Control of Stereospecificity in the Radical Polymerization of *N*-Methyl-*N*-(2-pyridyl)acrylamide by Conformational Switching of the Monomer with Protonation

Tomohiro Hirano, Akihiro Morikami, Koichi Ute

Department of Chemical Science and Technology, Institute of Technology and Science,

The University of Tokushima, 2-1 Minamijosanjima, Tokushima 770-8506, Japan

Correspondence to : T. Hirano (E-mail: hirano@chem.tokushima-u.ac.jp)

ABSTRACT: Radical polymerization of *N*-methyl-*N*-(2-pyridyl)acrylamide (MPyAAm) was carried out in dichloromethane at low temperatures in the presence of trifluoroacetic acid (TFA). The *m* dyad contents of the polymers obtained at 0°C increased linearly from 37% to 60% with increase in the $[TFA]_0/[MPyAAm]_0$ ratio from unity to 5. NMR analysis of MPyAAm-TFA mixtures in dichloromethane-d_2 revealed that the favorable conformation in terms of the pyridyl group to the carbonyl group in MPyAAm switched from s-trans to s-cis by protonation. The results suggest that controlling the conformation of MPyAAm resulted in control of the stereospecificity in radical polymerization of the monomer.

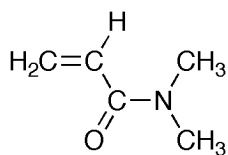**Keywords:** radical polymerization; stereospecific polymerization; isotactic;

syndiotactic; *N*-methyl-*N*-(2-pyridyl)acrylamide; monomer conformation;

Running Head: Stereospecific radical polymerization

INTRODUCTION

Radical polymerization of *N*-monosubstituted acrylamide generally gives atactic polymer. To prepare stereoregular polymers of *N*-monosubstituted acrylamide, it is necessary to use Lewis acids,[1,2] Lewis bases,[3,4] alkyl alcohols[5,6] or fluorinated alcohols[7,8] as an additive to the polymerization mixture. On the other hand, radical polymerization of *N*,*N*-disubstituted acrylamide affords stereoregular polymer without an additive. The stereospecificity in the polymerization depends on the structure of the *N*-substituent in the monomer; radical polymerization of *N*,*N*-dimethylacrylamide (DMAAm) provides isotactic polymer, whereas polymerization of *N*,*N*-diphenylacrylamide (DPhAAm) gives syndiotactic polymer.[9]

Recently we found that radical polymerization of *N*-methyl-*N*-phenylacrylamide (MPhAAm) gave syndiotactic polymer.[10] According to the conformational analysis of *N*-aryl-*N*-methylamide,[11-15] an *N*-aryl substituent favors the form s-trans to the carbonyl group and perpendicular to the planar amide group. This suggests that the *N*-substituent s-trans to the carbonyl group of *N*,*N*-disubstituted acrylamide should play a determining role in the stereospecificity of the radical polymerization.
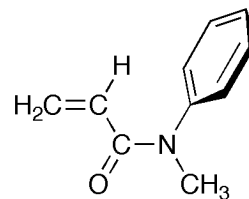
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DMAAm
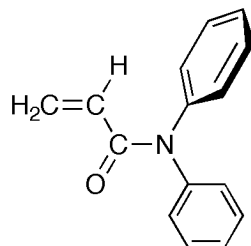
Isotactic

DPhAAm

Syndiotactic

MPhAAm

Syndiotactic

Monomer conformation can be one of important factors in the stereospecificity of radical polymerization. In fact, it is known that monomer conformation affects the stereochemistry in the propagating reaction in the radical polymerization of 1,1-disubstituted vinyl monomers with an optically active ester group, near the ceiling temperature.[16] Thus, it is assumed that stereospecificity of radical polymerization of *N*-aryl-*N*-methylacrylamides can be controlled by strategically controlling the monomer conformation, even when achiral monomers are used.

Recently, it was reported that *N*-methyl-*N*-(2-pyridyl)amides switched their conformation from s-trans to s-cis O=C-N-Py with protonation.[17,18] If *N*-methyl-*N*-(2-pyridyl)acrylamide (MPyAAm) undergoes similar conformational switching, addition of acid to the radical polymerization of MPyAAm is expected to change the stereospecificity from syndiotactic to isotactic. In this paper, we report the effect of trifluoroacetic acid (TFA) and methanesulfonic acid (MSA) on the stereospecificity of radical polymerization of MPyAAm. Conformational switching of MPyAAm with protonation is also discussed on the basis of NMR analysis of mixtures

of MPyAAm and TFA.

EXPERIMENTAL

Materials

MPhAAm was prepared according to literature methods.[10] Dimethyl 2,2'-azobisisobutyrate (MAIB) (supplied by Otsuka Chemical Co., Ltd, Japan) was recrystallized from methanol. Acryloyl chloride, triethylamine, anhydrous dichloromethane, anhydrous tetrahydrofuran (THF), anhydrous acetonitrile, HCl aqueous solution (12 N) (Kanto Chemical Co., Inc., Japan), trifluoroacetic acid (TFA), methanesulfonic acid (MSA), 2-(methylamino)pyridine (Tokyo Chemical Industry Co., Ltd, Japan), diethyl ether, methanol, and ethyl acetate (Kishida Chemical Co., Ltd, Japan) were used without further purification.

Synthesis of MPyAAm

To a stirred solution of acryloyl chloride (36.2 g, 0.40 mol) in THF (300 mL) were added 2-(methylamino)pyridine (21.6 g, 0.20 mol) and triethylamine (40.5 g, 0.40 mol) in THF (150 ml) dropwise at 3-5°C. After stirring the mixture for 24 h at room temperature, the solid precipitate that had formed was removed by filtration, and the solvent was evaporated. The residue was chromatographed (silica gel, ethyl acetate) to give 14.9 g of MPyAAm (46 %): red orange oil; ^{1}H NMR (400 MHz, CDCl$_3$ at 35°C), δ 8.51 (m, 1H), 7.74 (m, 1H), 7.21 (m, 1H), 7.19 (m, 1H), 6.41 (dd, 1H, ^2J = 2.0 Hz, ^3J = 16.8 Hz), 6.25 (dd, 1H, ^3J = 10.2 Hz, ^3J = 16.8 Hz), 5.61 (dd, 1H, ^2J = 2.0 Hz, ^3J = 10.2

Hz), 3.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$ at 35°C), δ 166.22, 155.90, 149.23, 138.16, 129.27, 127.89, 121.76, 120.92, 35.36. Anal. Calc. for C$_9$H$_{10}$NO: C, 66.64; H, 6.22; N, 17.28. Found: C, 66.38; H, 6.13; N, 17.22.

Polymerization

A typical polymerization procedure was as follows. MPyAAm (1.0948 g, 6.75 mmol) was dissolved in CH$_2$Cl$_2$ to prepare 3 mL of solution, and TFA (0.7697 g, 6.75 mmol) was dissolved in CH$_2$Cl$_2$ to prepare 3 mL of solution. Two milliliters of each solution were transferred to a glass ampoule cooled to 0°C. MAIB (0.0104 g, 4.52×10^{-2} mmol) was dissolved in CH$_2$Cl$_2$ to prepare 1 mL of solution and 0.5 mL of this solution was added to the mixture of MPyAAm and TFA in CH$_2$Cl$_2$ at 0°C, giving final concentrations: [MPyAAm]$_0$=1.0 mol L^{-1}, [TFA]$_0$=1.0 mol L^{-1}, [MAIB]$_0$=5.0×10^{-3} mol L^{-1}. The glass ampoule was degassed and filled with nitrogen three times. The mixture was irradiated at a distance of ~5cm from an UV-LED lamp (375nm, Optocode Co., Japan) to initiate polymerization. After 16 h, the polymerization mixture was poured into diethyl ether (500 mL). The precipitated polymer was collected by centrifugation, and dried *in vacuo*. The polymer yield was determined gravimetrically.

Measurements

^{1}H NMR spectra of the polymers were obtained using an EX-400 spectrometer (JEOL Ltd.). The tacticity of the polymers was determined from the ^{1}H NMR signals of the methylene groups in the main chain, as measured in deuterated dimethyl sulfoxide

(DMSO-d_6) at 150°C. ^{1}H and ^{13}C NMR spectra of MPyAAm monomer in the presence or absence of TFA were measured in CD_2Cl_2 at 0°C with an ECX-400 spectrometer (JEOL Ltd.) operated at 400 MHz for ^{1}H and 100 MHz for ^{13}C.

The molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC), using polystyrene samples as molecular weight standards. SEC was performed with an HLC 8220 chromatograph (Tosoh Co.) equipped with TSK gel columns (SuperHM-M (6.5 mm ID×150 mm) and SuperHM-H (6.5 mm ID×150 mm), Tosoh Co.) and UV detector (UV-8220, Tosoh Co.). Dimethylformamide containing LiBr (10 mmol L^{-1}) was used as eluent at 40°C with flow rate 0.35 mL min^{-1}. The initial polymer concentration was 1.0 mg mL^{-1}.

No peaks were observed in the chromatograms of poly(MPyAAm)s, probably because polymers containing pyridyl groups were absorbed by the stationary phase. Thus, the molecular weights of poly(MPyAAm)s were measured after poly(MPyAAm)s were converted into hydrochloride salts.

Preparation of poly(MPyAAm) hydrochloride

Poly(MPyAAm) (ca. 30 mg, 0.19 mmol of monomeric unit) was dissolved in 2 mL of HCl methanol solution (2.0 N, 4.0 mmol of HCl), and 4 mL of diethyl ether was added dropwise to the solution. After removal of the supernatant solution by decantation, the precipitated polymer was dried *in vacuo*. Signals of the pyridinium protons were not observed in the ^{1}H NMR spectrum of the precipitated polymer measured in DMSO-d_6 at 25°C, probably because of exchange with H_2O. However, the

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signals of the pyridyl group exhibited a slight down-field shift after treatment with HCl, suggesting that the pyridyl groups in poly(MPyAAm)s were converted into HCl salts.

RESULTS AND DISCUSSION

Radical Polymerization of MPyAAm in CH₃CN at 0 or –40°C in the Presence of TFA or MSA

Radical polymerization of MPyAAm was carried out in CH$_3$CN at 0°C in the absence of acids; however, no polymer was obtained. The polymerization was then carried out in CH$_3$CN in the presence of TFA (Table 1, runs 1-3), and polymers were obtained in moderate yields. The fact that hydrogen bonding formation between C=O and –OH significantly enhances k_p in radical polymerization of α,β-unsaturated ester monomers,[19-22] suggested that at least the carbonyl group in MPyAAm was protonated, resulting in formation of polymers.

Polymer with m dyad content 38% was obtained in the presence of an equimolar amount of TFA. This value (38%) is comparable to the m dyad content (34%) of poly(MPhAAm) prepared in CH$_2$Cl$_2$ at 0°C (cf. Table 3), suggesting that MPyAAm essentially favored the s-trans O=C-N-Py conformation and gave syndiotactic-rich polymers by a mechanism similar to that proposed for the MPhAAm polymerization[10]. The m dyad content increased to 44% with increase in the amount of added TFA. However, isotactic specificity was not induced even in the presence of a 5-fold amount of TFA, suggesting that only partial conformational switching of MPyAAm occurred in

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the presence of excess amounts of TFA at 0°C. Thus, the polymerization temperature was reduced to –40°C, in anticipation of an enhanced effect of TFA (Table 1, runs 4-6). A slight increase in the *m* dyad content of poly(MPyAAm) was observed regardless of the amount of added TFA, though the *m* dyad content did not exceed 50%.

<Table 1>

The effect of MSA (pKa: 1.6 in DMSO[23]), which is a stronger acid than TFA (pKa: 3.45 in DMSO[23]), was then examined (Table 1, runs 7-12). The *m* dyad content reached 49% in the presence of excess amounts of MSA at 0°C. By lowering the temperature to –40°C, however, the *m* dyad content decreased in the presence of excess MSA.

Radical Polymerization of MPyAAm in CH$_2$Cl$_2$ at Low Temperatures in the Presence of TFA

The radical polymerization of MPyAAm was carried out in CH$_2$Cl$_2$, a less polar solvent than CH$_3$CN, at 0°C in the presence or absence of TFA. As for polymerization in CH$_3$CN, no polymer was obtained in the absence of TFA and polymers were obtained in moderate yields in the presence of TFA (Table 2, runs 1-5). The addition of TFA significantly affected the stereoregularity of the poly(MPyAAm) obtained. The *m* dyad content of the polymer increased linearly with the amount of added TFA and reached 60%, although 4-fold and 5-fold amounts of TFA showed

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similar effects (Figure 1). The value (m=60 %) is comparable with the m dyad content (62%) of poly(DMAAm) prepared in toluene at 0°C.[24] This result suggested that MPyAAm favored the s-cis O=C-N-Py conformation in CH_2Cl_2 in the presence of excess amounts of TFA, and gave isotactic-rich polymers by a mechanism similar to that proposed for DMAAm polymerization[24].

<Table 2>

<Figure 1>

To confirm the involvement of the pyridyl group in the induction of isotactic specificity by TFA, radical polymerization of MPhAAm was carried out under the same conditions (Table 3). The addition of TFA scarcely influenced the stereoregularities of the polymers obtained, although slight decreases in the m dyad contents of the polymers obtained in the presence of equimolar and 2-fold amounts of TFA were observed. Thus, it is further suggested that the conformational switching of MPyAAm by protonation was responsible for the acid-induced isotactic specific polymerization, as expected.

<Table 3>

To examine the effect of the polymerization temperature on isotactic specificity, MPyAAm polymerizations in CH_2Cl_2 were carried out at –60°C to –20°C (Table 2, runs 6-20). Decrease in temperature slightly enhanced the isotactic specificity,

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but excess amounts of TFA were required to significantly induce isotactic specificity even at –60°C (Figure 2). The conformational switching of MPyAAm by protonation is assumed to proceed via multi-step and not single-step processes, as discussed later.

<Figure 2>

The tendency of increase in number-averaged molecular weight (M_n) of poly(MPyAAm) with increase in the amount of the added TFA was observed, although the addition of 5-fold amount of TFA decreased M_n compared with 4-fold amount of TFA. This tendency implies that polymerization was accelerated by protonation of the carbonyl group in MPyAAm as mentioned above and/or the rate of syndiotactic propagation differs from the rate of isotactic propagation, although the M_ns determined by SEC of poly(MPyAAm) hydrochlorides are not accurate enough to be discussed quantitatively.

NMR Analysis of Conformational Switching of MPyAAm

To further investigate the conformational switching of MPyAAm, we conducted ^{1}H NMR analysis of MPyAAm ([MPyAAm]$_0$=0.1 mol L^{-1}) in CD$_2$Cl$_2$ at 0°C in the absence or presence of TFA (Figure 3). The signals of pyridyl and vinyl groups shifted significantly upon adding TFA, suggesting interaction between MPyAAm and TFA. In the pyridyl group resonances, small signals were observed on adding an equimolar amount of TFA. The small signals were also observed in the presence of 2-

and 3-fold amounts, but disappeared in the presence of 4- and 5-fold amounts of TFA. It was assumed that the small signals were assignable to the pyridyl groups in the s-cis O=C-N-Py conformer that is in equilibrium with the original s-trans O=C-N-Py conformer, and the equilibrium exchange rate was enhanced by excess TFA. The details are discussed later.

<Figure 3>

In the vinyl group resonances, signals assignable to the s-cis O=C-N-Py conformer were not clearly observed, probably because of overlap of the signals due to the two conformers. Protonation of the carbonyl group would result in a down-field shift of the signals of the vinylidene protons and an up-field shift of the signal of the methine proton.[25] Indeed, the signals of the vinylidene protons moved gradually towards lower magnetic field with an increase in the amount of added TFA. However, the methine proton signal moved slightly towards higher magnetic field upon adding an equimolar amount of TFA, then moved towards lower magnetic field upon adding excess TFA. The down-field shift in the presence of excess TFA suggests conformational switching of MPyAAm by protonation, because the methine proton should become free from the shielding effect of the pyridyl ring in the s-trans O=C-N-Py conformation when conformational switching takes place.[26]

NOE difference spectroscopy was performed to confirm the conformational switching. Saturation of the *N*-methyl group led to significant NOE enhancement for

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both the H^c in the vinyl group and the H^d proton at the 3-position in the pyridyl group in the presence of TFA, although no NOE was observed in the absence of TFA (Figure 4). Furthermore, the NOE enhancement increased linearly with increase in the amount of added TFA, although 4-fold and 5-fold amounts of TFA exhibited similar NOE enhancements (Figure 5). It should be noted that this tendency was similar to the dependence of the m dyad content on the amount of the added TFA (*cf*. Figure 2).

<Figure 4>

<Figure 5>

^{13}C NMR spectra of MPyAAm ($[MPyAAm]_0$=0.1 mol L^{-1}) in the absence or presence of TFA were also measured in CD_2Cl_2 at 0°C. The ^{13}C NMR signals of MPyAAm shifted significantly on adding TFA as well as the ^1H NMR signals. Figure 6 displays the changes in the chemical shifts of the acryl group and the pyridyl group on adding TFA.

<Figure 6>

By adding equimolar and 2-fold amounts of TFA, the signals of the vinylidene and carbonyl carbons exhibited down-field shifts. This result supports protonation of the carbonyl group. Furthermore, the signal of the carbon at the 4-position in the pyridyl group exhibited a down-field shift, and those at the 2- and 6-positions in the pyridyl

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group exhibited up-field shifts. These results indicate that the pyridyl group was also protonated.[27]

By adding a 3-fold amount of TFA, the changes in the chemical shifts of all of the carbons were substantial. However, significant changes were not observed between 4-fold and 5-fold amounts of TFA. These results imply that the conformational switching of MPyAAm required at least a 3-fold amount of TFA.

Proposed Mechanism for Conformational Switching of MPyAAm with Protonation

It has been proposed that *N*-aryl-*N*-methylamides favor the s-trans O=C-N-Ar conformation, because the s-cis O=C-N-Ar conformation is destabilized by the electronic repulsion between the carbonyl lone-pair electrons and the aryl π-electrons in the aryl ring twisted by steric hindrance between the *N*-methyl group and the aryl ring.[15,28] In fact, the major conformation dramatically changed from the s-trans O=C-N-Ar to the s-cis O=C-N-Ar upon addition of TFA in the case of *N*-[3,5-bis(dimethylamino)phenyl]-*N*-methylacetamide, probably because of the decrease in the electronic repulsion with protonation at the amino groups.[28]

In the present system, conformational switching could occur via the following mechanism (Scheme 1):

1. both the carbonyl and pyridyl groups of structure **A** are protonated to become structure **C** *via* structure **B** or **B'**, resulting in a decrease in the electronic repulsion between the carbonyl and pyridyl groups;

2. the conformational switching of structure **C** will occur, but the repulsion between

the positive charges prevents structure **C** from converting;

3. however, structure **C** is transformed into structure **D**, accompanied by abstraction of one of the protons in structure **C**, probably catalyzed by the conjugate base of the third acid, to form double protonations of both the carbonyl and pyridyl groups by one proton.

If the conjugate base of the third acid catalyzed the conformational switching, excess TFA should enhance the equilibrium exchange. This corresponds to the result that the ^{1}H NMR signals of the s-trans and s-cis O=C-N-Py conformers were not distinguished in the presence of 4-fold and 5-fold amounts of TFA (cf. Figure 3). Furthermore, it is explicable that MSA exhibited the isotactic-specificity-inducing effect to a lesser extent than TFA (*cf*. Table 1).

When conformational switching takes place via the structure **B**, the concentration of **D** can be expressed by the following equation:

$$[\mathbf{D}]=K_{1B}K_{2B}K_3[\mathbf{A}][\mathrm{H}^+]$$

where K_{1B}, K_{2B}, and K_3 are the equilibrium constants for the protonation of **A** to **B**, and for **B** to **C**, and for conformational switching of **C** to **D**, respectively. Even when the conformational switching takes place via the structure **B'**, the concentration of **D** can be expressed by a similar equation:

$$[\mathbf{D}]=K_{1B}K_{2B}K_3[\mathbf{A}][\mathrm{H}^+]$$

These equations indicate that the concentration of **D** is proportional to the concentrations of **A** and H$^+$. This corresponds to linear increases of the *m* dyad content of the polymers obtained (cf. Figure 2) and of the NOE enhancement in ^{1}H NMR of

MPyAAm (cf. Figure 5), with the amount of added TFA. Furthermore, the conformational switching of **C** to **D** accompanies release of one of two H^+ in **C**. This means that increase in the concentration of H^+ dose not simply result in acceleration of the conformational switching, even though the conjugate base of the third acid catalyzed the conformational switching. Consequently, excess amount, such as 5-fold amount, of TFA was required to significantly induce the conformational switching.

CONCLUSION

MPyAAm was designed as a monomer that is conformationally switchable by protonation. The stereospecificity of radical polymerization of MPyAAm was changed from syndiotactic to isotactic by adding TFA in CH_2Cl_2 at low temperatures, as expected. NMR analysis of mixtures of MPyAAm and TFA revealed that MPyAAm favored the s-cis O=C-N-Py conformation in the presence of excess TFA, and the s-trans O=C-N-Py conformation in the absence of TFA. Consequently, it is suggested that conformational switching of the monomer with protonation was responsible for the change in the stereospecificity of the radical polymerization of MPyAAm. Successful control of stereospecificity of radical polymerization by conformational switching of monomer would allow development of novel methodology for control of stereospecificity of radical polymerization.

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25. The signals of vinylidene protons and methine proton of DMAAm, as measured in toluene-d_8 at 0°C, exhibited down-field and up-field shifts by mixing with diethyl L-tartrates which form a complex with DMAAm though double C=O•••H-O hydrogen bonding in toluene at low temperatures.

26. The signal of the methine proton of DMAAm was observed at lower magnetic field than those of MPyAAm and MPhAAm, as measured in $CDCl_3$ at 25°C.

27. In the ^{13}C NMR spectra of pyridine in $CDCl_3$ 25°C, on adding TFA the signal of the carbon at the 4-position shifted down-field, whereas the signals of the carbons

at the 2- and 6-positions shifted up-field.

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Table 1. Radical polymerization of MPyAAm in CH$_3$CN at low temperatures for 16 h in the presence of TFA or MSA.[a]

Run	Temp.	Additive	[Additive]$_0$	Yield	Dyad / %[b]		M_n[c]	M_w/M_n[c]
	°C		mol L^{-1}	%	m	r	$\times 10^{-4}$	
1	0	TFA	1.0	48	38	62	0.63	1.8
2	0	TFA	3.0	55	44	56	2.05	3.1
3	0	TFA	5.0	50	44	56	4.36	3.1
4	–40	TFA	1.0	60	44	56	2.59	2.6
5	–40	TFA	3.0	54	47	53	3.75	3.2
6	–40	TFA	5.0	30	47	53	5.20	4.4
7	0	MSA	1.0	>99	42	58	1.26	3.2
8	0	MSA	3.0	58	49	51	1.82	4.7
9	0	MSA	5.0	>99	49	51	3.08	5.1
10	–40	MSA	1.0	29	45	55	nd[d]	nd[d]
11	–40	MSA	3.0	49	48	52	0.73	2.9
12	–40	MSA	5.0	51	47	53	0.93	2.3

a. [MPyAAm]$_0$=1.0 mol L^{-1}, [MAIB]$_0$=5.0×10^{-3} mol L^{-1}.

b. Determined from the ^{1}H NMR signals of the main-chain methylene groups.

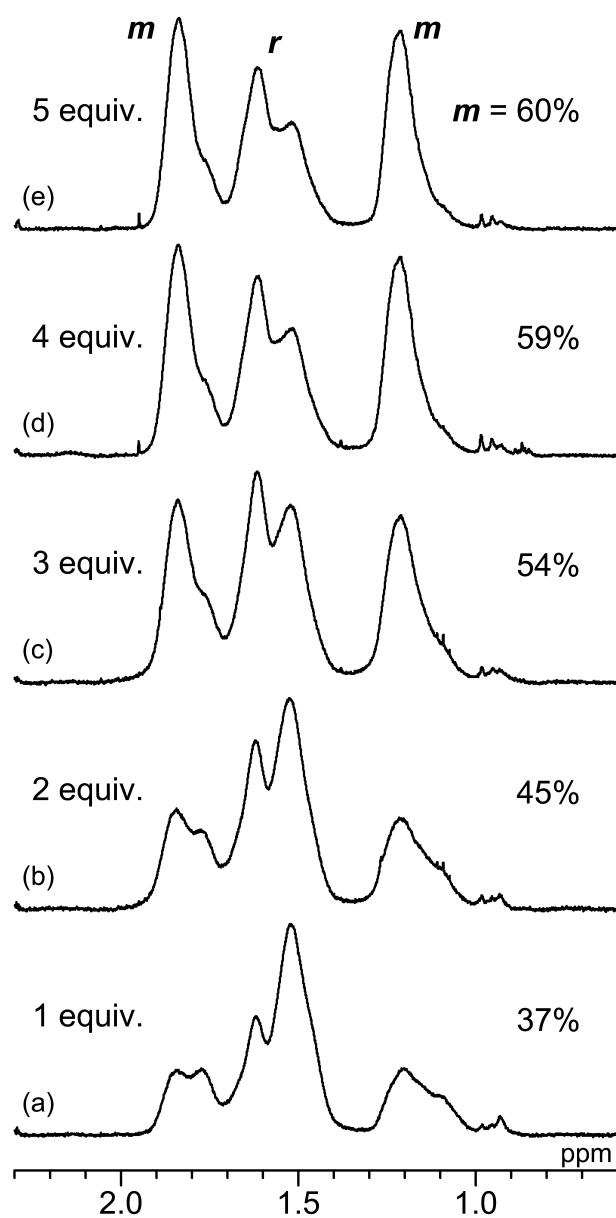c. Determined by SEC (polystyrene standards) for poly(MPyAAm) hydrochloride.

d. Not determined.

Table 2. Radical polymerization of MPyAAm in CH$_2$Cl$_2$ at low temperatures for 16 h in the presence of TFA[a].

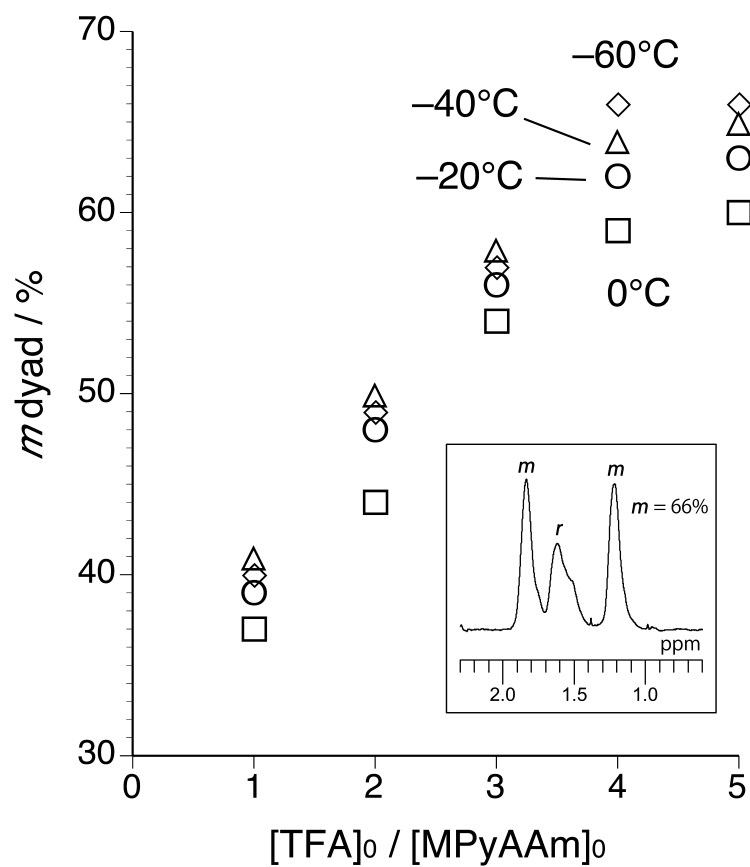| Run	Temp.	[TFA]$_0$	Yield	Dyad / %[b]		M_n[c]	M_w/M_n[c]
	°C	mol L^{-1}	%	m	r	$\times 10^{-4}$	
1	0	1.0	80	37	63	0.33	1.5
2	0	2.0	88	45	55	4.76	1.9
3	0	3.0	46	54	46	1.71	2.4
4	0	4.0	34	59	41	3.45	3.4
5	0	5.0	49	60	40	4.18	4.4
6	−20	1.0	84	39	61	2.57	4.3
7	−20	2.0	59	49	51	4.28	3.0
8	−20	3.0	37	57	43	7.44	4.2
9	−20	4.0	33	62	38	9.67	4.5
10	−20	5.0	57	63	37	5.22	4.9
11	−40	1.0	50	41	59	5.70	3.8
12	−40	2.0	26	50	50	3.87	6.2
13	−40	3.0	29	58	42	7.90	4.6
14	−40	4.0	40	65	35	8.28	3.5
15	−40	5.0	28	65	35	4.03	4.4
16	−60	1.0	66	40	60	6.13	4.4
17	−60	2.0	40	49	51	4.39	8.0
18	−60	3.0	44	57	43	13.8	4.1
19	−60	4.0	25	66	34	17.5	3.7
20	−60	5.0	14	66	34	7.59	3.6

a. [MPyAAm]$_0$=1.0 mol L^{-1}, [MAIB]$_0$=5.0×10^{-3} mol L^{-1}.

b. Determined from the ^{1}H NMR signals of the main-chain methylene groups.

c. Determined by SEC (polystyrene standards) for poly(MPyAAm) hydrochloride.

Table 3. Radical polymerization of MPhAAm in CH_2Cl_2 at 0°C for 16 h in the presence or absence of TFA[a].

Run	$[TFA]_0$	Yield	Dyad / %[b]		M_n[c]	M_w/M_n [c]
	mol L^{-1}	%	m	r	$\times 10^{-4}$	
1	0.0	57	34	66	5.29	1.6
2	1.0	84	27	73	5.26	1.9
3	2.0	61	29	71	3.91	1.8
4	3.0	37	32	68	2.76	1.7
5	4.0	32	33	67	2.25	1.5
6	5.0	21	35	65	1.96	1.4

a. $[MPhAAm]_0$=1.0 mol L^{-1}, $[MAIB]_0$=5.0×10^{-3} mol L^{-1}.

b. Determined from the ^1H NMR signals of the main-chain methylene groups.

c. Determined by SEC (polystyrene standards).

Figure 1. ¹H NMR spectra of the methylene groups in the main chain of poly(MPyAAm)s prepared in CH$_2$Cl$_2$ at 0°C in the presence of (a) 1 equiv., (b) 2 equiv., (c) 3 equiv., (d) 4 equiv., and (e) 5 equiv. of TFA, as measured in DMSO-d_6 at 150°C.
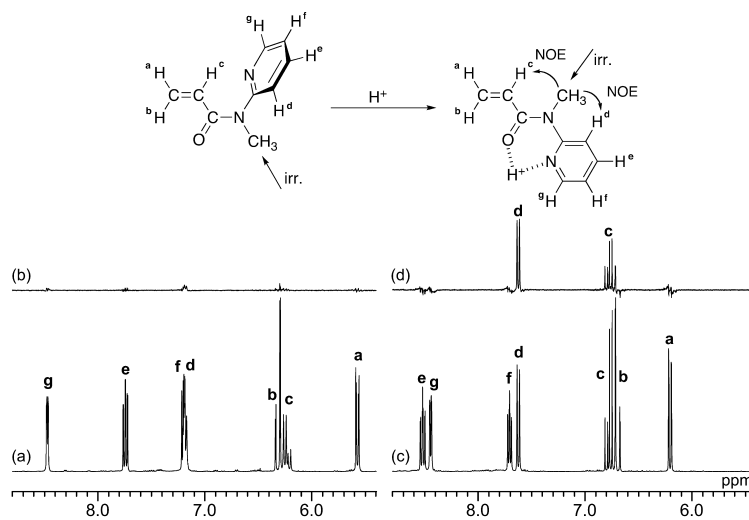
Figure 2. Relationship between the $[TFA]_0/[MPyAAm]_0$ ratio and the m dyad contents of poly(MPyAAm)s prepared at –60°C to 0°C. The inset shows ^1H NMR spectrum of the methylene group in the main chain of poly(MPyAAm) prepared in CH_2Cl_2 at –60°C in the presence of 5 equiv. of TFA, as measured in DMSO-d_6 at 150°C.
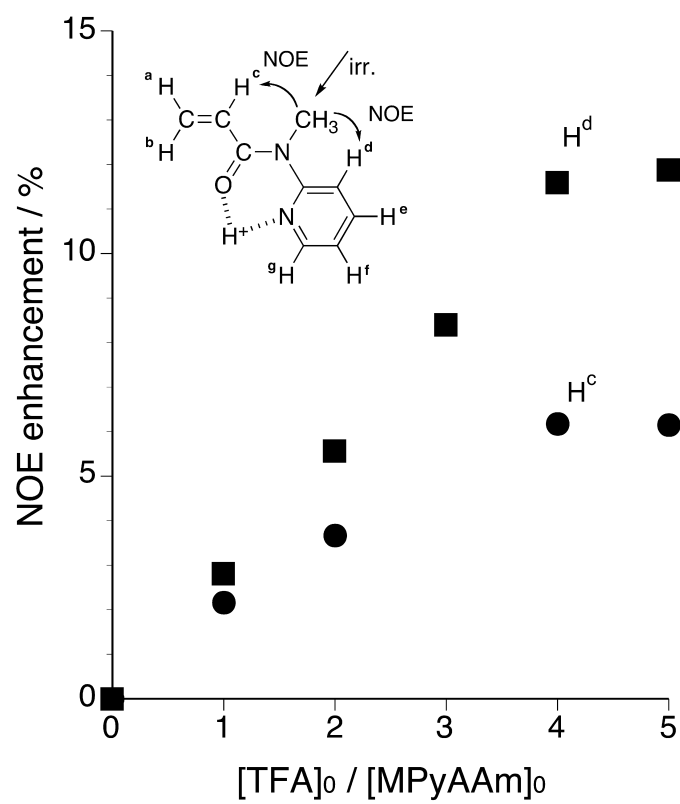
Figure 3. Expanded ^{1}H NMR signals of the vinyl group and the pyridyl group of MPyAAm (0.1 mol L^{-1}) in CD$_2$Cl$_2$ at 0°C. ([TFA]$_0$: (a) 0.0 mol L^{-1}, (b) 0.1 mol L^{-1}, (c) 0.2 mol L^{-1}, (d) 0.3 mol L^{-1}, (e) 0.4 mol L^{-1}, and (f) 0.5 mol L^{-1})
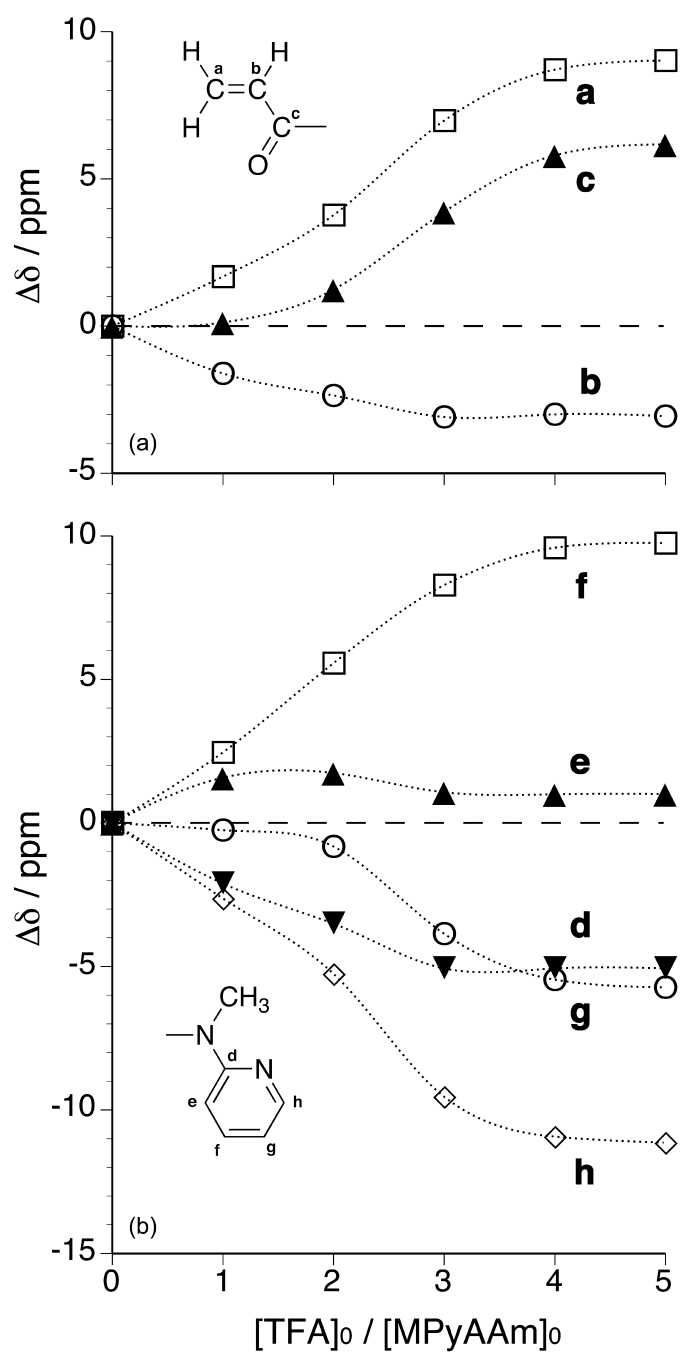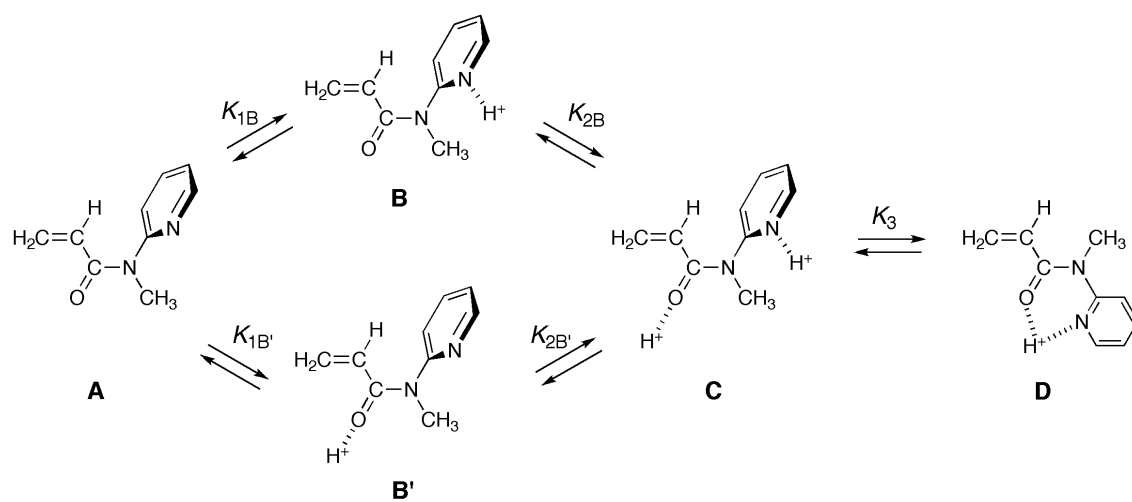
Figure 4. ^{1}H and NOE difference spectra of MPyAAm in CD_2Cl_2 at 0°C in the (a, b) absence or (c, d) presence of a 5-fold amount of TFA, saturating the signal of the *N*-methyl group.

Figure 5. Relationship between the $[TFA]_0/[MPyAAm]_0$ ratio and the NOE enhancements observed for the H^c in the vinyl group and the H^d in the pyridyl group.

Figure 6. Chemical shift changes in ^{13}C NMR spectra of (a) acryloyl group and (b) pyridyl group in MPyAAm upon addition of TFA.

Scheme 1. Proposed mechanism for the conformational switching of MPyAAm with protonation.