

Stereospecific Radical Polymerization of *N*-tert-Butoxycarbonylacrylamide in the Presence of Fluorinated Alcohols

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ABSTRACT: Radical polymerization of *N*-tert-butoxycarbonylacrylamide (NBocAAM) in toluene at low temperatures in the presence of the fluorinated alcohols, 2,2,2-trifluoroethanol, 1,1,1,3,3,3-hexafluoro-2-propanol and nonafluoro-*tert*-butanol, afforded atactic, heterotactic and syndiotactic polymers, respectively. NMR analysis revealed that the fluorinated alcohols formed hydrogen bonding-assisted complexes with NBocAAM, with different structures. The difference in the structures of the complexes was responsible for the differences in the induced stereospecificities. Based on the structures of the complexes between NBocAAM and the fluorinated alcohols, mechanisms for the three kinds of stereospecific radical polymerizations are proposed.

Keywords: hydrogen bonding; radical polymerization; stereospecific polymers;

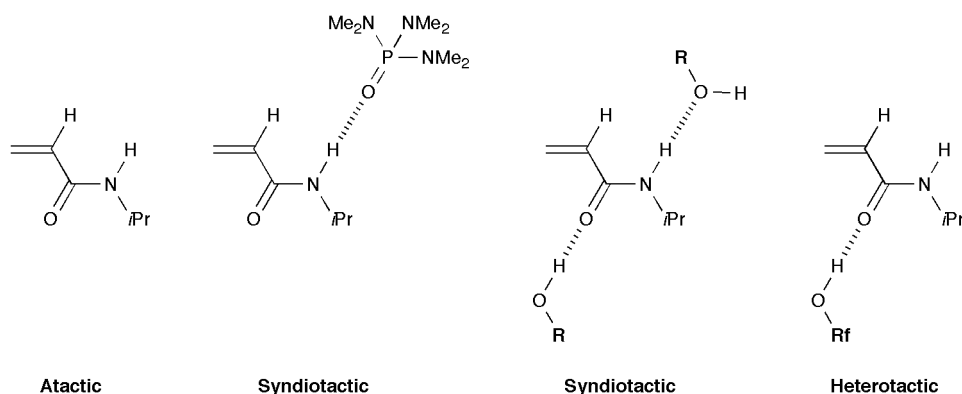
syndiotactic; heterotactic; *N-tert*-butoxycarbonylacrylamide

Running Head: Stereospecific Radical Polymerization

INTRODUCTION

The control of stereospecificity in radical polymerization has been considered to be difficult, probably because of the high activity of electrically neutral propagating species. However, recent developments in polymer synthesis are gradually overcoming the difficulty of stereocontrol of radical polymerization using a wide variety of methods.¹

We have reported that radical polymerization of vinyl monomers with amide groups, such as acrylamide derivatives and *N*-vinylacetamide, can be moderately well controlled by utilizing hydrogen bonding interaction.²⁻⁸ For example, complex formation of *N*-isopropylacrylamide (NIPAAm) with hexamethylphosphoramide (HMPA) or alkyl alcohol (ROH) such as 3-methyl-3-pentanol (3Me3PenOH) gave syndiotactic polymers. Furthermore, the addition of fluorinated alcohols (RfOH), such as 2,2,2-trifluoroethanol (**1**), 1,1,1,3,3,3-hexafluoro-2-propanol (**2**) and nonafluoro-*tert*-butanol (**3**), provided heterotactic polymers which had an alternating sequence of *meso* (*m*) and *racemo* (*r*) dyads.⁷ NMR analysis of mixtures of NIPAAm and those additives suggested that the induced stereospecificity depended on the structures of the hydrogen bonding-assisted complexes shown below.

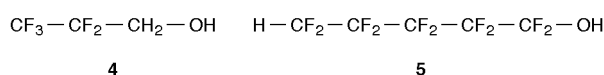
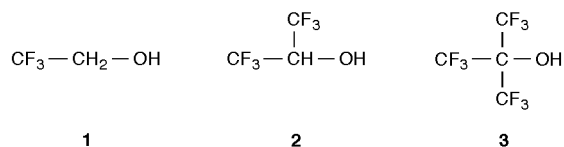


Recently, we found that stereospecificity of radical polymerization of *N*-*tert*-butoxycarbonylacrylamide ($\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CO}-\text{O}-t\text{Bu}$) (NBocAAM), which is a monomer with an imide group protected with the butoxycarbonyl (Boc) group, was significantly altered by changing the kind of fluorinated alcohol added to the polymerization system in toluene at low temperatures.⁹ Atactic, heterotactic and syndiotactic polymers were obtained by adding **1**, **2** and **3**, respectively, to the NBocAAM polymerization, assuming that the three kinds of fluorinated alcohols formed hydrogen bonding-assisted complexes with NBocAAM, with different structures. In the present study, we investigated radical polymerization of NBocAAM in more detail, and the structure of hydrogen bonding-assisted complexes between NBocAAM and fluorinated alcohols, to obtain insight into the unusual dependence of stereospecificity on the added fluorinated alcohols.

EXPERIMENTAL

Materials

Toluene was purified by washing with sulfuric acid, water and 5% aqueous NaOH, followed by fractional distillation. Dimethyl 2,2'-azobisisobutyrate (MAIB) (supplied by Otsuka Chemical Co., Ltd) was recrystallized from methanol. HMPA, **1** (Aldrich Chemical Co.), **2**, 1H, 1H-pentafluoropropanol (**4**), 1H, 1H, 5H-octafluoropentanol (**5**) (supplied by Daikin Industries, Ltd.), *tert*-butyl alcohol (tBuOH) (Wako Pure Chemical Industries, Ltd.), **3**, isopropyl alcohol (iPrOH), 3Me3PenOH, α,α,α -trifluorotoluene (Tokyo Chemical Industry Co., Ltd), dehydrated methanol (MeOH), dehydrated ethanol (EtOH), dehydrated tetrahydrofuran (THF), and dehydrated *N,N*-dimethylformamide (DMF) (Kanto Chemical Co., Inc.) were used without further purification for the polymerization reactions. NBocAAM was prepared as reported previously.⁹



Polymerization

A typical polymerization procedure was as follows. NBocAAM (0.481 g, 2.8 mmol) and **1** (1.694 g, 16.9 mmol) were dissolved in toluene to prepare 5 mL of solution. MAIB (0.103 g, 0.40 mmol) was dissolved in toluene to prepare 1 mL of solution. Four milliliters of the former solution and 0.5 mL of the latter solution were transferred to a glass ampoule and cooled to -50°C . The glass ampoule was degassed and filled with nitrogen three times. Polymerization was initiated by UV irradiation at the

polymerization temperature. After 12 h, the reaction mixture was poured into a large amount of hexane/diethyl ether mixture (1:1 vol:vol),⁹ and the precipitated polymer was collected by centrifugation or filtration and dried *in vacuo*. The polymer yield was determined gravimetrically.

Measurements

¹H and ¹³C NMR spectra were obtained with an EX-400 spectrometer or an ECX-400 spectrometer (JEOL, Ltd.). Triad tacticities were determined from ¹³C NMR signals due to the main-chain methine groups of the poly(AAm)s derived from poly(NBocAAm)s.⁹ Molecular weights and molecular weight distributions of the poly(NBocAAm)s 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.). DMF 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.

RESULTS AND DISCUSSION

Radical Polymerization of NBocAAm at Low Temperatures

Radical polymerization of NBocAAm was carried out in toluene at -40°C in the presence of alkyl alcohols or HMPA, which induced syndiotactic specificity in the radical polymerization of NIPAAm (Table 1).^{3,4} Radical polymerization in the absence

of alkyl alcohols or HMPA was unsuccessful, because of insolubility of NBocAAM in toluene under the given conditions. The polymers were obtained at high yields in the presence of less bulky alcohols (Table 1, runs 1-3). The polymer yield, however, decreased drastically as the bulkiness of the added alcohol increased, probably because the reactions were heterogeneous under some conditions (Table 1, runs 4 and 5). Addition of HMPA gave polymer in relatively high yield, but decreased the molecular weight (Table 1, run 6). Polymers slightly rich in *r* dyad were obtained, regardless of the kinds of the additives. Radical polymerization in MeOH, THF or DMF gave polymers slightly rich in *r* dyad, suggesting that NBocAAM essentially exhibited syndiotactic-specificity. Thus, it is assumed that no significant effect of the added alcohols and HMPA on the stereospecificity was observed in NBocAAM polymerization, in contrast to NIPAAm polymerization.

<Table 1>

The radical polymerization of NBocAAM was carried out in the presence of fluorinated alcohols which induced heterotactic specificity in the radical polymerization of NIPAAm (Table 2).⁷ The tacticity of the polymers obtained at 0°C varied widely with the structure of the added alcohols. Atactic, heterotactic and syndiotactic polymers were obtained in radical polymerization of NBocAAM with the addition of **1**, **2** and **3**, respectively (Table 2, runs 1, 5, 15). That tendency was enhanced by decrease in the polymerization temperature (Table 2, runs 2, 9, 19). However, reducing the temperature

to -60°C made the system heterogeneous and further enhancement was not observed, even though polymerization was carried out in $\text{C}_6\text{H}_5\text{CF}_3$ which was expected to increase the solubility of the system (Table 2, runs 3, 4, 13, 14, 21, 22).

<Table 2>

The effect of the amount of **2** and **3** added was examined. The *mr* content of the polymers obtained increased gradually as the amount of **2** increased. Furthermore, use of **2** as a solvent afforded polymer with almost the same tacticity as the polymer prepared in the presence of a six-fold amount of **2** (Table 2, runs 6-10). A similar tendency was observed in the case of **3** (Table 2, runs 16-20). Moreover, decreasing the monomer concentration scarcely affected the stereospecificity of the polymerization in the presence of **2** (Table 2, runs 11-12). It is assumed that to induce heterotactic or syndiotactic specificity, fluorinated alcohols need not be used as a solvent, but need only to be present in excess.

Addition of **4** and **5** afforded polymers with almost the same tacticity as were obtained in the presence of **1**, suggesting that induction of heterotactic and syndiotactic specificities requires not only increase in the number of fluorine atoms but also a branched structure at the 1 position of the fluorinated alcohol (Table 2, runs 3, 23, 24).

The *mr* content of the poly(AAm) directly obtained under corresponding conditions increased gradually with increase of the number of fluorine atoms in the added alcohols (Table 2, runs 25-27), although the heterotacticities were much lower

than those of poly(NIPAAm)s. Thus, the imide groups or the two carbonyl groups in the NBocAAM monomer bring about the unique dependence of the stereospecificity of the radical polymerization in the presence of the fluorinated alcohols.

NMR Analysis of the Mixtures of NBocAAM and Fluorinated Alcohols

The structures of the complexes between NBocAAM and fluorinated alcohols were investigated using NMR spectroscopy. The NMR measurement was conducted at 25°C, because NBocAAM was insoluble in toluene-*d*₈ at low temperatures. The signals of N-H protons, C=O carbons in the acryloyl groups (C=O_{acryl}) and C=O carbons in the Boc groups (C=O_{Boc}) exhibited downfield shifts with increase in the concentration of NBocAAM alone from 0.05 mol L⁻¹ to 0.2 mol L⁻¹, indicating self-association of NBocAAM monomer (Figure 1).

<Figure 1>

The effect of the addition of fluorinated alcohols was examined, keeping the concentration of NBocAAM at 0.2 mol L⁻¹. The signals of N-H protons exhibited upfield shifts which were enhanced with increase in the amount of fluorinated alcohol added, although the magnitude was small in the case of **1** (Figure 2a) compared with **2** and **3**. In addition, the signals of the quaternary carbons in the butoxy groups exhibited downfield shifts from mixing NBocAAM and fluorinated alcohols (Figure 2b), implying involvement of butoxy groups in hydrogen bonding interactions.

<Figure 2>

The signals of carbonyl carbons showed various behaviors depending on the kind of added alcohol. In the case of **3** (Figure 3c) the signals of C=O_{acryl} showed a large downfield shift, and those of C=O_{Boc} an upfield shift at low [3]₀/[NBocAAM]₀ ratios but a downfield shift at high ratios, suggesting that both C=O_{acryl} and C=O_{Boc} formed C=O•••H–O hydrogen bonds. In the case of **2** (Figure 3b) the signals of C=O_{Boc} showed an upfield shift, whereas those of C=O_{acryl} scarcely changed. Taking into account that the solubility of NBocAAM in toluene was improved by mixing with **2** and p*K*_a (9.6)¹⁰ of **2** is comparable to the calculated p*K*_a (10.34±0.46)^{11,12} of NBocAAM, it is assumed that only C=O_{acryl} formed C=O•••H–O hydrogen bonds. In the case of **1** (Figure 3a), the changes in the chemical shifts of both C=O_{acryl} and C=O_{Boc} were small compared with the cases of **2** and **3**. Thus it was not possible to draw any conclusions about hydrogen bonding interactions, although the solubility of NBocAAM in toluene was improved by mixing with **1**.

<Figure 3>

The stoichiometries of the complexes were evaluated by Job's method via Eq.

(1)¹³

$$[\text{NBocAAm} - \text{RfOH}] = \frac{\delta(\text{CH}_2=) - \delta(\text{CH}_2=)_f}{\delta(\text{CH}_2=)_c - \delta(\text{CH}_2=)_f} \times [\text{NBocAAm}]_0 \quad (1)$$

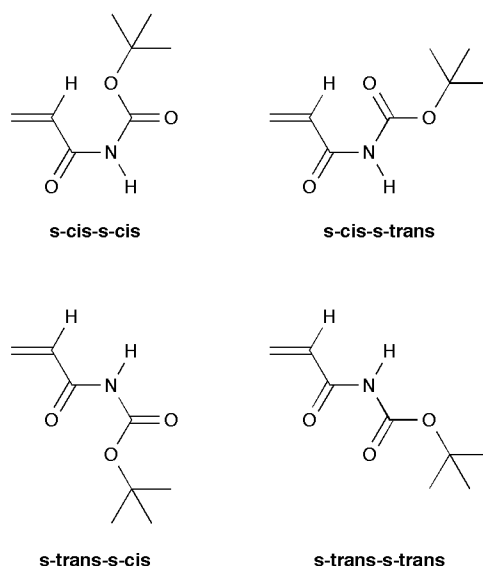
where $\delta(\text{CH}_2=)$ and $\delta(\text{CH}_2=)_f$ are the chemical shifts of methylene carbons of the sample mixture and NBocAAm alone, respectively, relative to TMS internal standard. As noted above, the chemical shift of NBocAAm alone also varied with concentration, since NBocAAm self-associates through a hydrogen bonding interaction. Thus, the chemical shifts of NBocAAm alone at the corresponding concentration were used as $\delta(\text{CH}_2=)_f$. The chemical shift for the saturated mixture [$\delta(\text{CH}_2=)_c$] was calculated from the intercept of quadratic fits to plots of the chemical shift versus the $[\text{NBocAAm}]_0$ fraction, since the saturation values should be independent of NBocAAm concentration.

In the case of **3** (Figure 4c), the calculated data were asymmetrically plotted, and a maximum was observed around $[\text{NBocAAm}]_0$ fraction=0.4. In the case of **2** (Figure 4b), the calculated data were symmetrically plotted, and a maximum was observed at $[\text{NBocAAm}]_0$ fraction=0.5. These results mean that NBocAAm and **3** afford both 1:1 and 1:2 complexes at 25°C, whereas NBocAAm and **2** form a 1:1 complex, corresponding to the result obtained from the dependence of the C=O chemical shift on the $[\text{RfOH}]_0/[\text{NBocAAm}]_0$ ratio (cf. Figure 3).

<Figure 4>

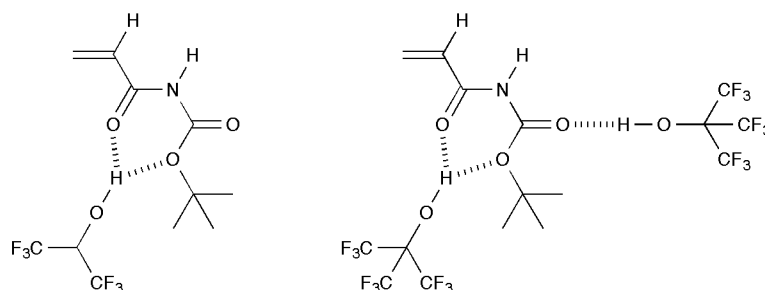
There are four conformers for NBocAAm as discussed below. It is known that imide compounds favor one s-trans O=C-N-H and one s-cis O=C-N-H conformation

in solution^{14,15}, although two O=C–N–H bonds favor the s-trans conformation in the solid state^{16,17}. Thus the predominant conformation of NBocAAm in solution would be the s-trans-s-cis or the s-cis-s-trans conformation. The steric repulsion between the methine hydrogen of vinyl group and the carbonyl oxygen of Boc group in the s-cis-s-trans conformation is larger than that between the methine hydrogen of vinyl group and the imide proton in the s-trans-s-cis conformation, suggesting that NBocAAm favors the s-trans-s-cis conformation in solution.



If NBocAAm favors the s-trans-s-cis conformation, the added alcohols can form hydrogen bonds with not only C=O_{acryl} but also the oxygen of the butoxy group due to a chelating effect, as supported by the downfield shift of the signals of the quaternary carbons in the butoxy groups (cf. Figure 2b). The formation of O–H•••O_{Boc} hydrogen bonds should result in reduction of the basicity of the C=O_{Boc}. Thus, it is assumed that **2** formed a 1:1 complex with NBocAAm as noted above, whereas **3**

formed a 1:2 complex, probably because the acidity of **2** is much lower than that of **3** ($pK_a=5.2$)¹⁰, as below.

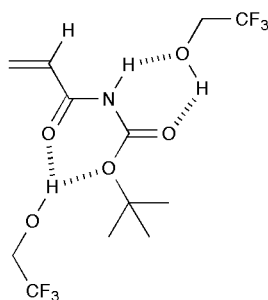


A maximum was also observed at about $[NBocAAm]_0$ fraction=0.4 in the case of **1** (Figure 4a). Thus it is suggested that NBocAAm and **1** formed both 1:1 and 1:2 complexes as well as a combination of NBocAAm and **3**, although not only is the acidity of **1** ($pK_a=12.4$)¹⁰ lower than that of **2** but also syndiotactic specificity was not induced. This suggests that the structure of the 1:2 NBocAAm-**1** complex is different from that of the 1:2 NBocAAm-**3** complex. One possible explanation for the difference in the structures is whether or not N-H...O-Rf hydrogen bonding was formed, for the following reasons.

- (1) the basicity of the oxygen of **1** is higher than those of **2** and **3**¹⁸
- (2) the upfield shift of N-H proton from mixing with **1** was smaller than the shifts with **2** and **3** (cf. Figure 2a)
- (3) the C=O_{acryl} signal exhibited a slight downfield shift from mixing with **1**, probably due to enhanced C=O...H-O hydrogen bonding by the cooperative effect of the N-H...O-Rf hydrogen bonding.¹⁹⁻²¹

Two-dimensional exchange spectroscopy (EXSY) measurements were

conducted for the mixtures of NBocAAm with **1** or **3** in toluene-*d*₈ at 0°C. A positive cross peak was observed between the protons of O–H and N–H groups only in the spectra of the mixture of NBocAAm and **1**, suggesting the formation of N–H•••O–Rf hydrogen bonds. Furthermore, it is assumed that **1** forming the N–H•••O–Rf hydrogen bonds also forms O–H•••O=C hydrogen bonds with C=O_{Boc}, because the upfield shift of the C=O_{Boc} from mixing with **1** was smaller than with **2** and **3** (cf. Figure 3),^{22,23} as shown below.



Proposed Mechanism for the Stereospecific Radical Polymerization of NBocAAm Induced by Fluorinated Alcohols

The heterotactic specificity in NBocAAm polymerization in the presence of **2** would be induced by a similar mechanism as for NIPAAm polymerization in the presence of fluorinated alcohols, because both systems included the 1:1 complex of the monomer and fluorinated alcohols through hydrogen bonding between the C=O of acryloyl group and the O–H group. When the complexed NBocAAm undergoes a propagating reaction, the fluorinated alcohol binding to the NBocAAm monomer remains at the newly formed propagating chain end. Thus, a propagating reaction should proceed between the propagating radical and the monomer, both of which are

bonded to fluorinated alcohols, in such a manner that the fluorinated alcohol binding to the incoming monomer is arranged at the opposite side from the fluorinated alcohol binding to the propagating chain-end. The single bond near the propagating chain end of the *r*-ended radicals rotates to reduce the repulsion of fluorine atoms in the fluorinated alcohols bound to the antepenultimate and chain-end monomeric units (Scheme 1). The conformationally rotated radicals can react with a new incoming monomer via two possible pathways: pathway **a** should form an *r* dyad and pathway **b** should form an *m* dyad. However, the imide group at the penultimate monomeric unit bound to RfOH limits the approach via pathway **a** by the next incoming monomer, so that *r*-ended radicals favor *m*-addition via pathway **b**.

<Scheme 1>

In the *m*-ended radicals, the single bond at the second dyad from the end rotates to reduce the repulsion of fluorine atoms in RfOHs bound to the antepenultimate and penultimate monomeric units (Scheme 2). These conformationally rotated radicals also can undergo the next propagating reaction via two possible pathways. However, side groups not only at the penultimate monomeric unit but also at the antepenultimate monomeric unit sterically prevent the radicals from propagating via pathway **b** so that *m*-ended radicals favor *r*-addition via pathway **a**. As a result, *m*-addition to *r*-ended radicals and *r*-addition to *m*-ended radicals both take place in an alternating manner, resulting in the formation of heterotactic stereosequences.

<Scheme 2>

In the NBocAAM polymerization in the presence of **3**, the single bond near the propagating chain end of the *r*-ended radicals rotates to reduce the repulsion of fluorine atoms in the fluorinated alcohols bound to the antepenultimate and chain-end monomeric units. In this case, however, the second RfOH binding to the antepenultimate monomeric unit is crowded out to the front free-space to reduce steric and/or electrostatic repulsions, and limits the approach via pathway **b** by the next incoming monomer more than the side group at penultimate monomeric unit, so that *r*-ended radicals favor *r*-addition via pathway **a** (Scheme 3). The *m*-ended radicals also favor *r*-addition in similar manner to NBocAAM polymerization in the presence of **2**, resulting in the formation of syndiotactic stereosequences. The stronger repulsion would be reflected in the lower molecular weights of the polymers obtained, as compared with those obtained in the presence of **1** and **2** (cf. Table 2).

<Scheme 3>

As mentioned above, NBocAAM and **1** are expected to form the 1:2 complex through two kinds of cyclic hydrogen bonding. In this case, the fluorine atoms on the two kinds of the bonded alcohols should exhibit almost the same repulsion effects, undercutting the basic premise that the incoming monomer approaches the propagating

chain-end, keeping the imide group of the monomer at the opposite side to that of the chain end. As a result, statistically completely atactic polymers were obtained, in particular by lowering the polymerization temperature.

CONCLUSIONS

The stereospecificity of radical polymerization of NBocAAM in toluene at low temperatures is scarcely affected by alkyl alcohols as additives or solvent, whereas fluorinated alcohols exhibit unique stereocontrolling power: atactic, heterotactic and syndiotactic polymers are obtained in the presence of **1**, **2**, and **3**, respectively. NMR analysis of mixtures of NBocAAM and the fluorinated alcohols shows that the individual alcohols form different complexes with NBocAAM through hydrogen bonding interaction, suggesting that different stereospecificity is induced depending on the structure of the complex. In other words, control of the mode of hydrogen bonding is the key to controlling the stereospecificity of the NBocAAM polymerization. The low stereospecificity of NBocAAM polymerization in the presence of alkyl alcohols contrasts with NIPAAm polymerization, for which stereospecificity can be moderately well controlled with alkyl alcohols.

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Table 1. Radical polymerization of NBocAAM at -40°C for 16 h in the presence of alkyl alcohols or HMPA^a

Run	Additive	Solvent	Yield %	Triad tacticity / % ^b			M_n^c $\times 10^{-4}$	M_w/M_n^c
				<i>mm</i>	<i>mr</i>	<i>rr</i>		
1	MeOH	C ₆ H ₅ CH ₃	98	17	48	35	3.8	8.8
2	EtOH	C ₆ H ₅ CH ₃	94	18	48	34	3.0	6.0
3 ^d	<i>i</i> -PrOH	C ₆ H ₅ CH ₃	90	18	49	33	1.7	3.1
4 ^d	<i>t</i> -BuOH	C ₆ H ₅ CH ₃	36	21	47	32	2.7	19.4
5 ^d	3Me3PenOH	C ₆ H ₅ CH ₃	12	-	-	-	1.2	1.6
6	HMPA	C ₆ H ₅ CH ₃	60	18	45	37	0.9	1.2
7	None	MeOH	>99	17	47	36	5.7	4.9
8	None	THF	90	19	40	41	1.3	2.1
9	None	DMF	>99	23	43	34	3.5	4.8

a. $[\text{MAIB}]_0 = 0.05 \text{ mol L}^{-1}$.

b. Determined by ^{13}C NMR signals due to the methine groups of poly(AAm)s derived from poly(NBocAAM).

c. Determined by SEC (polystyrene standards).

d. Polymerization proceeded heterogeneously.

Table 2. Radical polymerization of NBocAAm in toluene at low temperatures for 12 h in the presence of fluorinated alcohols^a

Run	Added alcohol	Solvent	[ROH] ₀ mol L ⁻¹	Temp. °C	Yield %	Triad tacticity / % ^b			M _n ^c x 10 ⁻⁴	M _w /M _n ^c
						<i>mm</i>	<i>mr</i>	<i>rr</i>		
1	1	C ₆ H ₅ CH ₃	3.0	0	91	20	46	34	5.68	3.4
2	1	C ₆ H ₅ CH ₃	3.0	-40	95	23	52	25	10.8	4.0
3 ^d	1	C ₆ H ₅ CH ₃	3.0	-60	93	21	50	29	9.66	3.6
4 ^d	1	C ₆ H ₅ CF ₃	3.0	-60	96	23	50	27	7.39	4.6
5	2	C ₆ H ₅ CH ₃	3.0	0	79	15	54	31	2.52	1.6
6 ^d	2	C ₆ H ₅ CH ₃	0.5	-40	95	24	50	26	4.45	4.5
7 ^d	2	C ₆ H ₅ CH ₃	1.0	-40	>99	23	56	21	6.01	3.6
8 ^d	2	C ₆ H ₅ CH ₃	1.5	-40	>99	20	58	22	5.36	2.9
9	2	C ₆ H ₅ CH ₃	3.0	-40	61	16	63	21	3.24	2.0
10 ^e	-	2	-	-40	>99	19	62	19	28.3	4.6
11 ^{d,f}	2	C ₆ H ₅ CH ₃	1.5	-40	78	19	59	22	3.72	1.9
12 ^f	2	C ₆ H ₅ CH ₃	3.0	-40	55	16	59	25	3.51	1.7
13 ^d	2	C ₆ H ₅ CH ₃	3.0	-60	37	19	57	24	4.08	2.2
14 ^d	2	C ₆ H ₅ CF ₃	3.0	-60	>99	20	63	17	10.4	7.9
15	3	C ₆ H ₅ CH ₃	3.0	0	81	18	37	45	1.11	2.1
16 ^d	3	C ₆ H ₅ CH ₃	0.5	-40	43	20	43	37	13.5	4.8
17 ^d	3	C ₆ H ₅ CH ₃	1.0	-40	98	15	44	41	3.43	4.0
18 ^d	3	C ₆ H ₅ CH ₃	1.25	-40	>99	16	45	39	3.36	4.0
19	3	C ₆ H ₅ CH ₃	3.0	-40	65	11	44	45	1.00	1.6
20 ^e	-	3	-	-40	97	9	45	46	4.0	1.8
21 ^d	3	C ₆ H ₅ CH ₃	3.0	-60	51	14	41	45	1.28	1.6
22 ^d	3	C ₆ H ₅ CF ₃	3.0	-60	56	11	39	50	2.50	1.8
23 ^d	4	C ₆ H ₅ CH ₃	3.0	-60	97	22	47	31	17.4	2.6
24 ^d	5	C ₆ H ₅ CH ₃	3.0	-60	>99	21	47	32	8.13	2.2
25 ^g	1	C ₆ H ₅ CH ₃	3.0	0	93	23	50	27	nd	nd
26 ^g	2	C ₆ H ₅ CH ₃	3.0	0	44	19	52	29	nd	nd
27 ^g	3	C ₆ H ₅ CH ₃	3.0	0	57	15	58	27	nd	nd

a. [MAIB]₀=0.05 mol L⁻¹.

b. Determined by ¹³C NMR signals due to the methine groups of poly(AAm)s derived from poly(NBocAAm).

c. Determined by SEC (polystyrene standards).

d. Polymerization proceeded heterogeneously.

e. [NBocAAm]₀=1.0 mol L⁻¹, for 16 h.

f. [NBocAAm]₀=0.25 mol L⁻¹.

g. [AAm]₀=0.5 mol L⁻¹.

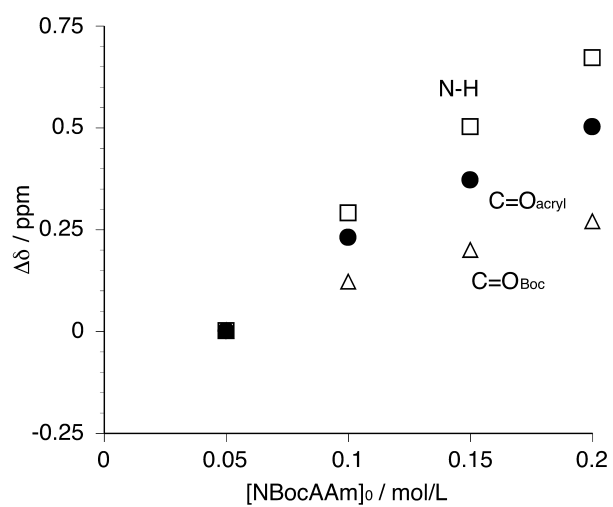


Figure 1. Chemical shifts of the N-H proton and the C=O carbons in acryloyl and Boc groups of NBocAAM, as a function of the concentration of NBocAAM in toluene-*d*₈ at 25°C.

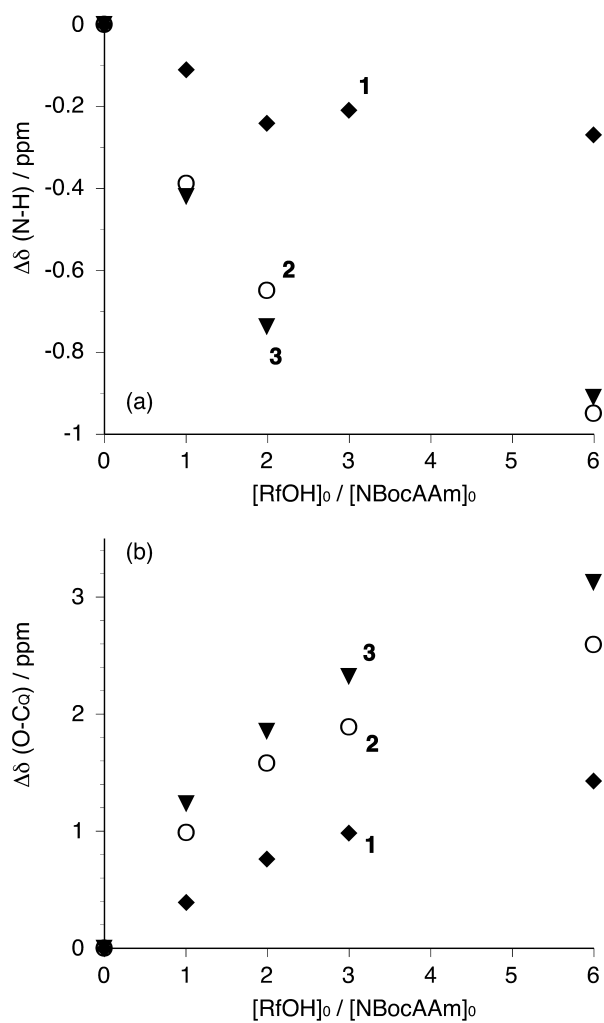


Figure 2. Chemical shifts of (a) the N-H proton and (b) the quaternary carbons in the butoxy groups of NBocAAM, as a function of the $[\text{RfOH}]_0/[\text{NBocAAM}]_0$ ratio in toluene- d_8 at 25°C ($[\text{NBocAAM}]_0=0.2 \text{ mol L}^{-1}$).

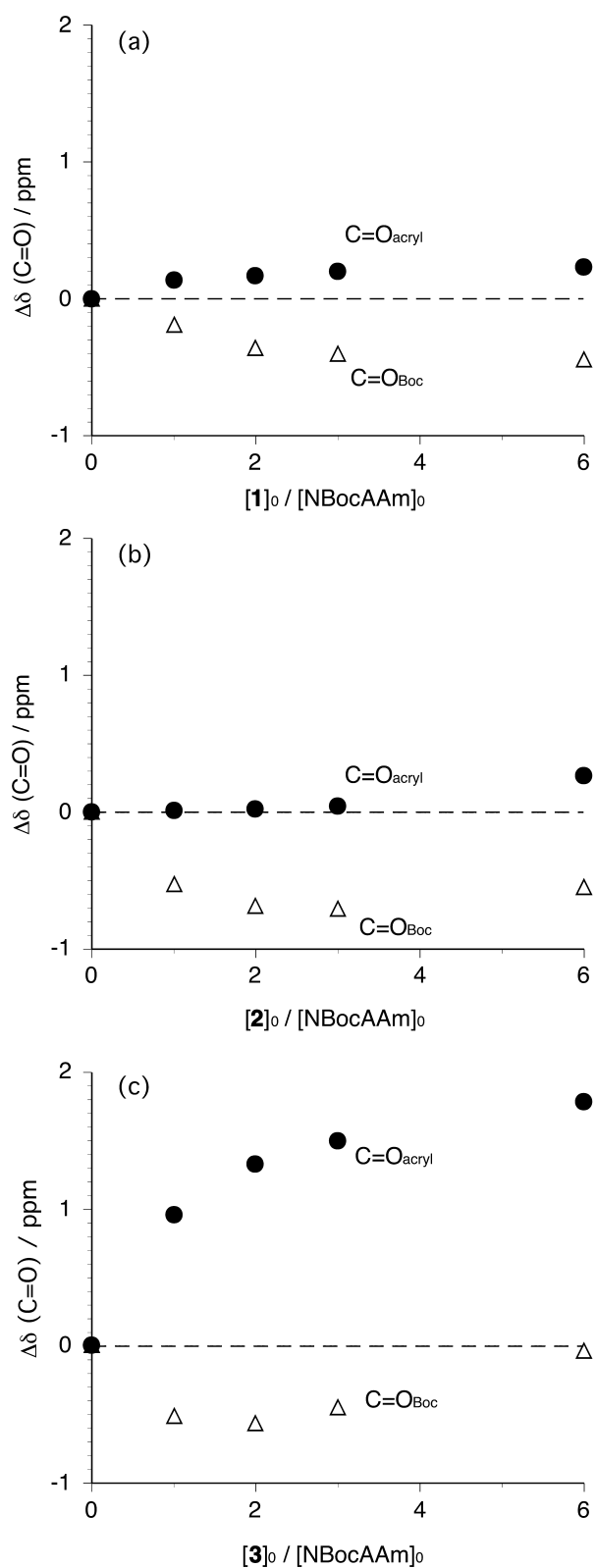


Figure 3. Chemical shifts of the C=O carbons in acryloyl and Boc groups of NBocAAm, as a function of the $[RfOH]_0/[NBocAAm]_0$ ratio in toluene- d_8 at 25°C; (a) **1**, (b) **2**, and (c) **3** ($[NBocAAm]_0=0.2 \text{ mol L}^{-1}$).

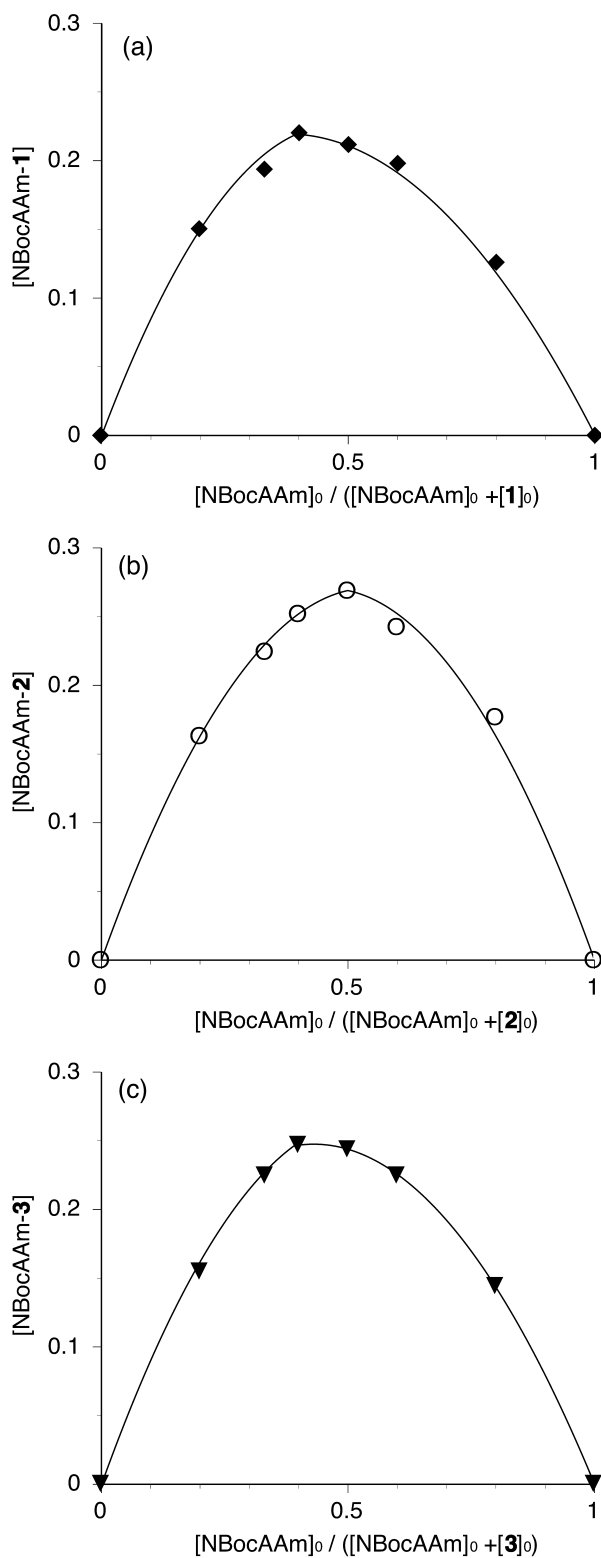
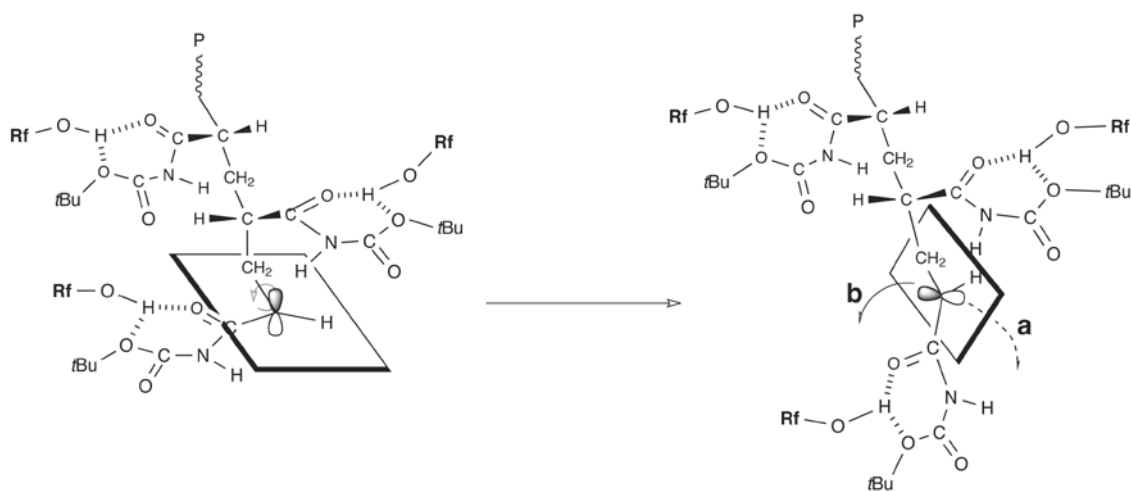
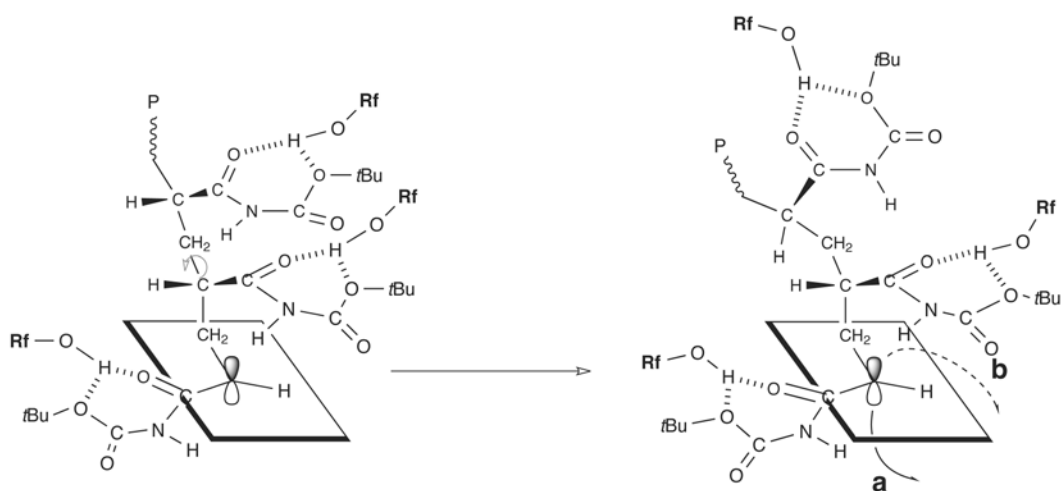


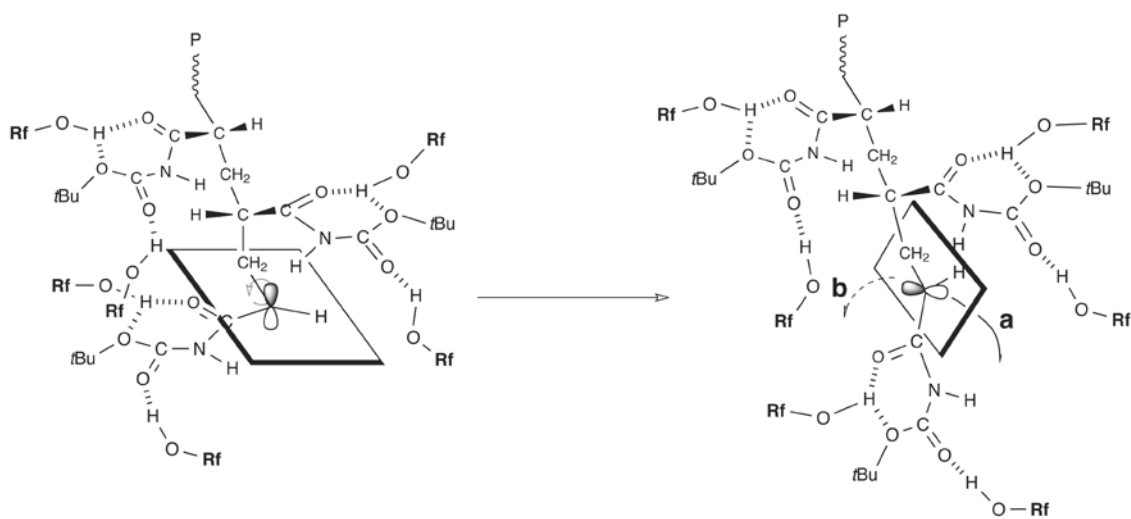
Figure 4. Job's plots for the association of NBocAAm with (a) **1**, (b) **2**, and (c) **3**, respectively, evaluated from the changes in the chemical shift of $\text{CH}_2=$ carbons of NBocAAm ($[\text{NBocAAm}]_0 + [\text{RfOH}]_0 = 0.25 \text{ mol L}^{-1}$, in toluene- d_8 , at 25°C).



Scheme 1. Proposed mechanism for *m*-addition to *r*-ended radicals in the heterotactic-specific radical polymerization of NBocAAM induced by **2**.



Scheme 2. Proposed mechanism for *r*-addition to *m*-ended radicals in the heterotactic-specific radical polymerization of NBocAAM induced by **2**.



Scheme 3. Proposed mechanism for *r*-addition to *r*-ended radicals in the syndiotactic-specific radical polymerization of NBocAAm induced by **3**.