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Reversible Addition−Fragmentation Chain Transfer Polymerization in Microemulsion

Shiyong Liu,[†] Kevin D. Hermanson,[‡] and Eric W. Kaler*

Center of Molecular Engineering and Thermodynamics, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

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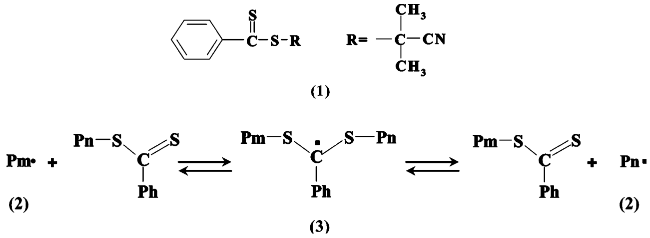
ABSTRACT: We have conducted reversible addition−fragmentation chain transfer (RAFT) polymerization of *n*-hexyl methacrylate solubilized in a microemulsion using dodecyltrimethylammonium bromide as surfactant and 2-cyanoprop-2-yl dithiobenzoate (**1**) as the RAFT agent. The resulting latex particles are stable and much smaller, ranging from 18 to 30 nm depending on the mole ratio of RAFT agent **1** to the free radical initiator, 2,2′-azobis(2-amidinopropane) hydrochloride (V50), than those produced by conventional microemulsion polymerization. The molecular weight increases linearly with conversion, and the polydispersity remains low when the number of RAFT agent molecules used is in excess of the initial number of swollen micelles. The RAFT technique can be successfully used in microemulsion polymerization to produce stable dispersions of small particles containing low molecular weight polymers. This is believed to be the first report of RAFT polymerization in microemulsion.

Introduction

Microemulsions are thermodynamically stable mixtures of oil, water, and surfactant. Their unique physical properties have led to the development of methods for the polymerization of organic monomers in microemulsions, with the primary goal of producing stable latexes with particle sizes close to those of the parent microemulsion droplets.[1−4] Such polymerizations typically show fast reaction rates and produce latex nanoparticles (10−50 nm) made of very high molecular weight polymers (∼15×10^6 Da). It would be beneficial to exert control on the microstructural properties (molecular weight, polydispersity, monomer sequences, chain ends, degree of branching, etc.) of the polymers during microemulsion polymerization, and living or controlled free radical polymerization offers a pathway to such control.[5]

Different approaches have been developed to carry out “living” free-radical polymerization, including nitroxide-mediated polymerization,[6−10] atom transfer radical polymerization (ATRP),[11−16] degenerative transfer (DT),[17] and reversible addition−fragmentation transfer (RAFT) polymerization.[18−22] In particular, RAFT polymerization has recently emerged as a promising controlled free radical polymerization technique due to its versatility and simplicity and because the polymer is free from the contamination of metal catalysts.[19,21] The RAFT process relies first on the chain transfer of active species ($P_m^\bullet$) to the RAFT agent, which then undergoes fragmentation to reinitiate polymerization. The active moiety from the RAFT agent is thus attached to the polymeric chain end, making it a dormant species. Once the RAFT agent is consumed, equilibrium is established between the active and dormant species (Scheme 1).[18−22]

Scheme 1. Chemical Structure of the Reversible Addition−Fragmentation Chain Transfer (RAFT) Agent Used in This Study (Top) and Mechanism of the RAFT Process (Bottom)



To produce polymers with narrow polydispersities via “living” free-radical polymerization in solution and bulk, the radical concentrations must be relatively low compared to the concentration of mediating agent (e.g., RAFT or DT) so as to limit biradical termination. However, low radical concentrations result in slow polymerization rates. Emulsion polymerization enables a potential solution to this problem because the compartmentalization of the radicals in individual particles produces high polymerization rates with low termination rates.[23,24] Theoretical analysis indicates that using either the RAFT or DT living mechanisms could take advantage of the radical segregation typical in emulsion polymerization without considerably decreasing the polymerization rate.[5,18,23−25]

Recently, RAFT agents have been used in free radical macro-[23−30] and miniemulsion polymerizations.[31−37] RAFT polymerization of macroemulsions stabilized by ionic surfactants, such as sodium dodecyl sulfate (SDS), resulted in emulsion destabilization at the very beginning of polymerization, leading to nonliving behavior.[23] This was suggested to reflect a combination of transport limitations and/or destabilization of the colloid particles through unknown interactions of the SDS surfactant with the RAFT agent. Droplet nucleation and polymerization are also postulated to lead to destabilization.[18,24,26] Miniemulsions stabilized with SDS also become unstable during polymerization.[36] Only when nonionic surfactants were used could destabilization be alleviated to some extent and “living polymers” successfully produced.[36,38]

Polymerizations in microemulsions are also compartmentalized, and microemulsions can remain stable during polymeri-

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* To whom correspondence should be addressed: Tel (302) 831-3553; e-mail kaler@che.udel.edu.

[†] Current address: Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, 230026, Anhui Province, P.R. China.

[‡] Current address: Department of Physics, E22-Biophysics, Technische Universität München, 85747 Garching, Germany.

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zation because they do not contain the large monomer droplets present in emulsion polymerization. Microemulsion polymerization uses a large amount of surfactant compared to emulsion polymerization, and consequently the number of monomer swollen micelles is much higher than the number of polymerizing particles. On average, there is only one (or at most a very few) radical entry per particle, in which case each entered radical is nearly perfectly "segregated" in well-separated polymerizing particles and biradical terminations are rare. Recently, Matyjaszewski et al. reported the polymerization of methyl methacrylate and styrene in a microemulsion via ATRP.[39] They found that the normal ATRP protocol does not work in microemulsions and that the resulting polymers have a bimodal distribution. Reverse ATRP led to monomodal polymer distributions, although they showed a broader molecular weight range than that given by ATRP in bulk. Only when the newly developed "activator generated by electron transfer" (AGET) ARTP[33,40] method was used did better control of the process and the particle size distribution emerge.

Here, we have carried out RAFT polymerization of *n*-hexyl methacrylate (C_6MA) solubilized in a microemulsion using the cationic surfactant dodecyltrimethylammonium bromide (DTAB) and 2-cyanoprop-2-yl dithiobenzoate (**1**) as the RAFT agent. Although it is generally believed that the RAFT polymerization of methacrylate monomers is more difficult to control than acrylates or styrene,[18,20,21] C_6MA was chosen as the monomer because the uncontrolled polymerization of C_6MA/DTAB microemulsions has been thoroughly studied and offers an ideal system for kinetic analysis.[23,41−46]

Materials and Methods

Materials. Dodecyltrimethylammonium bromide from TCI America with 99+% purity was used as received. *n*-Hexyl methacrylate (C_6MA) (Scientific Polymer Products, 99%) was vacuum-distilled and stored at −20 °C for less than 1 week before use. The initiator 2,2′-azobis(2-amidinopropane) hydrochloride (V50) (Wako Pure Chemical Industries, Ltd., 98.8%) was crystallized from hot water. The RAFT agent 2-cyanoprop-2-yl dithiobenzoate (**1**) was synthesized following literature procedures.[20,47,48] **1** was pure as checked by ^{1}H NMR δ: 1.96 (s, 6H, CH_3), 7.39 (2H, meta-Ar*H*), 7.57 (1H, para-Ar*H*) and 7.92 (2H, ortho-Ar*H*). Thin-layer chromatography of **1** shows only a single spot. Elemental analysis of **1** indicated a purity of ~98% based on carbon.

RAFT Polymerization in Microemulsions. A typical protocol for the RAFT polymerization in microemulsion was as follows. Microemulsions containing 12 wt % DTAB, 2.64 wt % of nitrogen-sparged C_6MA monomer, and 3 mM **1** in degassed water were prepared in a 500 mL three-necked flask. Following a common notation, compositions in weight percentages are reported as α = oil/(oil + water) × 100 and γ = surfactant/(surfactant + oil + water) × 100; the prepared microemulsion corresponded to α = 3% and γ = 12%. After the microemulsion was equilibrated at room temperature for 2 h, the mixture was purged with high-purity nitrogen for 30 min. To polymerize the microemulsion, the mixture was heated to 75 °C and initiated by injecting 1.0 mL of a degassed H_2O solution containing the amount of V50 initiator needed to give an overall initiator concentration of 0.50 mM. The conversion reached over 99% in ~3 h. Polymerizations were conducted at different molar ratios of [**1**]/[V50] (0, 0.7, 1.0, 1.5, 2.25, 3.0, 4.5, and 6.0) following the protocol described above.

Kinetic Analysis. For RAFT microemulsion polymerizations with [**1**]/[V50] ratio higher than 1.0, conversion of monomer to polymer was followed using dry solids (gravimetric) analysis. Samples were taken regularly through the polymerization, quenched with a few crystals of hydroquinone, cooled rapidly with liquid nitrogen, and dried in a vacuum oven at 50 °C. For polymerizations with [**1**]/[V50] ratio less than or equal to 1.0, conversions were monitored by calorimetry using a Mettler RC1 calorimeter with a 2L glass reactor. The detailed procedures have been described previously.[42,43]

Gel Permeation Chromatograph (GPC). After the samples were totally dried, they were dissolved in hot tetrahydrofuran (THF) and then cooled to crystallize the DTAB surfactant. The supernatant was filtered through a 0.45 μm polytetrafluorethylene filter and then dried under vacuum at room temperature. Molecular weight and molecular weight distributions were analyzed by GPC using THF (containing 2% triethylamine) as an eluent at a flow rate of 1.0 mL min^{-1} at 30 °C in a Waters chromatograph equipped with two PLgel 5 μm (30 cm) mixed D columns (molecular weight range 200−400 000), a WellChrom K-2301 refractive index detector operating at 950 ± 30 nm, and a Waters 2487 dual wavelength UV/vis absorbance detector. The reported number-average molecular weights are apparent values expressed in poly(methyl methacrylate) equivalents.

Quasielastic Light Scattering (QLS). QLS experiments were made using equipment manufactured by Brookhaven Instrument Corp. (BI9000). The scattering angle was fixed at 90°. Samples thermostated at 25 °C were irradiated with 488 nm light from a Lexal 2 W argon ion laser. Intensity correlation data were analyzed by the method of cumulants to provide the average decay rate, $\langle\Gamma\rangle$ ($= q^2D$), where D is the diffusion coefficient, and the normalized variance, ν ($= [(\langle\Gamma^2\rangle - \langle\Gamma\rangle^2)/\langle\Gamma\rangle^2]$, which is a measure of the width of the distribution of the decay rates. The measured diffusion coefficients were represented in terms of apparent radii by using Stokes' law and assuming the solvent has the viscosity of water. Latexes were diluted with 0.5 wt % DTAB solution up to 20 times to minimize interactions and filtered through 0.2 μm Millipore Acrodisc-12 filters to eliminate dust before QLS measurements.

Results and Discussion

Previous attempts at RAFT polymerization in emulsion and miniemulsion polymerization have shown that compartmentalization, RAFT agent diffusion, and droplet nucleation are important features of heterogeneous RAFT polymerizations.[24−39] Compartmentalization segregates each radical into a separate particle and produces fast reaction rates by reducing biradical termination. However, in RAFT polymerizations compartmentalization can also be a liability because it creates separate polymerizing domains that may each have a different RAFT concentration. These differences in RAFT concentration can be suppressed only if the transport rate of the RAFT agent and monomer are comparable. If transport of the RAFT agent is much faster than that of the monomer, then all of the RAFT agent will be consumed in the early stages of polymerization. This would result in the initial production of low molecular weight polymer and leave less RAFT agent available for the latter stages of polymerization. The higher molecular weight polymers produced in the latter stages will cause an increase in average molecular weight (MW) and polydispersity. On the other hand, if either the unreacted RAFT agent or monomer is too hydrophobic, transport through the aqueous domain of the microemulsion will be the limiting process, and the polymerization will be limited by mass transfer rather than reaction. Experiments show that in the case of RAFT agents with aqueous solubilities greater than 0.1 M[23] and for C_6MA monomer[41] there are no mass transfer limitations. The solubility of RAFT agent **1** in water was measured to be 0.12 M by UV adsorption, so these reactions will not be limited by mass transfer.

Kinetics. Unlike RAFT polymerization in a macroemulsion or miniemulsion, where the destabilization of either the emulsion or the latex during polymerization is always problematic, during RAFT polymerizations in microemulsions, both the microemulsion and the final latex remain thermodynamically or colloidally stable, respectively.

Conversions as a function of time for the microemulsion polymerization of C_6MA with and without RAFT agent **1** are

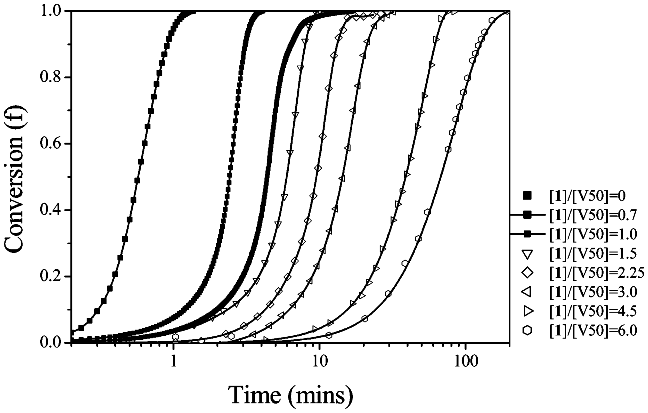


Figure 1. Experimental kinetics for *n*-hexyl methacrylate (C_6MA) solubilized in a microemulsion using the cationic surfactant, dodecyltrimethylammonium bromide (DTAB), and 2-cyanoprop-2-yl dithiobenzoate (**1**) as the RAFT (reversible addition−fragmentation chain transfer) agent. V50 is the initiator 2,2′-azobis(2-amidinopropane) hydrochloride. The microemulsions contained 3 wt % monomer on a surfactant-free basis and a DTAB weight fraction of 12 wt % and were initiated with 0.50 mM V50 initiator with different [**1**]/[V50] ratios at 75 °C.

shown in Figure 1. Microemulsion polymerization in the absence of RAFT agent **1** is completed in only 1 or 2 min, but there is a large drop in the reaction rate with increasing [**1**]/[V50]. Similar decreases in reaction rate have been observed to occur in the bulk polymerization of styrene and methyl methacrylate using RAFT agent **1**.[23,49−53] The decrease in reaction rate in bulk polymerization was attributed to termination of the macro-RAFT radical **3** and/or slow fragmentation. Because of the highly compartmentalized nature of microemulsion polymerization, termination of the macro-RAFT radical **3** is not possible, and the decrease in reaction rate can only be attributed to slow fragmentation or other effects caused by the interaction of the RAFT agents with the heterogeneous environment. These effects include a possible increase in radical exit rates or changes in initiator efficiency. Recently, Plummer et al.[49] reported that a RAFT agent, cumyl dithiobenzoate, synthesized and purified via conventional silica gel chromatography is not 100% pure. After further purification, they concluded that impurities in the RAFT agent can also dramatically inhibit or retard the RAFT polymerization process of methacrylates.

Modeling of Polymerization Kinetics. The fundamental rate equation for microemulsion polymerization is[44,45]

$$\frac{\partial f}{\partial t} = \frac{k_p C_{\mathrm{mon}}^{(\mathrm{part})} N^*}{M_0} \tag{1}$$

where f is the fractional conversion, M_0 is the initial concentration of monomer in moles per liter of microemulsion, k_p is the propagation rate constant, $C_{\mathrm{mon}}^{(\mathrm{part})}$ is the monomer concentration at the locus of polymerization within the growing polymer particles, and N^* is the concentration of propagating radicals. For typical microemulsions, the number of micelles is ∼1000 times more than the number of particles throughout the polymerization, so there is negligible biradical termination. RAFT agent, once added, can of course act as a chain transfer agent, but it will not change the number of propagating radicals. Therefore, if the reaction rate is fast compared to the half-life of the initiator, the number of free radicals will increase linearly with time, i.e.

$$N^* = \rho_0 t = 2k_d[\mathrm{I}]t\gamma_{\mathrm{eff}} \tag{2}$$

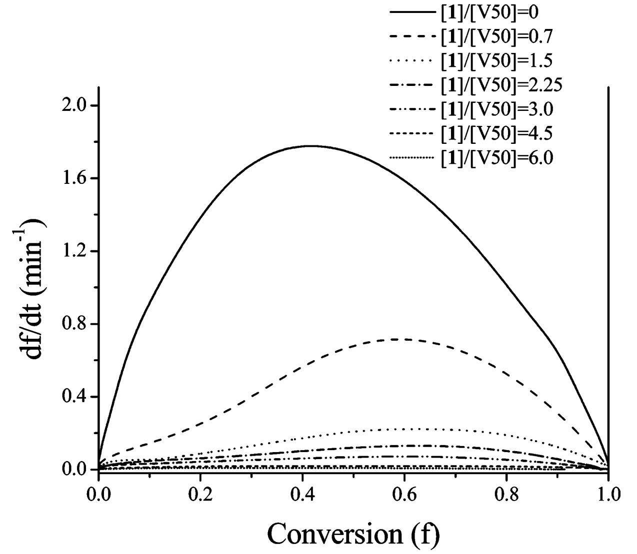


Figure 2. Experimental rate vs conversion profiles obtained by differentiating the data shown in Figure 1. Here 2-cyanoprop-2-yl dithiobenzoate is **1**, and V50 is the initiator 2,2′-azobis(2-amidinopropane) hydrochloride.

Here ρ_0 is the effective rate of radical generation, k_d and [I] are the decomposition rate constant and molar concentration of the initiator, respectively, and γ_{eff} is the initiator efficiency.

For a microemulsion containing 2.64% C_6MA monomer and 12% DTAB, previous SANS studies have confirmed that the concentration of monomer at the locus of polymerization in the polymer particles, $C_{\mathrm{mon}}^{(\mathrm{part})}$, changes linearly with conversion.[44,45]

$$C_{\mathrm{mon}}^{(\mathrm{part})} = C_{\mathrm{mon},0}^{(\mathrm{part})}(1 - f) \tag{3}$$

Substitution of eqs 2 and 3 into eq 1 results in the following analytical expression for the polymerization kinetics:

$$f = 1 - \exp\left(-\frac{k_p C_{\mathrm{mon},0}^{(\mathrm{part})} k_d[\mathrm{I}]\gamma_{\mathrm{eff}}}{M_0} t^2\right) \tag{4}$$

This model predicts that the maximum rate of polymerization occurs at a conversion of $1 - e^{-0.5} \approx 39\%$ for all microemulsion polymerizations and describes quantitatively the polymerization kinetics of C_6MA in microemulsions.[42−45]

Figures 2 and 3 show the polymerization rate vs conversion for the RAFT polymerization in microemulsion at eight different [**1**]/[V50] ratios. The maximum rate of the polymerization without RAFT agent ([**1**]/[V50] = 0) occurs at 41% conversion, in fair agreement with the model predicted rate maximum at 39%. As RAFT agent is added, the rate maximum first shifts to about 60%, but with further increasing RAFT agent concentration moves back to lower conversions (32% conversion at maximum rate for [**1**]/[V50] = 6.0). For a typical microemulsion polymerization under similar conditions without RAFT agent the maximum reaction rate is about 1.8 min^{-1}. At [**1**]/[V50] = 1.0 and [**1**]/[V50] = 1.5, the maximum polymerization rates are 0.34 and 0.22 min^{-1}, respectively (Figure 4), and at even higher [**1**]/[V50] ratios the maximum polymerization rate drops dramatically to about 0.01−0.02 min^{-1}.

Molecular Weights. Figure 5 shows the GPC traces of the products of RAFT microemulsion polymerization for different conversions at [**1**]/[V50] = 3.0. As the microemulsion polymerizes a clear shift in molecular weight is evident, and all the GPC peaks appear to be monomodal. The experimental molecular weight increases linearly with conversion and agrees well

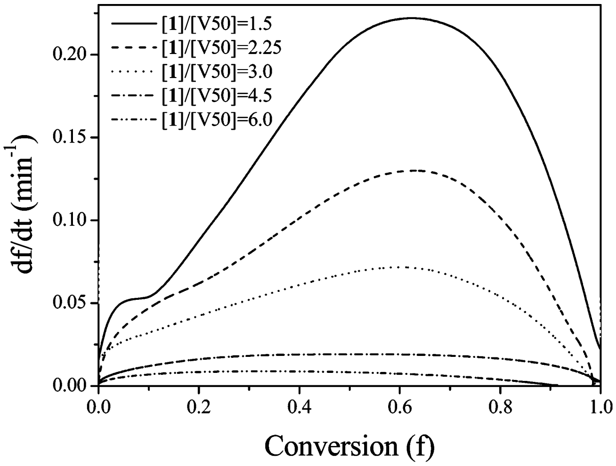


Figure 3. Expanded view of experimental rate vs conversion profiles for values of [**1**]/[V50] above 1.5. Here 2-cyanoprop-2-yl dithiobenzoate is **1**, and V50 is the initiator 2,2′-azobis(2-amidinopropane) hydrochloride.

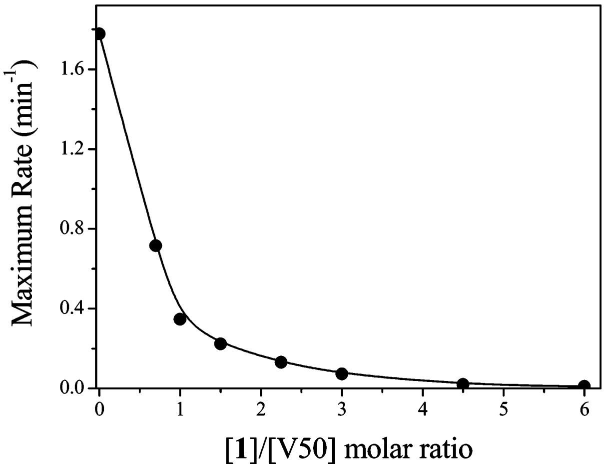


Figure 4. Maximum reaction rate (df/dt) vs [**1**]/[V50] molar ratio for n-hexyl methacrylate (C_6MA) solubilized in a microemulsion using the cationic surfactant, dodecyltrimethylammonium bromide (DTAB), and 2-cyanoprop-2-yl dithiobenzoate (**1**) as the RAFT (reversible addition−fragmentation chain transfer) agent. V50 is the initiator 2,2′-azobis(2-amidinopropane) hydrochloride. The microemulsions contained 3 wt % monomer on a surfactant-free basis and a DTAB weight fraction of 12 wt % and were initiated with 0.50 mM V50 initiator with different [**1**]/[V50] ratios at 75 °C.

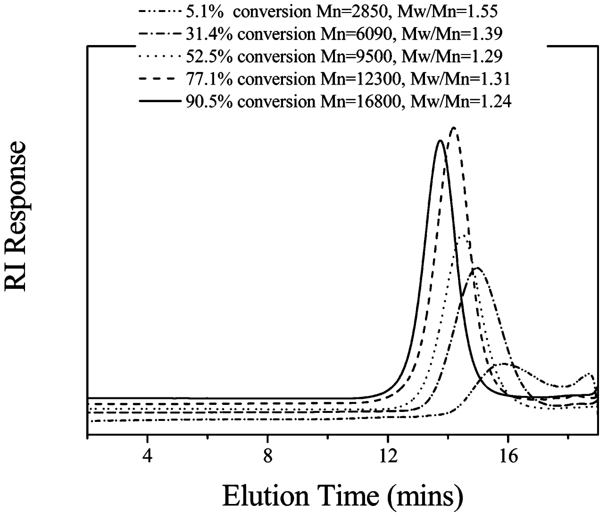


Figure 5. Evolution of gel permeation chromatography traces with conversion obtained from polymerization of n-hexyl methacrylate (C_6-MA) solubilized in a microemulsion using the cationic surfactant, dodecyltrimethylammonium bromide (DTAB), and 2-cyanoprop-2-yl dithiobenzoate (**1**) as the RAFT (reversible addition−fragmentation chain transfer) agent. V50 is the initiator 2,2′-azobis(2-amidinopropane) hydrochloride. The microemulsions contained 3 wt % monomer on a surfactant-free basis and a DTAB weight fraction of 12 wt % and were initiated with 0.50 mM V50 initiator and [**1**]/[V50] = 3.0. M_n and M_w are the number- and weight-average molecular weights, respectively.

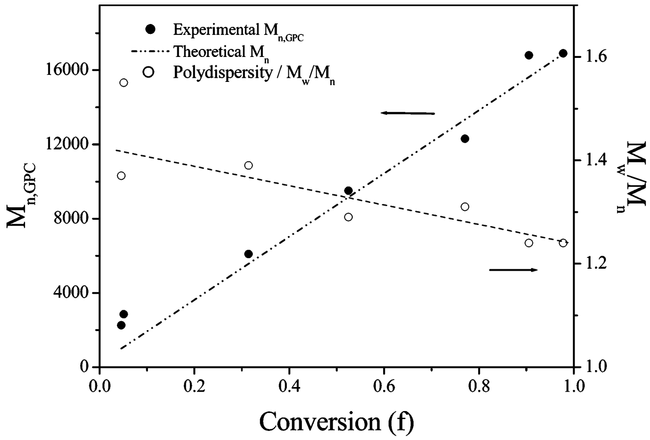


Figure 6. Measured number-average molecular weight ($M_{n,GPC}$) and ratio of the weight-average molecular weight to the number-average molecular weight as a function of conversion. The data are from polymerization of n-hexyl methacrylate (C_6MA) solubilized in a microemulsion using the cationic surfactant, dodecyltrimethylammonium bromide (DTAB), and 2-cyanoprop-2-yl dithiobenzoate (**1**) as the RAFT (reversible addition−fragmentation chain transfer) agent. V50 is the initiator 2,2′-azobis(2-amidinopropane) hydrochloride. The microemulsions contained 3 wt % monomer on a surfactant-free basis and a DTAB weight fraction of 12 wt % and were initiated with 0.50 mM V50 initiator and [**1**]/[V50] = 3.0 at 75 °C. The theoretical line represents the conversion calculated from $M_{n,theory} = FW_{RAFT} + (Mol_{mon}FW_{mon}f)/Mol_{RAFT}$, where FW_{mon} is the monomer molecular weight and Mol is the total moles of RAFT agent or monomer.

with the theoretical molecular weight given by $M_{n,theory} = FW_{RAFT} + (Mol_{mon}FW_{mon}f)/Mol_{RAFT}$, where FW_{mon} is the monomer molecular weight and Mol is the total moles of RAFT agent or monomer (Figure 6). This theoretical molecular weight assumes that all RAFT agent reacts early in the polymerization, and the observed linear increase of molecular weight with conversion hints that the RAFT polymerization in microemulsion at this [**1**]/[V50] molar ratio is relatively controlled.[18,20] More convincing evidence is the polydispersity of the product, which, with increasing conversion, decreases from 1.4 to about 1.2.

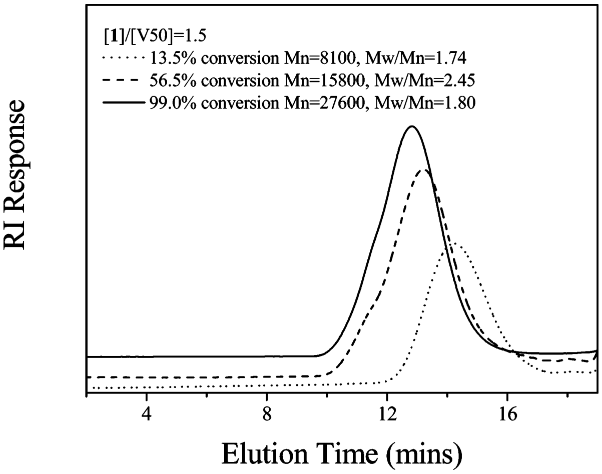
Figure 7 shows RAFT microemulsion polymerization GPC traces for different conversions at [**1**]/[V50] = 1.5. At this [**1**]/[V50] molar ratio, a shift in molecular weight with conversion is again observed, but a closer examination of Figure 7 shows that a slightly bimodal distribution develops, especially at high conversions. The experimental molecular weights at [**1**]/[V50] = 1.5 still increase with conversion, but they deviate substantially from the theoretical molecular weight (Figure 8). The polymerization yields polymers with a polydispersity ∼2, which demonstrates that the RAFT polymerization at this condition, i.e., low [**1**]/[V50] ratio, is not completely controlled.

Table 1 lists the molecular weights and polydispersities of C_6MA polymers prepared by RAFT/microemulsion polymerization at eight different ratios. In general, the molecular weights and polydispersity decrease with increasing [**1**]/[V50] ratio. This indicates that the RAFT process exerts some kind of control at all ratios, but for RAFT/microemulsion polymerizations at [**1**]/[V50] ratios below 1.5 the polymers show high polydispersity and a slightly bimodal GPC curve. Thus, RAFT/micro-

Table 1. Number-Average Molecular Weight (M_n), Polydispersity (Ratio of the Weight-Average Molecular Weight M_w to M_n), Particle Diameter, Number of Polymer Chains in Each Latex Particle, and Number Density of Latex Particles Resulting from Polymerization of a Microemulsion Containing the Monomer *n*-Hexyl Methacrylate and the Surfactant Dodecyltrimethylammonium Bromide[a]

[**1**]/[V50] molar ratio	0	0.7	1.0	1.5	2.25	3.0	4.5	6.0
M_n	$>1 \times 10^7$	4.7×10^4	3.4×10^4	2.8×10^4	2.3×10^4	1.7×10^4	1.2×10^4	8.7×10^3
M_w/M_n		5.06	3.85	1.80	1.43	1.24	1.20	1.25
particle size (nm)	45.0	21	18.5	20.5	20.7	22.6	29.4	30.0
no. of chains in each particle	1	65	62	102	128	225	700	1027
no. density of latex particles	5.3×10^{17}	5.2×10^{17}	7.6×10^{17}	5.6×10^{18}	5.4×10^{18}	4.2×10^{18}	1.9×10^{18}	1.8×10^{18}

[a] 2-Cyanoprop-2-yl dithiobenzoate (**1**) is the RAFT (reversible addition−fragmentation chain transfer) agent, and polymerization is carried out at different [**1**]/[V50] molar ratios. V50 is the initiator 2,2′-azobis(2-amidinopropane) hydrochloride. The microemulsions contain 3 wt % monomer on a surfactant-free basis and a surfactant weight fraction of 12 wt %. The microemulsions were initiated with 0.50 mM V50 initiator at 75 °C.



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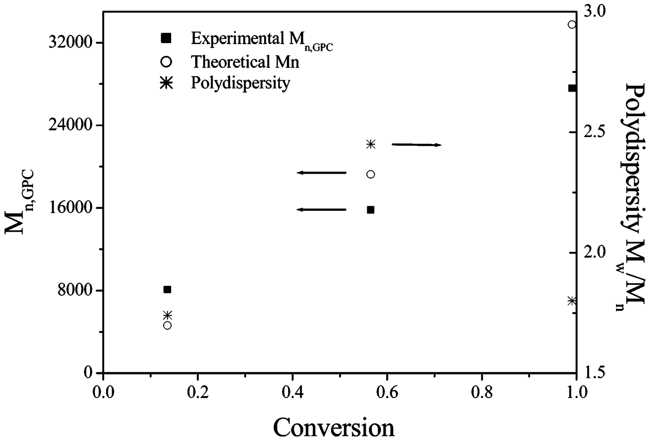

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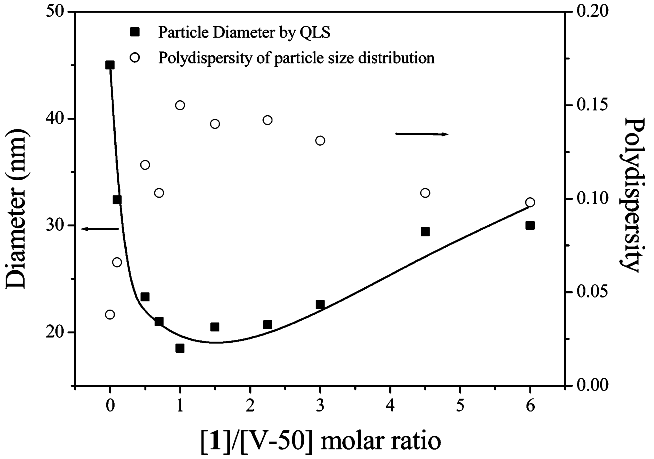

Figure 9. Average hydrodynamic diameter and polydispersity as measured by quasielastic light scattering (QLS) of the final latex particles as a function of the [**1**]/[V50] ratio. 2-Cyanoprop-2-yl dithiobenzoate (**1**) is the RAFT (reversible addition−fragmentation chain transfer) agent, and V50 is the initiator 2,2′-azobis(2-amidinopropane) hydrochloride.

emulsion polymerizations at lower [**1**]/[V50] ratios are not completely controlled.

The bimodal distribution of the GPC curves and high polydispersities at [**1**]/[V50] lower than 1.5 could result from either of two mechanisms. First, for a microemulsion with compositional values of $\alpha = 3\%$ and $\gamma = 12\%$, the number density of monomer-swollen micelles is calculated to be ~1.0 mM, assuming that the diameter of monomer-swollen micelles is ~15 nm[1,46] and the typical surface area per DTAB surfactant at the monomer/water interface is 0.65 nm^2.[54,55] For the polymerizations with [**1**]/[V50] exceeding 3.0 and demonstrating good control, the concentration of [**1**] exceeds the concentration of micelles. At [**1**]/[V50] = 1.5, the concentration of [**1**] is less than the concentration of micelles, and the polymerization is poorly controlled. In this case, once a radical enters a monomer swollen micelle, the polymerization may initially be uncontrolled since there will not necessarily be a RAFT molecule in the micelle. Such uncontrolled reactions could produce higher molecular weight polymers that could give a shoulder similar to those seen in the GPC plots (Figure 6). However, since the diffusion of **1** is fast, there are RAFT agents continuously entering the micelles, and the reaction will eventually come under control. Thus, the polymerization will not produce any of the ultrahigh molecular weight polymer (~10^7 Da) that characterizes conventional microemulsion polymerization. An alternative explanation of the high polydispersities at low RAFT concentration is that all of the RAFT agent could be consumed early in the polymerization, and particles nucleated later in the polymerization could be starved for RAFT. Further work is needed to clarify this situation.

Particle Size and Latex Properties. After polymerization, the resulting latex particles are colloidally stable for at least one year. Figure 9 shows the variation of latex particle diameter and size polydispersity as a function of [**1**]/[V50]. The addition of RAFT agent produced small particles, ranging in diameter from 18 to 30 nm. These are smaller than those produced by conventional microemulsion polymerization (without RAFT agent), which have a diameter of 45 nm under the same conditions. The particles made with **1** are also more monodisperse than those prepared by conventional microemulsion polymerization.

The number of chains per particle can be estimated from the particle diameter, the density of latex particles, and the molecular weight of polymer chains (Table 1). In conventional microemulsion polymerization the final latex particles are composed of one or at most a very few high molecular weight chains. In contrast, RAFT polymerizations in microemulsions yield latex particles made of hundreds of polymer chains with low molecular weight polydispersity.

Conclusion

RAFT polymerization of C_6MA monomer in a microemulsion using DTAB as surfactant and 2-cyanoprop-2-yl dithiobenzoate as the RAFT agent yields stable latex particles much smaller (18−30 nm) than those produced by conventional microemulsion polymerization. At high RAFT agent concentrations the polymerizations were controlled and living, producing polymer with a low final polydispersity and displaying a linear increase in molecular weight with conversion. At lower RAFT agent concentrations a mixture of polymers formed, suggesting that portions of the reaction are uncontrolled.

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