

Synthesis of Syndiotactic Poly(methacrylic acid) by Free-Radical Polymerization of the Pseudo-Divinyl Monomer Formed with Methacrylic Acid and Catechol

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ABSTRACT: Syndiotactic poly(methacrylic acid) (*Syn*-PMAA, r diad = 91 mol %) was synthesized by free radical polymerization of methacrylic acid (MAA) with catechol. The pseudo-divinyl monomer was formed with one catechol and two MAA molecules by the hydrogen bonding between OH groups of catechol and COOH group of MAA. When the free radical polymerization of the pseudo-divinyl monomer was carried out, *intra*- and *intermolecular* addition proceeded with racemic addition. The hydrogen bonding was the driving force to control tacticity. We discussed the effects of solvent, temperature, and the concentrations of MAA and catechol on the pseudo-divinyl monomer formation. The highly syndiotactic PMAA was successfully obtained. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

The industrial importance and the wide use of polyelectrolytes, such as poly(acrylic acid) and poly(methacrylic acid) (PMAA), have been well established. Syndiotactic PMAA (*Syn*-PMAA) has higher thermal and chemical resistance than atactic PMAA.^{1,2} Generally, syndiotactic polymers are synthesized by anionic polymerization. However, PMAA cannot be synthesized directly by anionic polymerization. For the synthetic methods of syndiotactic PMAA, hydrolysis of syndiotactic poly(*tert*-butyl methacrylate),³ radical polymerization with pH controlled solution,⁴ template polymerization with isotactic PMMA⁵ or α -cyclodextrin,⁶ and atom transfer radical polymerization (ATRP) with fluoroalcohol⁷ are known. However, these methods have serious disadvantages. In the case of poly(*tert*-butyl methacrylate), the hydrolysis is required to obtain PMAA. In the case of pH control, the syndiotacticity of resulting PMAAs was not so high (r diad < 80 mol %). In the cases of template polymerization with isotactic PMMA or α -cyclodextrin, mass production was almost impossible, because thin films of 3–5- μ m thickness are needed as the template molecules. In the case of ATRP with fluoroalcohol, the method cannot be used for acidic monomers such as MAA. Thus, the development of a synthetic method of syndiotactic PMAA, which can be applied to mass production, is needed.

Cyclopolymerization of divinyl monomers is one of the useful techniques to synthesize structure-controlled polymer.^{8–10} Chirality-controlled polymers have been synthesized by cyclopolymerization of divinyl monomers.^{11–13} Cyclopolymerization of divinyl monomers is a potentially useful synthetic method of syndiotactic polymer. In these cases, the tacticity of the backbone of polymers was frequently syndiotactic. For example, when *tert*-butyl- α -(hydroxymethyl) acrylate ether dimer was used as the divinyl monomer, the backbone of cyclopolymerized polymer was syndiotactic.¹⁴ When isopropylidene diallylmalonate was used, the backbone was *threo*-disyndiotactic.¹⁵

For cyclopolymerization, the concentration of divinyl monomer, polymerization temperature, and the arrangement of two vinyl groups of divinyl monomer are important factors.^{16,17} To control the arrangement, vinyl groups are generally connected to the template molecule by covalent bond, such as ester, amide, and ether. For the synthesis of syndiotactic PMAA by cyclopolymerization, the template molecules must be separated from the backbone of the cyclopolymerized polymer. However, the incomplete cleavage of these groups has been reported.^{18,19} In this work, vinyl groups and template molecule were connected by noncovalent bond to omit the hydrolysis.

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For cyclopolymerization, it is necessary for the distance between two vinyl groups to be lower than 5 Å.^{20,21} It is also important that the noncovalent bond in the pseudo-divinyl monomer is strong enough to control the arrangement of two vinyl groups.

Van der Waals bond, ionic bond, and hydrogen bond are well-known typical noncovalent bonds. Van der Waals's bond is too weak to connect the vinyl groups and the template molecule. Ionic bond is strong enough, but the pseudo-divinyl monomer formed by ionic bonds will be difficult to dissolve in solvents. On the other hand, hydrogen bond is strong enough to control the arrangement and the distance of vinyl groups. The strength of hydrogen bond can be controlled by varying the dielectric constants of the solvent.²² Thus, hydrogen bond will be useful for connecting two MAA molecules and the template molecule. The template molecule must have two functional groups, which can form hydrogen bonding with MAA, with a short distance apart from each other. The tacticity control of PMAA by using the pseudo-divinyl monomer with MAA and acetyl diaminocyclohexane has been reported.²³ However, the resulting PMAA was atactic, because the hydrogen bond between MAA and amide group was too weak to control the arrangement of vinyl groups. On the other hand, catechol has two OH groups, which can connect to the COOH group of MAA strongly, at *ortho*-position of benzene ring. Thus, catechol was chosen as the template molecule.

The aim of this work is to clarify the effects of the solvent, temperature, and the concentration of the pseudo-divinyl monomer on the tacticity of resulting PMAA. Conditions to form the pseudo-divinyl monomer of catechol and MAA were also investigated.

EXPERIMENTAL

Materials

Methacrylic acid (MAA, Kanto Chemical, 98%) was purified by distillation. Catechol (Aldrich, 99%), 1,4-anhydroerythritol (Aldrich, 99%), 2,2'-azobis(2,4-dimethyl-4-methoxyvaleronitrile) (V-70, Wako Pure Chemical Industries, 99%), 2,2'-azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%), ethyl iodoacetate (Aldrich, 98%), methanol (Kanto Chemical, 99.5%), *N,N*-dimethylacetamide (DMA, Kanto Chemical, 98.5%), sodium hydroxide (Kanto Chemical, 95.0%), nitric acid (Kanto Chemical, 60–61%), acetic acid (Kanto Chemical, 99.5%), (trimethylsilyl)diazomethane diethyl ether solution (Aldrich, 2.0 M), tetrahydrofuran (THF, Kanto Chemical, 99%), acetone (Kanto Chemical, 99%), methanol-*d*₄ (ACROS ORGANICS, 99.8%), chloroform-*d*₁ (ACROS ORGANICS, 99.8%), and dimethyl sulfoxide-*d*₆ (DMSO-*d*₆, Aldrich, 99.9%) were used as received.

Polymerization

A typical procedure is as follows. In the case of code 12, MAA (2.0 mL, 22.6 mmol) and catechol (1.24 g, 11.3 mmol) were added to a Pyrex reactor and stirred for 10 min. Next, DMA (10 mL) was added to the reactor, and the solution was kept under nitrogen flow for 10 min. V-70 was added to the reactor. The reactor was sealed under N₂ atmosphere and heated at 35°C for 5.0 h. After the polymerization, the product was precipitated with 3 *N*-nitric acid aq. (50 mL), collected, purified by

reprecipitation for three times from methanol (10 mL) into acetone (50 mL), and dried under vacuum. The product was a white powder.

FTIR Measurement

FTIR spectra of polymerization solutions were measured with an FTIR spectrometer (Jasco, FT/IR-410) using a CaF₂ cell (cell length is 0.1 mm).

NMR Measurement

NMR measurement was carried out with a NMR spectrometer (JEOL, GLX, 400 MHz) with methanol-*d*₄ for PMAA and dimethyl sulfoxide-*d*₆ or chloroform-*d*₁ for PMMA using the resonance of the deuterated solvent as lock and the internal standard for chemical shift data in the δ -scale relative to TMS.

Methylation of PMAAs

PMAA (0.015 g, 0.15 mmol of carboxyl group) was dissolved in methanol (0.5 mL). (Trimethylsilyl)diazomethane diethyl ether solution (0.15 mL, 0.30 mmol) was added to the solution. The solution was stirred at room temperature for 48 h. Then, acetic acid (0.1 mL, 1.75 mmol) was added to the solution. The precipitate was collected and washed with methanol (5 mL) and dried under vacuum. The product was a white powder. Yield: 58 wt %. ¹H-NMR: δ = 0.81–1.19 (3 H, —CH₃), 1.76–2.03 (2 H, —CH₂—), and 3.56–3.72 ppm (3 H, —OCH₃) (solvent: chloroform-*d*₁).

GPC Measurement

The molecular weight and molecular weight distribution of PMMA were measured by gel permeation chromatograph (GPC) with polystyrene standards. The GPC profiles were determined by GPC [TOSOH, column oven = CO-8020, RI detector = RI-8020, pump = DP-8020, degasser = SD0802, column = TSKgel G5000HHR (range < 4.0 × 10⁵), temperature = 35°C, eluent = THF, and flow rate = 1.0 mL/min].

RESULTS AND DISCUSSION

Formation of Pseudo-Divinyl Monomer

The hydrogen bond is strong in solvents with low-dielectric constants (<21).²⁴ To investigate the formation of the pseudo-divinyl monomer of MAA and catechol in various solvents, the FTIR spectra of MAA and catechol solutions were observed. The range of the dielectric constant of solvents was 2.21 (toluene) to 78.54 (H₂O). The dielectric constants of solvents are literature values.²⁵

Figure 1 shows the FTIR spectra of MAA–catechol solutions. In DMF, DMA, and DMSO with ϵ = 36.71, 37.78, and 46.45, respectively, new peak was observed at 3650 cm⁻¹. They are attributed to the hydrogen bond between the hydrogen of Ar—OH group of catechol and the carbonyl oxygen of MAA.²⁶ Thus, the formation of pseudo-divinyl monomer was expected in these solvents. In toluene, dioxane, and 2-butanone with ϵ = 2.21, 2.38, and 18.51, respectively, hydrogen bonding was not detected. This would be because of the low solubility of catechol. The catechol molecule was not dispersed in these solvents enough to form the pseudo-divinyl monomer. In H₂O (ϵ = 78.54), FTIR spectroscopy was inappropriate because of the dissolution of CaF₂ cell in H₂O.

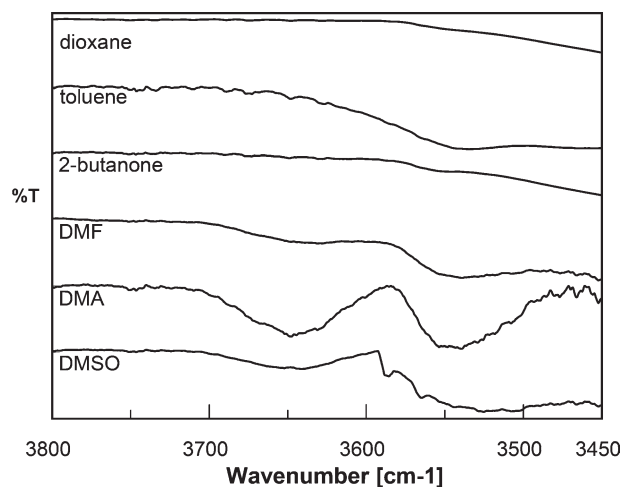


Figure 1. FTIR spectra of catechol and MAA solutions (catechol = 0.41 mol/L, MAA = 0.83 mol/L).

The formation of hydrogen bond in the solution was not quantitatively but qualitatively determined by FTIR. For the quantitative analysis of the formation of pseudo-divinyl monomer, the $^1\text{H-NMR}$ spectra of the catechol-MAA solutions were measured in $\text{DMSO-}d_6$ (Figure 2). The peak of OH groups of catechol (8.2–8.6 ppm) broadened by increasing the molar ratio of MAA to catechol. The broadening of peaks is a typical phenomenon for the formation of hydrogen bonding.^{10,27} To clarify the stoichiometry of the complex of catechol and MAA, Job plot²⁸ was measured by using the peak of OH group at 8.2–8.6 ppm. Figure 3 shows the Job plot. δ is the deference of the peak top between catechol solution and catechol/MAA mixture solution. The peak top was observed at 33 mol % of catechol. This means that one molecule of catechol and two molecules of MAA interacted with each other. This suggests the formation of pseudo-divinyl monomer in $\text{DMSO-}d_6$.

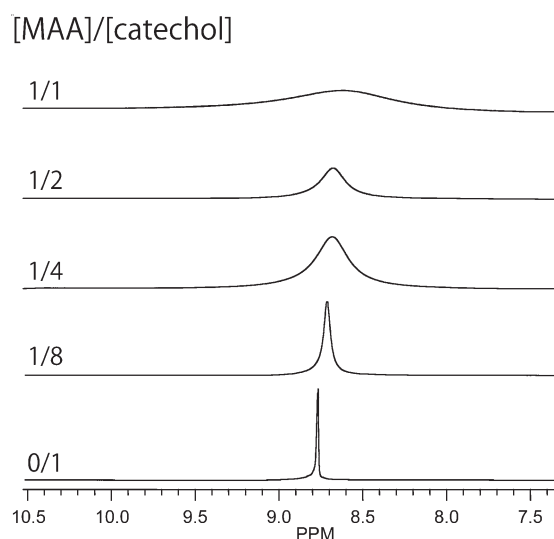


Figure 2. $^1\text{H-NMR}$ spectra of catechol and MAA solution (Ar—OH of catechol, solvent = $\text{DMSO-}d_6$, temp. = 35°C , [catechol] + [MAA] = 3.56 mol/L).

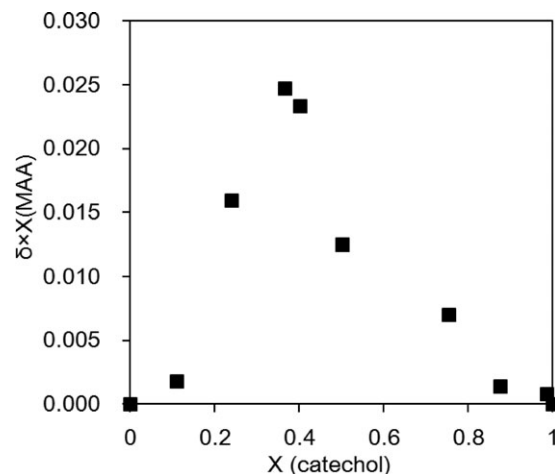


Figure 3. The Job plot of catechol and MAA (peak of Ar—OH of catechol at 8.58 ppm, solvent: $\text{DMSO-}d_6$, temp. = 35°C , [catechol] + [MAA] = 3.56 mol/L).

To clarify the structure of the complex with catechol and MAA, 2D-NMR with NOESY analysis was measured. Figure 4 shows the 2D-NMR of the mixture of catechol and MAA in $\text{DMSO-}d_6$. The resonance interaction between OH of catechol and COOH of MAA was observed at δ the cross-section of 8.7 and 12.2 ppm. Thus, the pseudo-divinyl monomer with one catechol molecule and two MAA molecules was formed by the hydrogen bond between OH groups of catechol and COOH group of MAA in DMSO .

Effect of Solvent on Polymerization of MAA

Table I shows the conditions and results of the polymerization of MAA with and without catechol. In the solvents with $\epsilon < 2.38$ (dioxane and toluene), the polymerization solutions gelled. Generally, PMAA is soluble in dioxane.^{29,30} On the other hand,

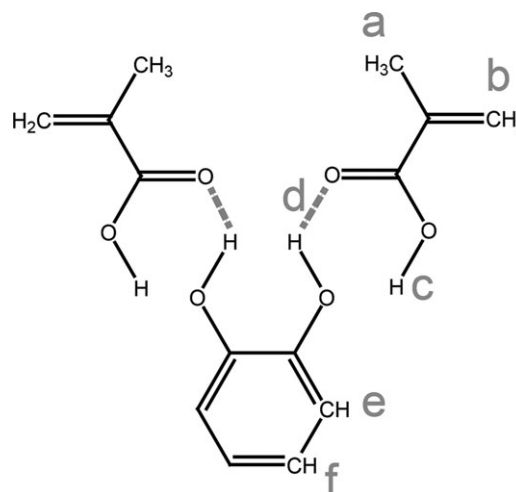


Figure 4. 2D NMR with NOESY of catechol and MAA solution (solvent = : $\text{DMSO-}d_6$, [catechol] = 1.16 mol/L, [MAA] = 2.32 mol/L, temp. = 35°C , and red circle is the NOE between Ar—OH of catechol and —COOH of MAA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. The Conditions and Results of Polymerization of MAA With and Without Catechol

Code	Solvent		[Catechol] (mol/L)	[MAA] (mol/L)	Yield (wt %)	Molecular weight ^b			Tacticity (triad) ^c			Tacticity (diad) ^d <i>r</i>
	Type	DC ^a				$M_n \times 10^4$	M_w/M_n	Gelation	<i>mm</i>	<i>mr</i>	<i>rr</i>	
1	Dioxane	2.21	-	2.32	38	2.37	1.96	Gelled	7	35	58	76
2	Toluene	2.38	-	2.32	23	3.21	2.54	Gelled	6	34	60	77
3	2-Butanone	18.51	-	2.32	55	1.98	2.34		12	28	60	74
4	DMF	36.71	-	2.32	61	2.54	2.48		9	32	58	74
5	DMA	37.79	-	2.32	38	2.60	2.79		9	32	58	74
6	DMSO	46.45	-	2.32	32	3.24	3.04		9	31	59	75
7	H ₂ O	78.54	-	2.32	95	4.25	3.40		8	37	55	74
8	Dioxane	2.21	1.16	2.32	91	2.56	1.92	Gelled	15	23	62	74
9	Toluene	2.38	1.16	2.32	71	2.66	2.02	Gelled	5	35	59	77
10	2-Butanone	18.51	1.16	2.32	64	3.97	1.98	-	4	31	65	81
11	DMF	36.71	1.16	2.32	66	3.30	1.66	-	1	22	77	88
12	DMA	37.79	1.16	2.32	60	2.59	1.50	-	1	17	82	91
13	DMSO	46.45	1.16	2.32	69	2.03	1.54	-	1	20	79	89
14	H ₂ O	78.54	1.16	2.32	79	2.24	1.53	-	3	27	70	84

Initiator = V-70; 23.7 $\mu\text{mol/L}$, temp. = 35°C, time = 5 h.

^aDielectric constant of solvents, ^bDetermined by GPC with PS standards, ^cDetermined by ¹H-NMR spectra by using the resonance of α -methyl at 0.90–1.10, 1.10–1.25, and 1.25–1.35 ppm for *mm*, *mr*, and *rr* triad, ^dCalculated from the triad values.

the hydrogen bonding of PMAA is stronghold in dioxane, and the viscosity of solution increases.²⁹ In this system, it is expected that PMAA was cross-linked by the hydrogen bonding between PMAA. As a result, the solution was gelled. Poor control of tacticity of PMAA was expected in these solvents. In the solvents with $\epsilon > 18.51$ (2-butanone, DMF, DMA, DMSO, and H₂O), the polymerization proceeded without gelation.

If the catechol remained in PMAA, PMAA may be cross-linked by catechol in aqueous phase. Thus, the PMAAs were converted to PMMA to determine the molecular weight with organic solvent by GPC. For GPC measurements, PMAAs were converted to PMMA by TMS diazomethane (¹H-NMR spectra of resulting PMMA is shown in Supporting Information Figure S1). The molecular weights of resulting PMMA were listed in Table I. In all cases, the molecular weights were in a range of 2.00×10^4 – 4.00×10^4 [g/mol]. The solvent and existence of catechol did not affect the molecular weight.

The tacticity of resulting PMAAs was determined by ¹H-NMR. Figure 5 shows the ¹H-NMR spectra of PMAA (code 12). The peaks $\delta = 0.65$ – 1.24 (3 H, $-\text{CH}_3$), 1.67 – 2.02 (2 H, $-\text{CH}_2-$), and 13.42 (1 H, $-\text{COOH}$) ppm were observed. The tacticity was calculated by using the peak areas of $-\text{CH}_3$ at 0.65–1.06, 1.06–1.19, and 1.19–1.24 ppm for *rr*, *mr*, and *mm* triad, respectively. The tacticity of other PMAAs was measured in the same way as code 12 and listed in Table I.

When MAA was polymerized without catechol, the *r* diad of the resulting PMAAs was constant at about 75 mol % and did not depend on the solvent. On the other hand, when DMF, DMA, and DMSO were used as solvents, the addition of catechol drastically increased the *r* diad (88–91 mol %). When H₂O was used, the *r* diad slightly increased (84 mol %). In contrast,

when dioxane, toluene, and 2-butanone were used, the *r* diads of resulting PMAAs were close to those of the PMAAs polymerized without catechol. The dielectric constants of DMF, DMA, and DMSO are around 40. In these solvents, the hydrogen bond between OH groups of catechol and COOH group of MAA molecule was observed by FTIR (Figure 1). Therefore, it is suggested that tacticity of the PMAAs was controlled by the formation of hydrogen bonding.

Effect of Temperature

It is well known that the strength of hydrogen bond is due to temperature. The hydrogen bond between Ar–OH and $-\text{COOH}$ group is at its strongest around 30°C.³¹ Thus, if the hydrogen bonding was the driving force of tacticity control, the tacticity of resulting PMAA would be effected by the polymerization temperature.

Table II shows the tacticity of resulting PMAAs polymerized in DMA with and without catechol. In the cases without catechol, the *r* diad decreased with the increase in the polymerization temperature. This agrees well with the research of Kocheneva and Roshupkin.³² In all the cases, the *r* diad increased by the addition of catechol. The *r* diad value and the margin of the increase of *r* diad value were highest at 35°C. Therefore, it can be said that the driving force of the synthesis of syndiotactic PMAA by using catechol is the hydrogen bond to form the pseudo-divinyl monomer.

The synthesis of isotactic-rich PMAA (*mm*/*mr*/*rr* diad = 16/49/35 mol %) by using diaminocyclohexane as the template molecule to form the pseudo-divinyl monomer was reported.³³ In the case of diaminocyclohexane, MAA and diaminocyclohexane were connected by ionic bond. Thus, two MAA molecules of the pseudo-divinyl monomer were repelled by electrostatic

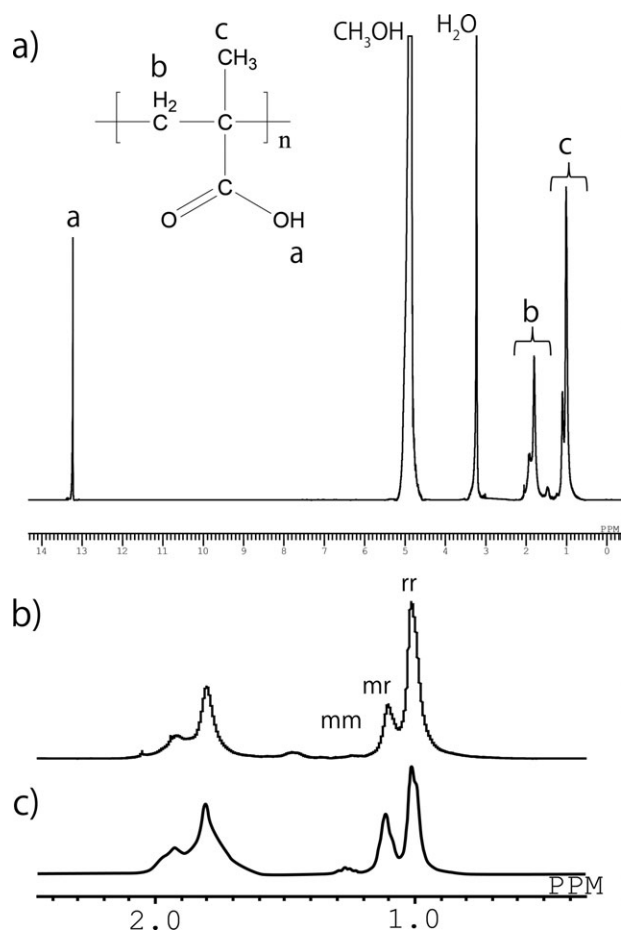


Figure 5. $^1\text{H-NMR}$ spectra of PMAA polymerized with catechol (a) and (b), code 12 and without catechol (c), code 5, solvent = methanol- d_4 , and temp. = r.t.

repulsion, and the arrangement of vinyl groups was not controlled strictly. As a result, the tacticity of the resulting PMAA was not controlled well. On the other hand, the pseudo-divinyl monomer of this work was formed by hydrogen bond. The arrangement of vinyl groups was not influenced by electrostatic repulsion. The arrangement of two vinyl groups on one pseudo-divinyl monomer was controlled racemo because of the

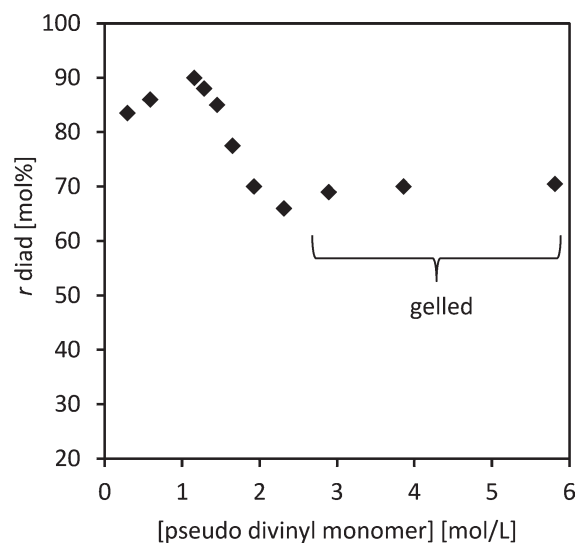


Figure 6. Syndiotacticity of PMAAs polymerized with catechol versus the concentration of the pseudo-divinyl monomer (solvent = DMA, initiator = V-70; 23.7 $\mu\text{mol/L}$, [catechol]/[MAA] = 1/2, and temp. = 35°C).

excluded volume effect of the α -methyl group of MAA. And intramolecular addition of polymerization of the pseudo-divinyl monomer proceeded racemic-like fashion because of the excluded volume effect of catechol. As a result, the syndiotactic PMAAs were synthesized.

Effect of Concentration of Pseudo-Divinyl Monomer

When polymerization is carried out with high concentration of divinyl monomer, the polymerization solution tends to gel.^{34,35} In the case of pseudo-divinyl monomer, the similar phenomenon was expected. In this work, tacticity control would be inhibited by gelation, because the arrangement of MAA would not be controlled by catechol. To clarify the range of concentration, in which the tacticity of resulting PMAAs is controlled, polymerizations were carried out with different concentrations of pseudo-divinyl monomer. Other polymerization conditions were the same as code 12 in Table I (solvent: DMA; initiator: V-70; 23.7 $\mu\text{mol/L}$; temp.: 35°C; and time: 5 h). Figure 6 shows the r diad values of PMAAs polymerized with catechol at different concentrations of the pseudo-divinyl monomer. It should be

Table II. The Conditions and Results of Polymerization of MAA With and Without Catechol at Different Temperature

Code	Catechol (mol/L)	Initiator ^a		Temp. (°C)	Yield (wt %)	Tacticity (triad) ^b			Tacticity (diad) ^c
		Type	$\mu\text{mol/L}$			<i>mm</i>	<i>mr</i>	<i>rr</i>	
15	-	EIA	23.7	20	59	5	31	64	80
5	-	V-70	23.7	35	38	9	36	55	73
16	-	AIBN	23.7	60	52	10	32	52	68
17	1.16	EIA	23.7	20	34	2	25	73	86
12	1.16	V-70	23.7	35	60	1	17	82	91
18	1.16	AIBN	23.7	60	47	3	27	70	84

MAA = [2.32 mol/L], [catechol]/[MAA] = 2/1 (code 12, 17, 18), solvent = DMA, and time = 5 h.

^aEIA, ethyl iodacetate; and V-70; [EIA]/[V-70] = 1/2; [EIA] = 23.7 mmol/L, ^bDetermined by $^1\text{H-NMR}$ spectra by using the resonance of α -methyl at 0.90–1.10, 1.10–1.25, and 1.25–1.35 ppm for *mm*, *mr*, and *rr* triad, ^cCalculated from the triad values.

noticed that “gelled” in Figure 6 indicates that the polymerization solution was macroscopically gelled. When the concentration was smaller than 1.56 mol/L, the r diad value was high (r diad = 85–91 mol %). The highest r diad value (91 mol %) was obtained at 1.56 mol/L. In a range of 1.56–2.89 mol/L, the r diad value decreased with the increase in the concentration of pseudo-divinyl monomer. This could be because of microscopically gelled solution. Over 2.89 mol/L, the polymerization solutions gelled, and atactic PMAAs (r diad, 69–70 mol %) were obtained. Thus, the tacticity control of PMAA by catechol was conducted when the concentration of pseudo-divinyl monomer was smaller than 1.56 mol/L.

CONCLUSIONS

The formation of pseudo-divinyl monomer of one catechol and two MAA molecules increased the syndiotacticity of PMAA (r diad = 90 ± 2 mol %) polymerized by free radical polymerization. The pseudo-divinyl monomer of two MAA and one catechol molecule was formed by hydrogen bonding in aprotic solvents such as DMF, DMA, and DMSO. In these solvents, the intra- and intermolecular addition of the pseudo-divinyl monomer was controlled racemically because of the specific hindrance of the α -methyl group of MAAs in the pseudo-divinyl monomer and the specific hindrance of catechol, respectively. In other solvents, the resulting PMAAs were atactic, because the catechol and MAA did not form the pseudo-divinyl monomer by hydrogen bond. The pseudo-divinyl monomer formation did not affect the tacticity when the concentration of the pseudo-divinyl monomer was higher than 1.56 mol/L because of the micro- and macrogelation.

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REFERENCES

- Krull, L. P.; Yakimtsoca, L. B.; Egorova, E. L.; Matusевич, Y. I.; Polikaropob, A. P. *Russ. J. Appl. Chem.* **2011**, *84*, 8596.
- Lazzari, M. *Polym. Bull.* **1997**, *39*, 85.
- Ramireddy, C.; Tuzar, Z.; Prochazka, K.; Webber, S. E.; Munk, P. *Macromolecules* **1992**, *25*, 2541.
- Bovey, F. A. *J. Polym. Sci. Part A: Gen. Pap.* **1963**, *1*, 843.
- Ajiro, H.; Kamei, D.; Akashi, M. *Macromolecules* **2009**, *42*, 3019.
- Miura, T.; Kida, T.; Akashi, M. *Macromolecules* **2011**, *44*, 3723.
- Miura, Y.; Satoh, T.; Narumi, A.; Nishizawa, O.; Okamoto, Y.; Kakuchi, T. *Macromolecules* **2005**, *38*, 1041.
- Klopp, J. M.; Pasini, D.; Byers, J. D.; Willson, C. G.; Fréchet, J. M. *J. Chem. Mater.* **2001**, *13*, 4147.
- Coluccini, C.; Metrangolo, R.; Parachini, M.; Pasini, D.; Resnati, G.; Righetti, P. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 5202.
- Cagnoni, E.; Pasini, D.; Galbiati, A.; Ricci, M.; Righetti, P. *Macromolecules* **2003**, *36*, 8894.
- Coates, G. W.; Waymoth, M. *J. Mol. Catal.* **1992**, *76*, 189.
- Anders, U.; Krause, J. O.; Wang, D.; Nuyken, O.; Buchmeiser, M. R. *Des. Monom. Polym.* **2004**, *7*, 151.
- Krause, J. O.; Wang, D.; Anders, U.; Weberskirch, R.; Zarka, M. T.; Nuyken, O.; Jäger, C.; Haarer, D.; Buchmeiser, M. R. *Macromol. Symp.* **2004**, *217*, 179.
- Mathias, L. J.; Warren, R. M.; Huang, S. *Macromolecules* **1991**, *24*, 2036.
- Miyamura, Y.; Kinbara, K.; Yamamoto, Y.; Praveen, V. K.; Kato, K.; Takata, M.; Takano, A.; Matsushita, Y.; Lee, E.; Lee, M.; Aida, T. *J. Am. Chem. Soc.* **2010**, *132*, 3292.
- Edizer, S.; Veronesi, B.; Karahan, O.; Aviyente, V.; Dęgirmenci, I.; Galbiati, A.; Pasini, D. *Macromolecules* **2009**, *42*, 1860.
- Sharma, A. K.; Cornaggia, C.; Pasini, D. *Macromol. Chem. Phys.* **2010**, *211*, 2254.
- Shaw-Chang, C.; Butler, G. B. *J. Polym. Sci. Polym. Let. Ed.* **1977**, *15*, 277.
- Saito, R.; Yamaguchi, K.; Hara, T.; Saegusa, C. *Macromolecules* **2007**, *40*, 4621.
- Ochiai, B.; Ootani, Y.; Endo, T. *J. Am. Chem. Soc.* **2008**, *130*, 10832.
- Saito, Y.; Saito, R. *Polymer*, **2011**, *52*, 3565.
- Ligon, A. C.; Millen, D. *J. Chem. Soc. Rev.* **1987**, *16*, 467.
- Karakovoyak, M. G.; Anufrieva, E. V.; Sycheva, E. A.; Sheveleva, T. V. *Macromolecules*, *193*, 26, 7375.
- Vertes, A.; Nagy-Czako, I. Burger, K. *J. Phys. Chem.* **1976**, *80*, 1314.
- Burton, A. F. M. *Chem. Rev.* **1975**, *75*, 731.
- Li, C.; Hai-Ming, G.; Zi, Z.; Shi-Xuan, D.; Don-Xia, S.; Hong-Jun, G. *Chin. Phys. B* **2009**, *18*, 1622.
- Saito, R.; Iijima, Y.; Yokoi, Y. *Macromolecules*, **2006**, *39*, 6838.
- Huang, C. Y. *Methods Enzymol.* **1982**, *87*, 509.
- Dire, C.; Charleus, B.; Magnet, S.; Couvreur, L. *Macromolecules* **2007**, *40*, 1897.
- Dire, C.; Magnet, S.; Couvreur L.; Charleux, B. *Macromolecules* **2009**, *42*, 95.
- Fukuda, H.; Diem, T.; Stefely, J.; Kezdy, F. J.; Regen, S. L. *J. Am. Chem. Soc.* **1986**, *108*, 2321.
- Kocheneva, T. S.; Roshupkin, V. P. *Polym. Sci.* **1991**, *33*, 2104.
- Krakovoyak, M. G.; Anufrieva, E. V.; Sycheva, E. A.; Sheveleva, T. V. *Macromolecules* **1993**, *26*, 7375.
- Park, S.; Okada, T.; Takeuchi, D.; Osakada, K.; *Chem. Eur. J.* **2010**, *16*, 8662..
- Hashimoto, T.; Ohashi, M.; Kodaira, T. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 4002.