Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Tang, Ruiting , Xue, Yin , Yang, Wuli , Zha, Liusheng and Fu, Shoukuan(2007) 'Rich-Syndiotacticity of Poly(cyclohexyl methacrylate) Prepared by Modified Microemulsion Polymerization', Journal of Macromolecular Science, Part A, 44: 6, 569 — 575

To link to this Article: DOI: 10.1080/10601320701283586

URL: http://dx.doi.org/10.1080/10601320701283586

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2007) **44**, 569–575

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320701283586

Rich-Syndiotacticity of Poly(cyclohexyl methacrylate) Prepared by Modified Microemulsion Polymerization

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Received andReceived and accepted January, 2007

Nanoscale poly(cyclohexyl methacrylate) (PCHMA) particles were prepared by a modified microemulsion polymerization procedure. ^{13}C-NMR analysis suggested that such PCHMA samples were higher in syndiotactic content (61–72% rr) and lower in isotactic content (1–3% mm). The glass transition temperatures (T_g's) of the products were also higher than that reported in the literature. The polymer properties, such as particle size, molecular weight, tacticity, and T_g were affected by the reaction conditions. The smaller the particle size, the higher the syndiotacticity, the lower the isotacticity and the greater the molecular weight, then the higher the T_g of the PCHMA samples. Possible mechanism of rich-syndiotacticity was also discussed.

Keywords: Modified microemulsion polymerization; poly(cyclohexyl methacrylate); nanoparticles; tacticity; glass transition temperature

1 Introduction

By use of different surfactants and co-surfactants, various microlatexes with particle sizes ranging from 20 to 50 nm can easily be obtained by microemulsion polymerization (1–3). Traditional microemulsion polymerization usually produces microlatexes with relatively low polymer contents (<10 wt%) and low weight ratios of polymer to surfactant ($\leq$1), with only limited application in industry. Recently, our laboratory developed a modified microemulsion polymerization procedure by which nanosized (15–50 nm)poly (methyl methacrylate) latexes with low surfactant content (1–2 wt%) and high polymer content (15–35 wt%) could be prepared (4, 5).

Polymerization of a nonpolar monomer, such as styrene, in a traditional microemulsion system starts from monomer-swollen micelles that are typically 6 nm in diameter (6). The resulting latex particles are often 20–30 nm in diameter, which are much smaller than those obtained by traditional emulsion polymerization (7–12). The molecular weights of the polymers usually exceed 10^6g/mol, and each particle contains only one or a few macromolecules. In a Θ solvent or in the bulk amorphous phase, the unperturbed root-mean-square end-to-end distance of PMMA($M_w = 1 \times 10^6$g/mol) molecule is about 55 nm (13), therefore, the polymer chains in the particles of polymerized microemulsions, which's diameter is around 20–30 nm, are tightly collapsed into a restricted volume. As the chain propagates in such a restricted volume, the resulting polymers are conformationally restricted and their properties are affected.

It is the same case in a modified microemulsion polymerization procedure. As we have reported before, PMMA and poly(ethyl methacrylate) (PEMA) polymerized by modified microemulsion polymerization procedure had higher glass transition temperatures (over 120°C and 75°C, respectively) and were rich in syndiotactic and lower in isotactic contents (61–64% rr, 5–6% mm, respectively) (5, 14).

In this paper, the study were extended to poly(cyclohexyl methacrylate) (PCHMA), which has a relatively higher glass-transition temperature and is extensively used as a component for special coatings (15). PCHMA latex could also be prepared by this modified microemulsion polymerization process. The reaction conditions which affect the PCHMA properties including particle size, molecular weight, tacticity and glass transition temperature etc. were discussed and the possible mechanism was proposed.

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2 Experimental

2.1 Materials

Cyclohexyl methacrylate (CHMA, 98%, Aldrich) was purified by running through alumina column before use. Sodium dodecyl sulfate (SDS) was purchased from Shanghai Shenggong Bioengineering Co. and used as received. Ammonium persulfate (APS) from Shanghai Aijian Reagent Factory was purified by recrystallization in water. Ascorbic acid from Shanghai Chemical Reagent Co. and a 30% hydrogen peroxide aqueous solution from Shanghai Taopu Chemical Factory were used as received. 1-pentanol (POH), methanol and chloroform from Shanghai Chemical Reagent Co. were used as received. Deionized water was used for all experiments.

2.2 Polymerization

The recipes of modified microemulsion polymerizations under various conditions are shown in Tables 1 and 2. The general procedure of modified microemulsion polymerization with SDS/POH as the surfactant/cosurfactant combination and APS as the initiator can be described as follows. The so-called pre-microemulsion, composed of the 2.1 g of SDS, 0.3 g of POH, 38 g of water, and a small fraction of CHMA (0.5 g) was added into a 100-mL, three-necked flask equipped with a reflux condenser, an addition funnel, a nitrogen gas inlet and outlet, and a magnetic stirring bar. The pre-microemulsion was heated to $70 \pm 2°C$ and stirred under a nitrogen atmosphere for 1 h until a transparent microemulsion was obtained. Then, 0.114 g of APS, which was dissolved in 4 g of water, was added to initiate the polymerization. After adding the initiator, the appearance of the microemulsion changed to slightly bluish, but still transparent. Then, the rest of the monomer (5 g) in the addition funnel were added dropwise into the reaction system in 1 h. After the post-addition of monomer was completed, stirring was continued for another 2 h at the reaction temperature to essentially complete the conversion of monomer.

To precipitate the polymer, 10 mL of the latex dispersion was added dropwise to 100 mL of vigorously stirred methanol and the mixture was allowed to stand overnight. The precipitated polymer was vacuum filtered, washed successively with methanol and water, then dried in vacuo at ambient temperature for 24 h.

2.3 Characterization

Particle size (D_z) and polydispersity of the size distribution(PDI)16 of polymer microlatexes were determined by dynamic light scattering (DLS) on a Malvern 4700 from Malvern Instruments, Ltd. The morphology of the particles was observed by JEM2010 transmission electron microscope (TEM), and the sample was negative stained by phosphate-tungstic acid. Molecular weight (M_w) and molecular weight distribution (M_w/M_n) were determined by Agilent 1100 gel permeation chromatography (GPC), with polystyrene as the calibration standard. To determine the tacticities of the PCHMA samples, a Bruker DMX 500 NMR spectrometer was used for ^{13}C-NMR analysis with $CDCl_3$ as a solvent. The glass transition temperature (T_g) values of the samples were measured by Perkin Elmer Pyris 1 differential scanning calorimeter (DSC) at a heating rate of 10°C/min followed by rapid cooling.

2.4 Calculations of N_d and n_p

The number of latex particles per milliliter of microlatex (N_d) and the number of polymer chains per latex particle (n_p) can

Table 1. Characterization of PCHMA microlatexes prepared by modified microemulsion polymerization at 35°C

Sample	A1	A2	A3	A4	A5	A6	A7
SDS/POH (g)	2.1/0.3	2.1/0.3	2.1/0.3	2.1/0.3	2.1/0.3	2.1/0.3	2.1/0.3
H_2O_2/ascorbic-acid (g)	0.06/0.09	0.06/0.09	0.06/0.09	0.06/0.09	0.06/0.09	0.12/0.18	0.30/0.45
CHMA (g)^a	0.5 + 5	0.5 + 5	0.5 + 5	0.5 + 3	0.5 + 1	0.5 + 5	0.5 + 5
H_2O (ml)	42	42	42	42	42	42	42
Time (min)^b	60	30	12	6	3	12	12
D_z (nm)	14	14	17	18	16	12	12
PDI	0.23	0.22	0.14	0.17	0.18	0.34	0.36
N_d (10^{16})	8.3	8.3	4.6	2.5	1.5	13.1	13.1
n_p	10.1	4.9	4.7	4.2	3.4	4.9	6.6
$M_w(10^5)$	0.94	1.93	3.64	4.87	4.21	1.21	0.90
M_w/M_n	3.3	2.7	2.7	2.2	2.5	2.4	2.6
T_g(°C)	113	113	113	114	114	113	111
Tacticity (mm/mr/rr)	1/27/72	1/27/72	1/29/70	1/29/70	1/30/69	1/28/71	1/28/71

^{a}The first part of the monomer was in the pre-microemulsion and the second part was post-added.
^{b}Feeding time of the post-added CHMA monomer.

Table 2. Characterization of the PCHMA microlatexes prepared by modified microemulsion polymerization at different temperatures

Sample	A8	A9	A10	A11	A12
SDS/POH (g)	2.1/0.3	2.1/0.3	2.1/0.3	2.1/0.3	2.1/0.3
Initiator (g)	APS (0.114)	APS (0.114)	APS (0.114)	APS (0.6)	AIBN (0.07)
Reaction temp. (°C)	60	70	80	70	70
CHMA (g)[a]	$0.5+5$	$0.5+5$	$0.5+5$	0.5+5 (SH 0.06g)[c]	$0.5+5$
H_2O (ml)	42	42	42	42	42
Time (min)[b]	60	60	60	60	30
D_z (nm)	21	20	21	22	34
PDI	0.19	0.26	0.23	0.17	0.14
N_d (10^{16})	2.5	2.8	2.5	2.1	0.58
n_p	9.5	16.7	36.5	205	24.0
M_w (10^5)	3.37	1.66	0.88	0.18	5.68
M_w/M_n	2.1	3.0	3.3	1.7	1.8
T_g (°C)	113	113	110	103	112
Tacticity (mm/mr/rr)	3/32/65	3/33/64	3/36/61	2/35/63	3/33/64

[a] The first part of the monomer was in the pre-microemulsion and the second part was post-added.

[b] Feeding time of the post-added CHMA monomer.

[c] SH was used as the chain-transfer agent to reduce the molecular weight of the polymer.

be estimated from the following equations: (17)

$$N_d = 6\omega/(\pi d_p D_w^3)$$

$$n_p = (1/6)\pi D_w^3 d_p/(M_w/N_A)$$

In the equations above, ω refers to the weight of polymer per milliliter of microlatex, d_p is the density of polymer microlatex particles (1.1 g/cm^3 for PCHMA microlatex), M_w is the weight-average molecular weight and N_A is Avogadro's constant with D_z instead of D_w used as an estimation.

3 Results and Discussion

3.1 General Characteristics of PCHMA Microlatexes

The particle sizes (D_z), polydispersity of the size distribution (PDI), weight-average molecular weights (M_w), glass transition temperatures (T_g) and tacticities of PCHMA microlatexes polymerized by modified microemulsion polymerization under various conditions are shown in Tables 1 and 2. Diameters of these PCHMA latexes were in the range of 10–40 nm and most of the PDIs were in the range of 0.10–0.30. The weight-average molecular weights (M_w) were about $\sim 10^5$ g/mol, except sample (A11) polymerized at the presence of a chain-transfer agent dodecanethiol (SH), which had the M_w of 1.8×10^4 g/mol. This could be attributed to the chain-transfer to SH, which resulted in a decrease in the molecular weight and dramatically increase in the number of polymer chains per particle ($n_p = 205$). The PCHMA samples were higher in syndiotactic content (61–72% rr), lower in isotactic content (1–3% mm), and had higher T_g values than reported before (18). The effect of polymerization conditions on particle sizes,molecular weights, tacticities and glass transition temperatures were discussed below separately.

3.3 Particle Size and Molecular Weight of PCHMA Samples

3.3.1 Effect of the Amount of Post-added Monomer

The weight-average molecular weights (M_w) just varied slightly and the particle sizes (D_z) almost did not change as the amount of post-added monomer increased from 1 g to 5 g (Table 1, A5 → A4 → A3), which is also proved by the TEM photographs (Figure 1). The number of polymer particles per milliliter of latex (N_d) continuously increased and the number of polymer chains per latex particle (n_p) almost kept constant with increased amount of post-added monomer. Usually, the polymerizations are postulated to occur in monomer-swollen micelles, which behave as nanoreactors (19). Polymer particles formed initially in the pre-microemulsion system are viewed to act as "seeds" for further seeding polymerization with the constant supply of monomer via dropwise post-addition. But as the latexes formed throughout the polymerization process, radicals generated in the aqueous phase were trapped by those newly-formed monomer-starved latexes and chain propagation proceeded there because of which's great totally surface. As a result, N_d increased and D_z kept unchanged with increase amount of post-added monomer.

3.3.2 Effect of the Speed of Monomer Post-addition

As reported in Table 1, the particle sizes increased slightly and the weight-average molecular weights (M_w) of the PCHMA samples increased obviously with increased speed of monomer post-addition (A1 → A2 → A3), as was shown in Table 1 and Figure 2. The number of polymer particles per milliliter of latex (N_d) decreased from 8.3×10^{16} to 4.6×10^{16} as the speed of monomer post-addition increased from 5 g/60min (A1) to 5 g/12min (A3), it seems that with increased speed of monomer post-addition, less number of latexes were formed throughout the polymerization process and the particle sizes increased accordingly. The monomer post-addition process was a "monomer starved" procedure for the modified microemulsion polymerization as we have reported before (19, 20). When the post-addition speed was very slow, the supply of monomer couldn't satisfy the need of the propagating chain radicals in their lifetime and the chain radicals died in starving. On one hand the resulting polymer had low M_w of 0.9×10^5 g/mol (A1), on the other hand there would be more polymer chains per latex particle ($n_p = 10.1$). As the post-addition was applied at a proper speed and the need of the propagating chain radicals was satisfied, n_p of the PCHMA sample decreased to 4.7(A3) and M_w increased dramatically to 3.6×10^5 g/mol. It could be concluded that in order to obtain PCHMA products with high molecular weight, adjusting the monomer post addition to a proper speed is very important in this modified microemulsion polymerization procedure.

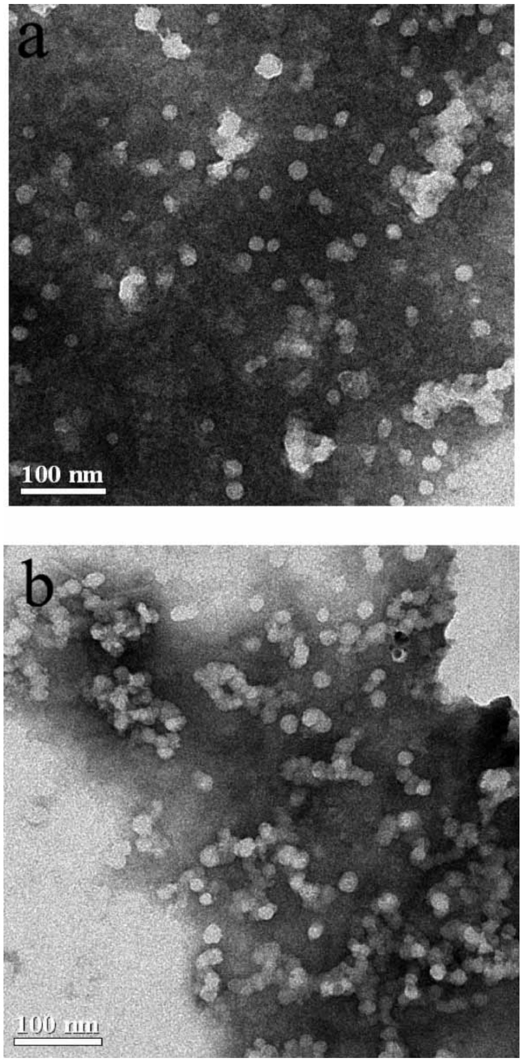

Fig. 1. TEM photographs of PCHMA sample A4(a) and A3(b).

3.3.3 *Effect of the Amount of Initiator*

Both the particle sizes and the molecular weights (M_w) of the PCHMA samples decreased as the amount of H_2O_2/ascorbic increased from 0.06 g/0.09 g to 0.30 g/0.45 g(A3 → A6 → A7). According to Table 1, the number of polymer particles per milliliter of latex (N_d) increased dramatically from 4.6×10^{16} to 13.1×10^{16}. This result indicated that more particles were formed with increased amount of initiator. As the reaction temperature of this redox initiated system was relative low (35°C), it was less possible for the inter-particle aggregation to occur, then the number of nucleating particles increased, the particle size of PCHMA microlatex decreased. Meanwhile, the M_w of the resulting polymers decreased from 3.64×10^5 g/mol to 0.90×10^5 g/mol (Table 1, A3 → A6 → A7), which may be attributed to the larger number of initiation centers and reaction centers at higher initiator concentration.

3.3.4 *Effect of the Initiator Type and the Reaction Temperature*

The PCHMA particle sizes varied dramatically with the type of initiator and the reaction temperature as shown in Table 1 and Table 2. Generally, the particle sizes of PCHMA prepared by redox initiators (A1–A7) were smaller than those of the PCHMA prepared by thermal initiators (A8–A12). PCHMA microlatexes prepared with oil-soluble AIBN initiator (A12) had the largest particle size. It seems that smaller particles are liable to be formed at lower reaction temperature. This may be attributed to the less possibility of aggregation between the nucleating particles at lower temperature.

The M_w of the PCHMA samples varied with the type of initiator, too. PCHMA prepared with oil-soluble AIBN initiator (A12) had the highest M_w. As reported in Table 2, when the reaction temperature increased from 60°C to 80°C (A8 → A9 → A10), the M_w of the PCHMA samples decreased from 3.37×10^5 g/mol to 0.88×10^5 g/mol. This may be attributed to the larger number of initiation centers and reaction centers formed at higher reaction temperatures.

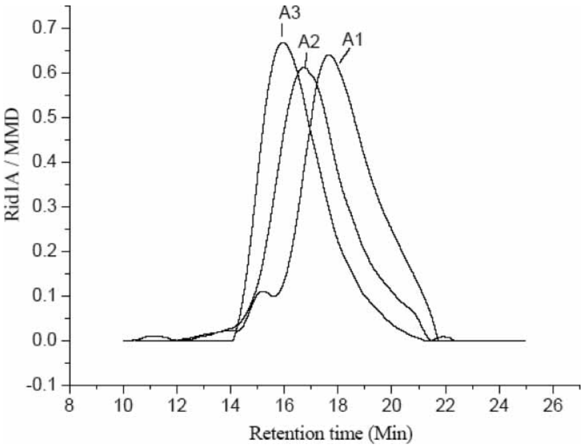

Fig. 2. GPC of PCHMA sample (A1, A2, A3).

3.4 Glass Transition Temperature and Tacticitiy of PCHMA Samples

Both Table 1 and Table 2 showed that the T_g values of PCHMA samples prepared by modified microemulsion polymerization were about 113°C, which were generally higher than the T_g value reported before (83°C) (18). It could be compared with the T_g value (115°C) of the rich-syndiotactic PCHMA sample (rr = 97% and $M_w = 2.58 \times 10^5$ g/mol) polymerized by solution polymerization at rather lower reaction temperature (−78°C) with a unique initiator ($S_mM_e(C_5Me_5)_2$) (21). To explain the high T_g's, the microstructure of the obtained polymers was determined by the ^{13}C-NMR spectrum. Figure 3 is the ^{13}C-NMR spectrum of PCHMA sample A1, the contents of rr, mr and mm triad were calculated by the tacticity splittings in the 175–179 ppm region, corresponding to the carbonyl carbon resonances. The intensities of mm, mr, and rr triad resonances in the spectrum of the ^{13}C-NMR data were measured by integrating the spectral regions of 175.5–176.2, 176.5–177.1, and 177.1–178.1 ppm, respectively, according to literature (22). The relative error is around 1%.

One aim of the present research was to determine whether the polymerization of methacrylate monomers with bulkier side-group than methyl methacrylate and ethyl methacrylate in a restricted volume would more affect the tacticities of the polymers. As was shown in Tables 1 and 2, the PCHMA samples prepared by modified microemulsion polymerization were more rich-syndiotactic than PMMA and PEMA samples polymerized at the same temperature as reported before (4, 5, 14) (Table 3). PCHMA samples were obtained with triad tacticity rr = 61–72% and mm = 1–3% under different reaction temperatures.

This rich-syndiotacticity may be caused by both the restricted volume effect of nanoparticles and the activation enthalpy effect during the propagation process. It is considered that in the small volume of a latex particle formed in microemulsion, the propagating polymer chains must have more gauche conformations than in its unperturbed state, especially near the surface of the particle, the path of its random walk would be forced to fold back into the particle (25). Therefore, the polymer formed in a microemulsion was conformationally restricted and the potential energy was higher. To compensate for this effect, the propagating chain would be liable to have smaller root-mean-square end-to-end distance and lower potential energy during the propagation process (26). According to the discussions above, we can suppose that the rr contents of the PCHMA samples would be affected by the particle sizes, as was validated by experimental results.

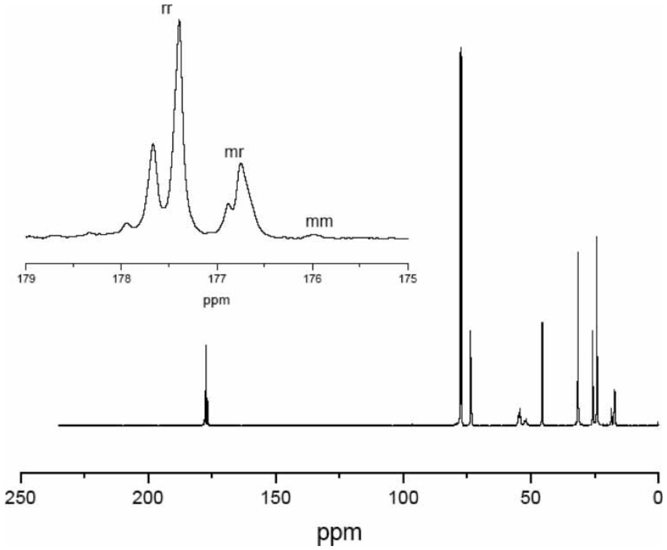

Fig. 3. ^{13}C-NMR spectrum (500MHz) of PCHMA sample A1.

Table 3. The NMR, DSC dData of poly(methacrylate)s prepared by modified microemulsion polymerization

Sample	rr	mr	mm	Reaction temp. (°C)	Tg (°C)	Tg^a (°C)
PMMA1	0.56	0.35	0.09	70	124	105^{23}
PMMA2	0.61	0.33	0.06	35	130	105
PEMA1	0.61	0.34	0.05	70	82	65^{24}
PEMA2	0.64	0.31	0.05	35	83	65

^{a}Tg values, adopted from the literature (23, 24), the polymers were prepared by common radical polymerization.

The difference in activation enthalpy ($\Delta H^{\ddagger}$) and that in activation entropy ($\Delta S^{\ddagger}$) between the isotactic and syndiotactic specific propagations in modified-microemulsion polymerization systems (A1, A8, A9, A10) were discussed. According to literature (27), $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be determined by the plot according to the following equation:

$$\ln\left(\frac{P_i}{P_s}\right) = \frac{\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}}{R} - \frac{\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}}{RT}$$

Where P_i and P_s are the mole fractions of isotactic and syndiotactic dyads (square root value of mm and rr content),

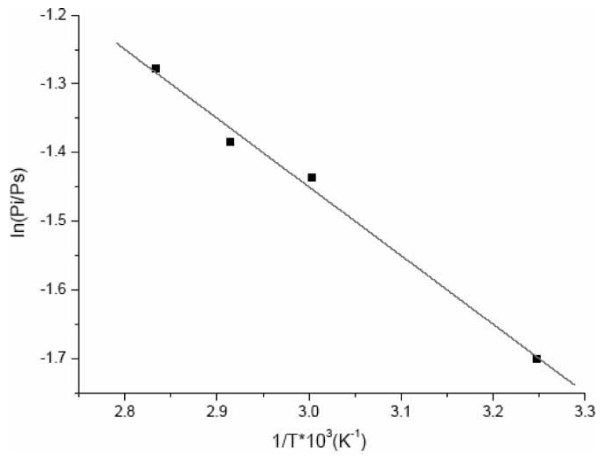

Fig. 4. Plots for the polymerizations of CHMA under different polymerization temperatures.

respectively, R is the gas constant (1.987 cal/mol · K), T is the polymerization temperature (K). Figure 4 is the plot of $\ln(P_i/P_s)$ to 1/T:

It can be obtained from Figure 4 that $\Delta H_s^{\ddagger} - \Delta H_i^{\ddagger} = -2185 \pm 153$ cal/mol for modified microemulsion polymerization. The rather negative value of $\Delta H_s^{\ddagger} - \Delta H_i^{\ddagger}$ indicated that the syndiotactic propagation was more favored by enthalpy in a restricted volume of a modified microemulsion polymerization system.

It can also be obtained from Figure 4 that $\Delta S_s^{\ddagger} - \Delta S_i^{\ddagger} = -3.65 \pm 0.46$ cal/mol · K for modified microemulsion polymerization. The negative values of $\Delta S_s^{\ddagger} - \Delta S_i^{\ddagger}$ indicated that the syndiotactic propagation was slightly disadvantaged by entropy, but in general, it was more favored by activation energy in a modified microemulsion polymerization system as we took both enthalpy and entropy into account.

Glass-transition temperatures about 113°C were obtained for most of the PCHMA samples polymerized by modified microemulsion polymerization as compared with values of 83°C (18) reported previously. As we have discussed above, the polymerization conditions can affect the particle sizes, molecular weights and tacticities of PCHMA samples. The glass transition temperatures are affected by all of them. It was shown in Tables 1 and 2 that the ratio of triads (rr, mr, mm) and the molecular weights are the major influencing factors of the glass transition temperature. The higher the content of rr triad, the lower the content of mm triad and the greater the molecular weight, then the higher the T_g value. The PCHMA sample polymerized at the presence of a chain-transfer agent dodecanethiol (SH) (A11) had slightly lower syndiotacticity than that polymerized without it (A9), but the molecular weight decreased dramatically and accordingly, the T_g value, too.

PCHMA samples were also polymerized by traditional microemulsion polymerization as reported in Table 4 to compare with the PCHMA samples polymerized by modified microemulsion polymerization in Tables 1 and 2. It could be concluded that the tacticities of these samples prepared by either method at the same temperature were almost identical.

Table 4. Compositions and polymer properties of the PCHMA samples prepared by traditional microemulsion polymerization

Sample	D1	D2	D3
SDS/POH (g)	5.4/0.7	5.4/0.7	5.4/0.7
Initiator (g)	H_2O_2/ascorbic acid (g) 0.06/0.09	H_2O_2/ascorbic acid (g) 0.06/0.09	APS(g) 0.114
Reaction Temp. (°C)	35	35	70
CHMA (g)	1	1 (SH 0.02g)	1
H_2O (ml)	44	44	44
D_z (nm)	21	21	29
PDI	0.07	0.07	0.10
N_d (10^{16})	0.43	0.43	0.16
n_p	7.1	133	7.3
M_w (10^5)	4.51	0.24	11.5
M_w/M_n	1.8	1.6	2.4
T_g (°C)	113	106	111
Tacticity (mm/mr/rr)	2/28/70	1/30/69	3/33/64

The PCHMA sample polymerized by traditional microemulsion polymerization (Table 4) also had high glass-transition temperatures except for sample D2, which was prepared at the presence of a chain-transfer agent dodecanethiol (SH). Sample D2 had slightly lower syndiotacticity than sample D1 polymerized without it, but the molecular weight decreased dramatically and the T_g value decreased accordingly.

4 Conclusions

This is the first report of polymerizations of PCHMA by modified microemulsion polymerization procedures. The polymerizations were carried out with thermal initiators APS, AIBN and redox initiator ascorbic acid/hydrogen peroxide at various temperatures. Polymerization in modified microemulsion systems gave a relatively higher molecular weight ($\sim 10^5$ g/mol) and the resulting polymers had higher syndiotacticity (rr), lower isotacticity(mm). The particle size, molecular weight, triad (rr, mr, mm) ratio and T_g of the PCHMA samples were influenced by the reaction conditions. The smaller the particle size, the higher the syndiotacticity, the lower the isotacticity, the greater the molecular weight, then the higher the T_g of PCHMA. The PCHMA from this research had higher glass-transition temperatures (113°C) than reported before, probably due to their richer syndiotacticity and lower isotacticity.

5 Acknowledgments

The authors thank the National Natural Science Foundation of China 20374011 and the Major State Basic Research Development program (G1999064802) for their financial supports.

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