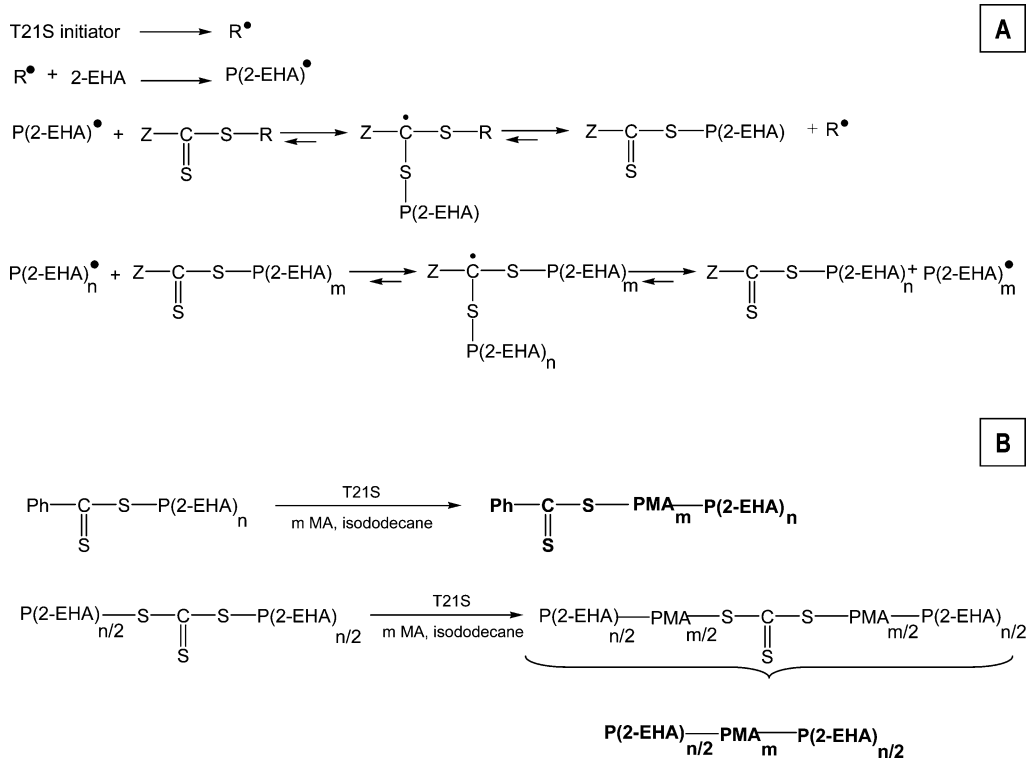


Table 1. Experimental Conditions for the RAFT-Mediated Bulk Polymerizations of 2-Ethylhexyl Acrylate and Dispersion Polymerizations of Methyl Acrylate Initiated by the Initiator T21S in the Presence of Various Chain Transfer Agents

expt	monomer	RAFT agent	process	solvent	[M], mol L^{-1}	[RAFT agent], mol L^{-1}	[T21S], mol L^{-1}	T, °C
1	2-EHA	DTB	bulk		4.8	4.5×10^{-2}	1.5×10^{-2}	80
2	2-EHA	DTB	bulk		4.8	4.4×10^{-2}	1.5×10^{-2}	80
3	MA	P(2-EHA)-$DTB_{expt\ 2}$	dispersion	isododecane	2.0	1.3×10^{-3}	1.4×10^{-3}	80
4	MA	P(2-EHA)-$DTB_{expt\ 2}$	dispersion	isododecane	2.0	3.9×10^{-3}	1.5×10^{-3}	80
5	MA	P(2-EHA)-$DTB_{expt\ 2}$	dispersion	isododecane	2.0	7.9×10^{-3}	1.4×10^{-3}	80
6	2-EHA	TTC	bulk		4.8	4.4×10^{-2}	4.6×10^{-3}	60
7	MA	P(2-EHA)-$TTC_{expt\ 6}$	dispersion	isododecane	2.0	1.3×10^{-3}	1.4×10^{-3}	80
8	MA	P(2-EHA)-$TTC_{expt\ 6}$	dispersion	isododecane	2.0	3.9×10^{-3}	1.5×10^{-3}	80
9	MA	P(2-EHA)-$TTC_{expt\ 6}$	dispersion	isododecane	2.0	7.7×10^{-3}	1.4×10^{-3}	80

triethylamine (20 mL, 0.143 mol) in 100 mL of anhydrous diethyl ether. The solution was stirred at 15 °C for 3 h until the reaction was complete. Additional water (100 mL) was added to dissolve the triethylamine bromohydrate salts. The organic phase was extracted with diethyl ether, washed with a saturated aqueous solution of $NaHCO_3$ (1 × 50 mL) and water (3 × 50 mL) until neutral pH of the aqueous phase was reached, dried over $MgSO_4$, and filtered, and solvent was evaporated. The yield of this reaction was estimated at 94 wt %. In a second step, the recovered (2-ethylhexyl)-2-bromopropionate and the crude aqueous solution of disodium trithiocarbonate were used without any further purification for the synthesis of the desired trithiocarbonate. (2-Ethylhexyl)-2-bromopropionate (34 g, 0.128 mol), tetrabutylammonium hydrogensulfate (2.17 g, 6.409 mmol) as phase transfer catalyst, toluene (75 mL), and the solution of sodium trithiocarbonate in water (54.6 mL, 0.064 mol) were introduced into a round-bottom flask. The mixture was stirred at 55 °C for 24 h. The bright yellow organic phase was washed with water (4 × 50 mL), dried over $MgSO_4$, and filtered, and solvent was evaporated. The crude product was purified by column chromatography on silica gel, using a 3:1 (v:v) hexane:dichloromethane mixture as an eluent, to give 6.2 g of pure product (yield = 45 wt %, purity = 99.9%). ^{1}H NMR (d_6-acetone; 200 MHz) δ (ppm): 0.18 (m, 6H, C**H**$_3$), 0.59 (m, 8H, C**H**$_2$), 0.86 (d, 3H, C**H**$_3$), 1.32 (m, 1H, C**H**), 3.33 (m, 2H, O−C**H**$_2$), 4.06 (q, 1H, S−C**H**-C═O). ^{13}C NMR (d_6-acetone; 125.7 MHz) δ (ppm): 11.03, 14.04, 16.61, 23.30, 24.11, 30.75, 39.27, 48.69, 67.92, 170.50, 220.57.

RAFT Polymerization of 2-Ethylhexyl Acrylate (2-EHA). A typical polymerization procedure was applied, and experiment 2 (Table 1) is described in detail below. A mixture of T21S (34.1 mg, 1.6×10^{-4} mol), TTC (717 mg, 1.5×10^{-3} mol), and 2-EHA (30.01 g, 1.6×10^{-1} mol) was stirred for 5 min and subsequently poured into several tubes sealed with Rotaflo. Oxygen was removed by five freeze−vacuum−thaw cycles. The tubes were immersed into an oil bath thermostated at 80 or 60 °C when using DTB or TTC, respectively, as a chain transfer agent. Samples were withdrawn at regular time intervals, quenched by cooling in water and exposed to air. A fraction of the crude sample served to determine the monomer conversion by ^{1}H NMR (250 MHz, in $CDCl_3$) using the ratio of the three vinylic proton peak area of the 2-EHA monomer (5−6 ppm) over the two methylene ester proton peak area (3−4 ppm) of both the monomer and the polymer. The remaining part of the crude fraction was dried to provide polymer for subsequent SEC measurements. To prepare a large amount of polymer for the dispersion polymerization experiments, the polymerization of 2-EHA was carried out in a round-bottom flask sealed with a rubber septum. Oxygen was removed from the mixture by 30 min nitrogen bubbling before immersing the reactor into the thermostated oil bath. The crude P(2-EHA) was purified by dissolving it into a minimum volume of dichloromethane prior to

Table 2. Molar Mass and Polydispersity Index of the (Co)polymers as a Function of Time and Monomer Conversion

expt	time, h	conv, %	M_n(theo),[a] g mol^{-1}	M_n(exp), g mol^{-1}	M_w/M_n	(co)polymer nature
1	5	80	15 800	17 900[b]	1.17	P(2-EHA)
				20 050[c]		
2	4	83	16 420	18 230[b]	1.14	P(2-EHA)
				21 160[c]		
3	2	1	22 480	21 480[b]	1.37	mixture of diblock copolymer and homopolymers
	8	100	152 930	56 060[b]	18	
4	2	6	23 670	22 820[b]	1.21	mixture of diblock copolymer and homopolymers
	4	11	25 950	23 170[b]	1.43	
	8	25	32 510	32 150[b]	1.76	
	16	62	49 020	55 190[b]	4.2	
	24	85	59 040	46 440[b]	6.0	
5	1	3	21 840	20 340[b]	1.17	Mixture of diblock copolymer and homopolymers
	4	8	22 850	20 290[b]	1.19	
	20	36	28 870	29 980[b]	1.51	
	24	42	30 330	28 920[b]	1.67	
	48	48	31 530	28 940[b]	1.76	
6	5	89	18 250	19 200[c]	1.06	P(2-EHA)
7	0.2	6	27 730	29 100[c]	1.11	triblock copolymer
	2	91	140 610	99 670[c]	2.7	
8	0.25	4	20 960	20 840[c]	1.09	triblock copolymer
	3	92	60 390	52 630[c]	1.60	
9	0.25	7	20 850	19 610[c]	1.08	triblock copolymer
	0.5	27	25 500	24 810[c]	1.07	
	4	100	42 030	39 960[c]	1.21	

[a] $M_{n,theoretical} = M_{RAFT} + ([monomer]/[RAFT]) \times conversion \times M_{monomer}$, with M_{RAFT} the molar mass of the molecular RAFT agent for the bulk polymerizations of 2-EHA (experiments 1, 2, and 6) or the number-average molar mass of the first P(2-EHA) block (LS detector) for the dispersion polymerizations of MA. [b] M_n(exp) corresponds to the experimental M_n determined by SEC using a PS calibration. [c] M_n(exp) corresponds to the experimental M_n determined by SEC using a LS detector.

precipitation into cold methanol (below 0 °C). A soft polymer was recovered and subsequently dried under vacuum. The experimental conditions of 2-EHA homopolymerization are reported in Table 1 (experiments 1, 2, and 6).

The precipitated P(2-EHA) homopolymers, which corresponded to the samples at final conversion (see Tables 1 and 2, experiments 2 and 6), were characterized by ^{1}H NMR or UV−vis spectroscopy to determine the amount of thiocarbonylthio end or middle group preserved in the polymer chains. Proton NMR was the technique of choice to determine the amount of dithiobenzoate functions present at the chain end because the ortho-aromatic proton signal ($\delta = 8.0$ ppm) was well distinct from those of all other protons of the polymer chain (see Supporting Information, Figure SI-1). For the final polymer of experiment 2 (see Table 2), knowing the absolute number-average degree of polymerization from the SEC ($DP_n = 114$, $M_n = 21\,160$ g/mol), the proton NMR analyses allowed the chain-end functionality to be evaluated at 0.86. Moreover, chain extension of a P(2-EHA)-DTB macro(RAFT agent) with 2-EHA in bulk was successfully performed (see Supporting Information Figure SI-2), and the complete shift of the SEC peak proved the absence of residual P(2-EHA), which consequently confirmed a close to quantitative chain-end functionality. Concerning the P(2-EHA) recovered from the TTC-mediated polymerization (experiment 6), UV−vis spectroscopy appeared to be a suitable technique to measure the concentration of the trithiocarbonate mid-function for two reasons: first, we could use the TTC molecular RAFT agent as an ideal model to determine the molar extinction coefficient of the functional polymer (see Scheme 1), and second, characteristic signals of protons in the vicinity of the TTC group were not visible in the polymer ^{1}H NMR spectrum. The absorbance of the polymer solution at $\lambda = 430$ nm (see Supporting Information, Figure SI-3) was consistent with a rather high degree of trithiocarbonate incorporation (>0.70).

Dispersion Polymerization of Methyl Acrylate (MA). For experiment 8 as an example, a mixture of T21S (8.9 mg, 4.1×10^{-5} mol), the P(2-EHA) macro(RAFT agent) (2.02 g, 1.05×10^{-4} mol, $M_n = 19\,200$ g mol^{-1}, experiment 6, Table 2), MA (4.70 g, 5.5×10^{-2} mol), and isododecane (15.11 g, 20.3 mL) was stirred until the P(2-EHA) macro(RAFT agent) was well dissolved. The homogeneous mixture was poured into several tubes sealed with Rotaflo and degassed by five freeze−vacuum−thaw cycles. The tubes were immersed into an oil bath thermostated at 80 °C, and the polymerizations proceeded under stirring at 250 rpm using a magnetic bar. For the experiments 3 and 4, the final dispersion was turbid, whereas for the experiments 5, 7, 8, and 9, it was clear. In experiment 9, moreover, the dispersion became very viscous after 30 min of reaction. The conversion of methyl acrylate was determined by gravimetry from the crude aliquots, which were also used for particle size analysis. Those crude aliquots were dried before measuring the average molar mass of poly(2-ethyhexyl acrylate)-*b*-poly(methyl acrylate) (P(2-EHA)-*b*-PMA) and poly(2-ethyhexyl acrylate)-*b*-poly(methyl acrylate)-*b*-poly(2-ethyhexyl acrylate) (P(2-EHA)-*b*-PMA-*b*-P(2-EHA)) block copolymers. The experimental conditions are reported in Table 1 (experiments 3−5 and 7−9).

Size Exclusion Chromatography. The number-average molar mass (M_n), the weight-average molar mass (M_w), and the molar mass distributions (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}. Two types of SEC apparatus were used in this study: (i) A routine SEC apparatus equipped with a Viscotek VE 5200 automatic injector, two columns thermostated at 40 °C (PSS SDV, linear M, 8 mm × 300 mm; bead diameter: 5 μm), 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: 260−2×10^6 g mol^{-1}). (ii) A more sophisticated apparatus with a triple detector array (TDA, model 302 from Viscotek) equipped with a two angle light scattering (LS) detector (LALS, $\theta = 7°$, RALS, $\theta = 90°$, laser $\lambda = 670$ nm), a refractive index detector, and two Polymer Laboratories Mixed C columns (5 μm) thermostated at 40 °C (the online viscosimeter was not used in this work). The average molar masses were calculated from the LS signal with the OmniSec software, using the average refractive index increment (d*n*/d*c*) measured for each sample with the online refractometer. (d*n*/d*c* for P(2-EHA) in THF at 40 °C is 0.072, and it is 0.065−0.072 for the block copolymers.) All polymers were first analyzed using the routine SEC, and only when more accurate data were needed were the samples also injected in the other system. For experiments 3−5, the SEC analyses were performed with the routine system only, and consequently the molar masses were derived from

a polystyrene calibration curve. For the experiments 1, 2, and 6−9, the provided SEC results are based on an absolute molar mass determination given by the light scattering detection.

Liquid Adsorption Chromatography. The chemical composition of the block copolymers was qualitatively examined by liquid adsorption chromatography (LAC). This technique enables the chains to be separated depending on their chemical composition and not on their molar mass. Even though the LAC detector did not allow a quantitative study to be made in the present work, the LAC technique was the appropriate method to confirm the formation of block copolymer and to detect the presence of either residual P(2-EHA) macro(RAFT agent) or PMA homopolymer. The samples were prepared by dissolving the polymer in THF (1 mg mL^{-1}) before injection. The Waters LAC apparatus included a degasser, a pump, an injector, and an evaporative light scattering detector (ELSD, from Polymer Laboratories) used with the Millenium32 software. For the experiments 3−5 and 7−9, the samples were injected through PLRP-S columns (150 × 4.6 mm, 5 μm, Polymer Laboratories) 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}.

Dynamic Light Scattering. The *z*-average particle diameter of the diluted organic dispersions was measured by dynamic light scattering (DLS) at a temperature of 20 °C using a Zetasizer Nano S90 from Malvern (90° angle, 4 mW He−Ne laser at 633 nm). The value noted σ corresponds to the polydispersity directly provided by the Zetasizer Nano S90, using a second-order cumulant analysis. The particle size distribution is generally considered as monodisperse and narrow when σ is below 0.10. For calculation, the refractive index of isododecane was $n = 1.421$ and the viscosity was $\eta = 1.4$ cP.

UV−Vis Spectroscopy. UV−vis spectrophotometric analysis of the P(2-EHA)-TTC homopolymer was performed in toluene solution using a CARY-1G spectrophotometer from Varian. The molar extinction coefficient (ϵ) of the trithiocarbonate midchain group at 25 °C was considered to be the same as that of the *S*,*S*′-bis[1-(2-ethylhexyloxycarbonyl)ethyl] trithiocarbonate RAFT agent ($\epsilon = 40$ L mol^{-1} cm^{-1} in toluene at 434 nm).

NMR Spectroscopy. Three models of Brüker spectrometers (AC200, AC250, DRX500) were used for the NMR analyses performed at room temperature, in 5 mm diameter tubes.

Results and Discussion

Various dithiobenzoates and trithiocarbonates have proven to be suitable RAFT agents for the polymerization of alkyl acrylates.[30−37] For this reason, *tert*-butyl dithiobenzoate (DTB)[30] and the symmetrical *S*,*S*′-bis[1-(2-ethylhexyloxycarbonyl)ethyl] trithiocarbonate (TTC) were selected here for the synthesis of the P(2-EHA)-*b*-PMA diblock copolymers and the P(2-EHA)-*b*-PMA-*b*-P(2-EHA) triblock copolymers, respectively, in isododecane, a good solvent for the P(2-EHA) block but a poor solvent for the PMA sequence. The advantage of dithioesters is their larger chain transfer constant compared to trithiocarbonates,[38] but the drawback is a more pronounced rate retardation.[30,35]

Synthesis of the Poly(2-ethylhexyl acrylate) Macro(RAFT agent)s. Polymerization of 2-ethylhexyl acrylate was initiated by *tert*-butyl peroxy-2-ethylhexanoate (T21S) and carried out under RAFT control using either DTB at 80 °C or TTC at 60 °C (Scheme 1). In both cases, high monomer conversions (80−90%) were reached within 5 h (Figure 1). The conversion vs time plots exhibit an S-shape with an evident induction period of ca. 1 h for the polymerization carried out at 60 °C with the TTC RAFT agent. The polymer was well controlled in both cases, as shown by the linear increase of the experimental number-average molar masses (M_ns) with monomer conversion and the low polydispersity indexes (Figures 2 and 3). The experimental M_ns, measured by SEC using a light scattering detector (see Experimental Part), were above the predicted values for the DTB-mediated polymerization and perfectly matched the theoretical values when using the TTC RAFT agent. The polydispersity indexes were invariably below 1.2, but a broadening of the molar mass distribution was observed at 80% conversion when using DTB as a RAFT agent (Figure 2). Despite the fact that free-radical polymerization of 2-EHA is

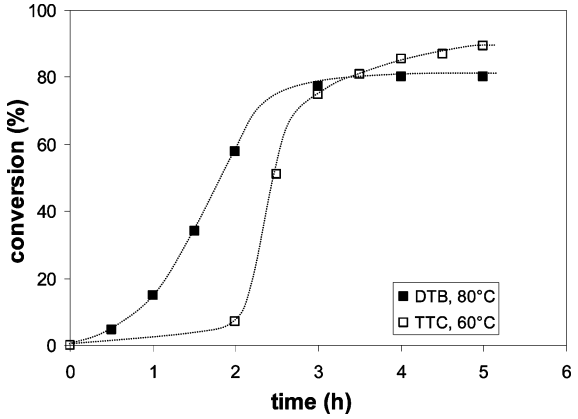


Figure 1. Monomer conversion vs time for the RAFT polymerizations of 2-EHA carried out in bulk. See Table 1, experiment 1 (DTB) and experiment 6 (TTC) for experimental conditions.

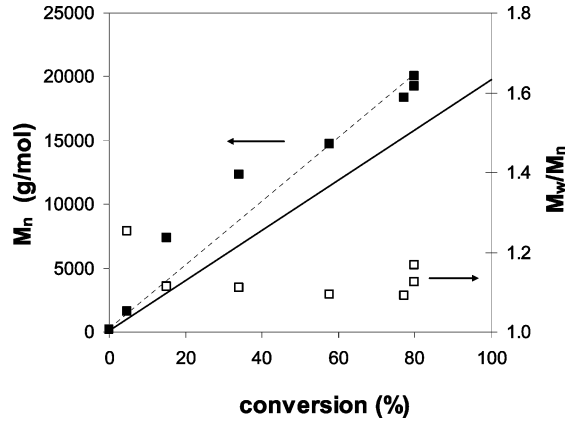


Figure 2. Number-average molar mass (M_n, ■) and polydispersity index (M_w/M_n, □) vs monomer conversion for the polymerization of 2-EHA carried out in bulk at 80 °C using DTB as a RAFT agent. See Table 1, experiment 1 for experimental conditions. The straight line corresponds to the theoretical M_n (efficiency of the RAFT agent = 0.79).

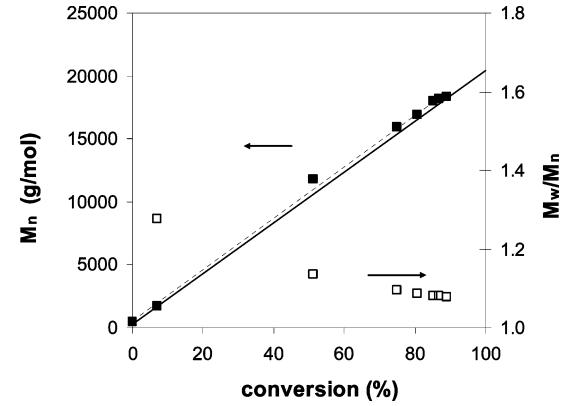


Figure 3. Number-average molar mass (M_n, ■) and polydispersity index (M_w/M_n, □) vs monomer conversion for the polymerization of 2-EHA carried out in bulk at 60 °C using TTC as a RAFT agent. See Table 1, experiment 6 for experimental conditions. The straight line corresponds to the theoretical M_n (efficiency of the RAFT agent = 0.99).

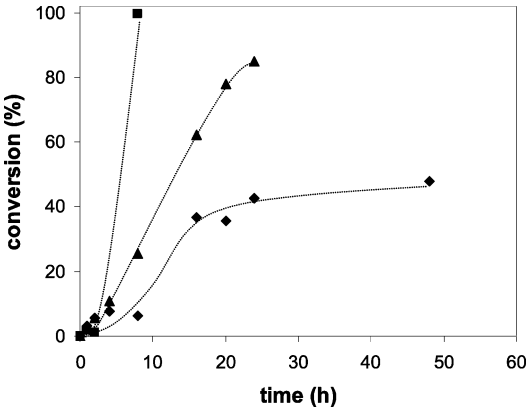


Figure 4. Conversion vs time for the dispersion polymerizations of MA carried out in isododecane at 80 °C using various concentrations of the P(2-EHA)-DTB macro(RAFT agent). See Table 1 for experimental conditions of experiment 3 (■, 1.3 mM), experiment 4 (▲, 3.9 mM), and experiment 5 (◆, 7.9 mM).

highly prone to chain transfer reactions[39] and that the *tert*-butoxy radicals are known to favor hydrogen abstraction,[2] the polymerization of 2-EHA under the RAFT process fulfilled all the criteria of a well-controlled one, particularly because low molar masses were targeted.

The well-defined and living P(2-EHA)-DTB and P(2-EHA)-TTC homopolymers (see Scheme 1) were subsequently used as macro(RAFT agent)s to allow the synthesis of block copolymers by chain extension in nonaqueous dispersion polymerization.

Dispersion Polymerization of MA Using Poly(2-ethylhexyl acrylate) as a Macro(RAFT agent): Experimental Observations. The dispersion polymerizations of methyl acrylate, performed in isododecane at 80 °C, were initiated by T21S in the presence of either P(2-EHA)-DTB or P(2-EHA)-TTC as macro(RAFT agent). The initial polymerization medium was a homogeneous solution as both methyl acrylate and P(2-EHA) are fully soluble in isododecane. Because of poly(methyl acrylate) nonsolublility in isododecane, a dispersion polymerization process was expected with production of stable micelle-like aggregates. Ideally, in a living polymerization process such as the RAFT-mediated free-radical polymerization selected here, well-defined block copolymer chains should form and self-assemble into micelles with a PMA core and a P(2-EHA) soluble shell playing the role of the steric stabilizer. With DTB, a diblock copolymer is expected with the dithiobenzoate group at the PMA solvophobic block end, whereas with TTC, one anticipates the formation of a triblock copolymer with the trithiocarbonate function in the middle of the PMA central block (Scheme 2). In both cases, the study focused on the macromolecular characteristics of the polymer chains and on the particle size and stability.

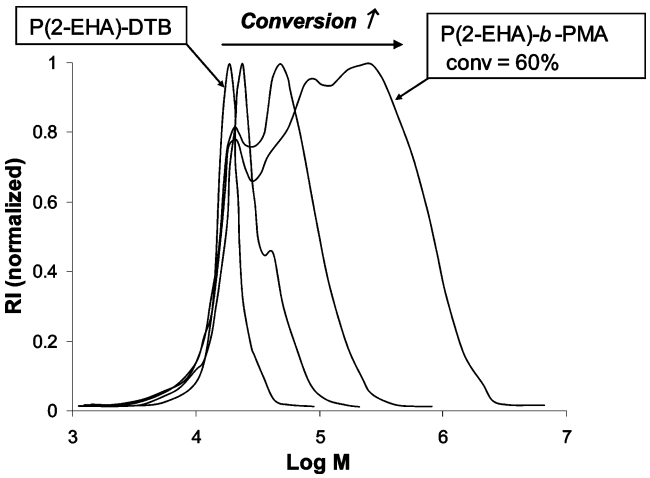


Figure 5. Size exclusion chromatograms for the dispersion polymerization of MA carried out in isododecane at 80 °C using P(2-EHA)-DTB as a macro(RAFT agent). See Table 1, experiment 4 for experimental conditions.

P(2-EHA)-DTB Macromolecular RAFT Agent. The conversion vs time plots of the dispersion polymerizations carried out at 80 °C in the presence of the P(2-EHA)-DTB macromolecular chain transfer agent (Figure 4) highlighted a significant rate retardation effect since the polymerization drastically slowed down when the concentration of the macro(RAFT agent) was increased. Indeed, the reaction was completed within 10 h when the polymerization was performed with the lowest macro(RAFT agent) concentration (Table 1, experiment 3), whereas less than 60% conversion was reached after 50 h with the highest P(2-EHA)-DTB concentration (Table 1, experiment 5). For the latter, the plateau is explained by a complete consumption of the initiator as half-lifetime of TS21 at 80 °C is 4 h.[40] This retardation phenomenon had been previously observed for the RAFT polymerization of acrylates mediated by a dithioester derivative.[30,35] It was also particularly pronounced for the dispersion polymerization of 4-vinylpyridine in cyclohexane, when a dithiobenzoate-terminated polystyrene was used as a macromolecular RAFT agent.[27] Nevertheless, stable polymer particles were always recovered and their average diameter ranged from 39 to 93 nm (Table 3, experiments 3−5). The highest average particle diameter and the narrowest particle size distribution were obtained with the lowest macro(RAFT agent) concentration (Table 3, experiment 3). The same experiment showed in the meantime a very broad molar mass distribution ($M_w/M_n = 18$), characteristic of noncontrolled polymerization.

Table 3. Molecular and Colloidal Characteristics of the Polymer Dispersions in Isododecane

						final DLS data	
expt	conv, %	solids, wt %	DP_n,P(2-EHA)[a]	DP_n,PMA[a]	(co)polymer structure	*Z*-average (nm)	σ
3	100	25	114		$P(2\text{-EHA})_{114}$-*b*-PMA + $P(2\text{-EHA})_{114}$ + PMA	93	0.09
4	85	28	114		$P(2\text{-EHA})_{114}$-*b*-PMA + $P(2\text{-EHA})_{114}$ + PMA	51 (bimodal)[b]	0.22
5	48	30	114		$P(2\text{-EHA})_{114}$-*b*-PMA + $P(2\text{-EHA})_{114}$ + PMA	39 (bimodal)[b]	0.18
7	6	5	102	115	$P(2\text{-EHA})_{51}$-*b*-PMA_{115}-*b*-$P(2\text{-EHA})_{51}$	21	0.10
	91	23	102	936	$P(2\text{-EHA})_{51}$-*b*-PMA_{936}-*b*-$P(2\text{-EHA})_{51}$	50	0.03
8	4	10	102	19	$P(2\text{-EHA})_{51}$-*b*-PMA_{19}-*b*-$P(2\text{-EHA})_{51}$	14	0.16
	92	29	102	389	$P(2\text{-EHA})_{51}$-*b*-PMA_{389}-*b*-$P(2\text{-EHA})_{51}$	30	0.03
9	7	19	102	5	$P(2\text{-EHA})_{51}$-*b*-PMA_5-*b*-$P(2\text{-EHA})_{51}$	NA	NA
	27	24	102	65	$P(2\text{-EHA})_{51}$-*b*-PMA_{65}-*b*-$P(2\text{-EHA})_{51}$	18	0.13
	100	39	102	241	$P(2\text{-EHA})_{51}$-*b*-PMA_{241}-*b*-$P(2\text{-EHA})_{51}$	54	0.10

[a] The number-average degrees of polymerization, $DP_{n,P(2-EHA)}$ and $DP_{n,PMA}$, were calculated using M_n of the P(2-EHA) homopolymer and M_n of the copolymer. For these values, the M_n data were measured by SEC using a LS detector. $DP_{n,PMA} = (M_{n,copolymer} - M_{n,P(2-EHA)})/M_{MA}$. [b] A second population at $D = 230$ nm is visible in the particle size intensity distribution, but not in the number distribution.

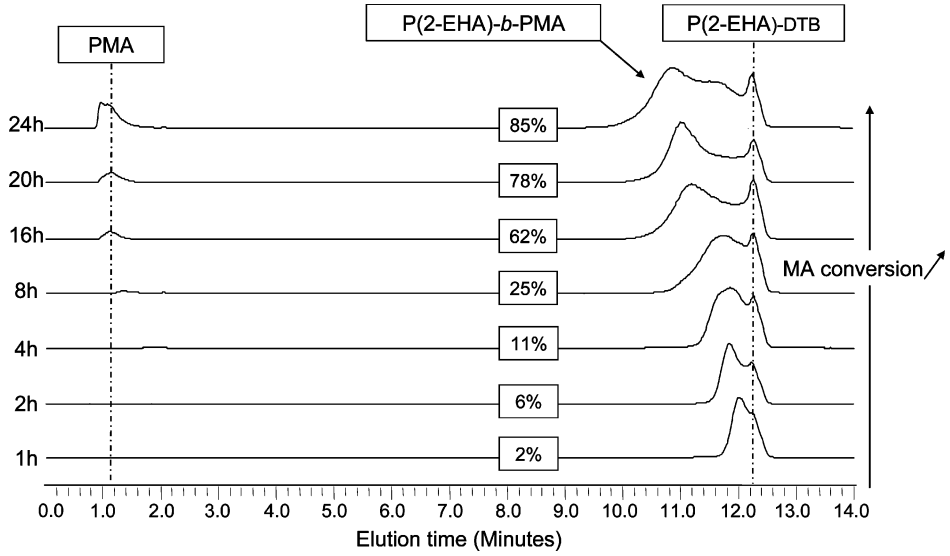


Figure 6. Liquid adsorption chromatograms for the dispersion polymerization of MA carried out in isododecane at 80 °C using P(2-EHA)-DTB as a macro(RAFT agent). See Table 1, experiment 4 for experimental conditions.

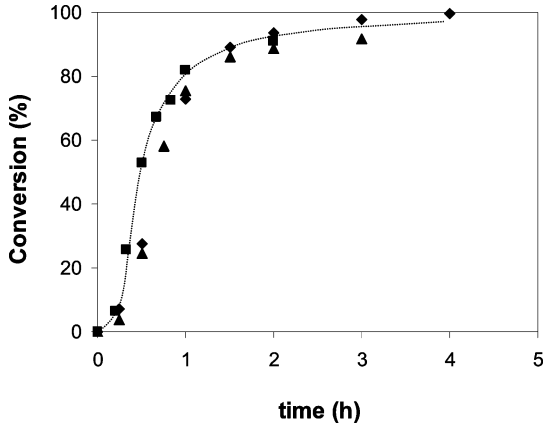


Figure 7. Conversion vs time for the dispersion polymerizations of MA carried out in isododecane at 80 °C using various concentrations of P(2-EHA)-TTC macro(RAFT agent). See Table 1 for the experimental conditions of experiment 7 (■, 1.3 mM), experiment 8 (▲, 3.9 mM), and experiment 9 (◆, 7.7 mM).

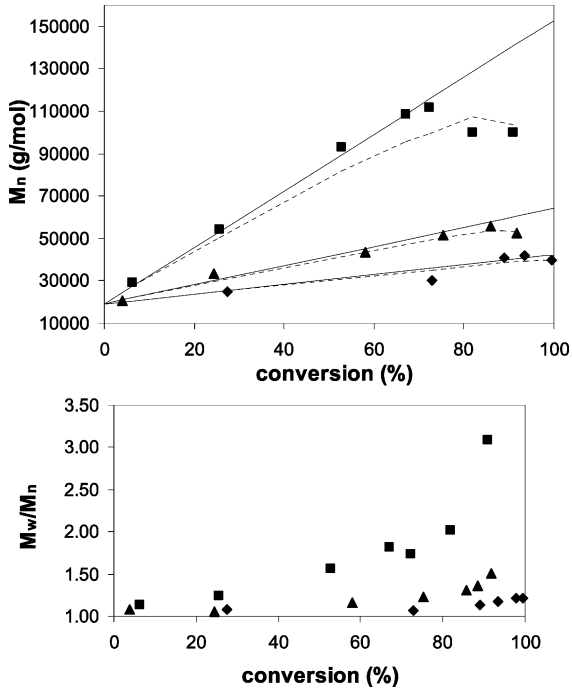


Figure 8. M_n and M_w/M_n vs monomer conversion for the dispersion polymerizations of MA carried out at 80 °C in isododecane using P(2-EHA)-TTC as a macro(RAFT agent) and T21S as an initiator. See Table 1 for experimental conditions of experiment 7 (■), experiment 8 (▲), and experiment 9 (◆). The straight lines and the dashed lines correspond to the theoretical molar masses calculated on the basis of the monomer/P(2-EHA)-TTC initial concentration ratio, excluding or not the chains generated by the initiator, respectively (see ref 42).

When higher P(2-EHA)-DTB concentrations were used, polydispersed polymer particles were recovered (Table 3, experiments 4 and 5), but the narrowing of the molar mass distribution was obvious (Table 2, experiment 4, $M_w/M_n = 6.0$, and experiment 5, $M_w/M_n = 1.76$). It was noticeable from both the SEC and LAC results of experiment 4 shown in Figures 5 and 6, respectively (the SEC and LAC of experiments 3 and 5 appear in the Supporting Information in Figures SI-4 to SI-7), that the polymer was made of a mixture of a nonnegligible proportion of unreacted P(2-EHA) homopolymer, a fraction of PMA homopolymer, and the expected P(2-EHA)-*b*-PMA diblock copolymer, suggesting that a large part of the P(2-EHA)-DTB macro(RAFT agent) was not involved in the RAFT process during the dispersion polymerization of MA in isododecane. An additional experiment (not presented in this article) was carried out with a shorter P(2-EHA)-DTB to match the block length of one arm of the TTC counterpart. Similar results of incomplete consumption of the macro(RAFT agent) and poor control over the copolymerization were observed.

P(2-EHA)-TTC Macromolecular RAFT Agent. The P(2-EHA)-TTC macro(RAFT agent) behaved in a very different manner when compared with its dithiobenzoate-ended homologue. The dispersion polymerization of MA was indeed much faster (see Figure 7) as more than 80% conversion was achieved within 4 h at 80 °C. Moreover, no rate retardation was observed for any of the macro(RAFT agent) initial concentrations as the superimposition of conversion vs time plots indicates (Figure 7). With the exception of the experiment with the lowest P(2-EHA)-TTC concentration (Table 2, experiments 7−9), the dispersion polymerization of methyl acrylate occurred in a well-controlled fashion up to high conversion, as all criteria of a controlled polymerization were indeed fulfilled.

Figure 8 shows the increase of M_n vs monomer conversion. The experimental molar masses were however below the theoretical line when the latter was classically calculated from

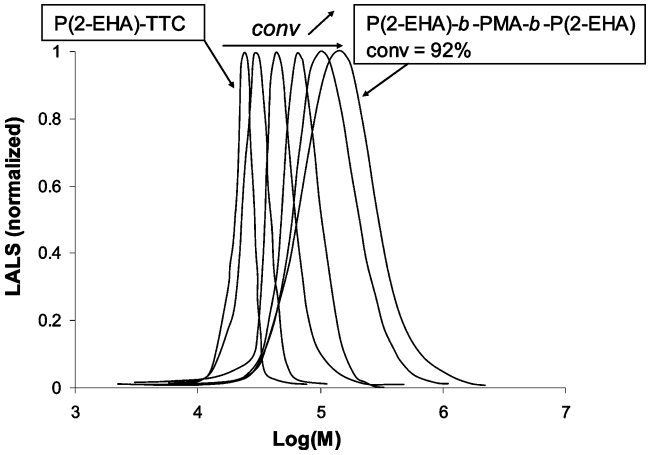


Figure 9. Size exclusion chromatograms for the dispersion polymerization of MA carried out in isododecane at 80 °C using P(2-EHA)-TTC as a macro(RAFT agent). See Table 1, experiment 8 for experimental conditions.

the ratio of monomer/P(2-EHA)-TTC initial concentrations. This was likely due to an underestimation of the calculated number of chains. Nevertheless, when the number of chains created by the initiator was taken into account in the theoretical calculation (especially for experiment 7 in which the concentration of T21S was similar to the concentration of the macro(RAFT agent) (Table 1)), the experimental molar masses were in better agreement with the theoretical trend. The polydispersity index values were significantly lower than those found in the presence of the P(2-EHA)-DTB transfer agent (see experiments 3, 4, 5 and experiments 7, 8, 9 in Table 2, respectively, for comparison): they increased with conversion up to 2.7 with the lowest P(2-EHA)-TTC concentration (experiment 7) but remained very low with the highest P(2-EHA)-TTC concentration (Table 2, experiment 9).

The shift of the narrow size exclusion chromatograms (Figure 9 and Supporting Information Figures SI-8 and SI-10) together with the monomodal LAC distributions and the continuous shift of the peaks toward a higher proportion of MA units (Figure 10 and Supporting Information Figures SI-9 and SI-11) were in accordance with the synthesis of pure P(2-EHA)-*b*-PMA-*b*-P(2-EHA) triblock copolymers with a homogeneous chemical composition. No trace of homopolymers, the P(2-EHA)-TTC transfer agent, or the PMA homopolymer generated by the initiation step were detected by the LAC analysis of the final samples (see Figure 10 and Supporting Information Figures SI-9 and SI-11). The extremely small amount of P(2-EHA) homopolymer observed by LAC from the lowest P(2-EHA)-TTC concentration experiment (experiment 7, see Supporting Information, Figure SI-9) indicates that the macro(RAFT agent) was not completely consumed before ~70% monomer conversion in this case.

As PMA is not soluble in isododecane, the so-formed triblock copolymer chains self-assembled to form micelles that were sterically stabilized by the P(2-EHA) chains. Those micelles appeared early in the polymerization process (typically below 10% MA conversion, see Table 3) and further grew by PMA block extension. The final average particle diameters ranged between 30 and 50 nm with polydispersity (σ) lower than 0.1 for all three experiments, and the particle diameters logically increased with the increase in PMA block length (see Table 3, experiments 7−9). In the experiment 9, for which the macro(RAFT agent) concentration was high and the solids content reached 40 wt %, the average diameters were particularly high for only 240 MA units in the PMA block. The increase in the particle polydispersity factor σ indicated that a limited flocculation probably occurred due to the high concentration in polymer particles.

Influence of the Thiocarbonylthio Group on the Dispersion Polymerization Mechanism. Despite the fact that both systems led to stable polymer nanoparticles with hydrodynamic diameters below 100 nm, all other experimental data indicate clear differences in the RAFT dispersion polymerizations of MA when they were conducted in the presence of P(2-EHA)-DTB or in the presence of P(2-EHA)-TTC. The P(2-EHA)-DTB was never completely converted, it was unable to produce well-defined copolymer structure and in addition, it induced a pronounced rate retardation. In contrast, all polymerizations performed with P(2-EHA)-TTC were fast and well controlled with complete crossover efficiency. Such results are particularly surprising and in contradiction with the well-known ability of the dithiobenzoate group to bring about a living free-radical polymerization mechanism. Moreover, a solution polymerization of 2-EHA in isododecane in the presence of a P(2-EHA)-DTB

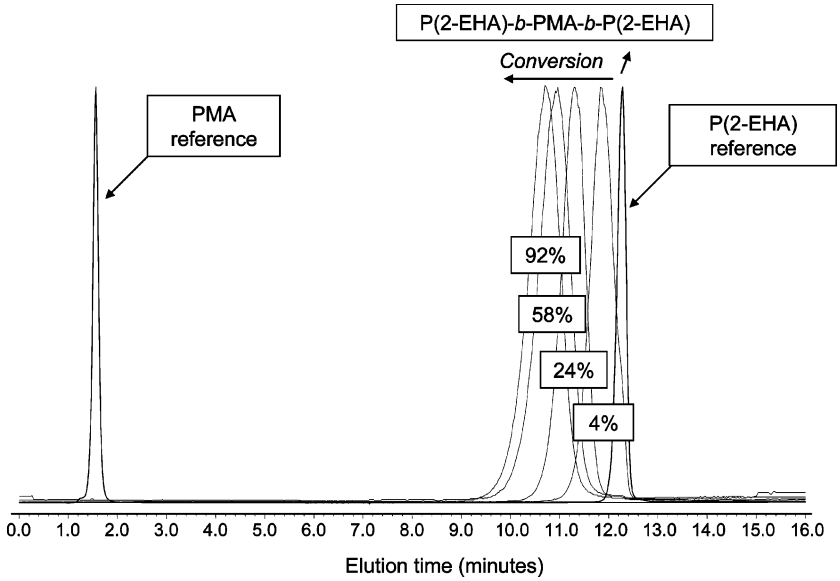


Figure 10. Liquid adsorption chromatograms for the dispersion polymerization of MA carried out in isododecane at 80 °C using P(2-EHA)-TTC as a macro(RAFT agent). See Table 1, experiment 8 for experimental conditions.

led to a much more efficient chain extension process than the corresponding dispersion polymerizations of MA (see Supporting Information, Figure SI-12). Interpretation of the data has thus to be found in the dispersed state of the system rather than in the polymerization mechanism itself.

Complete consumption of the P(2-EHA) macro(RAFT agent) strongly depends on the kinetics in the continuous phase, where block copolymers are initially generated, providing the reversible chain transfer reaction is fast enough. When the PMA block reaches a critical size and concentration of the block copolymer is large enough, self-assembly occurs and micellar aggegates form, which swell with monomer owing to favorable partitioning. In the presence of those particles, the propagating homopoly(methyl acrylate) oligoradicals created in the continuous phase from the radical initiator have two main possible fates (besides self-termination): either they react with soluble macro(RAFT agent) via reversible transfer reaction or they adsorb onto a nanoparticle surface. The first event remains favored as long as the chain length reached before chain transfer reaction is lower than the critical degree of polymerization for adsorption. The chain length before chain transfer reaction corresponds to the ratio of the rate of propagation over the rate of transfer in the continuous medium and thus depends upon the monomer and macro(RAFT agent) concentrations and the chain transfer constant.

The experimental results of incomplete consumption of the dithiobenzoate-terminated P(2-EHA) indicate that the transfer reaction in the continuous phase is not favored, whereas it is very efficient for the P(2-EHA)-TTC macro(RAFT agent). This might be related to the chain transfer constant being significantly larger for the trithiocarbonate derivative than for the dithiobenzoate one, but this is not very likely and in direct opposition to the trend reported in the literature.[38] We propose then another possible explanation, which relies on the structure of the formed block copolymers rather than on the reactivity.

With P(2-EHA)-*b*-PMA-DTB block copolymers, the reactive group is located at the solvophobic block end, buried inside the particles. When they preferentially adsorb at the particle surface, the PMA oligoradicals grow by addition of MA units and subsequently undergo a transfer reaction to the reactive group of a dormant block copolymer, which then releases a P(2-EHA)-*b*-PMA radical (Scheme 2). Because of its structure, the latter is trapped inside the particle and might be unable to exit to further react with the P(2-EHA)-DTB chains located in the continuous phase. In such conditions, reaction of the soluble macro(RAFT agent) molecules is slow and incomplete, and the overall quality of control of the copolymer is poor.

With P(2-EHA)-TTC, the reactive group is located at the center of the chain and the solvophobic PMA blocks grow on both sides of this central function (it is actually an individual growth of the separated arms). One cannot thus exclude that block copolymers start to self-assemble when only one of the two P(2-EHA) leaving groups has reacted. In this situation, the reactive trithiocarbonate function remains close to the interface. The adsorption of a PMA oligoradical is then followed by a fast chain transfer reaction, which might then release a P(2-EHA) homopolymer radical. The latter is able to exit the micelle and further grow by monomer addition in the continuous solution and undergo multiple chain transfer reactions, allowing a more complete consumption of the macro(RAFT agent). In other words, the adsorption phenomenon can be regarded as a reversible step.

The second important difference between both systems is the polymerization rate. With DTB-based RAFT agents, rate retardation has very often been observed, although the true reason for this has not been completely elucidated yet.[41] In the particle core, concentration of the dithiobenzoate functions is much higher than in the solution and might explain the strong retardation observed in our dispersed systems. This was also reported by Zheng et al.[27] for the dispersion polymerization of 4-vinylpyridine in cyclohexane in the presence of a dithiobenzoate-terminated polystyrene. In comparison to TTC, longer polymerization times with DTB lead to the dissociation of a larger fraction of the initiator and hence to an accumulation of PMA homopolymer chains.

Conclusion

The RAFT-mediated dispersion polymerization of methyl acrylate in isododecane, using two thiocarbonylthio-functionalized poly(2-ethylhexyl acrylate) macro(RAFT agent)s, allowed stable particles with very small hydrodynamic diameter to be produced. When the trithiocarbonate macro(RAFT agent) was used, the polymerization of MA fulfilled all the criteria of a controlled system. Thanks to this control, well-defined P(2-EHA)-*b*-PMA-*b*-P(2-EHA) triblock copolymer chains were formed and self-assembled, which resulted in monodisperse micelles with a PMA core and soluble P(2-EHA) hair. However, when the dithiobenzoate derivative was used, formation of polydisperse particles, strong rate retardation, and very poor control over the polymer structure were observed together with an incomplete consumption of the macro(RAFT agent). Such a result was quite surprising and in contradiction with the behavior of the poly(2-ethylhexyl acrylate)-DTB, when used as a macro(RAFT agent) for the polymerization of 2-ethylhexyl acrylate, either in bulk or in isododecane solution. Only a major influence of the dispersed state of the system could explain the difference in apparent reactivity of the macro(RAFT agent)s used in this work. In conclusion, this study highlighted the great importance of the nature of the RAFT agent (trithiocarbonate vs dithioester) to simultaneously control the colloidal parameters and the macromolecular characteristics in dispersion polymerization. With a judicious choice of the macro(RAFT agent), the process is thus very efficient to directly form block copolymer micelles in situ, with high solids content.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; Wiley-Interscience: Hoboken, NJ, 2002.
(2) Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*, 2nd ed.; Elsevier: Amsterdam, 2006.
(3) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661.
(4) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.
(5) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.
(6) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379.
(7) Monteiro, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3189.
(8) Favier, A.; Charreyre, M. T. *Macromol. Rapid Commun.* **2006**, *27*, 653.
(9) Qiu, J.; Charleux, B.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 2083.
(10) (a) Cunningham, M. F. *Prog. Polym. Sci.* **2002**, *27*, 1039. (b) Cunningham, M. F. *C. R. Chimie* **2003**, *6*, 1061.

(11) Monteiro, M.; Charleux, B. In *Chemistry and Technology of Emulsion Polymerisation*; van Herk, A., Ed.; Blackwell Publishing Ltd.: Oxford, UK, 2005; pp 111−139.
(12) McLeary, J. B.; Klumperman, B. *Soft Matter* **2006**, *2*, 45.
(13) Save, M.; Guillaneuf, Y.; Gilbert, R. G. *Aust. J. Chem.* **2006**, *59*, 693.
(14) Cawse, J. L. *Dispersion Polymerization* in *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A., El-Aasser, M. S., Eds.; John Wiley & Sons: Chichester, England, 1997; p 744.
(15) Hoelderle, M.; Baumert, M.; Muelhaupt, R. *Macromolecules* **1997**, *30*, 3420.
(16) Xia, J.; Johnson, T.; Gaynor, S. G.; Matyjaszewski, K.; DeSimone, J. *Macromolecules* **1999**, *32*, 4802.
(17) Gabaston, L. I.; Jackson, R. A.; Armes, S. P. *Macromolecules* **1998**, *31*, 2883.
(18) Oh, S.; Kim, K.; Lee Byung, H.; Shim, S. E.; Choe, S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 62.
(19) McHale, R.; Aldabbagh, F.; Zetterlund, P. B.; Minami, H.; Okubo, M. *Macromolecules* **2006**, *39*, 6853.
(20) Minami, H.; Kagawa, Y.; Kuwahara, S.; Shigematsu, J.; Fujii, S.; Okubo, M. *Des. Monomers Polym.* **2004**, *7*, 553.
(21) Shim, S. E.; Jung, H.; Lee, H.; Biswas, J.; Choe, S. *Polymer* **2003**, *44*, 5563.
(22) Song, J. S.; Winnik, M. A. *Macromolecules* **2006**, *39*, 8318.
(23) Saikia, P. J.; Lee, J. M.; Lee, B. H.; Choe, S. *Macromol. Symp.* **2007**, *248*, 249.
(24) (a) McHale, R.; Aldabbagh, F.; Zetterlund, P. B.; Okubo, M. *Macromol. Rapid Commun.* **2006**, *27*, 1465. (b) McHale, R.; Aldabbagh, F.; Zetterlund, P. B.; Minami, H.; Okubo, M. *Macromolecules* **2006**, *39*, 6853.
(25) Jeong, K. J. S.; Kim, K.; Ahn, Y.; Quirk, R. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 3277.
(26) Wang, X.; Hall, J. E.; Warren, S.; Krom, J.; Magistrelli, J. M.; Rackaitis, M.; Bohm, G. G. A. *Macromolecules* **2007**, *40*, 499.
(27) Zheng, G.; Pan, C. *Macromolecules* **2006**, *39*, 95.
(28) Farcet, C. French Patent FR 2881648, 2006.
(29) Ladavière, C.; Dörr, N.; Claverie, J. P. *Macromolecules* **2001**, *34*, 5370.
(30) Chernikova, E.; Morozov, A.; Leonova, E.; Garina, E.; Golubev, V.; Bui, C.; Charleux, B. *Macromolecules* **2004**, *37*, 6329.
(31) Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754.
(32) Postma, A.; Davis, T. P.; Li, G.; Moad, G.; O'Shea, M. S. *Macromolecules* **2006**, *39*, 5307.
(33) Zhang, L.; Katapodi, K.; Davis, T. P.; Barner-Kowollick, C.; Stenzel, M. H. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 2177.
(34) Quinn, J. F.; Rizzardo, E.; Davis, T. P. *Chem. Commun.* **2001**, *11*, 1044.
(35) Perrier, S.; Barner-Kowollik, C.; Quinn, J. F.; Vana, P.; Davis, T. P. *Macromolecules* **2002**, *35*, 8300.
(36) Toy, A. A.; Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Macromolecules* **2004**, *37*, 744.
(37) Hua, D.; Sun, W.; Bai, R.; Lu, W.; Pan, C. *Eur. Polym. J.* **2005**, *41*, 1674.
(38) Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273.
(39) Sato, E.; Emoto, T.; Zetterlund, P. B.; Yamada, B. *Macromol. Chem. Phys.* **2004**, *205*, 1829.
(40) Akzo Nobel Polymer Chemicals; *Initiators for High Polymers, BTB Communication*; Issue: June 2006.
(41) Barner-Kowollik, C.; Buback, M.; Charleux, B.; Coote, M. L.; Drache, M.; Fukuda, T.; Goto, A.; Klumperman, B.; Lowe, A. B.; Mcleary, J. B.; Moad, G.; Monteiro, M. J.; Sanderson, R. D.; Tonge, M. P.; Vana. P. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5809.
(42) The linear theoretical number-average molar mass (straight line) was calculated according to $M_n(\text{theor}) = M_{n,P(2-EHA)-TTC} + ([MA]_0/[P(2\text{-}EHA)\text{-}TTC]_0) \times \text{conv} \times M_{MA}$ with $M_{n,P(2-EHA)-TTC}$ the number-average molar mass of the macro(RAFT agent) and $[P(2\text{-}EHA)\text{-}TTC]_0$ its initial concentration; M_{MA} the molar mass of the monomer MA, and $[MA]_0$ its initial concentration. When the initiator concentration was included into the equation (dashed line), it led to $M_n(\text{theor}) = M_{n,P(2-EHA)-TTC} + \text{conv} \times M_{MA} \times [MA]_0/([P(2\text{-}EHA)\text{-}TTC]_0 + [T21S]_0 \times f \times (1 + \delta) \times (1 - e^{-k_d t}))$ in which k_d denotes the dissociation rate constant of TS21 ($k_d = 5.1 \times 10^{-5}$ L mol^{-1} s^{-1} at 80 °C [Akzo Nobel Polymer Chemicals, *Initiators for High Polymers, BTB Communication*, Issue: June 2006]). The best fit in Figure 8 is obtained with the factor $f \times (1 + \delta) = 1.2$ (f is the efficiency of T21S, and $(1 + \delta)$ indicates the termination mechanism: when termination proceeds exclusively by combination $\delta = 0$ and exclusively by disproportionation $\delta = 1$).

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