Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 3999–4004

polymer

www.elsevier.com/locate/polymer

Radical copolymerization of (−)-menthyl 2-acetamidoacrylate and styrene or methyl methacrylate near ceiling temperature

Miki Niwa, Hitoshi Tanaka*

Institute of Technology and Science, University of Tokushima, Minamijosanjima-cho, Tokushima 770-8506, Japan

Received 28 March 2007; received in revised form 7 May 2007; accepted 18 May 2007
Available online 25 May 2007

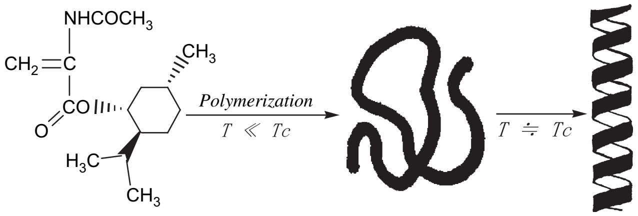
Abstract

Radical copolymerization of chiral monomer, (−)-menthyl 2-acetamidoacrylate (**1**), with low ceiling temperature ($T_c = 62.0$ °C in [monomer] = 1.0 mol/L) and styrene or methyl methacrylate (MMA) has been studied near ceiling temperature (60 °C) and at the temperature lower than T_c (30 °C). Monomer reactivity ratios and Alfrey–Price Q and e-values of **1** are estimated to be $r_1 = 0.27$, $r_2 = 0.067$, $Q = 3.0$, and $e = 1.2$ at 30 °C, and $r_1 = 0.32$ and $r_2 = 0.046$ at 60 °C for the copolymerization of **1** (M_1) and styrene (M_2), suggesting an alternating tendency at both temperatures, whereas for the copolymerization of **1** (M_1) and MMA (M_2) r_1 and r_2 are estimated to be 2.9 and 0.019 at 30 °C, respectively, indicating longer sequence length of **1**. Specific rotation and circular dichroism of the resulting copolymer indicate that styrene, in particular, is effectively incorporated into a helical copolymer structure at 60 °C and even only 25 mol% incorporation of the acetamidoacrylate unit in the copolymer induces the helix formation in solution.

Keywords: Radical copolymerization; Ceiling temperature; Helical copolymer

1. Introduction

Generation of helical polymer through a radical polymerization has attracted much attention, in particular, for mechanistic interest [1] and practical advantage in radical polymerization, e.g., high accessibility for a number of monomers and solvents, high reproducibility, and easy procedures [2]. Okamoto and his coworkers have reported that the methacrylates bearing bulky aryl substituents at the ester moiety including achiral arylmethyl methacrylates produce a helical polymer in radical polymerization [3] and one-handed chiral helical polymer is successfully obtained in the presence of the chiral reagents including (+)- and (−)-menthol, (−)-2-octanol, and so on [4]. Influence of other additives including comonomers as well as a chiral reagent on helicity induction has also been examined in a radical copolymerization of achiral bulky *N*-[(4-butyl)triphenylmethyl]methacrylamide with the chiral monomers including *N*-[(*R*)-(+)-1-(1-naphthyl)ethyl]methacrylamide, *N*-((*R*)-(−)-1-cyclohexylethyl)methacrylamide, and so on, and it has been found that the optically active monomeric units can induce a single-handed helical conformation of the achiral monomeric sequence via copolymerization [5]. Such a copolymerization has received a renaissance by a mechanistic interest and for a preparation of multi-functional polymer. Recently, we found that the captodatively (cd) substituted acrylates including (−)- and (+)-menthyl 2-acetamidoacrylate would give a helical polymer in the polymerization near ceiling temperature (T_c) [6].



1

---

* Corresponding author.
E-mail address: tanaka@opt.tokushima-u.ac.jp (H. Tanaka).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.05.054

In the present paper, we will study an influence of achiral less bulky vinyl comonomers including styrene and methyl methacrylate (MMA) on the copolymerization of (−)-menthyl 2-acetamidoacrylate (**1**) and their helicity induction.

2. Experimental

2.1. Materials

Basic chemicals were purchased from Wako Pure Chemical Industries Ltd. Commercial grade azo initiators including 2,2′-azobis(isobutyronitrile) (AIBN) and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) were purified by recrystallization from ethanol. Styrene and MMA were washed with aq. sodium sulfite, water, NaOH (aq. 5%), NaCl (aq. 20%), and dried over magnesium sulfate, then distilled under reduced pressure just before use. Deuterated solvent $CDCl_3$ used for NMR measurement was purchased from Acros Organics Co. and used without further purification.

Compound **1** was prepared according to the previous paper [6], and purified by column chromatography using a mixture of *n*-hexane and ethylacetate (4:1) as a developing solvent, $[\alpha]_D = -81.0°$ in $CHCl_3$. ^1H NMR ($CDCl_3$, TMS, ppm): 0.76 (d, $J = 7.1$ Hz, 3H, CH_3), 0.90 (d, $J = 7.1$ Hz, 3H, CH_3), 0.92 (d, $J = 6.6$ Hz, 3H, CH_3), 1.0–2.0 (m, 9H, menthyl), 2.13 (s, 3H, $COCH_3$), 4.80 (dt, $J = 4.5$, 11 Hz, 1H, menthyl), 5.85 (s, 1H, CH=), 6.57 (s, 1H, CH=), 7.94 (br s, 1H, NH). Anal. Calcd for $C_{15}H_{25}NO_3$: C, 68.04; H, 9.41; N, 4.87. Found: C, 67.90; H, 9.38; N, 5.02.

2.2. Copolymerization

Copolymerization was usually carried out in benzene in a sealed ampoule with shaking at a given temperature. The ampoule containing required amounts of reagents including initiator, solvent, and monomers was degassed several times by a freeze–thaw method and then sealed under reduced pressure and placed in a constant temperature bath. The resulting copolymer was isolated by pouring the contents of the ampoule into a large amount (ca. 20-fold) of methanol, and purified by reprecipitations from tetrahydrofuran into methanol for the NMR measurement and elemental analysis.

2.3. Measurements

^1H NMR spectrum was recorded on JEOL EX-400 (400 MHz) spectrometer at 23 °C in $CDCl_3$. Specific rotation $[\alpha]_D$ at $\lambda = 589.3$ nm (Na-D) was measured on JASCO DIP-360 digital polarimeter in $CHCl_3$ at ambient temperature. Circular dichroism (CD) was recorded on JASCO J-820 spectropolarimeter in *n*-hexane at 20 °C. Copolymer composition was determined from the nitrogen content found by elemental analysis of the purified copolymer, and monomer reactivity ratio was estimated by the curve fitting method.

3. Results and discussion

3.1. Copolymerization of **1** and styrene

Copolymerization of **1** (M_1) and styrene (M_2) was carried out at 30 and 60 °C in benzene using AMVN and AIBN as radical initiators, respectively. It is clear from Table 1 that the specific rotation $[\alpha]_D$, levorotation, of the resulting copolymer tends to increase monotonously with increasing contents of **1** in the copolymer at 30 °C, whereas it takes the maximum value of $[\alpha]_D = -72.8°$ in 73.7 mol% M_1 containing copolymer in the copolymerization at 60 °C. Fig. 1 illustrates clearly an influence of the comonomer content on the specific rotation of the copolymer. In the copolymerization at 30 °C, levorotation of poly(**1**-*co*-styrene) increases linearly with increasing contents of **1** in the copolymer, whereas at 60 °C it would deviate from the linear line near 45 wt% (ca. 25 mol%) M_1 containing copolymer. Exceptional non-linear relationship between $[\alpha]_D$ and M_1 contents of the copolymer in the copolymerization at 60 °C might be correlated to the structural change in the copolymerization near T_c [5,6]. That is, propagating polymer chain of **1** has been reported to change gradually its secondary structure from random coil to helix with an elevating polymerization temperature, and finally **1** converts predominantly to the helical structure showing dextrorotation near T_c of **1** [6]. The present copolymerization temperature (60 °C) is far from T_c of styrene ($T_c = 150$ °C in benzene and $[\text{styrene}] = 9.1 \times 10^{-4}$ mol/L [7]), but close to T_c of **1**

Table 1
Copolymerization of **1** (M_1) and styrene (M_2) in benzene at 30 and 60 °C and specific rotation of copolymer

$[M_1]$ in feed (mol%)	Temp.[a] (°C)	Time (h)	Yield[b] (%)	$[M_1]$ in copolymer[c]		$[\alpha]_D$[d] (deg)
				mol%	wt%	
10.0	30	1.7	2.8	38.5	61.6	−61.0
30.0	30	1.3	4.6	49.3	71.4	−67.5
50.0	30	0.9	4.4	56.7	77.1	−78.5
70.0	30	0.9	7.5	64.1	82.1	−80.0
90.0	30	0.4	3.9	73.0	87.4	−94.0
98.0	30	0.5	3.8	93.4	97.3	−95.4
100	30	0.3	1.8	100	100	−98.5
0.20	60	2.0	3.5	3.7	9.0	−6.0
0.60	60	2.0	3.4	8.0	18.3	−16.3
1.00	60	0.9	1.7	12.5	26.9	−28.5
3.00	60	1.0	3.0	24.9	46.0	−45.0
5.00	60	0.9	3.6	37.6	60.7	−55.0
10.0	60	1.3	6.5	42.5	65.5	−53.0
30.0	60	1.3	9.9	48.1	70.4	−62.5
50.0	60	1.0	11.3	57.0	77.3	−65.5
70.0	60	1.0	11.6	62.0	80.7	−72.5
90.0	60	1.0	9.0	73.7	87.8	−72.8
98.0	60	0.5	3.9	84.9	93.5	−71.9
100	60	1.3	9.7	100	100	−61.5

[a] AMVN and AIBN were used for the copolymerization at 30 and 60 °C, respectively. $[\text{Initiator}] = 5.0 \times 10^{-3}$ mol/L.

[b] Yield of methanol-insoluble polymer.

[c] Copolymer composition was determined by the nitrogen content in elemental analysis.

[d] $[\text{Polymer}] = 0.2$ g/dL in $CHCl_3$ at ambient temperature.

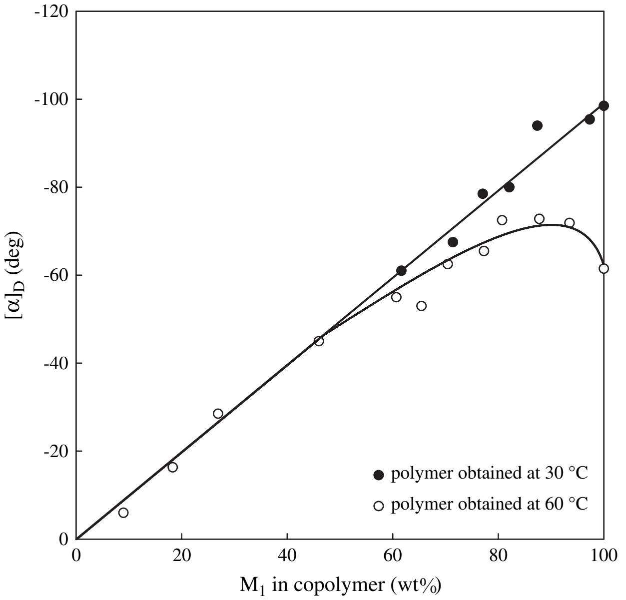


Fig. 1. Dependence of specific rotation of poly(**1**-*co*-styrene) on M_1 contents in copolymer.

($T_c = 62.0$ °C in benzene and [**1**] = 1.0 mol/L [8]). Such a structural change can be eventually demonstrated in the CD spectrum as seen in Fig. 2. That is, the [θ] value of the copolymer obtained at 60 °C shifts toward the positive and negative Cotton effects at 202 and 220 nm, respectively, compared with that obtained at 30 °C [9], which is a characteristic behavior of a helical polymer [6].

Figs. 3 and 4 represent the copolymer composition curves for the copolymerizations of **1** (M_1) and styrene (M_2) at 30 and 60 °C, respectively, where the theoretical curves are calculated for the Mayo–Lewis and Lowry's Case 1 and Case 2 [10] mechanisms. Monomer reactivity ratios, r_1 and r_2, estimated for all these models are shown in Table 2, in which the equilibrium constants K used for the calculations of the Lowry's Case models were 4.06 and 1.18 at 30 and 60 °C, respectively, which were determined using the correlation $K = 1/[M]_e$ and the equilibrium monomer concentration $[M]_e$ of 0.247 and 0.850 mol/L at 30 and 60 °C, respectively [11]. Although every curve illustrated is not so much deviated from the experimental results, the Lowry's Case 1 and Case 2 are rather satisfactory at 30 and 60 °C, respectively, and the best fit monomer reactivity ratios were $r_1 = 0.27$ and $r_2 = 0.067$, and $r_1 = 0.32$ and $r_2 = 0.046$ at 30 and 60 °C, respectively. It is noted that an alternating tendency of the copolymer sequence is observed in both systems. Indeed, the absorption due to the phenyl protons of the styryl unit in the ^{1}H NMR spectrum of poly(**1**-*co*-styrene) was observed as a single peak with small shoulder near 7.2 ppm, which indicates

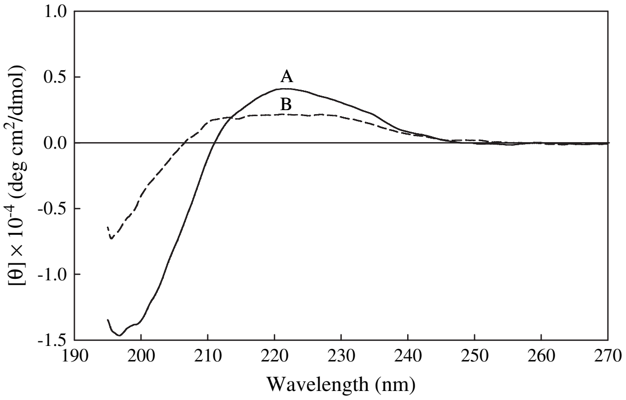


Fig. 2. CD spectra of poly(**1**-*co*-styrene) obtained at (A) 30 °C ([**1**] = 93.4 mol%) and (B) 60 °C ([**1**] = 84.9 mol%). Spectra were measured in *n*-hexane at 20 °C.

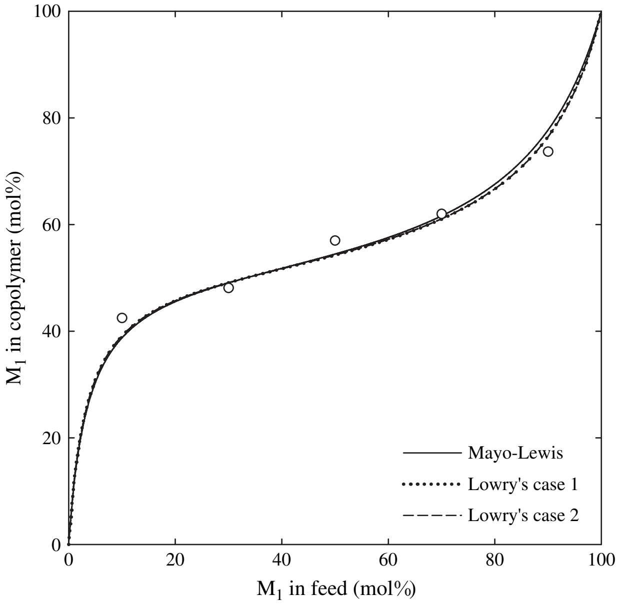


Fig. 3. Copolymer composition curves for the copolymerization of **1** and styrene at 30 °C in benzene and [**1**] + [styrene] = 2.0 mol/L.

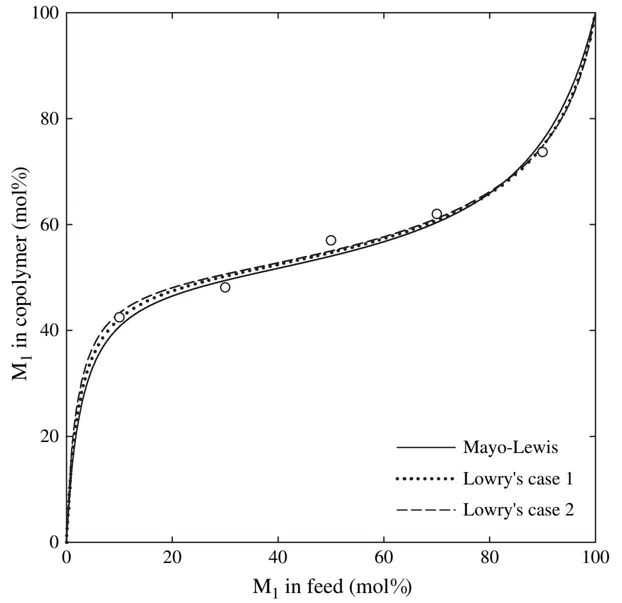


Fig. 4. Copolymer composition curves for the copolymerization of **1** and styrene at 60 °C in benzene and [**1**] + [styrene] = 2.0 mol/L.

Table 2
Reactivity ratio for **1** (M_1) and styrene (M_2)

Method	Temp. (°C)	r_1	r_2	σ[a]
Mayo–Lewis	30	0.28	0.070	2.75
Lowry's case 1	30	0.28	0.067	2.39
Lowry's case 2	30	0.27	0.067	2.37
Mayo–Lewis	60	0.24	0.055	2.05
Lowry's case 1	60	0.32	0.046	1.58
Lowry's case 2	60	0.28	0.039	1.60

[a] Standard deviation.

a very short styrene sequence length in the copolymer [12]. Johnston and Rudin have pointed out that the depropagation effects are not important in the copolymerization when the monomer with low T_c takes a short sequence length [13]. Little variation of the monomer reactivity ratios at 30 and 60 °C may be interpreted by such a short sequence length of **1**.

Lowry's Case 1

$$\sim\sim\sim M_2M_1^{\bullet} + M_1 \rightleftharpoons \sim\sim\sim M_2M_1M_1^{\bullet}$$

Lowry's Case 2

$$\sim\sim\sim M_2M_1M_1^{\bullet} + M_1 \rightleftharpoons \sim\sim\sim M_2M_1M_1M_1^{\bullet}$$

From the monomer reactivity ratios, Alfrey–Price *Q* and *e*-values [14] of **1** were calculated to be 3.0 and 1.2, respectively, at 30 °C. Since the *Q* value has been correlated to not only a resonance effect but also a steric one [15], the large *Q* value of **1** obtained might be due to a large steric hindrance of **1** as well as the captodative resonance stabilization [16]. Opposite polarity in *e*-value for each monomer and large steric hindrance of **1** presumably induce a preferential cross-propagation to give an alternating copolymer. Less bulky styryl units existed in an alternating position in copolymer chain and facile formation of helical structure of, in particular, isotactic polystyrene in the solid [17] or gel state [18], therefore, should be favorable for the helical copolymerization, and styryl unit can be effectively incorporated into the copolymer.

*3.2. Copolymerization of **1** and MMA*

Table 3 shows the copolymerization of **1** (M_1) and MMA (M_2) at 30 and 60 °C, respectively.

Table 3
Copolymerization of **1** (M_1) and MMA (M_2) in benzene at 30 and 60 °C and specific rotation of copolymer

$[M_1]$ in feed (mol%)	Temp.[a] (°C)	Time (h)	Yield[b] (%)	$[M_1]$ in copolymer[c]		$[\alpha]_D$[d] (deg)
				(mol%)	(wt%)	
10.0	30	2.6	0	–	–	–
30.0	30	1.4	6.2	66.6	84.2	−86.5
50.0	30	0.8	5.9	78.2	90.5	−91.5
70.0	30	0.6	5.7	87.0	94.7	−95.5
90.0	30	0.4	5.9	96.5	98.6	−101.0
100	30	0.4	6.2	100	100	−105.5
10.0	60	4.0	0	–	–	–
30.0	60	2.0	2.9	54.3	76.0	−77.5
50.0	60	1.2	4.7	66.9	84.4	−78.5
70.0	60	1.0	5.3	80.1	91.5	−80.0
90.0	60	1.0	7.4	90.5	96.2	−77.0
100	60	0.8	5.7	100	100	−65.5

[a] AMVN and AIBN were used for the copolymerization at 30 and 60 °C, respectively. $[\text{Initiator}] = 5.0 \times 10^{-3}$ mol/L.

[b] Yield of methanol-insoluble polymer.

[c] Copolymer composition was determined by the nitrogen content in elemental analysis.

[d] $[\text{Polymer}] = 0.2$ g/dL in $CHCl_3$ at ambient temperature.

Relationship between $[\alpha]_D$ and M_1 content of the copolymer displays a tendency similar to the copolymerization with styrene, but the levorotation of the resulting copolymer takes the maximum value of $[\alpha]_D = -80.0°$ in 80.1 mol% M_1 containing copolymer in the copolymerization at 60 °C. Fig. 5 illustrates the influence of the comonomer content on the specific rotation of the copolymers. In the copolymerization at 30 °C, the levorotation of poly(**1**-*co*-MMA) increases linearly with increasing contents of **1** like styrene system, but at 60 °C it would deviate from the linear line near 70 wt% (ca. 50 mol%) M_1 containing copolymer. In this case, it would also be correlated to the structural change of the copolymer since the copolymerization temperature (60 °C) is far from T_c of MMA ($T_c = 155.5$ °C in *o*-dichlorobenzene and $[\text{MMA}] = 0.82$ mol/L [7]). Fig. 6 actually demonstrates such a structural change, in which the variation of the CD intensity at 202 and 220 nm is similar to that observed for poly(**1**-*co*-styrene) [9].

Figs. 7 and 8 show the copolymer composition curves of **1** (M_1) and MMA (M_2) at 30 and 60 °C, respectively. The copolymerization was also analyzed according to the three models, and the calculated curves are depicted in both figures. In contrast to the copolymerization of styrene, Lowry's case 1 is not the best fit model for the copolymerization of MMA as seen in Table 4 and Figs. 7 and 8, and Lowry's case 2 or Mayo–Lewis model is rather predominant for the copolymerization

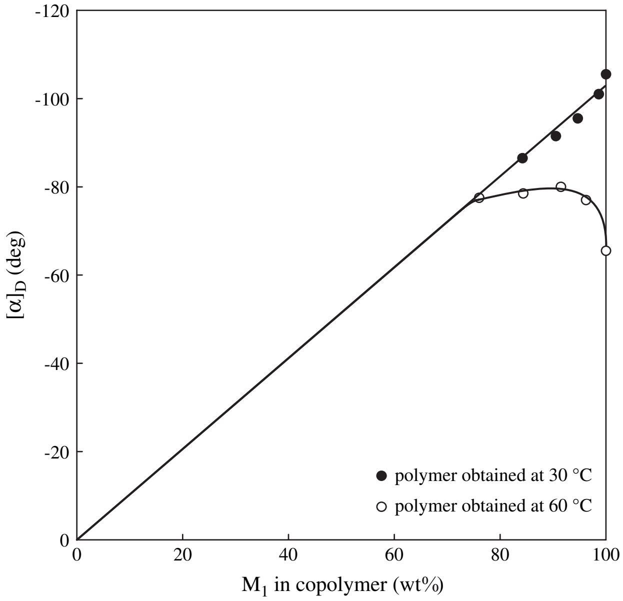


Fig. 5. Dependence of specific rotation of poly(**1**-*co*-MMA) on M_1 contents in copolymer.

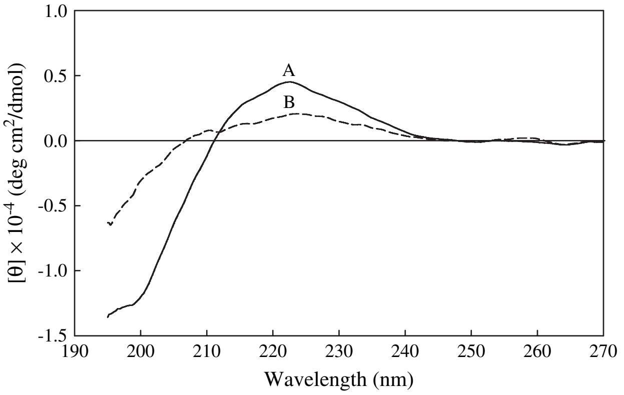


Fig. 6. CD spectra of poly(**1**-*co*-MMA) obtained at (A) 30 °C ([**1**] = 96.5 mol%) and (B) 60 °C ([**1**] = 90.5 mol%). Spectra were measured in *n*-hexane at 20 °C.

mechanism. Therefore, poly(**1**-*co*-MMA), compared with poly(**1**-*co*-styrene), has a longer sequence length of **1**, e.g., a block sequence tendency, and the best fit monomer reactivity ratio was estimated to be $r_1 = 2.9$ and $r_2 = 0.019$, and $r_1 = 2.0$ and $r_2 = 0.16$ at 30 and 60 °C, respectively, for Lowry's case 2. Such a copolymerization reactivity may be due to the positive polarity ($e = 0.40$) of MMA in analogy with **1** [7]. In addition, monomer reactivity ratios for the copolymerization with MMA were varied with the polymerization temperatures in contrast to the copolymerization with styrene. Longer sequence length of **1** and larger steric effect of MMA in the copolymerization of **1** with MMA compared with that of styrene might reduce the r_1 value, but increase the r_2 value. Deviation of $[\alpha]_D$ from the linear line in relatively higher M_1 content (ca. 50 mol%) in poly(**1**-*co*-MMA) than poly(**1**-*co*-styrene) also indicates a relatively large steric hindrance of MMA, which is unfavorable for the formation of helical structure. The inhibition or retardation of the polymerization by admixture of MMA to **1** was indeed observed in higher MMA concentration (90 mol% of MMA in monomer feed) as in Table 3 in contrast to the admixture of styrene, in which no polymer was produced and it demonstrates feasible depropagation presumably due to a larger steric hindrance of MMA.

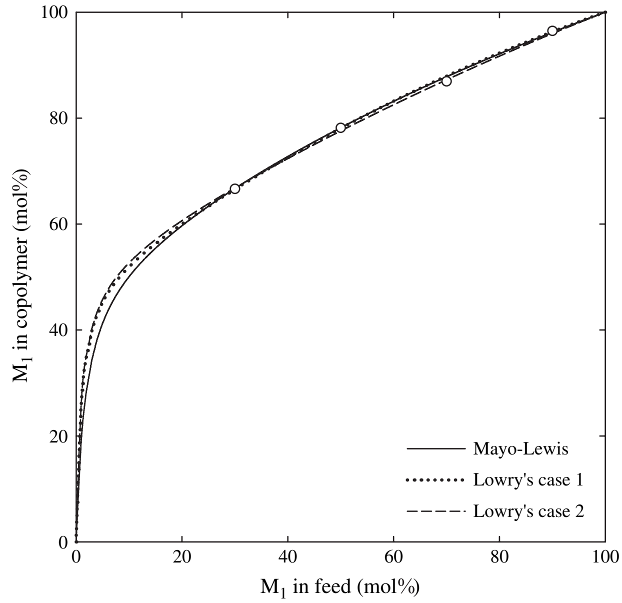


Fig. 7. Copolymer composition curves for the copolymerization of **1** and MMA at 30 °C in benzene and [**1**] + [MMA] = 2.0 mol/L.

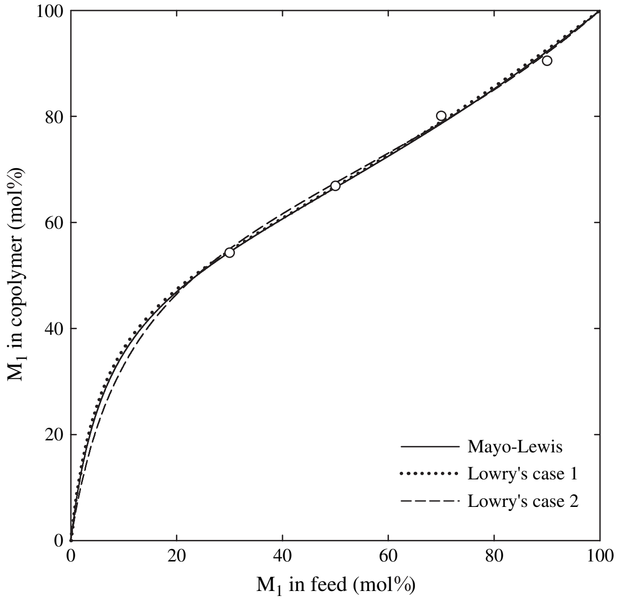


Fig. 8. Copolymer composition curves for the copolymerization of **1** and MMA at 60 °C in benzene and [**1**] + [MMA] = 2.0 mol/L.

Table 4
Reactivity ratio for **1** (M_1) and MMA (M_2)

Method	Temp. (°C)	r_1	r_2	σ[a]
Mayo–Lewis	30	2.7	0.033	0.45
Lowry's case 1	30	3.2	0.019	0.49
Lowry's case 2	30	2.9	0.019	0.42
Mayo–Lewis	60	1.2	0.12	1.16
Lowry's case 1	60	2.3	0.11	1.21
Lowry's case 2	60	2.0	0.16	1.07

[a] Standard deviation.

4. Conclusion

Styrene and MMA formed a helical copolymer in conventional free radical vinyl copolymerization with captodatively substituted chiral acrylate, (−)-menthyl 2-acetamidoacrylate, near T_c. It is noted that styrene tends to undertake an alternating copolymerization with the chiral acrylate and is effectively incorporated into a helical structure, and even only 25 mol% of the chiral acrylate unit in the copolymer could make styrene to induce a helical structure in solution in the copolymerization near T_c. That is, the present chiral acrylate would serve as a good reagent to promote a helical structure.

References

[1] Bennani YL, Hanessian S. Chem Rev 1997;97:3161.

[2] Okamoto Y, Nakano T. Chem Rev 1994;94:349.

[3] (a) Nakano T, Shikisai Y, Okamoto Y. Polym J 1996;28:51;
(b) Nakano T, Matsuda A, Okamoto Y. Polym J 1996;28:556.

[4] (a) Hoshikawa N, Hotta Y, Okamoto Y. J Am Chem Soc 2003;125:12380;
(b) Hoshikawa N, Yamamoto C, Hotta Y, Okamoto Y. Polym J 2006;38:1258.

[5] Azam AKMF, Kamigaito M, Tsuji M, Okamoto Y. Polym J 2006;38:1173.

[6] Tanaka H, Niwa M. Polymer 2005;46:4635.

[7] Brandrup J, Immergut EH, Grulke EA, editors. Polymer handbook. 4th ed. New York: Wiley; 1999.

[8] The T_c value of 62.0 °C was estimated by the plot of ln($R_p k_d^{-0.5}$[initiator][monomer]) vs reciprocal of the absolute temperature T according to the literature (Yamada B, Sugiyama S, Mori S, Otsu T. J Macromol Sci Chem 1981;A15:339.), which is very similar to that of 58.5 °C in Ref. [6], where R_p and k_d denote polymerization rate and rate constant of initiator decomposition, respectively.

[9] Helicity induction in the copolymerization at 60 °C is strongly supported since a characteristic CD spectrum of helical conformation is observed for the copolymer containing small amounts of M_1 unit as seen for spectrum B in Figs. 2 and 6.

[10] Lowry GG. J Polym Sci 1960;42:463.

[11] Equilibrium monomer concentrations $[M]_e$ at 30 and 60 °C were estimated by calibration which was drawn on the basis of 1.00, 2.00, and 3.70 mol/L of $[M]_e$ at 62.0, 75.4, and 98.0 °C, respectively, in which their values have already been obtained in Ref. [6] and in the present study.

[12] Mochel VD, Claxton WE. J Polym Sci A-1 1971;9:345.

[13] Johnston H, Rudin A. Macromolecules 1971;4:661.

[14] Alfrey T, Price CC. J Polym Sci 1947;2:101.

[15] Ueda M, Suzuki T, Takahashi M, Li ZB, Koyama K, Pittman Jr CU. Macromolecules 1986;19:558.

[16] Tanaka H. Prog Polym Sci 2003;28:1171.

[17] (a) Natta G, Corradini P. Makromol Chem 1955;16:77;
(b) Zhao C-T, Do Rosario Ribeiro M, Portela MF. Macromol Chem Phys 2002;203:1983.

[18] Nakaoki T, Katagiri C, Kobayashi M. Macromolecules 2002;35:7708.