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Notes

Stereospecific Free-Radical Polymerization of Methacrylic Acid Calcium Salt for Facile Preparation of Isotactic-Rich Polymers

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In this study, we found stereospecific free-radical polymerization of an ionic vinyl monomer such as methacrylic acid calcium salt (MAA−Ca) in organic solvents for facile preparation of isotactic-rich polymers. The polymerization of MAA−Ca was performed with 2,2′-azobisisobutyronitrile (AIBN) as an initiator in N,N-dimethylformamide (DMF) under argon atmosphere at 60 °C. The obtained poly(MAA−Ca) was converted into poly(methyl methacrylate) (PMMA), which contained approximately 60% of the mm triad (mm/mr/rr = 59/33/8). When free-radical polymerization of MAA−Ca was carried out in toluene/DMF(2:1) mixed solvent, the mm triad of the resulting PMMA (mm/mr/rr = 65/30/5) was increased more than that of the polymer obtained in DMF. These results indicate that the ionic interaction affected stereocontrol in the free-radical polymerization of MAA−Ca for production of the isotactic-rich polymers.

Introduction

Radical polymerization of vinyl monomers is one of the main practical procedures for preparation of industrial polymeric materials. Because the properties of the polymers are affected by their molecular weight and stereostructure, their controls are considered to be important.[1] The control of the molecular weight has been achieved by living radical polymerization such as atom transfer radical polymerization (ATRP),[2−5] nitroxide-mediated polymerization (NMP),[6,7] and reversible addition-fragmentation chain transfer (RAFT) polymerization.[8,9] Furthermore, a combination of living and stereospecific radical polymerizations has permitted the simultaneous control of the molecular weight and the stereostructure of the resulting polymers.[10−12] However, it is generally difficult to control the stereostructure of the polymers in radical polymerization, even though several studies have been conducted on the stereospecific radical polymerization described above. General radical polymerization allows polymers which are relatively rich in syndiotacticity due to steric repulsion. Therefore, recent years have seen developments in the syndiotactic-specific radical polymerizations by changing the substituents in monomers.[13,14] On the other hand, isotactic-rich polymers have only been obtained in limited cases. In particular, isotactic-specific radical polymerization of methacrylic monomers was hard to attain. Therefore, it is one of the important topics in the research field of synthetic polymer chemistry.

One of the examples for isotactic-specific radical polymerizations is a method using bulky methacrylates, such as triphenylmethyl methacrylate and 1-phenyldibenzosuberyl methacrylate, giving rise to polymers with 98.2% and 99.9% of the isotactic (*mm*) triad, respectively.[15,16] The isotactic-specificity in these cases has been explained in terms of a larger steric effect between the entering monomer and the growing polymer-chain end, which prevents syndiotactic addition. As the other example of isotactic-specific radical polymerization, the polymerization of methyl methacrylate (MMA) has been reported using a stereoregular template of poly(methacrylic acid) (PMAA), leading to poly(MMA) (PMMA) with 97% of the *mm* triad.[17]

However, the methods described above have required tedious processes such as preparation of specific monomers and a stereoregular template. Therefore, the development of stereospecific radical polymerization by a simple method is expected for both academic and application reasons. So far, the stereocontrolled radical polymerization of MMA in the presence of Lewis acids such as rare earth metal salts of trifluoromethanesulfonic acid has been reported.[18−20] This method provided PMMA with approximately 10−22% of the *mm* triad, which is higher than that of PMMA obtained by the general free-radical polymerization of MMA. Formation of complexes between monomer and Lewis acids may affect stereocontrol in radical polymerization. As with the other methods, it has been reported to control the tacticity in the polymerization of zinc methacrylate coordinated with a bidentate ligand (*mm* = 12%),[21] and the polymerization of similar monomers containing chiral ligands was also used to obtain chiral polymers.[22] Furthermore, radical polymerization of methacrylic acid (MAA) in the presence of amine compounds (*mm* = 16%)[23] and chitosan (*mm* = 29%)[24] afforded the polymers which were relatively rich in isotacticity. However, these procedures are not enough to provide isotactic-rich polymers, compared with the polymerization procedures using specific monomers and a template described above.[15−17]

In this paper, we report the stereospecific free-radical polymerization of the methacrylic acid calcium salt (MAA−Ca) in organic solvents, which can be considered as a new and facile preparation method for isotactic-rich polymers. The isotactic-specificity in this polymerization manner is caused by ionic interaction in organic solvent. It is noted that the facility of this method provides a possibility for extension to other monomers, leading to various isotactic-rich polymers.

Experimental Section

Materials. Solvents, *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), were purified by distillation. Diazomethane was generated by reaction of *N*-methyl-*N*′-nitro-*N*-nitrosoguanidine with 20 wt % aqueous sodium hydroxide. Monomer, MAA−Ca (purity; >97%) was commercially available as its hydrate from Tokyo Chemical Industry Co., Ltd. Methacrylic acid magnesium and lithium salts (MAA−Mg and MAA−Li) were

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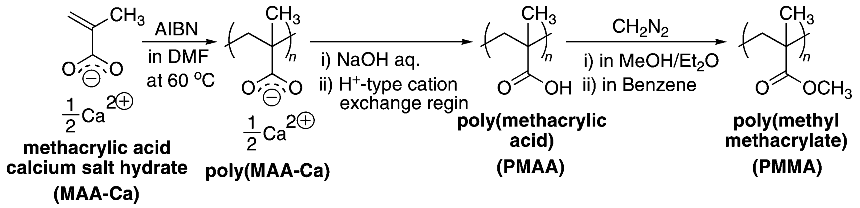
Table 1. Results of Free-Radical Polymerizations of Methacrylic Acid Salts[a]

run	monomer	initiator	solvent(mL)	yield[b] (%)	M_n[c]	M_w/M_n[c]	tacticity[d] (*mm*/*mr*/*rr*)
1	MAA−Ca[e]	AIBN[f]	DMF[g](1)	67.5	45 500	4.31	59/33/8
2	MAA−Ca[e]	AIBN[f]	DMF[g](2)	63.3	40 800	3.98	60/34/6
3	MAA−Ca[e]	AIBN[f]	DMF[g](3)	53.5	39 300	3.08	60/35/5
4	MAA	AIBN[f]	DMF[g](1)	97.0	11 700	2.76	5/30/65
5	MAA−Ca[e]	KPS[h]	water(1)	99.0	58 700	2.40	6/36/58
6	MAA−Ca[e]	AIBN[f]	DMF[g](2)/water(1)	94.0	55 500	3.07	30/47/23
7	MAA−Ca[e]	AIBN[f]	DMF[g](1.5)/water(1.5)	97.6	52 300	3.35	22/45/33
8	MAA−Ca[e]	AIBN[f]	DMF[g](1)/water(2)	91.8	55 300	3.40	17/41/42
9	MAA−Ca[e]	AIBN[f]	toluene(1)/DMF[g](1)	52.4	32 800	4.60	65/29/6
10	MAA−Ca[e]	AIBN[f]	toluene(2)/DMF[g](1)	56.4	22 700	4.62	65/30/5
11	MAA−Mg[i]	AIBN[f]	DMF[g](1)	72.0	39 700	2.26	20/48/32
12	MAA−Li[j]	AIBN[f]	DMSO[k](1)	97.8	32 000	3.22	29/53/18

[a] Polymerization conditions: monomer = 1.0 mmol, initiator = 0.025 mmol, reaction temperature = 60 °C, reaction time = 14 h. [b] On the basis of the weight of the original polymers, i.e., poly(MAA−Ca) for runs 1−3, 5−10, PMAA for run 4, poly(MAA−Mg) for run 11, and poly(MAA−Li) for run 12. [c] Number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated by GPC measurements of the purified PMMA derived from the original polymer using polystyrene standards. [d] Determined by the integrated ratio of α-methyl signals in the ^{1}H NMR spectrum ($CDCl_3$) of purified PMMA derived from the original polymer. [e] Methacrylic acid calcium salt hydrate. [f] 2,2′-Azobisisobutyronitrile. [g] *N*,*N*-Dimethylformamide. [h] Potassium peroxodisulfate. [i] Methacrylic acid magnesium salt hydrate. [j] Methacrylic acid lithium salt hydrate. [k] Dimethyl sulfoxide.

Scheme 1. Free-Radical Polymerization of MAA−Ca Initiated with 2,2′-Azobisisobutyronitrile (AIBN) in *N*,*N*-Dimethylformamide (DMF) at 60 °C to Produce Poly(MAA−Ca), Followed by Conversion to PMMA



prepared by mixing methacrylic acid (10.0 and 5.0 mmol, respectively) and the corresponding metal hydroxides (5.0 mmol) in water (10 mL) for 1 h at room temperature, followed by evaporating the water, and then dried under reduced pressure at room temperature. Because contents of hydrated water in all monomers were unknown, feed amounts of monomers were calculated based on molecular weights of their anhydride formulas, which were regarded as those of monomers in this study. Initiator, 2,2′-azobisisobutyronitrile (AIBN) (purity; >98%) was purchased from Wako Pure Chemical Industries, Ltd., which were used as received. Other reagents and solvents were used as received.

Polymerization of MAA−Ca. A typical polymerization was performed as follows (run 1 in Table 1). Under argon, a mixture of MAA−Ca (105.1 mg, 1.0 mmol) and AIBN (4.1 mg, 0.025 mmol) in DMF (1 mL) was heated at 60 °C. After the reaction was carried out for 14 h, the mixture was suspended in water. The precipitated product was isolated by filtration, washed with water, and then dried under reduced pressure at room temperature to yield 70.9 mg (0.675 mmol unit, 67.5%) of poly(MAA−Ca).

Conversion of Poly(MAA−Ca) to PMMA. The obtained poly(MAA−Ca) (21.0 mg, 0.2 mmol unit) was dissolved in 0.1 mol/L aqueous sodium hydroxide (40 mL), and this solution was passed through a glass column on an H^+-type ion-exchange resin (Amberlite IR120B Na treated with 1.0 mol/L aqueous hydrochloric acid) to convert PMAA. The obtained aqueous solution was evaporated and dried under reduced pressure at room temperature to yield 15.7 mg (0.182 mmol unit, 91.0%) of PMAA. Methylation of the dried PMAA (8.6 mg, 0.1 mmol unit) was carried out using diazomethane in methanol/diethyl ether (4.5 mL/0.5 mL) mixed solvent, followed by using diazomethane in benzene (4.0 mL) to yield 8.2 mg (0.082 mmol unit, 82.0%) of PMMA.

Measurements. The ^{1}H NMR spectra (400 MHz) were recorded using a JEOL ECX400 spectrometer under the following parameters: temperature = 25 °C, relaxation delay = 5 s, pulse angle = 45°, acquisition time = 2.73215 s, repetition time = 7.73215 s. The triad tacticity was determined by the integrated ratio of α-methyl signals in the ^{1}H NMR spectrum ($CDCl_3$) of purified PMMA derived from the original polymer. Gel permeation chromatographic (GPC) analyses were performed by using a HITACHI pump L-2130 and a HITACHI RI detector L-2490 under the following conditions: Shodex GPC KF-804L (bead size 7 μm and measurable molecular weight range (10^2)−(4×10^5)) and KF-803L (bead size 6 μm and measurable molecular weight range (10^2)−(7×10^4)) columns with chloroform as the eluent at a flow rate of 1.0 mL/min at 40 °C.

Results and Discussion

Free-radical polymerization of MAA−Ca was performed with AIBN in DMF under an argon atmosphere at 60 °C to produce poly(MAA−Ca) (see Scheme 1). The clear solution of the reaction mixture turned into a gelic form with progress of the polymerization. For solubilization of the gelic product, the resulting poly(MAA−Ca) was converted into PMAA by treatment with an H^+-type ion-exchange resin in 0.1 mol/L aqueous sodium hydroxide of poly(MAA−Ca). The tacticity of methacrylic polymers is generally determined by the integrated ratio of α-methyl signals in the ^{1}H NMR spectrum. However, because those signals of PMAA were broadened and overlapped each other, the tacticity of PMAA could not be determined. Therefore, methylation of PMAA was carried out using diazomethane in methanol/diethyl ether (9/1) mixed solvent, followed by using diazomethane in benzene to obtain PMMA. Its tacticity can be quantitatively determined by ^{1}H NMR analysis.

The integrated ratio of α-methyl signals in the ^{1}H NMR spectrum ($CDCl_3$) of the obtained PMMA indicates approximately 60% of the *mm* triad (*mm*/*mr*/*rr* = 59/33/8) (Figure 1, run 1 in Table 1). The *mm* triad of PMMA obtained from lower concentrations of MAA−Ca and AIBN scarcely changed (runs 2 and 3 in Table 1).

Since our consideration has focused on ionic interaction of methacrylate with the calcium ion, which may affect the *mm*

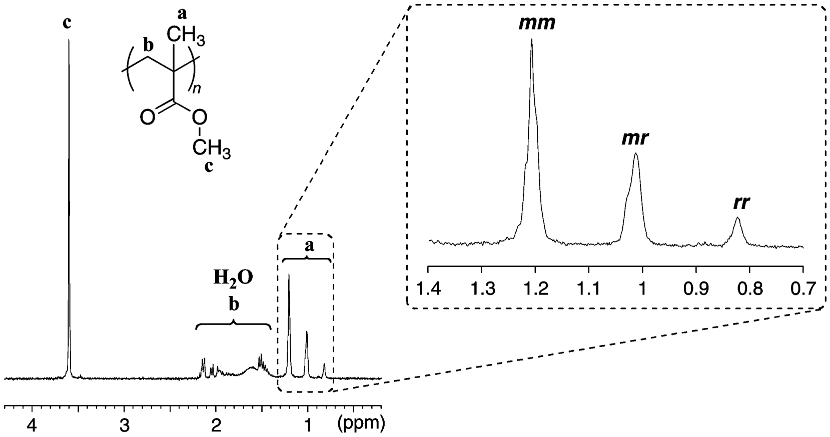


Figure 1. ^{1}H NMR spectrum in $CDCl_3$ of PMMA derived from poly(MAA−Ca) prepared by polymerization of MAA−Ca in *N,N*-dimethylformamide (DMF) at 60 °C (run 1 in Table 1).

triad, the polymerization of a nonionic monomer, MAA, initiated with AIBN in DMF was investigated. From the results, PMMA derived from the resulting PMAA contained only 5% of the *mm* triad (run 4 in Table 1). Furthermore, radical polymerization of MAA−Ca was performed in water, because ionic interaction has generally been weakened in the solvents with high polarity such as water. The *mm* triad of PMMA derived from poly(MAA−Ca) obtained by polymerization of MAA−Ca initiated with potassium peroxodisulfate (KPS) in water was 6% (run 5 in Table 1). These values are much lower than those of the polymers obtained by polymerization of MAA−Ca in DMF (runs 1−3 in Table 1), indicating that the ionic interaction of methacrylate with calcium ion strongly affected the stereocontrol in radical polymerization.

To confirm the effects of the solvent polarities on the tacticity, we performed free-radical polymerization of MAA−Ca initiated with AIBN in mixed solvents of DMF and water in varying ratios (runs 6−8 in Table 1). Consequently, the *mm* triads increased for a higher ratio of DMF/water, indicating that the polarity of the solvent affected the tacticity on the present polymerization system.

To obtain the stronger ionic interaction between methacrylate and the calcium ion, the polymerization of MAA−Ca was performed in the solvent of DMF mixed with toluene having a lower polarity.[25] The obtained poly(MAA−Ca)s were treated with the same procedures as described above to obtain PMMA. The *mm* triads of the obtained PMMAs (approximately 65%) were higher than that in DMF (runs 9 and 10 in Table 1), indicating that the stronger ionic interaction using the solvents with lower polarity affected the isotactic-specificity in radical polymerization. The *mm* triads of the resulting polymers in the present study were considerably high compared with those of polymers obtained by the facile radical polymerizations of versatile methacrylic monomers such as MMA and MAA (including its salt) as previously reported.[18−21,23,24]

To investigate the effect of countercations of methacrylate, we employed MAA−Mg and MAA−Li, which were dissolved in DMF and DMSO, respectively. The *mm* triads of PMMAs obtained from these monomers were lower than that of PMMA obtained from MAA−Ca (runs 11 and 12 in Table 1). These results indicate that the MAA−Ca specifically affected stereocontrol in free-radical polymerization to produce an isotactic-rich polymer, although the detailed reasons are not yet clear.

On the basis of the data described above, the following mechanism for isotactic-specific radical polymerization of MAA−Ca was speculated. Calcium ion strongly interacts with carboxylates of a growing polymer chain in DMF or toluene/DMF mixed solvent, because such organic solvents prevent solvation of each ion of calcium and carboxylate compared with solvation in water. In addition, divalent calcium ion can coordinate with the neighboring two segments (carboxylates) of a growing polymer chain end, regulating the direction of these carboxylates. Therefore, monomer addition would preferentially occur with keeping the meso configuration of the segments of a growing polymer chain end. The above mechanism would also be supported by the following result in the previous paper, in which isotactic PMAA has the higher affinity with divalent cations such as cupric ion, compared with syndiotactic PMAA.[26]

The polymerization results are summarized in Table 1. The molecular weights (M_n) evaluated by means of gel permeation chromatography (GPC) were in the range of 11−59 k (M_w/M_n = 2.26−4.62). The polymer yields as the water-insoluble fractions were not quantitative. The ^{1}H NMR spectra of the water-soluble parts of the products in polymerization revealed the existence of an unreacted monomer and a trace amount of oligomer.

Conclusion

In this study, we found that the stereospecific free-radical polymerization of MAA−Ca in organic solvents such as DMF and toluene/DMF mixed solvent resulted in the facile preparation of isotactic-rich polymers. The polymerization of MAA−Ca was performed with AIBN as an initiator in organic solvents described above to obtain poly(MAA−Ca). The *mm* triads of PMMAs derived from the resulting poly(MAA−Ca)s were approximately 60−65%. These results indicate that the ionic interaction affected stereocontrol in the free-radical polymerization of MAA−Ca for production of the isotactic-rich polymers.

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