Macromonomer Preparation by Radical Polymerization and Copolymerization of the Unsaturated Tetramer of Methyl Acrylate

Tomoyuki HIRANO, Per B. ZETTERLUND, and Bunichiro YAMADA[†]

Department of Applied and Bioapplied Chemistry, Graduate School of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558–8585, Japan

(Received December 20, 2002; Accepted March 30, 2003)

ABSTRACT: The unsaturated tetramer of methyl acrylate ($\text{CH}_2=\text{CXCH}_2\text{CHXCH}_2\text{CHXCH}_2\text{CH}_2\text{X}$, where $\text{X}=\text{CO}_2\text{Me}$: MATE) was homo- and copolymerized by radical means as a polymerizable acrylic ester bearing a bulky α -substituent. MATE homopolymerization in bulk yielded low molecular weight polymer consisting of the MATE units and 2-carbomethoxy-2-propenyl ($\text{CH}_2=\text{C}(\text{CO}_2\text{Me})\text{CH}_2-$) ω -end groups as a result of addition of propagation and simultaneous β -fragmentation of propagating radicals, expelling $\cdot\text{CHXCH}_2\text{CHXCH}_2\text{CH}_2\text{X}$ which adds to MATE to initiate a new chain. The end groups, introduced almost quantitatively in bulk at 60°C or above, were partly consumed by propagating radical addition. Copolymerizations of MATE with cyclohexyl acrylate (CHA) revealed that MATE is as reactive as CHA toward the poly(CHA) radical, and MATE is less reactive than CHA radical toward poly(MATE) radical by a factor of only 1.4. These results suggest that the poly(MATE) bearing the unsaturated end group can be a macromonomer copolymerizable with CHA to yield a highly branched structure because of the similarity in structure with the unsaturated end group of MATE. Comparison of MATE with unsaturated trimer and dimer of methyl acrylate indicated that the more significant steric hindrance of the α -substituent of MATE in homo- and copolymerization considerably facilitates introduction of the propenyl end group.

KEY WORDS End Group / Fragmentation / Chain Transfer / Steric Hindrance / Molecular Weight / Monomer Reactivity Ratios /

Methyl α -ethylacrylate homopolymerizes at an extremely low rate to low molecular weight because the steric hindrance of the α -ethyl group significantly suppresses propagation but not termination.^{1,2} However, a variety of α -(substituted methyl)acrylic esters readily polymerize despite the presence of larger α -substituents than the ethyl group. The polymerizabilities of the α -(substituted methyl)acrylates are accounted for by the favorable balance of slow propagation and slow termination arising from the steric hindrance.^{3,4} Some α -(substituted methyl)acrylates such α -(bromomethyl)-,^{5–7} α -(alkylsulfenylmethyl)-,^{8–10} and α -(arylsulfonylmethyl)acrylates¹¹ do not homopolymerize nor copolymerize with common monomers because of fast addition fragmentation chain transfer (AFCT). The radicals formed by addition of propagating radicals from common monomers to these acrylates readily undergo fragmentation to introduce the 2-carbalkoxy-2-propenyl ($\text{CH}_2=\text{C}(\text{CO}_2\text{R})\text{CH}_2-$) ω -end group and the corresponding α -end groups. Furthermore, methyl α -(chloromethyl)acrylate,¹² methyl α -(2-carbomethoxyethyl)acrylate (the dimer of methyl acrylate, MAD),^{13,14} and methyl α -(2,4-dicarbomethoxybutyl)acrylate (the trimer of methyl acrylate, MAT)^{15,16} function as polymerizable

monomers and AFCT agents, simultaneously.

α -(Substituted methyl)acrylic esters acting as AFCT agents, *e.g.*, methyl α -(bromomethyl)acrylate (MBMA), can introduce the ω -propenyl end group and the α -end group (both moieties of the AFCT agent) at the chain ends of poly(acrylic ester), poly(styrene), and poly(methyl methacrylate).^{5,17} The same unsaturated end group is formed by disproportionation of poly(methyl methacrylate) radicals.¹⁸ However, the unsaturated end group bound to high molecular weight poly(methyl methacrylate) has never drawn much attention as a reactive functional group for further reaction. Oligomers bearing substituted propenyl end groups can be prepared by catalytic chain transfer polymerization (CCTP) of α -methylvinyl monomers such as methyl methacrylate and α -methylstyrene using cobalt catalysts.^{19,20} Polymer or oligomer formed by CCTP has the propenyl end group bound to a quaternary carbon, and radical addition to the unsaturated end group tends to result in cleavage of the bond between the end group and the quaternary carbon to generate the propagating radical of the α -methylvinyl monomer.^{21,22} In order to use this type of polymer as macromonomer, β -fragmentation of the adduct radical must be suppressed. However, effective suppression of the fragmentation is impractical.

An alternative route to obtain polymer bearing the

[†]To whom correspondence should be addressed.

Table I. Homopolymerization of MAtE in bulk

[MAtE] mol L ⁻¹	[I] mol L ⁻¹	Temp. °C	Time h	Conv. %	<i>M_n</i> (GPC)	<i>M_w</i> / <i>M_n</i>
3.2	AIBN, 0.05	60	10	2.6	2300	1.4
3.2	ACN, 0.05	90	6	6.7	2100	1.4

ω -propenyl end group is high temperature polymerizations of acrylic ester and styrene.^{23,24} During the polymerizations, mid-chain radicals formed primarily by backbiting undergo β -fragmentation resulting in low molecular weight polymer bearing the propenyl end group.^{25–28} In order to attain sufficiently fast β -fragmentation of the mid-chain radicals the polymerization should be conducted at high temperature. It is noteworthy that the propagating radicals of MAD and MAT are structurally similar to the mid-chain radicals in acrylate polymerization, and the behavior of MAD and MAT and their propagating radicals can be regarded as models of the propenyl end group and the adduct radicals derived, respectively. MAD and MAT, which are unsaturated oligomers of methyl acrylate (MAOL), both undergo homopolymerization resulting in polymers with the unsaturated ω -end group arising from fragmentation of propagating radicals, particularly at 100 °C or above.^{13–15}

Our recent studies^{14,22} have revealed that the propenyl end groups bound to poly(acrylic ester) and poly(styrene) chains are as reactive as acrylic esters and styrene toward the respective polymer radicals to form copolymers. Therefore, AFCT introducing the ω -propenyl end group can be an efficient route to prepare radically copolymerizable macromonomers by radical polymerization. Although MAD mainly functions as monomer forming the polymer main chain at 60 °C due to the fragmentation reaction not being sufficiently fast, the efficiency of the ω -end group introduction increases with temperature as confirmed by ¹H NMR structural analysis and *M_n* measurement by gel permeation chromatograph (GPC).¹³ Polymerization of MAT, on the other hand, yields macromonomer more efficiently than MAD.¹⁵ MAOLs such as MAT and MAD, with the same chemical composition as monomeric methyl acrylate (MA), are considered to be more attractive AFCT agents for acrylate polymerization than MBMA, which introduces bromine as the α -end group *via* AFCT. However, the polymerization conditions should be carefully chosen to enhance the fragmentation rate of the MAOL radicals.

This paper describes the polymerization and copolymerization of methyl acrylate tetramer (MAtE) as a polymerizable AFCT agent as a means of macromonomer preparation. The reactivities of the se-

ries of MAOLs of MAD, MAT, and MAtE were estimated based on polymerization and copolymerization data, and compared as models for the propenyl end group.

EXPERIMENTAL

MAtE was synthesized by the Mannich reaction of MAT as previously reported.^{16,30} Cyclohexyl acrylate (CHA) was commercially available and was used after distillation under reduced pressure. 2,2-Azobisisobutyronitrile (AIBN) and 1,1-azobiscyclohexane-1-carbonitrile (ACN) were commercially available. Homopolymerizations (in bulk) and copolymerizations (in benzene) were carried out in Pyrex ampoules sealed under vacuum. After polymerization of MAtE, the solvent was evaporated from the polymerization mixture using a rotary evaporator. A preparative high performance liquid chromatography (HPLC) was employed to remove the unreacted MAtE from the polymerization mixture, and poly(MAtE) obtained was submitted for ¹H NMR and GPC analysis. In the case of polymerizations of MAT, the polymer was precipitated by a large amount of hexane. It was confirmed by GPC that no oligomeric products remain in the hexane solution. The monomer conversion was calculated from the weight of the dried polymer.

A Japan Analytical Industry LC-908 equipped with JAIGEL columns using chloroform as eluent. 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. Molecular weights were measured using a Tosoh 8000 series high-performance liquid chromatograph equipped with TSK-gel columns G5000HHR, GMultiporeHXL-M, and GMHHR-L connected in this order, and THF was used as eluent. Molecular weights were calibrated by poly(styrene) standards (*M_n* = 5.0 × 10² ~ 1.09 × 10⁶).

RESULTS AND DISCUSSION

Homopolymerization

MAtE polymerized slowly to low *M_n* as summarized in Table I. The ¹H NMR spectrum of poly(MAtE), which exhibits resonances due to the propenyl end

group as shown in Figure 1, is similar to that of poly(MA) with the propenyl end group except for the presence of the more intense resonances due to the methoxy groups. The spectral intensity ratio of the resonances ascribed to the olefinic protons (5.45–5.80 and 6.08–6.35 ppm) to that of the methoxy protons (3.45–3.80 ppm) allowed calculation of the end group content relative to the MATE units incorporated in the main chain. The k_p/k_f values for the polymerization of MATE at 60 and 90 °C were calculated from eq 1:

$$\frac{[\text{MAOL unit}]}{[\text{CH}_2=\text{C}]} = \frac{k_p[\text{MAOL}\cdot][\text{MAOL}]}{k_f[\text{MAOL}\cdot]} = \frac{k_p[\text{MAOL}]}{k_f} \quad (1)$$

Figure 1. ^1H NMR spectrum of the polymer obtained at 60 °C under the conditions of $[\text{MATE}] = 3.2 \text{ mol L}^{-1}$, and $[\text{AIBN}] = 5.0 \text{ mmol L}^{-1}$.

where k_p and k_f denote the rate constants of propagation and fragmentation, respectively (Scheme 1), and $[\text{MAOL unit}]$ and $[\text{CH}_2=\text{C}]$ are the contents of MAOL units in the main chain and unsaturated end groups, respectively. Eq 1 is based on the assumption that the unsaturated end groups do not undergo further reactions. The radical expelled by β -fragmentation, $\text{X}\cdot$, would smoothly add to MAOL to initiate a new chain. If the structure of poly(MAOL) is given by **1**, *i.e.*, if fragmentation is the main end forming event as opposed to bimolecular termination, then the degree of polymerization is given by $([\text{MAOL unit}]/[\text{CH}_2=\text{C}]) + 1 = DP(\text{N})$, where the “1” accounts for the unsaturated end group. The degree of polymerization determined by GPC is given by $DP(\text{G})$.

Table II summarizes the results of ^1H NMR structural analysis of the polymers, GPC measurements showing unimodal elution curves, and k_p/k_f values obtained according to eq 1 for polymerizations of MATE together with data for MAT and MAD.^{13,15} At 60 °C, the values of $DP(\text{G})$ and $DP(\text{N})$ increase in the order $\text{MATE} < \text{MAT} < \text{MAD}$. If AFCT is the main chain stopping reaction in the MATE polymerization, $DP(\text{G})/DP(\text{N})$ which can be the efficiency of the ω -end group introduction would be unity. The MATE polymerizations yielded $DP(\text{G})/DP(\text{N}) = 0.80$ (60 °C) and 0.92 (90 °C), significantly greater than for MAT and MAD, suggesting almost quantitative introduction of the ω -end groups during the MATE polymerizations. The $DP(\text{G})/DP(\text{N})$ values for MAT are considerably lower than unity, indicating that β -fragmentation is not sufficiently rapid for bimolecular termination to be negligible.¹⁵ The values of $DP(\text{G})$ and $DP(\text{N})$ for MAD are much greater than for MATE and MAT, in conformity

Scheme 1.

Table II. Results of GPC and ^1H NMR analysis of polymers of MATe, MAT, and MAD

MAOL (MW)	Temp. °C	Initiator ^a	$\frac{[\text{MAOL unit}]}{[\text{CH}_2=\text{C}]} + 1$ (= $DP(\text{N})^b$)	k_p/k_t L mol^{-1}	$M_n \times 10^{-3}^c$ ($DP(\text{G})^d$)	$DP(\text{G})$ $DP(\text{N})$
MATe (344 ^e)	60	AIBN	8.4	2.03	2.3(6.68)	0.80
MAT (258 ^e)	60	AIBN	18	4.25	2.3(8.91)	0.50
MAD ^f (172 ^e)	60	MAIB	1001	161	38.0(221)	0.22
MATe	90	ACN	6.6	1.75	2.1(6.10)	0.92
MAT ^g	90	ACN	6.4	1.33	1.0(3.88)	0.62
MAD ^f	100	ATMP	104	16.6	13.0(76)	0.73

^aPolymerizations were carried out in bulk: $[\text{Initiator}] = 0.05 \text{ mol L}^{-1}$, $[\text{MATe}] = 3.2 \text{ mol L}^{-1}$, $[\text{MAT}] = 4.0 \text{ mol L}^{-1}$, and $[\text{MAD}] = 6.2 \text{ mol L}^{-1}$. ^b $DP(\text{N})$ is degree of polymerization calculated from unsaturated end group content. ^cCalculated from unimodal elution curves showing $M_w/M_n = 1.3\text{--}1.9$. ^d $DP(\text{G})$ is degree of polymerization calculated from $M_n(\text{GPC})$. ^eMonomer molecular weight. ^fRef. 15. ^gRef. 13.

Scheme 2.

with faster fragmentation for MATe and MAT.

Although the MATe polymerization is slow (Table I), fragmentation of **2** can be utilized to introduce the propenyl end group by radical polymerization at 60°C (Scheme 2). The values of $DP(\text{G})/DP(\text{N})$ increase in the order $\text{MAD} < \text{MAT} < \text{MATe}$, revealing that the importance of bimolecular termination as an end forming event decreases in the same order. These re-

sults are consistent with the values obtained for k_p/k_t , which increase as $\text{MAD} > \text{MAT} > \text{MATe}$, with the values for MAT and MATe being much lower than for MAD. This suggests that the increase in the size of the α -substituent suppresses propagation and/or facilitates fragmentation, probably both. The situation at 90 and 100°C is however somewhat different; the lowest values of k_p/k_t , $DP(\text{G})$, $DP(\text{N})$, and $DP(\text{G})/DP(\text{N})$ are

here obtained for MAT, whereas the reaction behaviors for MAD and MATe are qualitatively consistent with the data at 60 °C. The value of k_p/k_f is expected to decrease with an increase in temperature since the activation energy for fragmentation (a unimolecular reaction) is greater than for propagation (a bimolecular reaction).^{13, 15, 31} The trend in k_p/k_f with temperature is as anticipated for MAD and MAT, but the value for MATe decreases much less than expected upon a temperature increase by as much as 30 °C. It should be recalled that the increase in the size of the α -substituent from MAD to MAT resulted in a decrease in the activation energy for the fragmentation.¹⁵

The similarity in the structures of the end groups and MAOL, in particular MATe, deserves attention. The k_p/k_f value for MATe being slightly greater than that for MAT at 90 °C in Table II suggests consumption of end groups by further reaction with propagating and expelled radicals in the case of MATe, leading to incorporation of the macromonomer moiety (**7** in Scheme 2). More precisely, the data suggest that the extent of end group reaction is greater for MATe than for MAT. Steric congestions of the end groups (**3** and **6**) and the radical centers (**2** and **5**) are compared in Scheme 2.

The reason for this is thought to be that the end group formed by fragmentation during MATe polymerization **6** is similarly or less congested than monomeric MATe. Although fragmentation of the MATe radical **2** to form poly(MATe) bearing the propenyl end group **3** and the small radical **4** is facilitated relative to propagation by an increase in temperature from 60 to 90 °C, **3** might be consumed by further reaction with **2** and **4** leading to an increase in [MATe unit]/[CH₂=C group], and thus underestimation of the true k_p/k_f value. In the case of MAT, on the other hand, the end group attached to the poly(MAT) chain **6** would be less reactive than monomeric MAT because the poly(MAT) chain and the C₄-group bearing two carbomethoxy groups are bound to the double bond as the α -substituents. The ω -end groups of poly(MAT) were found to be involved in further reactions during the MAT polymerization resulting in bimodal GPC curves.¹⁵

Copolymerization

Radical **2** readily undergoes β -fragmentation to yield polymer consisting of the MATe units and **3**. It was confirmed by inspection of the ¹H NMR spectra of the copolymers of MATe and MAT (Figures 2 and 3), which exhibit resonances assigned to the olefinic protons of the end group that **2** undergoes rapid β -fragmentation also during copolymerization. Results of copolymerizations of MATe, MAT, and MAD¹⁴ with CHA are summarized in Table III. The monomer reac-

Figure 2. ¹H NMR spectrum of CHA–MATe copolymer ($M_n=4100$) prepared by copolymerization in benzene for 3 h at 90 °C under the conditions of [MATe]=1.0 mol L⁻¹, [CHA]=1.0 mol L⁻¹, and [ACN]=5.0 mmol L⁻¹.

Figure 3. ¹H NMR spectrum of CHA–MAT copolymer ($M_n=3200$) prepared by copolymerization in benzene for 2 h at 90 °C under the conditions of [MAT]=1.0 mol L⁻¹, [CHA]=1.0 mol L⁻¹, and [ACN]=5.0 mmol L⁻¹.

tivity ratios were calculated from the copolymer compositions data obtained at low conversions (< 10%) (Figure 4). The quantity $1/r_1$ ($M_1 = \text{CHA}$, $M_2 = \text{MAOL}$) denotes the reactivities of MATe, MAT, and MAD toward the poly(CHA) radical relative to CHA. The CHA-terminated radicals add more rapidly to the MAOLs than to CHA, consistent with the propenyl end groups being as reactive as acrylic ester and styrene toward the respective propagating radicals.²² MATe and MAT are slightly less reactive than MAD towards the

Table III. Monomer reactivity ratios and GPC data for copolymerization of CHA (M_1) with MATE, MAT, and MAD (M_2)

M_2	Temp.	r_1	r_2	$1/r_1$	$1/r_2$	$\frac{M_n(G)^a}{M_n(N)}$	Ref
	$^{\circ}\text{C}$						
MATe	60	0.83	0.71	1.20	1.41	0.70 ^b	This work
MAT	60	0.83	0.56	1.20	1.79	0.60	15
MAD	60	0.68	1.28	1.47	0.78	0.44	14
MATe	90	0.86	0.63	1.16	1.58	0.88 ^c	This work
MAT	90	0.96	0.47	1.04	2.13	0.72	This work
MAD	100	0.66	1.00	1.52	1.00	0.62	14

^a $[M_1] = 0.6 \text{ mol L}^{-1}$, $[M_2] = 1.4 \text{ mol L}^{-1}$ in benzene. ^b3.3% conversion (4 h). ^c6.4% conversion (1 h).

Figure 4. Copolymer compositions curves for copolymerizations of CHA (M_1) with MATE and MAT (M_2) at 60 (●) and 90 °C (△).

poly(CHA) radical in accordance with the size of the α -substituents.

The value of $1/r_2$ represents the reactivity of CHA towards poly(MAOL) radicals such as **2** or **5** (Scheme 2) relative to MAOL. The r_2 values are less than unity for

the copolymerizations with MATE and MAT indicating that CHA is somewhat more reactive than MAOL towards the corresponding poly(MAOL) radicals. In the case of MATE, the $1/r_2$ value at 60 and 90 °C indicates that CHA is more reactive than MATE itself by factors of only 1.41 and 1.58, respectively. Considering the large differences in k_p values between MAOL (k_p for MAD and MAT at 60 °C are 19 and $2.43 \text{ L mol}^{-1} \text{ s}^{-1}$, respectively)^{13,15,16} and CHA ($k_p = 16000 \text{ L mol}^{-1} \text{ s}^{-1}$ at 30 °C),³² large differences in the k_{12} and k_{21} values can be predicted. Although $1/r_1$ for the copolymerization of CHA with MAD are greater than unity, the $1/r_2$ values are 0.78 (60 °C) and 1.00 (100 °C) showing that CHA is as reactive as MAD toward the poly(MAD) radical.

The values of $1/r_1$ are relatively unaffected by a temperature increase from 60 to 90 °C for MAD and MATE, although a decrease is observed for MAT. An increase in temperature for the MAT and MATE copolymerizations causes less incorporation of MAOL units into the copolymers relative to CHA, as seen in the observed increases in r_1 and decreases in r_2 . This may be related to the ceiling temperatures for homopropagation of MAT and MATE being close to 90 °C under the copolymerization conditions.^{13,15} As mentioned earlier, the efficiency of unsaturated end group introduction can be assessed by examination of the quantity $M_n(G)/M_n(N)$, which approaches unity as the efficiency increases. For all MAOLs, $M_n(G)/M_n(N)$ increases with temperature consistent with higher temperatures favoring fragmentation relative to propagation. Moreover, at both 60 and 90 °C, $M_n(G)/M_n(N)$ increases with the size of the α -substituent of MAOL, *i.e.*, in the order MAD < MAT < MATE, indicating suppressed propagation and/or increased rates of fragmentation in the same order.

Results of copolymerizations of MATE and MAT with CHA over a wide range of monomer feed compositions at 60 and 90 °C are summarized in Table IV

Table IV. Results of copolymerizations at 60 °C

[M ₂] in comonomer (mol%)	CHA (M ₁)–MATE (M ₂) ^a (<i>r</i> _{CHA} = 0.83, <i>r</i> _{MATE} = 0.71)			CHA (M ₁)–MAT (M ₂) ^a (<i>r</i> _{CHA} = 0.83, <i>r</i> _{MAT} = 0.50)		
	<i>M_n</i> × 10 ^{-3b}	[MATE unit] [CH ₂ =C]	<i>P_n</i> (MATE) <i>P_n</i> (CHA)	<i>M_n</i> × 10 ^{-3c}	[MAT unit] [CH ₂ =C]	<i>P_n</i> (MAT) <i>P_n</i> (CHA)
	(GPC)			(GPC)		
5	76.1 ^d	87.7 ^d	13.7/463	144.5 ^d	87.6 ^d	36.4/876
10	34.8	23.9	12.1/199	54.5	44.8	23.6/314
30	9.3	18.6	8.2/42.0	11.5	29.9	13.2/52.5
50	4.8	14.1	6.7/16.1	5.7	21.5	10.2/20.0
70	3.3	11.2	6.4/7.2	2.4	11.5	5.9/5.7
90	2.3	8.7	5.8/1.9	1.9	9.1	5.2/1.6

^a[M₁] + [M₂] = 2 mol L⁻¹ and [AIBN] = 5 mmol L⁻¹. ^bCalculated from unimodal elution curves showing *M_w*/*M_n* = 1.5–2.0. ^cCalculated from unimodal elution curves showing *M_w*/*M_n* = 1.4–2.5.

^d[M₁] + [M₂] = 3 mol L⁻¹ and [AIBN] = 5 mmol L⁻¹.

Table V. Results of copolymerization of MATE and MAT at 90 °C^a

[M ₂] in comonomer (mol%)	CHA (M ₁)–MATE (M ₂) (<i>r</i> _{CHA} = 0.86, <i>r</i> _{MATE} = 0.63)			CHA (M ₁)–MAT (M ₂) (<i>r</i> _{CHA} = 0.96, <i>r</i> _{MAT} = 0.47)		
	<i>M_n</i> × 10 ^{-3b}	[MATE unit] [CH ₂ =C]	<i>P_n</i> (MAT) ^c <i>P_n</i> (CHA)	<i>M_n</i> × 10 ^{-3d}	[MAT unit] [CH ₂ =C]	<i>P_n</i> (MAT) ^c <i>P_n</i> (CHA)
	(GPC)			(GPC)		
10	24.4	23.7	7.5/142	24.2	24.2	9.5/141
30	6.8	14.6	5.8/31	6.6	15.5	7.0/31
50	4.1	10.7	5.9/14	3.2	10.1	5.2/12
70	3.0	7.9	5.6/6.9	1.8	6.9	4.2/4.7
90	2.3	6.4	5.7/2.2	1.2	5.1	3.9/1.3

^a[CHA] + [M₂] = 2 mol L⁻¹ and [AIBN] = 5 mmol L⁻¹. ^bCalculated from unimodal elution curves showing *M_w*/*M_n* = 1.4–1.9. ^cCalculated from copolymer composition and *M_n*(GPC). ^dCalculated from unimodal elution curves showing *M_w*/*M_n* = 1.3–1.6.

Table VI. Results of CHA (M₁)–MAD (M₂) copolymerizations^a at 60 and 100 °C

[M ₂] in comonomer (mol%)	60 °C ^b (<i>r</i> _{CHA} = 0.68, <i>r</i> _{MAD} = 1.28)			100 °C ^c (<i>r</i> _{CHA} = 0.66, <i>r</i> _{MAD} = 1.00)		
	<i>M_n</i> × 10 ^{-3d}	[MAD unit] [CH ₂ =C]	<i>P_n</i> (MAD) <i>P_n</i> (CHA)	<i>M_n</i> × 10 ^{-3e}	[MAD unit] [CH ₂ =C]	<i>P_n</i> (MAD) <i>P_n</i> (CHA)
	(GPC)			(GPC)		
10	150	–	74/527	67	135	12/84
30	53	359	89/169	17.4	29.9	36/72
50	37	173	76/62	9.1	21.5	30/26
70	20	143	72/25	6.9	11.5	29/12
90	13	101	64/6	4.3	9.1	23/3

^a[M₁] + [M₂] = 2 mol L⁻¹. ^b[MAIB] = 10 mmol L⁻¹. ^c[ATMP] = 10 mmol L⁻¹. ^dCalculated from unimodal elution curves showing *M_w*/*M_n* = 1.6–1.8. ^eCalculated from unimodal elution curves showing *M_w*/*M_n* = 1.6–3.0.

and V, respectively. For comparison, the results of the copolymerization with MAD reported in our previous paper are shown in Table VI.¹⁴ An increase in the MATE or MAT content in the monomer feed results in a reduction in *M_n* because of the AFCT function of MAOL. An increase in CHA content in the monomer feed facilitated incorporation of a larger amount of MAOL as

monomer units to increase the [MAOL unit]/[CH₂=C] value because simultaneous addition of poly(MAOL) radicals to CHA and MAOL decreases the fragmentation of poly(MAOL) radicals relative to propagation. The copolymer composition given by the number of monomer units per chain, *P_n*(MAOL)/*P_n*(CHA), increases in the order of MATE < MAT < MAD at 60 and

90 °C. This can be explained by the r_1 and r_2 values together with the AFCT function of MAOL. The value of $[\text{MATE unit}]/[\text{CH}_2=\text{C}]$ is almost the same as $[\text{MAT unit}]/[\text{CH}_2=\text{C}]$ at each comonomer composition at both temperatures. The values of $[\text{MATE unit}]/[\text{CH}_2=\text{C}]$ and $[\text{MAT unit}]/[\text{CH}_2=\text{C}]$ are consistently higher at 60 than 90 °C, indicating that the rate of fragmentation relative to crosspropagation increase with temperature.

The value of k_{22}/k_f for copolymerization, corresponding to k_p/k_f for homopolymerization, was evaluated using eq 2, which can be derived in analogy with eq 1 by considering competition between propagation and β -fragmentation.^{13,14} It was assumed that penultimate effects on propagation and fragmentation are negligible.

$$\frac{[\text{MAOL unit}]}{[\text{CH}_2=\text{C}]} = \frac{k_{21}[\text{MAOL}\cdot][\text{M}_1] + k_{22}[\text{MAOL}\cdot][\text{MAOL}]}{k_f[\text{MAOL}\cdot]} \quad (2)$$

$$\frac{[\text{MAOL unit}]}{[\text{CH}_2=\text{C}][\text{MAOL}]} = \frac{k_{22}}{k_f} + \frac{k_{21}[\text{M}_1]}{k_f[\text{MAOL}]} = \frac{k_{22}}{k_f} \left(\frac{[\text{M}_1]}{r_2[\text{MAOL}]} + 1 \right) \quad (3)$$

Figure 5. Plots of $[\text{MAOL unit}]/[\text{CH}_2=\text{C}][\text{MAOL}]$ vs. $[\text{CHA}]/[\text{MAOL}]$ according to eq 2 for copolymerization of MAOL with CHA at 60 (MAT; ●, MATE; ○) and 90 °C (MAT; ▲, MATE; △).

Plots according to eq 3 for copolymerizations of MATE and MAT with CHA at 90 °C are shown in Figure 5, and Table VII lists the values of k_{22}/k_f obtained from the y-intercepts. Although a significant difference between k_p/k_f for the homopolymerizations of MATE and MAT was observed at 60 °C (Table II), the k_{22}/k_f values for the CHA copolymerizations of MATE and MAT are the same at both 60 and 90 °C suggesting underestimation of the k_{22}/k_f values arising from consumption of the end group by further reaction (Table VII). The k_{22}/k_f values for MAD are considerably greater than those for MATE and MAT, indicating that the MATE and MAT radicals undergo faster fragmentation than the radical from MAD not only in homopolymerization but also in copolymerization with CHA. The k_p/k_f values (Table II), the $M_n(\text{G})/M_n(\text{N})$ values (Table III), and the k_{22}/k_f values (Table VII) reveal that the propenyl end groups are almost quantitatively introduced in the copolymers involving MATE at 60 and 90 °C, and by the copolymerization with MAT at 90 °C. Finally, it is also noteworthy that the slopes (*i.e.*, k_{21}/k_f) decrease with increasing temperature as expected, and that k_{21}/k_f (MATE) $>$ k_{21}/k_f (MAT), suggesting that fragmentation is faster and/or crosspropagation is slower for MATE than for MAT.

CONCLUSIONS

MATE homopolymerization and copolymerization with CHA have been studied with the focus on macromonomer formation by β -fragmentation of the MATE propagating radical. The results were compared with polymerizations and copolymerizations of MAT and MAD, as summarized in Table VIII with brief remarks. The ratio of the degree of polymerization determined by GPC ($DP(\text{G})$) to that calculated from the end group content ($DP(\text{N})$) denotes the efficiency of end group introduction. The ratios of the rate constants for propagation to fragmentation (k_p/k_f), which closely relates to $DP(\text{G})/DP(\text{N})$, were evaluated to show the balance between the two reactions. The end groups were introduced almost quantitatively in poly(MATE) at low conversion at 60 and 90 °C. The values of $1/r_1$

Table VII. k_{22}/k_f and k_{21}/k_f values for copolymerizations of CHA (M_1) with MATE, MAT, and MAD (M_2)

MAOL (M_2)	k_{22}/k_f (L mol^{-1})			k_{21}/k_f (L mol^{-1})			Ref
	60 °C	90 °C	100 °C	60 °C	90 °C	100 °C	
MATE	4.5	3.1	—	11.9	9.5	—	This work
MAT	4.4	3.1	—	4.6	2.3	—	This work
MAD	82.8	—	20.0	115	—	31.6	14

Table VIII. Comparison of MATE, MAT, and MAD from different points of view

Item	Observed order	Factors considered
$DP(G)/DP(N)$ at 60 °C	MATe > MAT > MAD	Facilitation of fragmentation as the main end forming reaction by α -substituent.
$DP(G)/DP(N)$ at 90 °C	MATe > MAD (100 °C) > MAT	Facilitation of fragmentation by α -substituent + Further reaction of end group formed.
k_p/k_f at 60 °C	MATe < MAT < MAD	Decrease and increase in k_p and k_f , respectively, by α -substituent.
k_p/k_f at 90 °C	MAT < MATE < MAD (100 °C)	Decrease and increase in k_p and k_f , respectively, by α -substituent + Further reaction of end group formed
$1/r_1$ at 60 °C	MATe = MAT < MAD	Decrease in reactivity toward poly(CHA) radical by α -substituent.
$1/r_1$ at 90 °C	MAT < MATE < MAD (100 °C)	Decrease in reactivity toward poly(CHA) radical by α -substituent + Further reaction of end group after fragmentation.
$1/r_2$ at 60 °C	MAT > MATE > MAD	Decrease in k_{22} by bulky by α -substituent of propagating radical + Further reaction of end group after fragmentation.
$1/r_2$ at 90 °C	MAT > MATE > MAD (100 °C)	Decrease in k_{22} by α -substituent of propagating radical + Further reaction of end group after fragmentation.
k_{22}/k_f at 60 °C	MAD $\gg$ MATE $\sim$ MAT	Increase in k_f by internal strain arising from α -substituent + Further reaction of end group after fragmentation.

and $1/r_2$ were calculated from the monomer reactivity ratios to estimate the steric hindrance of the additions of the poly(CHA) radical to MATE and MAT, and for the additions of the corresponding propagating radicals to CHA. The α -substituents of MATE and MAT appear to suppress addition despite the acceleration of the β -fragmentation. Consequently, copolymerization of MATE with CHA was confirmed to be an efficient route to prepare macromonomer bearing the propenyl end group. However, the end group introduced to poly(MATE) copolymerizes with MATE since the level of steric congestion of the end group is similar to that of monomeric MATE.

Acknowledgment. Financial support from Toagosei Co., Ltd. is gratefully acknowledged.

REFERENCES

1. J. Penelle, J. Collot, and G. Rufford, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 2407 (1993).
2. S. Kobatake and B. Yamada, *Polym. J.*, **28**, 535 (1996).
3. B. Yamada and S. Kobatake, *Prog. Polym. Sci.*, **19**, 1089 (1994).
4. B. Yamada, D. G. Westmoreland, S. Kobatake, and O. Konosu, *Prog. Polym. Sci.*, **24**, 565 (1999).
5. B. Yamada and S. Kobatake, *Polym. J.*, **24**, 281 (1992).
6. G. F. Meijs, E. Rizzardo, and S. H. Thang, *Polym. Bull.*, **24**, 501 (1990).
7. S. A. F. Bon, S. R. Morseley, C. Waterson, and D. F. M. Haddleton, *Macromolecules*, **33**, 5819 (2000).
8. G. F. Meijs, E. Rizzardo, and S. H. Thang, *Macromolecules*, **21**, 3122 (1988).
9. G. F. Meijs, T. C. Morton, E. Rizzardo, and S. H. Thang, *Macromolecules*, **24**, 3689 (1999).
10. E. Rizzardo, Y. K. Chong, R. A. Evans, G. Moad, and S. H. Thang, *Macromol. Symp.*, **111**, 1 (1996).
11. T. Sato, M. Seno, M. Kobayashi, T. Kohono, and H. Tanaka, *Eur. Polym. J.*, **31**, 29 (1995).
12. B. Yamada, S. Kobatake, and S. Aoki, *Macromolecules*, **26**, 5099 (1993).
13. S. Kobatake and B. Yamada, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 95 (1996).
14. T. Harada, P. B. Zetterlund, and B. Yamada, *J. Polym. Sci.*,

Part A: Polym. Chem., in press.

15. T. Hirano and B. Yamada, *Polymer*, **44**, 347 (2003).
16. S. Kobatake and B. Yamada, *Macromol. Chem. Phys.*, **198**, 2825 (1997).
17. B. Yamada, S. Kobatake, and S. Aoki, *Polym. Bull.*, **31**, 263 (1993).
18. K. Hatada, T. Kitayama, K. Ute, Y. Terawaki, and T. Yanagida, *Macromolecules*, **30**, 754 (1997).
19. A. A. Gridnev and S. D. Ittel, *Chem. Rev.*, **101**, 3611 (2001).
20. J. P. A. Heuts, G. E. Roberts, and J. D. Biosutti, *Aust. J. Chem.*, **55**, 381 (2002).
21. B. Yamada, S. Tagashira, and S. Aoki, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 2745 (1994).
22. B. Yamada, F. Oku, and T. Harada, *J. Polym. Sci., Part A: Polym. Chem.*, **41**, 645 (2003).
23. J. Chiefari, J. Jeffery, R. T. A. Mayadunne, G. Moad, E. Rizzardo, and S. H. Thang, *Macromolecules*, **32**, 7700 (1999).
24. J. Chiefari, J. Jeffery, R. T. A. Maydunne, G. Moad, E. Rizzardo, and S. H. Thang, 'Preparation of Macromonomers via Chain Transfer with and without Added Chain Transfer Agent', in "Controlled/Living Radical Polymerization. Progress in ATRP, NMP, and RAFT", K. Matyjaszewski, Ed., ACS Symposium Series No. 768, American Chemical Society, Washington, D.C., 2000, p 21.
25. B. C. Gilbert, J. R. L. Smith, E. C. Milne, A. C. Whitwood, and P. Taylor, *J. Chem. Soc. Perkin Trans. 2*, 1759 (1994).
26. B. Yamada, M. Azukizawa, H. Yamazoe, D. J. T. Hill, and P. J. Pomery, *Polymer*, **41**, 5611 (2000).
27. M. Azukizawa, B. Yamada, D. J. T. Hill, and P. J. Pomery, *Macromol. Chem. Phys.*, **201**, 774 (2000).
28. A. M. van Herk, *Macromol. Rapid Commun.*, **22**, 687 (2001).
29. D. J. Trumbo and R. A. Zander, *J. Polym. Sci., Part A: Polym. Chem.*, **29**, 1053 (1991).
30. B. A. Feit, *Eur. Polym. J.*, **8**, 321 (1972).
31. J. Fossey, D. Lefort, and J. Sorba, "Free Radicals in Organic Chemistry", John Wiley & Sons, Ltd., Chichester, 1995, p 148.
32. K. Tanaka, B. Yamada, R. Willemse, and A. M. van Herk, *Polym. J.*, **34**, 692 (2002).