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The Relationship of Reaction Temperature, T_g and Rich-Syndiotacticity of Poly(alkyl methacrylate)s in Modified Microemulsion Polymerization

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Nanoscale poly(alkyl methacrylate)s including poly(methyl methacrylate), poly(ethyl methacrylate), poly(cyclohexyl methacrylate), poly(iso-butyl methacrylate) and poly(benzyl methacrylate) were prepared by a modified microemulsion polymerization procedure. NMR analysis suggested that these poly(methacrylate)s samples were higher in syndiotactic content, lower in isotactic content and the glass transition temperatures (T_gs) of them were also higher than those reported in the literature. The tacticities of the poly(methacrylate)s, beside the restricted volume effect of nanoparticles during the modified microemulsion polymerization, were mainly influenced by the reaction temperature, the lower the reaction temperature, the higher the syndiotacticity of the products. The syndiotacticity of the product decreased obviously when the polymerization was carried out at a temperature far above the T_g of the resulting polymer. It was also shown that the tacticity of the polymer was affected by the monomer structure, a monomer with the bulkier alkyl side group would liable to result in a polymer with richer syndiotacticity. Possible mechanism of rich-syndiotacticity was also discussed.

Keywords: modified microemulsion polymerization; poly(methacrylate)s; nanoparticles; tacticity; glass transition temperature

1 Introduction

Radical polymerization is one of the most widely employed methods for producing polymers because of its versatility and availability, (1–3) while the control of the stereochemistry is hard to attain because the growing radical species is a planar-like sp^2-carbon, which induces a non-stereospecific propagation. It was reported that stereospecific addition could occur for monomers with bulky substituents, as these substituents influenced the addition direction via steric repulsion. With increasing bulky substituents in methacrylates (4) and methacrylamides, (5) rich-isotactic polymers were obtained by radical polymerizations, while the syndiotacticity was enhanced in the 1,1-disubstituted vinyl ester polymerizations (6). However, all these stereospecific radical polymerizations relied on the structure of the monomers.

On the other hand, by use of polar solvents, such as bulky fluoroalcohols and aprotic solvents, which can interact with the polar substituents of the monomers such as methacrylates, vinyl esters, and acrylamides, polymers with rich-syndiotacticity were obtained by radical polymerizations via steric repulsion (7–9). Lewis acids, such as magnesium halides and metal triflates, can lead to isospecific radical polymerization of methacrylates and (meth)acrylamides owing to the multiple site coordination to the chain propagation species (10). But all these polymerization methods require hard reaction conditions (very low reaction temperature, oxygen-free, water-free, long reaction period etc.), unique solvent or catalyst, and the resulting polymers always have low molecular weights, which might limit their application.

A modified microemulsion polymerization method was developed by our group (11, 12) and poly(methyl methacrylate), (13) poly(ethyl methacrylate) (14) and poly(cyclohexyl methacrylate) (15) with rich-syndiotacticity and high glass transition temperature were easily prepared. The resulting polymers were nano-sized, the molecular weights of which could reach $\sim 10^5$ g/mol, and polymers with different molecular weights could be obtained by varied post-addition speeds.

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In this paper, we extend our study to other methacrylates with different alkyl side groups, such as iso-butyl methacrylate (i-BMA), hexyl methacrylate (HMA) and benzyl methacrylate (ByMA). The relationship of reaction temperature, T_g and syndiotacticity of the product was discussed and effects of the monomer side groups on the rich-syndiotacticities of the resulting polymers were studied.

2 Experimental

2.1 Materials

Methyl methacrylate (MMA) and ethyl methacrylate (EMA) from Shanghai Chemical Reagent Co. were distilled under reduced pressure before polymerization. Cyclohexyl methacrylate (CHMA, 98%, Aldrich), iso-butyl methacrylate (i-BMA, 98%, Aldrich), hexyl methacrylate (HMA, 98%, Tokyo Chemical Industry Co.) and benzyl methacrylate (ByMA, 98%, Tokyo Chemical Industry Co.) were purified by running through an alumina column before use. Sodium dodecyl sulfate (SDS) was purchased from Shanghai Shenggong Bioengineering Co. and used as received. 1-Pentanol (POH) and methanol from Shanghai Chemical Reagent Co. were used as received. Ammonium persulfate (APS) from Shanghai Aijian Reagent Factory was purified by recrystallization in water. Ascorbic acid (Vc) from Shanghai Chemical Reagent Co. and a 30% hydrogen peroxide aqueous solution (H_2O_2) from Shanghai Taopu Chemical Factory were used as received. Deionized water was used for all experiments.

2.2 Polymerization

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 surfactant and the co-surfactant, water and a small fraction of monomer 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 $70 \pm 2^\circ$C and stirred under a nitrogen atmosphere for 1 h until a transparent microemulsion was obtained. Then, the requisite amount of initiator, which was dissolved in a minimum quantity of water, was added to initiate the polymerization. After adding to the initiator, the appearance of the microemulsion changed to slightly bluish, but still transparent. Then the rest of the monomer in the addition funnel was added dropwise into the reaction flask with a proper speed. After the post-addition of monomer, stirring was continued for another 2 h at the reaction temperature to essentially complete the conversion of monomer. It is the same case for polymerizations initiated by Vc/H_2O_2 system.

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 size distribution of polymer microlatexes were determined by dynamic light scattering (DLS) on a Malvern 4700 from Malvern Instruments, Ltd. 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 poly(methacrylate) samples, a Bruker DMX 500 NMR spectrometer was used for ^{1}H-NMR and ^{13}C-NMR analysis with $CDCl_3$ as a solvent. The glass transition temperatures (T_g) of the samples were measured by a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC) at a heating rate of 10°C/min followed by rapid cooling.

3 Results and Discussion

3.1 Polymerization of Various Poly(alkyl methacrylate)s at Different Reaction Temperatures

We have reported the modified microemulsion polymerization of methyl methacrylate (13), ethyl methacrylate (14) and cyclohexyl methacrylate (15). The particle sizes (D_z), weight-average molecular weights (M_w), glass transition temperatures (T_g) and tacticities of PMMA, PEMA, and PCHMA samples polymerized at various reaction temperatures were shown in Tables 1, 2 and 3, respectively. Diameters of these poly(methacrylate)s latexes were in the range of 12–25 nm. The weight-average molecular weights (M_w) were about $\sim 10^5$ g/mol, except PEMA samples polymerized at relative low monomer post-addition speeds (14), which had the M_w of $\sim 10^4$ g/mol. This could be attributed to the “monomer starved addition” procedure of the modified microemulsion polymerization as discussed previously (15). The T_g of these PMMA, PEMA, and PCHMA samples were higher than those reported in the literature (16–18). It seems that these poly(methacrylate)s were rich in syndiotacticity and their tacticities, beside the restricted volume effect of nanoparticles during the modified microemulsion polymerization, were mainly affected by the reaction temperatures. The lower the reaction temperature, the higher the rich-syndiotacticity of the poly(methacrylate).

In this paper, modified microemulsion polymerization of other methacrylates with different side groups, including iso-butyl methacrylate (i-BMA), benzyl methacrylate (ByMA) and hexyl methacrylate (HMA) were studied. The characteristics of the Pi-BMA, PByMA, and PHMA samples prepared at different reaction temperatures were listed in Tables 4–7, respectively. It was shown that the

Table 1. Characterization of PMMA microlatexes prepared by modified microemulsion polymerization at different reaction temperatures

Sample	A1	A2	A3	A4	A5
[a]SDS/POH (g)	0.7/0.1	0.7/0.1	0.7/0.1	0.7/0.1	0.7/0.1
Initiator (g)	Vc/H_2O_2 0.09/0.06	APS 0.114	APS 0.114	APS 0.114	APS 0.114
[b]MMA (g)	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5
H_2O (mL)	42	42	42	42	42
Post-addition rate (g/min)	0.08	0.08	0.08	0.08	0.08
Reaction temp. (°C)	35	60	70	80	90
D_z (nm)	13	19	17	16	21
M_w (10^5)	1.87	5.26	1.76	1.05	0.35
M_w/M_n	2.6	2.9	4.7	2.5	1.4
[c]T_g (°C)	127	126	126	124	121
Tacticity (mm/mr/rr)	5/34/61	6/37/57	10/35/55	6/39/55	8/39/53

[a]POH was used as cosurfactant.
[b]The first part of monomer was in the initial microemulsion and the second part was post-added.
[c]The T_g reported in literature is 105°C (16).

diameters of these poly(methacrylate)s latexes were in the range of 19–31 nm, the weight-average molecular weights (M_w) were about ~10^5 g/mol, The T_g of the resulting Pi-BMA and PByMA samples were higher than those reported by the literature (19) and the products were rich-syndiotactic, while the T_g of the PHMA samples kept almost constant with the literature value (19) and the tacticites of the PHMA samples prepared by modified microemulsion polymerization and bulk polymerization were almost the same. It was reported in our earlier studies that the tacticity of the poly(methacrylate)s was influence by particle size (13) and reaction temperature (14, 15). But it seems that for all the alkyl methacrylates systems we studied, the tacticity of the polymer was also affected by other factors, as discussed in the following text.

3.2 Polymerizations Carried Out Below and Above T_g of the Resulting Polymers

As was shown in Tables 1, 2 and 3, the modified microemulsion polymerization of MMA, EMA (14), and CHMA (15) were carried out below or near the T_gs of the resulting polymers. As was discussed before, the rich-syndiotacticity of the resulting polymers may be caused by the restricted

Table 2. Characterization of PEMA microlatexes prepared by modified microemulsion polymerization at different reaction temperatures

Sample	B1	B2	B3	B4
[a]SDS/POH (g)	1.05/0.15	1.05/0.15	1.05/0.15	1.05/0.15
Initiator (g)	Vc/H_2O_2 0.09/0.06	APS 0.114	APS 0.114	APS 0.114
[b]EMA (g)	1 + 5	1 + 5	1 + 5	1 + 5
H_2O (mL)	42	42	42	42
Post-addition rate (g/min)	0.04	0.04	0.04	0.04
Reaction temp. (°C)	35	60	70	80
D_z (nm)	13	20	22	25
M_w (10^5)	0.48	0.67	0.51	0.52
M_w/M_n	2.8	2.9	1.3	2.8
[c]T_g (°C)	80	78	78	77
Tacticity (mm/mr/rr)	5/31/64	4/35/61	5/35/60	6/35/59

[a]POH was used as cosurfactant.
[b]The first part of monomer was in the initial microemulsion and the second part was post-added.
[c]The T_g reported in literature is 65°C (17).

Table 3. Characterization of the PCHMA microlatexes prepared by modified microemulsion polymerization at different reaction temperatures

Sample	C1	C2	C3	C4
[a]SDS/POH (g)	2.1/0.3	2.1/0.3	2.1/0.3	2.1/0.3
Initiator (g)	Vc/H_2O_2 0.09/0.06	APS 0.114	APS 0.114	APS 0.114
[b]CHMA (g)	0.5 + 5	0.5 + 5	0.5 + 5	0.5 + 5
H_2O (mL)	42	42	42	42
Post-addition rate (g/min)	0.08	0.08	0.08	0.08
Reaction temp. (°C)	35	60	70	80
D_z (nm)	14	21	20	21
M_w (10^5)	0.94	3.37	1.66	0.88
M_w/M_n	3.3	2.1	3.0	3.3
[c]T_g (°C)	113	113	113	110
Tacticity (mm/mr/rr)	1/27/72	3/32/65	3/33/64	3/36/61

[a]POH was used as cosurfactant.
[b]The first part of monomer was in the initial microemulsion and the second part was post-added.
[c]The T_g reported in literature is 83°C (18).

Table 4. Characterization of the Pi-BMA microlatexes prepared by modified microemulsion polymerization at different reaction temperatures

Sample	D1	D2	D3	D4	D5	D6
[a]SDS/POH (g)	2.8/0.4	2.8/0.4	2.8/0.4	2.8/0.4	2.8/0.4	2.8/0.4
Initiator (g)	Vc/H_2O_2 0.09/0.06	APS 0.114	APS 0.114	APS 0.114	APS 0.114	APS 0.114
[b]i-BMA (g)	0.4 + 4	0.4 + 4	0.4 + 4	0.4 + 4	0.4 + 4	0.4 + 4
H_2O (mL)	42	42	42	42	42	42
Post-addition rate (g/min)	0.16	0.16	0.16	0.16	0.16	0.16
Reaction temp. (°C)	35	50	60	70	80	90
D_z (nm)	24	31	29	25	24	19
M_w (10^5)	1.99	17.5	11.3	6.57	2.81	0.69
M_w/M_n	2.7	2.2	2.2	2.0	3.0	1.8
[c]T_g (°C)	74	72	72	71	71	68
Tacticity (mm/mr/rr)	4/31/65	4/32/64	4/33/63	5/35/60	5/36/59	6/37/56

[a]POH was used as cosurfactant.

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

[c]The T_g reported in literature is 53°C (19).

volume effect of nanoparticles (13) and the rich-syndiotactic propagation was favored by activation free energy during the polymerization process (14, 15). 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 (20). Therefore, the polymer formed in a microemulsion was conformationally restricted and the potential energy was higher, to compensate 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. For MMA, EMA, and CHMA systems, at the begin of the chain propagation, the propagating chains had low molecular weights and low T_g values, accordingly, the restricted volume effect was relatively not so obvious at this stage. Then, as the molecular weights and T_gs of the propagating chains increasing during the propagation, the T_gs of the propagating chains would finally exceed the reaction temperature, the propagating chains would pass a glass transition procedure and their free walks would be more restricted. So the restricted volume effect became obvious, resulting in products with rich-syndiotacticities and higher glass transition temperatures. Consequently, the contents of rr, mr, and mm triad calculated by ^{1}H-NMR or ^{13}C-NMR spectrum of the products were mean values of the chains during the whole propagation process.

On the other hand, the difference in activation enthalpy ($\Delta H^\ddagger$) and that in activation entropy ($\Delta S^\ddagger$) between the isotactic and syndiotactic specific propagations in these modified-microemulsion polymerization systems were discussed. According to the literature (21) $\Delta H^\ddagger$ 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), respectively, R is the gas constant (1.987 cal/mol · K), T is the polymerization temperature (K). Figure 1 contains the plots of $\ln(P_i/P_s)$ to $1/T$ (Fordham Plots) for MMA, EMA, and CHMA modified microemulsion polymerization systems.

The difference in activation enthalpy ($\Delta H^\ddagger$) and that in activation entropy ($\Delta S^\ddagger$) between the isotactic and syndiotactic specific propagations in MMA, EMA, and CHMA modified-microemulsion polymerization systems were calculated and listed in Table 8. 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

Table 5. Characterization of the PByMA microlatexes prepared by modified microemulsion polymerization at different reaction temperatures

Sample	E1	E2	E3	E4
[a]SDS/POH (g)	2.8/0.4	2.1/0.3	2.1/0.3	2.1/0.3
Initiator (g)	Vc/H_2O_2 0.09/0.06	APS 0.114	APS 0.114	APS 0.114
[b]ByMA (g)	0.4 + 4	0.4 + 4	0.4 + 4	0.4 + 4
H_2O (mL)	42	42	42	42
Post-addition rate (g/min)	0.08	0.08	0.08	0.08
Reaction temp. (°C)	35	60	80	90
D_z (nm)	21	27	25	26
M_w (10^5)	1.37	6.77	2.06	0.90
M_w/M_n	2.6	2.8	5.0	4.7
[c]T_g (°C)	69	69	69	65
Tacticity (mm/mr/rr)	6/33/61	5/36/59	6/37/57	8/39/53

[a]POH was used as cosurfactant.

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

[c]The T_g reported in literature is 57°C (19).

Table 6. The recipes of typical modified microemulsion and bulk polymerization of HMA

Sample	Surfactant[a] (g)	Initiator (g)	Reaction temperature (°C)	H_2O (mL)	HMA[b] (g)	Post-addition rate (g/min)
F1	SDS/n-Pt 2.1/0.3	Vc/H_2O_2 0.09/0.06	35	42	0.5 + 4	0.16
F2	SDS/n-Pt 2.1/0.3	APS 0.114	60	42	0.5 + 4	0.16
F3	SDS/n-Pt 2.1/0.3	APS 0.114	70	42	0.5 + 4	0.16
F4	SDS/n-Pt 2.1/0.3	APS 0.114	80	42	0.5 + 4	0.16
F5	—	AIBN 0.03	50	42	3	—
F6	—	AIBN 0.03	60	42	3	—
F7	—	AIBN 0.03	70	42	3	—
F8	—	AIBN 0.03	80	42	3	—

[a] POH was used as cosurfactant.
[b] The first part of monomer was in the initial microemulsion and the second part was post-added.

microemulsion polymerization system, and the syndiotactic propagation in CHMA system was most favored in these three systems. The negative values of $\Delta S_s^{\ddagger} - \Delta S_i^{\ddagger}$ indicated that the syndiotactic propagation was slightly disadvantaged by entropy, and the syndiotactic propagation in CHMA system was most disadvantaged in these three systems. Poly (methacrylate)s with richer syndiotacticities were prepared at lower reaction temperatures as the disadvantage of entropy was relatively smaller then. In general, syndiotactic propagations in CHMA system was most favored by activation free energy in these three polymerization systems as we took both enthalpy and entropy into account.

In this paper, the modified microemulsion polymerization of iso-butyl methacrylate (i-BMA) and benzyl methacrylate (ByMA) were also carried out as were shown in Tables 4 and 5. The tacticities of the products were determined by ^{1}H-NMR spectrum (Figures 2 and 3). The contents of rr, mr, and mm traid were calculated according to literature (22). The tacticity of Pi-BMA was determined from the relative intensity of R-CH_3 resonances due to rr, mr, and mm triads. The intensities of mm, mr, and rr triad resonances in every spectrum of the ^{1}H-NMR data were measured by integrating the spectral regions of 1.18–1.28, 0.98–1.07, and 0.82–0.92 ppm, respectively. The ester CH_3 resonance overlapped with the R-CH_3 resonance due to rr triad, thus the intensity of rr triad resonance was evaluated by subtracting three times the intensity of the ester OCH_2 resonance at 3.6–3.8 ppm from the intensity of the spectral region 0.82–0.92 ppm (Figure 2), because the theoretical relative intensity of ester CH_3 and OCH_2 resonances is 3.0:1.0. The contents of rr, mr, and mm triad of PByMA were calculated by the tacticity splittings in the 0.6–1.3 ppm region, as was shown in Figure 3, similar to PMMA samples (13). The relative error was around 1%.

Table 7. Characterization of the PHMA samples

Sample	D_z (nm)	M_w (10^5)	M_w/M_n	[a]T_g (°C)	Tacticity (mm/mr/rr)
F1	21	3.80	3.5	−3	3/29/68
F2	28	7.24	2.5	−5	4/32/64
F3	24	5.09	3.3	−2	4/34/62
F4	19	2.68	3.5	−5	5/34/61
F5	—	16.9	2.7	−4	4/31/65
F6	—	7.86	2.7	−5	4/33/63
F7	—	2.75	2.0	−3	5/35/60
F8	—	1.87	1.9	−7	6/37/57

[a] The T_g reported in literature is −5°C (19).

The Fordham plots of i-BMA and ByMA modified microemulsion polymerization systems were shown in Figure 4. The $\ln(P_i/P_s)$ to $1/T$ didn't remain linear during the range of the reaction temperatures for these two systems. It could be seen that a mutation occurred respectively near the T_g values of the resulting polymers (Figure 4).

For these monomers whose glass transition temperatures of the resulting polymers were in the range of the reaction temperatures, when the polymerization was carried out above the glass transition temperatures of product, it was found that the syndiotacticity of the resulting polymer decrease obviously, as was shown in Tables 4 and 5. A possible explanation may

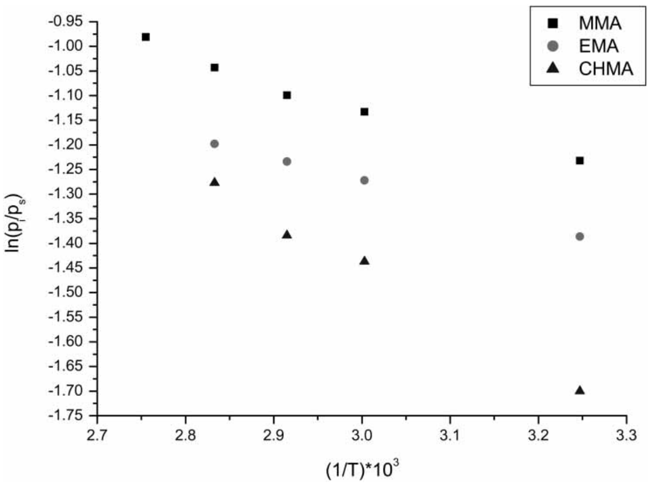

Fig. 1. Fordham plots for the modified microemulsion polymerizations of MMA, EMA, and CHMA under different reaction temperatures.

Table 8. 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

Monomer	EMA	MMA	CHMA
$\Delta H_s^{\ddagger} - \Delta H_i^{\ddagger}$ (cal/mol)	-885 ± 7	-978 ± 96	-2185 ± 153
$\Delta S_s^{\ddagger} - \Delta S_i^{\ddagger}$ (cal/mol · K)	-0.13 ± 0.02	-0.71 ± 0.28	-3.65 ± 0.46

be the less restricted volume effect on the propagating chains when the polymerization was carried out above the T_g values of them. In this case, although the molecular weights and T_gs of the propagating chains increasing during the propagation, the T_gs of the propagating chains would never exceed the reaction temperature during the whole chain propagation. Accordingly, the propagating chains would not pass a glass transition procedure, the free walk of them was less restricted and the restricted volume effect was weakened, resulting in products with lower syndiotacticities.

Modified microemulsion and bulk polymerizations of hexyl methacrylate were carried out as a contrast, the recipes and characteristics of the PHMA samples were listed in Tables 6 and 7. The tacticities of the PHMA samples (Figure 5) were determined similar to Pi-BMA samples according to the literature (22). For HMA monomer, whose polymerization were carried out far above the glass transition temperatures of the products (the T_g of PHMA reported was $-5°C$ (19)), the polymers prepared by modified microemulsion and bulk polymerization at the same temperature had almost the same T_gs and the difference of their tacticities was not obvious, as the restricted volume effect on the propagating chains was further weakened.

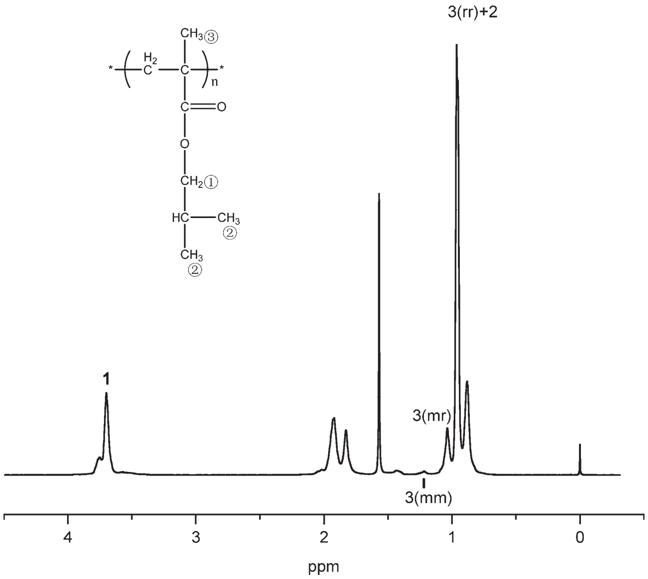

Fig. 2. ^{1}H-NMR spectrum (500 MHz) of Pi-BMA sample D4.

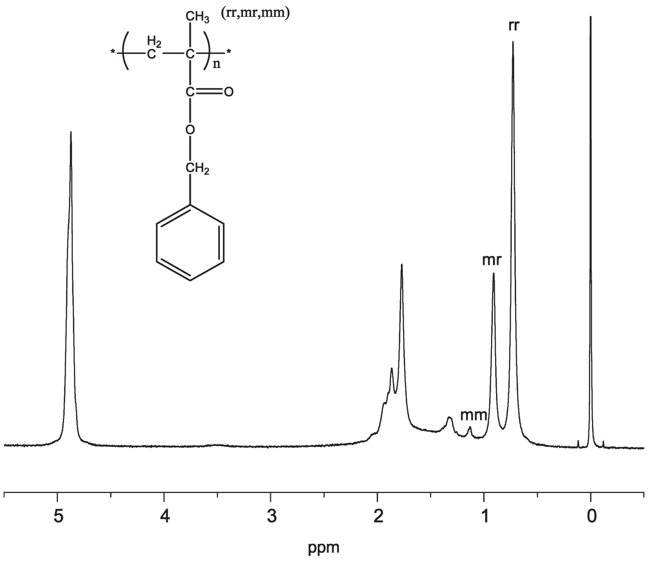

Fig. 3. ^{1}H-NMR spectrum (500 MHz) of PByMA sample E1.

3.3 Monomer Structure and Tacticities of Polymer

It could be concluded that most of the alkyl methacrylates we studied, such as MMA, EMA, i-BMA, CHMA, and ByMA, resulting in polymers with rich-syndiotacticity and higher glass transition temperature by modified microemulsion polymerization. The exception was HMA system, whose polymerization were all carried out far above the T_g of the PHMA products.

As discussed above, tacticities of poly(alkyl methacrylate)s prepared by modified microemulsion polymerization, beside the restricted volume effect of nanoparticles during the modified microemulsion polymerization, were mainly affected by reaction temperature, it was the case for all the methacrylate systems we studied that the lower the reaction temperature, the higher the rich-syndiotacticity of the poly (methacrylate). Effect of the reaction temperature on the

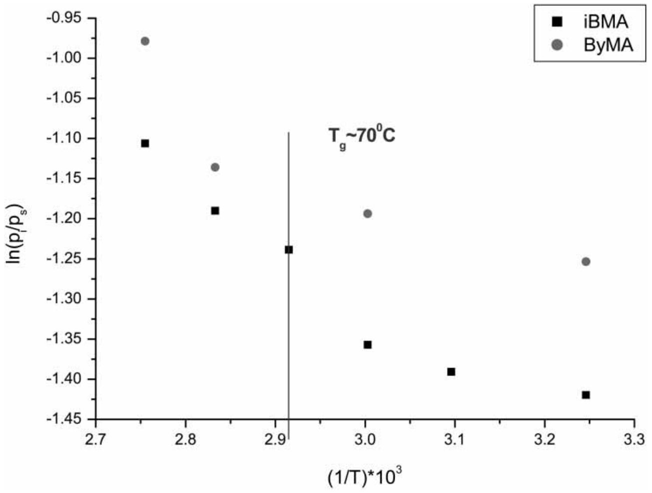

Fig. 4. Fordham plots for the modified microemulsion polymerizations of i-BMA and ByMA under different reaction temperatures.

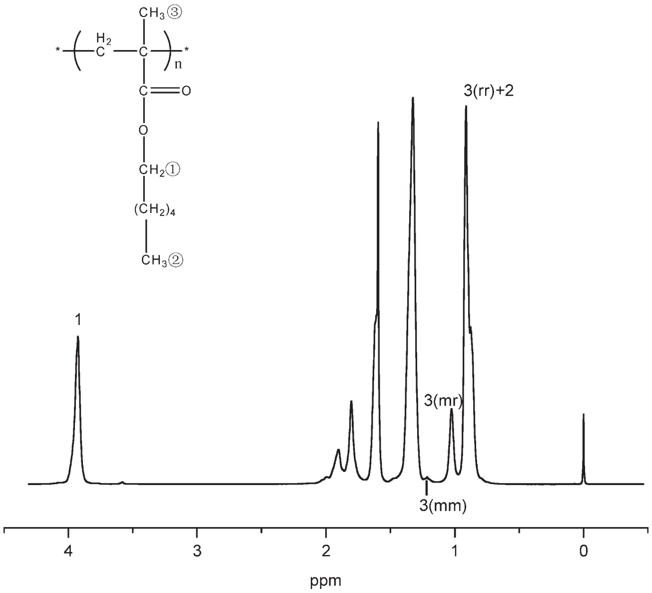

Fig. 5. ^{1}H-NMR spectrum (500 MHz) of PHMA sample F1.

rich-syndiotacticity of the polymers varied with methacrylate types as was shown in their different $\Delta H_s^{\ddagger} - \Delta H_i^{\ddagger}$ and $\Delta S_s^{\ddagger} - \Delta S_i^{\ddagger}$ values. The Fordham plots of various methacrylate systems were shown in Figure 6.

It was also discussed that the tacticities of the polymers prepared above and below the T_g of the products were different. It was indicated in Figure 6 that $\ln(P_i/P_s)$ to $1/T$ remained linear for MMA, EMA, CHMA, and HMA systems as all the polymerizations were carried out below or far above the T_gs of the corresponding products, while it was not the case for i-BMA and ByMA system as some of the polymerizations were carried out below the T_gs of the corresponding products and the others were carried out above them. It can be concluded that both the reaction temperature and the T_g of the product should be considered if we want to compare the tacticities of different poly(methacrylate)s. So, the tacticities of poly(methacrylate)s prepared at 35°C were taken into account, as all the poly(methacrylate)s but PHMA were prepared below the T_g of the corresponding products at this temperature.

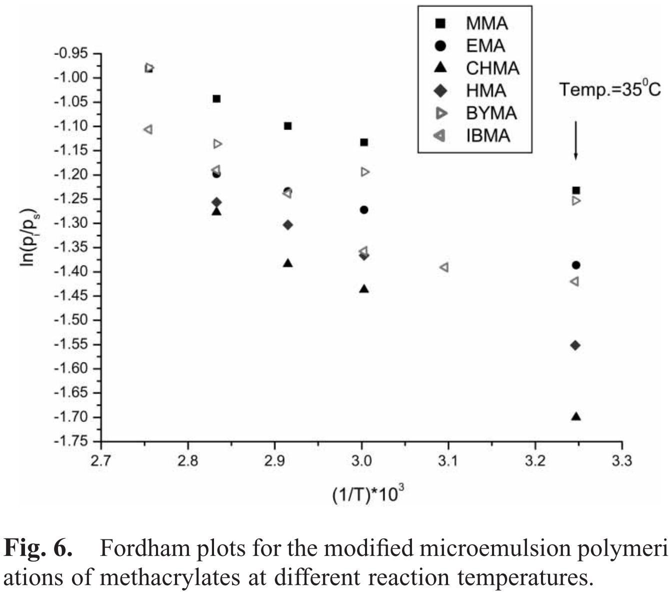

Fig. 6. Fordham plots for the modified microemulsion polymerizations of methacrylates at different reaction temperatures.

It was shown in Figure 6 that the highest syndiotacticity was obtained in CHMA system, then HMA, i-BMA, and EMA system, the relatively lower syndiotacticity was obtained in MMA and ByMA system. It seems that for methacrylates with alkyl side groups, including MMA, EMA, i-BMA, HMA, and CHMA, the bulkier the side group, the higher the syndio-tacticity of the resulting polymer. But it is not the case for ByMA which also has a bulk side group. This may be attributed to the methylene (-CH_2-) group between the phenyl side group and the main chain. The free rotation of the methylene group weakened the bulky effect of phenyl side group on the main chain conformation, resulting in polymers with less rich-syndiotacticity.

Methacrylate monomers with bulky aryl side groups, such as phenyl methacrylate and 1-naphthyl methacrylatewere were polymerized in microemulsions by Ford et al. (23). It was found that the tacticities of poly(phenyl methacrylate) (PPhMA, ~55% rr) and poly(1-naphthyl methacrylate) (P-1-NM, ~47% rr) were the same as those of the polymers prepared in toluene solutions. PphMA samples from microemulsion polymerizations and solution polymerizations had the same T_g of 127°C, and P-1-NM from microemulsion polymerizations had T_g of 145–147°C compared with T_g of 142°C for P-1-NM from solution polymerizations. In our opinion, it may be attributed to the less flexible ester group of phenyl methacrylate and 1-naphthyl methacrylate, the ester groups of them were very bulky with p-π conjugation. These less flexible ester groups may cause a rather large steric effect between the entering monomer and the propagating chain end, and may cause a more rigid conformation of growing polymer chain, it may be impossible for the propagating chain to reach lower potential energy through syndiotactic propagation. On the contrary, PbyMA polymerized by modified microemulsion polymerization had some rich-syndiotacticity and higher T_g values, as there was a methylene (-CH2-) group between the phenyl side group and the main chain, which made the effect of the side group on the main chain act like alkyl side groups, as was discussed before.

4 Conclusions

Poly(alkyl methacrylate)s, with rich-syndiotacticity and higher glass transition temperature were easily obtained by a modified microemulsion polymerization procedure.

For the monomers whose polymerization carried out below or near the glass transition temperatures of the resulting polymers, such as methyl methacrylate, ethyl methacrylate and cyclohexyl methacrylate, propagating polymer chains were restricted during the reaction process, resulted in products with rich-syndiotacticity and higher glass transition temperature. For the monomers whose glass transition temperatures of the resulting polymers were in the range of the reaction temperatures, i.e., iso-butyl methacrylate and benzyl methacrylate, when the polymerization was carried out above the glass transition temperature of product, the syndiotacticity of the resulting polymer would decrease obviously because of the less restricted volume effect on the propagating chains. For the monomers whose polymerization were carried out far above the glass transition temperatures of the products, i.e., hexyl metharylate, the resulting polymers had almost the same T_gs with bulk polymerized poly(hexyl metharylate)s. Although both of the methods resulting in polymers with rather higher syndiotacticity, the difference of their tacticities was not obvious, as the restricted volume effect on the propagation chains was further weakened.

Tacticities of the methacrylate polymers seemed to be affected by the monomer structure. At the same reaction temperature, monomers with bulkier alkyl side groups resulted in polymers with richer syndiotacticities. The influence of the bulky side group on the main chain may be weakened if there are other alkyl groups between them (i.e., in the case of benzyl methacrylate).

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