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Stereospecifity in radical polymerization of methyl α-(chloromethyl)acrylate

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Abstract

Poly(methyl α-(chloromethyl)acrylate)s (PMCMAs) obtained by homopolymerizations of methyl α-(chloromethyl)acrylate (MCMA) in benzene at different temperatures were converted to poly(methyl methacrylate)s (PMMAs) by reduction with tributyltin hydride. The reduction proceeded smoothly to yield PMMA exhibiting no ^{1}H NMR resonance due to the CH_2Cl group. The tacticity of the PMCMA obtained at 40 °C was determined using the ^{1}H NMR resonances of the α-methyl group of PMMA derived: *mm*/*mr*/*rr* = 8/56/36. Apparently, the propagation of MCMA preferred *r* addition to a lower extent in comparison with that of MMA. The more polar and the bulkier α-substituent $ClCH_2$ (relative to CH_3) would diminish the effect of the carbomethoxy group, thus resulting in a lower level of synditacticity than in MMA polymerization. The tacticity of MMA–MCMA copolymers estimated after conversion to PMMA varied from that of PMMA to that of PMCMA; an increase in MCMA content in the feed resulted in a decrease in *rr* content. Coisotactic parameters for copolymerization of MCMA with MMA-d_8 were determined according to Hatada's procedure for determination of these parameters [Polym J 19 (1987) 1105].

Keywords: Tacticity; α-Substituent; Deuterated monomer

1. Introduction

Stereochemistry of propagation in radical polymerization has been studied using mainly methacrylic esters, and the tacticity has been determined by ^{1}H and ^{13}C NMR spectroscopy [1,2]. It has been shown that for methyl methacrylate (MMA) polymerization at 60 °C, syndiotactic (*r*) addition is preferred over isotactic (*m*) addition, and that the syndiotactic triad (*rr*) content increases with decreasing temperature [1,2]. Merely the bulkiness of the ester alkyl group of methacrylate cannot effectively control the stereochemistry of propagation. Methacrylic triarylmethyl esters which fulfill the requirements to form helix structure of polymer chains yield isotactic polymers; e.g. almost perfectly isotactic polymers from tripehnylmethyl methacrylate, 1-phenldibenzosuberyl methacrylate, and some other triarylmethyl methacrylates [3–5]. Although the effects of solvents [6] and Lewis acids [7–9] on the tacticity of methacrylic polymer has been observed, highly isotactic or syndiotactic radical polymer has never been obtained by polymerization of methacrylic esters with the exception of triarylmethyl methacrylates. In order to accomplish significant substituent effects on the tacticity of radical polymer, the direction of the approaching propagating radical to the carbon–carbon double bond of the monomer has to be stericaly controlled with respect to the configuration of the α-carbon newly bound to the incoming monomer unit. Acrylamide bearing an asymmetric auxiliary group as *N*,*N*-disubstituents yielded highly isotactic (dyad) polymer as confirmed by ^{1}H NMR spectroscopy after conversion to poly(methyl acrylate) [10]. The auxiliary substituents involving the asymmetric center as the moieties of the monomer and the propagating radical selectively allow the addition to form *m* placement.

The tacticities of α-(phenoxymethyl)acrylate [11,12], α-(methoxymethyl)acrylate [7,13], ethyl α-(benzoyloxymethyl)acrylate [14], di-*n*-butyl itaconate [15], and α-(benzyl)- and α-(substituted benzyl)acrylates [16] obtained by radical polymerization have been determined, showing that the stereochemistries of these polymerizations are different from MMA polymerization. The effects of the substituents on the tacticity of the substituted acrylic esters were estimated, and most of the results showed that

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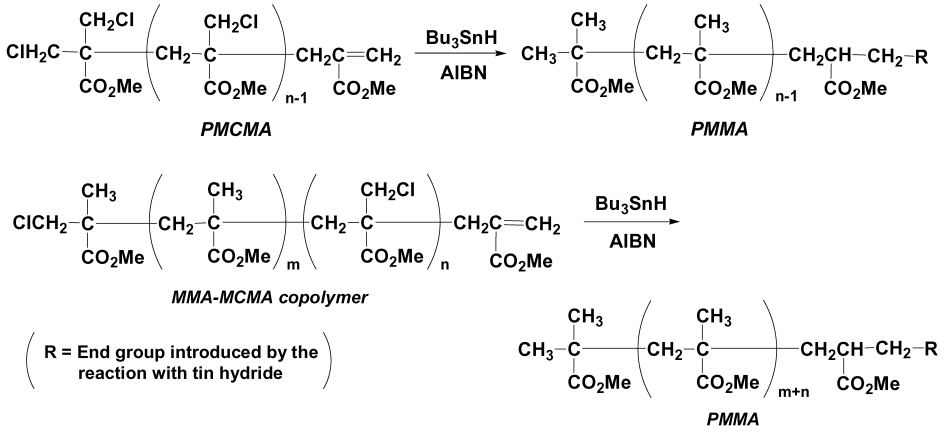


Scheme 1.

introduction of an α-substituent other than an α-methyl group caused a decrease in the preference of *r* addition in most cases, approaching random propagation. An exception was benzoyloxymethylacrylate polymerization, where *m* addition was preferred. Although the tacticity of poly(methyl α-(2-carbomethoxymethyl)acrylate) was not determined, the change in the ^{13}C NMR resonances of the acryloyl carbonyl carbon suggested that the tacticity varies from almost random propagation at 60 °C to an increased *mm* content at 100 °C [17]. Steric hindrance has been noted as one of the important factors affecting the reactivity and the reaction mode of the monomers and radicals in the polymerization of α-(substituted methyl)acrylic esters [18]. The reactivities of a large number of substituted acrylates have been investigate, whereas only a limited number of α-(substituted methyl)acrylates have been studied with respect to tacticity. Further work is required to clarify the effects of substituted methyl groups on the tacticity of polymer formed by radical polymerization in relation to the steric effect of the substituent.

In the present study, polymerizations of methyl α-(chloromethyl)acrylate (MCMA) and MCMA copolymerizations with MMA have been carried out. MCMA is a polymerizable addition-fragmentation chain transfer agent that yields homopolymer and copolymers bearing the 2-carbomethoxy-2propenyl ω-end group [19]. However, the end group formation may not affect the tacticity of polymer and copolymer of MCMA because only one ω-end group would be introduced per chain. The polymer and copolymer formed were converted to poly(MMA) (PMMA), and the triad tacticity of the PMMA derived was determined by ^1H NMR spectroscopy.

Table 1
Results of homopolymerization of MCMA in benzene at various temperatures

Initiator	Temperature (°C)	Time (h)	Conversion (%)	$M_n \times 10^{-3}$	M_w/M_n
n-Bu_3B	10	120	27.3	4.2	1.53
AVN	40	72	36.9	37.0	1.46
AIBN	60	48	57.8	24.6	1.34
CAN	90	48	81.8	12.4	1.16

[MCMA] = 5 mol/l, [Initiator] = 0.01 mol/l.

2. Experimental

MCMA was prepared by reaction of methyl α-(hydroxylmethyl)acrylate with thionyl chloride as described in the literature [20] and was distilled under reduced pressure. The structure of MCMA was verified by ^1H NMR spectroscopy. Commercially available MMA and MMA-d_8 were distilled under reduced pressure before use. Commercial 2,2′-azobis(2,4-dimethylvaleronitrile) (AVN), 2,2′-azobis(isobutyronitrile) (AIBN), and 1,1′-azobis(cyclohexane-1-carbonitrile) (ACN) were recrystallized from methanol. Tri-*n*-butyl boron was commercially available.

Polymerizations of MCMA and copolymerizations of MCMA with MMA or MMA-d_8 were carried out in glass tubes sealed under vacuum at 5 mol/l of monomer or comonomer concentration in benzene. After polymerization, the contents of the tube were poured into a large amount of methanol to precipitate the polymer formed. Polymer purification was carried out by reprecipitation using benzene as solvent and methanol as precipitant. The MCMA polymers and copolymers were allowed to react with tri-*n*-butyltin hydride by refluxing benzene solutions containing a small amount of AIBN.

GPC measurements were carried out using a Tosoh 8000 series high-performance liquid chromatograph equipped with TSK-gel columns G5000HHR, GMultiporeHXL-M, and GMHHR-L connected in this order. The molecular weight was calibrated by poly(styrene) standards. ^1H NMR spectra were recorded on a JEOL JNM-A 400 spectrometer at 400 MHz. Deuteriochloroform and tetramethylsilane were used as solvent and internal standard, respectively.

Table 2
Triad tacticity of poly[α-(substituted methyl)acrylate] prepared by radical polymerization at various temperatures

Monomer	Temperature (°C)	Triad tacticity (%)			$4(mm)(rr)/(mr)^2$	Reference
		mm	*mr*	*rr*		
MCMA	10	8	58	34	0.32	This work
MCMA	40	8	56	36	0.35	This work
MCMA	60	10	57	33	0.36	This work
MCMA	90	14	58	28	0.47	This work
Benzyl α-(methoxymethyl)acrylate	30	30	48	22	1.14	[8]
Methyl α-(methoxymethyl)acrylate	30	25	51	24	0.92	[8]
Methyl α-(phenoxymethyl)acrylate	30	25	50	25	1.07	[12]
Methyl α-(phenoxymethyl)acrylate	60	23	49	28	1.07	[11]
Ethyl α-(benzoyloxymethyl)acrylate	50	51	35	14	2.33	[14]
Di-*n*-butyl itaconate	40	6	42	52	0.67	[15]
Methyl α-benzylacrylate	40	13	32	55	2.79	[16]
Methyl α-(*p*-methoxybenzyl)acrylate	40	9	33	58	1.92	[16]
Methyl α-(*p*-chlorobenzyl)acrylate	40	9	24	67	4.19	[16]
MMA	60	3	31	66	0.82	[5]

3. Results and discussion

The homopolymerizations of MCMA at various temperatures were carried out under the conditions shown in Table 1, and the results obtained are summarized in the same table. Poly(methyl α-(chloromethyl)acrylate)s (PMCMAs) were converted to PMMAs as shown in Scheme 1, and the ^{1}H NMR spectra of the polymer before and after the reaction with tin hydride are compared in Fig. 1. The resonances of the CH_2Cl (3.7–4.3 ppm) in Fig. 1A disappeared after the reduction (Fig. 1B), and quantitative conversion of the α-CH_2Cl group to the CH_3 group can be confirmed. After the reaction, the resonance assigned to the olefinic protons of the ω-unsaturated end group of the PMCMA introduced by addition fragmentation chain transfer also disappeared because the end group is feasible to radical addition [19]. The tin radical attacked to the CH_2Cl group and the configuration of the backbone quaternary-carbons would be preserved.

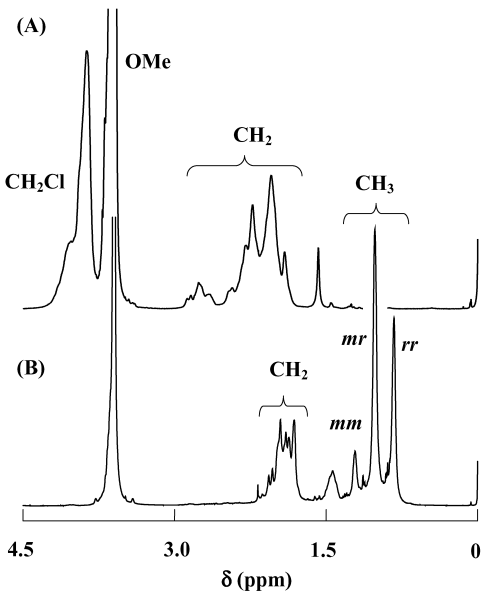


Fig. 1. ^{1}H NMR spectra of PMCMA before (A) and after (B) reduction with tributyltin hydride.

The triad tacticities of the PMMAs from the PMCMAs obtained at various temperatures were calculated from the intensities of the resonances due to the α-CH_3 (Fig. 1B). The results are summarized in Table 2 together with the tacticities of various poly[α-(substituted methyl)acrylate]s from the literatures. The tacticities of PMCMA indicate that the propagation is closer to random ($mm : mr : rr = 25 : 50 : 25$) in comparison with PMMA. An increase in temperature brought about an increase and decrease in *mm* and *rr*, respectively, whereas *mr* remained almost constant. These tendencies suggest that *r* addition is slightly preferred in comparison with *m* addition in propagation of MCMA. Table 2 indicates that the *rr* content of PMCMA and poly[α-(methoxymethyl)acrylate]s are considerably lower than for PMMA. Furthermore, poly(itaconate) [15] and poly(α-benzylacrylate)s [16] also showed lower *rr*. These results can be explained by a decrease in the preference of *r* addition arising from repulsion between not only the carbalkoxy groups, but also the polar and/or bulky α-substituents of the monomers and the propagating radicals. However, the higher *mm* content of poly[ethyl α-(benzoyloxymethyl)acrylate determined using ^{13}C NMR spectroscopy suggests stronger influence of the benzoyloxymethyl group to prefer *m* addition ($\sigma = 0.70$ at 50 °C) than carbomethoxy group to prefer *r* addition in MMA polymerization ($\sigma = 0.21$ at 40 °C) [22].

When addition of the propagating radical to monomer proceeds stereochemically independent of the structure of propagating radical, the tacticity of the polymer obtained would obey Bernoullian statistics. According to these statistics, $mm = \sigma^2$, $mr = 2\sigma(1-\sigma)$, and $rr = (1-\sigma)^2$, where σ denotes the probability of *m* (dyad) formation [21]. The values of $4(mm)(rr)/(mr)^2$, which would be unity for a

Table 3
Results of MMA and MMA-d_8 (M_1)–MCMA (M_2) copolymerizations at 40 °C

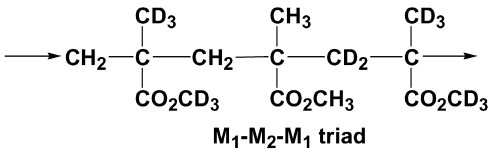
M_1	[M_1] in comonomer (mol%)	[M_1] in copolymer (mol%)	Time (h)	Conversion (%)	$M_n \times 10^{-3}$	M_w/M_n
MMA	10	18.9	20	13.1	7.3	1.42
MMA	30	41.6	15	11.0	9.8	1.72
MMA	70	75.4	5	11.1	34.0	1.68
MMA	100[a]	100[a]	8	39.7	116.0	2.02
MMA-d_8	95	96.7[b]	10	31.9	63.7	1.86

[MMA] + [MCMA] = 5.0 mol/l, [AVN] = 0.01 mol/l.
[a] MMA homopolymerization.
[b] Obtained from copolymerization of MMA (95 mol%)–MCMA (5 mol%).

Bernoullian system, were less than unity for most of the polymerizations in Table 2 including the MCMA polymerization. The polymerization of MCMA might follow higher order statistics affected by the structure of the PMCMA radical including the penultimate group.

The MMA–MCMA copolymers obtained (Table 3) were converted to the corresponding MMA homopolymers by the reduction with tributyltin hydride prior to tacticity determination (Scheme 1). MCMA functions as polymerizable monomer and addition-fragmentation chain transfer agent, simultaneously [19]. Although chain transfer would compete with bimolecular termination as an end forming reaction, the tacticity would not be influenced by the transfer to MCMA. The ^{1}H NMR spectra of the copolymer and the PMMA derived are shown in Fig. 2. The resonance due to the CH_2Cl group disappeared in the spectrum of the PMMA. Fig. 3 shows the expanded ^{1}H NMR spectra of the α-CH_3 resonances of the PMMAs derived from the copolymers obtained from different comonomer compositions, and the tacticities were estimated as summarized in Table 4. The *rr* content increases with increasing MMA content in the copolymer, and the triad tacticity of the copolymer gradually changed from that of PMCMA to that of PMMA with increasing MMA content.

According to the procedure reported by Hatada et al. [22], the probabilities of the *m* placement for additions of PMMA radical to MCMA and PMCMA radical to MMA can be estimated separately. In order to remove the resonances due to the α-CH_3 and CH_2 group of the MMA unit, MMA-d_8 was used instead of MMA for copolymerization with MCMA. The MMA-d_8 (M_1)–MCMA (M_2) copolymer formed during copolymerization a small amount of MCMA (5 mol%) (Table 3) and a lager amount of MMA-d_8 (95 mol%) was allowed to react with tirbutyltin hydride for conversion into a MMA-d_8–MMA copolymer which contained the MMA (M_1) unit almost exclusively as the MMA centered triad sequence, $M_1M_2M_1$, as shown below.



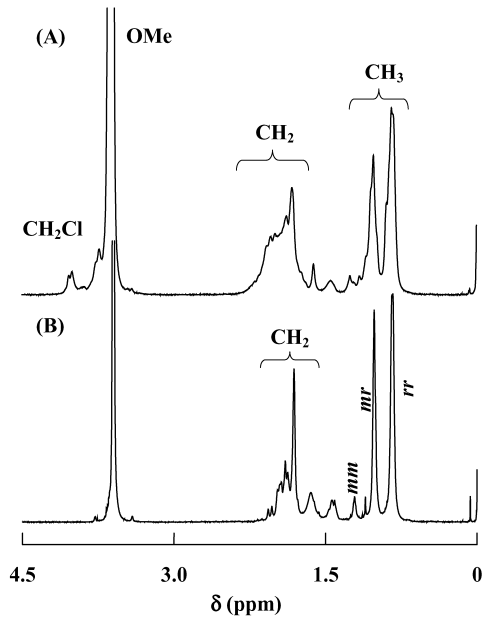


Fig. 2. ^{1}H NMR spectra of MMA–MCMA copolymer prepared by copolymerization of comonomer containing MMA (3.5 mol/l) and MCMA (1.5 mol/l) (A) and PMMA (B) derived by reduction with tributyltin hydride.

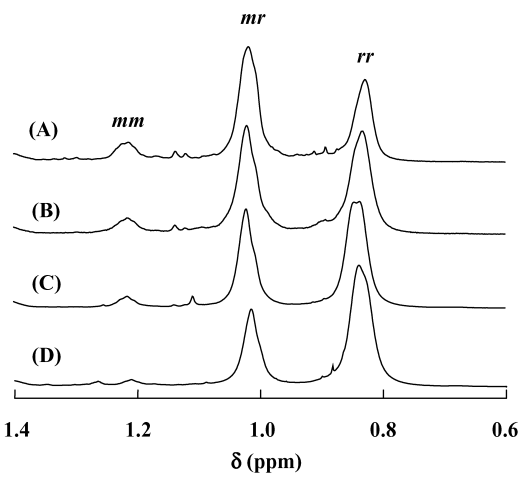


Fig. 3. Expanded ^{1}H NMR resonances of α-CH_3 of PMMA derived from PMCMA (A) and MMA–MCMA copolymer obtained from comonomer containing 30 (B), 70 (C), and 100 mol% (D) of MMA.

Table 4
Triad tacticity of MMA (M_1)–MCMA (M_2) copolymer obtained in benzene at 40 °C

[M_1] in copolymer (mol%)	Triad tacticity (%)		
	mm	*mr*	*rr*
0	8	56	36
18.9	7	51	42
41.6	6	46	48
75.4	4	40	56
100	3	34	63

[MCMA] + [MMA] = 5.0 mol/l, [AVN] = 0.01 mol/l.

The content of the isotactic, heterotactic, and syndiotactic triads of $M_1M_2M_1$ sequence ($m'm'$, $m'r'$, and $r'r'$, respectively) can be expressed in terms of the coisotactic parameters, σ_{12} and σ_{21}, according to Eqs. (1)–(3) if the system obeys Bernoullian statistics. The values of σ_{12} and σ_{21} denote the probabilities of *meso* (m') additions of M_1· and M_2· to M_2 and M_1, respectively (Scheme 2). The probabilities of *racemo* (r') additions of M_1· and M_2· to M_2 and M_1may be given by $(1-\sigma_{12})$ and $(1-\sigma_{21})$, respectively. The contents of $m'm'$, $m'r'$, and $r'r'$ triads were calculated from the intensities of the ^{1}H NMR resonances due to the α-CH_3 group

$$m'm' = \sigma_{12} \times \sigma_{21} \quad (1)$$

$$m'r' = \sigma_{12}(1-\sigma_{21}) + \sigma_{21}(1-\sigma_{12}) \quad (2)$$

$$r'r' = (1-\sigma_{12}) \times (1-\sigma_{21}) \quad (3)$$

The propagating radical chain end in *r* or *m* configurations with respect to the penultimate unit might affect the mode of addition to MCMA (the first-order Markov statistics [21]). Formation and participation to propagation of the MCMA propagating radical bound to the MCAM penultimate unit can be neglected in the copolymerization because of the small amount of MCMA (5 mol%) in the feed. It was assumed that the radical chain ends consisting of the MMA-d_8 (M_1) unit as the penultimate unit and the MCMA (M_2) terminal unit add to MMA-d_8 (M_1) to generate the MMA-d_8–MCMA–MMA-d_8 (M_1–M_2–M_1). The triad tacticity of PMCMA deviated from Bernoullian statistics as shown in Table 2, and the α-CH_2Cl group larger and more polar than

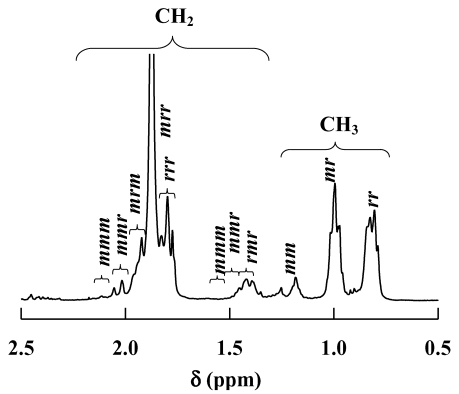
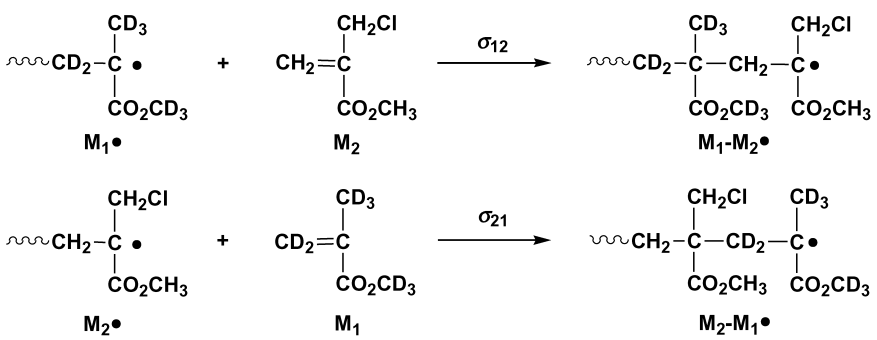


Fig. 4. ^{1}H NMR resonances of α-CH_3 and CH_2 protons of MMA-d_8–MMA copolymer derived from MMA-d_8–MCMA copolymer.

the α-CH_3 might be the cause for the deviation. Addition of the MCMA radical to MMA is sterically less hindered than the addition to MCMA and Eqs. (1)–(3) based on the Bernoullian statistics were assumed to be applicable to the tacticity of MMA-d_8–MCMA copolymer.

The expanded ^{1}H NMR resonances of the α-CH_3 and CH_2 protons of the MMA unit originated from the MCMA unit are shown in Fig. 4 [12]. Since the resonances ascribed to the CH_3 group exhibit different chemical shifts depending on the tacticity, a set of unassigned σ_{12} and σ_{12} values can be estimated as the solutions of the simultaneous Eqs. (1)–(3). If the σ_{12} and σ_{12} values are not too close [22], the individual values could be obtained from the intensity ratios of the resonances of the backbone CH_2 assigned as can be seen from Fig. 4 [7]. Table 5 summarizes the values of σ_{12}, σ_{21}, and σ_{22} for the MMA-d_8–MCMA copolymerization and other related copolymerizations. Formation of the r' dyad is only slightly favored for the addition of MMA-d_8 radical (M_1·) to MCMA (M_2), whereas formation of the r' dyad is clearly dominant in the case of addition of the MCMA radical (M_2·) to MMA-d_8 (M_1). The value of σ_{12} for MCMA (0.44) is greater than that for MMA (ca. 0.2) [22] by more than a factor of two, indicating that the CH_2Cl group causes the MMA-d_8 radical to approach the planar MCMA monomer from the above and below with almost the same probability to give σ_{12} close to 0.5. However, σ_{21} for the copolymerization of MCMA is only slightly lower than that for the polymerization with MMA. The σ_{22} calculated from



Scheme 2.

Table 5
Triad tacticity and coisotactic parameter for MMA-d_8 (M_1)–MCMA (M_2) copolymerization

Copolymerization		Tacticity (%)[a]			Coisotactic parameter			Reference
M_1	M_2	*mm*	*mr*	*rr*	σ_{12}	σ_{21}	σ_{22}	
MMA-d_8	MCMA	8	47	45	0.44	0.19	0.28	This work
MMA-d_8	MMA	4.4	33.2	62.4	0.20[b]	0.22[b]	0.21	[22]
MMA-d_8	Triphenylmethyl methacrylate	6.3	62.0	31.7	0.10	0.65	0.75	[22]

[a] Tacticity of M_2 centered triad sequence.
[b] These values were not assigned to either parameter [22].

the tacticity of the PMCMA lies in between the values of σ_{12} and σ_{21} in agreement with the findings that the triad tacticity of the MMA–MCMA copolymer gradually changed from that of PMCMA to that of PMMA with increasing MMA content (Table 4). The value of σ_{22} for the polymerization of triphenylmethyl methacrylate is greater than σ_{12} and σ_{21} in conformity with the contribution of the polymer chain in the helix structure controlling isotactic specific polymerization [22].

4. Conclusions

PMCMAs obtained by radical polymerization at different temperatures were successfully converted to PMMAs by reduction with tri-*n*-butyltin hydride, and the PMMAs derived were submitted for the tacticity measurement by ^{1}H NMR spectroscopy. Propagation of MCMA proceeded with similar probabilities of *m* and *r* additions, and the tacticity of PMCMA is closer to the result of random propagation than for PMMA. The presence of the carbomethoxy group and the chloromethyl group as the substituents of MCMA and the MCMA radical diminished the dominant effect of the former group on the tacticity. The tacticity of MMA–MCMA copolymers determined after conversion to PMMA varied between the tacticities of PMCMA and PMMA depending on copolymer composition. Furthermore, MMA-d_8 (M_1) instead of MMA was copolymerized with MCMA (M_2), and the coisotacticities of addition of the MCMA radical to MMA-d_8 and of MMA-d_8 radical to MCMA were estimated. The ^{1}H NMR spectrum of the MMA-d_8–MMA copolymer derived from the copolymer of MMA-d_8–MCMA indicated that the addition of the MMA-d_8 radical to MCMA more predominantly forms *m* dyad than that of the MCMA radical to MMA-d_8. The probability of *m* addition in homopolymerization of MCMA, σ_{22}, lies between those for addition of the MMA-d_8 radical to MCMA, σ_{12}, and addition of the MCMA radical to MMA-d_8, σ_{21}, and no effect of the polymer chain of MCMA on the tacticity was observed.

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