

De-tert-butylation of Poly(*N*-tert-butyl-*N*-*n*-propylacrylamide): Stereochemical Analysis at the Triad Level

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ABSTRACT

The stereochemical analysis of polymers derived from *N,N*-disubstituted acrylamides is usually difficult. The diad tacticity can be determined from the ^1H NMR signals of the main-chain methylene groups. However, the splitting because of the configurational sequences is poor, even in ^{13}C NMR, which does not allow determination of the tacticity at the triad level. In contrast, the stereochemical analysis of polymers derived from *N*-monosubstituted acrylamides is easily conducted and the triad tacticity can be determined from the ^{13}C signals of the main-chain methine groups. Thus, stereochemical analysis of *N,N*-disubstituted polymers should be able to be conducted if the polymers are transformed into *N*-monosubstituted polymers with retention of the configurational sequence. Poly(*N*-tert-butyl-*N*-*n*-propylacrylamide) [poly(TBNPAAm)] was radically prepared, and de-tert-butylation was conducted by treatment with $\text{Sc}(\text{OTf})_3$ in a mixed solvent of CH_3CN and 1,4-dioxane at 50, 80, and 110 °C. ^1H NMR analysis of the resulting polymers indicated quantitative conversion after 72 h, regardless of the temperature. ^{13}C NMR analysis of the transformed polymers confirmed that the configurational sequences were retained during the reaction. Thus, the triad stereochemical analysis of *N,N*-disubstituted polymers was successfully conducted by de-tert-butylation as a polymer reaction, followed by ^{13}C NMR analysis of the transformed polymers.

KEYWORDS: polymer reaction, de-tert-butylation, acrylamide, tacticity, NMR

INTRODUCTION

Stereospecific radical polymerization is still one of the challenging topics in the field of polymer synthesis.¹⁻³ Nuclear magnetic resonance (NMR) spectroscopy has been extensively used to investigate the configurational sequences of the obtained polymers, since the first reports on the triad tacticities of poly(methyl methacrylate) (PMMA) polymers determined by ^1H NMR in 1960.⁴⁻⁶

We have previously reported stereocontrol of the radical polymerization of (meth)acrylamides

via complex formation of the monomers with alcohols,⁷⁻⁹ Lewis bases,^{10,11} and lithium salts.^{12,13} For example, addition of lithium bis(trifluoromethanesulfonyl)imide (LiNTf_2) induced heterotactic specificity in the radical polymerization of *N*-*n*-propylmethacrylamide (NNPMAAm) in CH_3CN , whereas syndiotactic polymers were obtained in CH_3OH .¹³

Job's plots based on the NMR chemical shifts of NNPMAAm- LiNTf_2 mixtures revealed that the stoichiometry of the complex depended on the solvent: a 2:1 complex was formed in CH_3CN ,

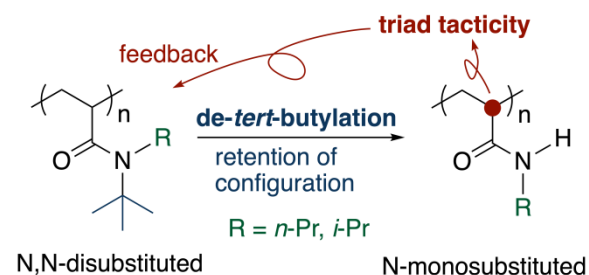
whereas a 1:1 complex was formed in CH₃OH. This result suggests that a 2:1 complex provides heterotactic polymers, probably because the 2:1 complex behaves like a pseudo-divinyl monomer.¹⁴

Similar to NNPMAAm, *N,N*-dimethylacrylamide (DMAAm) formed a 2:1 complex with LiNTf₂ in CH₃CN.¹² The radical polymerization of the complexed monomer gave a polymer with a *r* diad content of 57%. This diad tacticity was comparable to that of poly(DMAAm) prepared in toluene at -60 °C in the presence of half the amount of di-*n*-butyl L-tartrate (L-BuTar) (55%).⁹ However, the spectral patterns of the ¹H signals of the main-chain methylene group, particularly the signals assigned to the *r* diad, were quite different from each other. An excess amount of L-BuTar induced syndiotactic specificity in the DMAAm polymerization in toluene at lower temperatures.⁹ Conversely, LiNTf₂ induced heterotactic specificity in NNPMAAm in CH₃CN as mentioned above. Thus, it is suggested that the changes in the spectral pattern reflect the differences in the triad configurational sequences.

The first NMR study on the stereochemistry of poly(DMAAm) was reported by Huynh and McGrath in 1980, in which 90 MHz ¹H NMR spectra were recorded in chloroform-*d* (CDCl₃) at 34 °C.¹⁵ Even though the signal assignments were unclear, it was suggested that anionic polymerization afforded isotactic polymers as was reported by Butler and co-workers¹⁶ in 1960. Increasing the resonance frequency to 360¹⁷ or 500 MHz¹⁸ improved the peak resolution, but quantitative analysis of the tacticity was unable to be conducted even at the diad level. A successful quantitative analysis of diad tacticity was achieved from the ¹H signals of the main-chain methylene groups by increasing the measurement temperature in deuterated dimethyl sulfoxide (DMSO-*d*₆).¹⁹⁻²¹ However, it has been difficult to conduct quantitative analysis of the triad tacticity of poly(DMAAm), even using ¹³C NMR, which has a wider spectral width than ¹H NMR.^{17-19,22,23}

The diad tacticity of poly(*N*-isopropylacrylamide) [poly(NIPAAm)], however, was able to be determined from the ¹H signals of the main-chain methylene groups, measured in DMSO-*d*₆ at elevated temperatures.^{20,21,24} Furthermore, a successful quantitative analysis of triad tacticity can be achieved from the ¹³C signals of the main-chain methine groups, measured in a mixed solvent of DMSO-*d*₆, deuterium oxide (D₂O), and HCF₂CF₂CF₂CF₂CH₂OH at elevated temperatures.^{8,25} These results indicated that the splitting because of the stereochemical configuration strongly depends on the number of substituents on the nitrogen atom in polyacrylamide derivatives.

Recently, it has been reported that the *tert*-butyl group on the nitrogen atom in *N,N*-disubstituted amide compounds can be deprotected by treatment with a metal triflate, such as scandium triflate [Sc(OTf)₃].²⁶ Even if the amide compound has both *tert*-butyl and isopropyl groups, the *tert*-butyl group can be selectively deprotected. It was therefore proposed that *N,N*-disubstituted polyacrylamides can be transformed into *N*-monosubstituted polyacrylamides by applying this de-*tert*-butylation as a polymer reaction. As a result, the triad tacticity of *N,N*-disubstituted polyacrylamides should be able to be determined from the ¹³C signals of the main-chain methine groups of the transformed polymers, if the stereochemical configurations are retained during the reaction (SCHEME 1). In this paper, we report the successful quantitative analysis of the triad tacticity of poly(*N-tert*-butyl-*N-n*-propylacrylamide) [poly(TBNPAAm)] by de-*tert*-butylation, followed by ¹³C NMR analysis of the resulting polymers.



SCHEME 1 The strategy for the triad stereochemical analysis of *N,N*-disubstituted polyacrylamides by de-*tert*-butylation, followed by ¹³C NMR analysis of the resulting polymers.

EXPERIMENTAL

Materials

2,2'-Azobisisobutyronitrile (AIBN) (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) was recrystallized from CH₃OH (Kanto Chemical Co., Inc., Tokyo, Japan) that had been fractionally distilled. 1-Bromopropane, 2-bromopropane, *tert*-butylamine, tetrabutylammonium iodide, adiponitrile, acryloyl chloride (Tokyo Chemical Industry, Tokyo, Japan), Sc(OTf)₃, CDCl₃ (Sigma-Aldrich Japan, Tokyo, Japan), CH₂Cl₂, tetrachloroethylene (Cl₂C=CCl₂), diethyl ether, DMSO-*d*₆ (FUJIFILM Wako Pure Chemical Corporation), D₂O, CH₃CN, *N,N*-dimethylformamide (DMF; high-performance liquid chromatography grade), tetrahydrofuran (THF; high-performance liquid chromatography grade) (Kanto Chemical Co., Inc.), acetone, 1,4-dioxane, lithium bromide (LiBr, anhydride) (Kishida Chemical Co., Ltd, Osaka, Japan), and 4,4,5,5,5-pentafluoro-1-pentanol (PenOH-F₅) (Daikin Industry Ltd., Osaka, Japan) were used as received.

Measurements

The ¹H and ¹³C NMR spectra of the monomers were measured in CDCl₃ at 25 °C using an ECZ-400 spectrometer (JEOL Ltd., Tokyo, Japan). The ¹H NMR spectra of the polymers were measured in a mixed solvent (CDCl₃/DMSO-*d*₆ = 2/1 vol/vol) to dissolve the original poly(TBNPAAm), copolymers obtained during the reaction and the completely transformed poly(NNPAAm)s. The ¹³C NMR spectra of the transformed poly(NNPAAm)s were measured using an ECA-500 spectrometer (JEOL Ltd.) in a mixed solvent (DMSO-*d*₆/D₂O/PenOH-F₅ = 75/10/15 wt%), because a mixed solvent of DMSO-*d*₆, D₂O, and a fluorinated alcohol has been found to be effective for the triad stereochemical analysis of poly(NIPAAm)s.^{8,25} The ¹H chemical shifts were referenced to internal tetramethylsilane (δ = 0.00 ppm). The ¹³C chemical shifts were

referenced to PenOH-F₅ (CF₃CF₂-CH₂-CH₂CH₂OH: δ = 26.99 ppm).

The number-average molecular weights (*M*_ns) and molecular weight distributions (*M*_w/*M*_n) of the polymers were determined using size exclusion chromatography (SEC) using PMMA samples as molecular weight standards. For poly(TBNPAAm), SEC was performed on an HLC 8220 chromatograph (Tosoh Corp., Tokyo, Japan). THF was used as the eluent. For poly(NNPAAm)s, SEC was performed with a PU-4185 pump (JASCO, Tokyo, Japan) connected to a refractive index detector (RI-4035, JASCO) and column oven (380-B, Chemco Plus Scientific Co., Ltd., Osaka, Japan). DMF containing LiBr (10 mmol/L) was used as the eluent. TSK gel columns [SuperHM-M (150 × 6.5 mm, i.d) and SuperHM-H (150 × 6.5 mm, i.d)] (Tosoh Corp.) were used in both systems. Measurements were conducted at 40 °C with a flow rate of 0.35 mL/min. The initial polymer concentration was set at 3.0 mg/mL.

Synthesis of *N-tert-butyl-N-n-propylacrylamide* (TBNPAAm) and *N-tert-butyl-N-isopropylacrylamide* (TBIPAAm)

The disubstituted acrylamide monomers were prepared from the corresponding amine compounds and acryloyl chloride, according to procedures described in the literature.²⁶ TBIPAAm: ¹H NMR (400 MHz, CDCl₃, δ): 6.55 (dd, *J* = 16.7, 10.3 Hz, 1H), 6.17 (dd, *J* = 16.7, 2.0 Hz, 1H), 5.51 (dd, *J* = 10.3, 2.0 Hz, 1H), 3.93 (sept, *J* = 7.1 Hz, 1H), 1.47 (s, 9H), 1.39 (d, *J* = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, δ) 168.66, 134.03, 124.40, 58.31, 46.71, 29.53, 23.71.

De-*tert*-butylation of poly(TBNPAAm)

Poly(TBNPAAm) (113 mg, 6.6 × 10⁻¹ mmol of the monomeric unit), Sc(OTf)₃ (33 mg, 6.6 × 10⁻² mmol), and solvent (10 mL) were added to a 100-mL round-bottom flask equipped with a condenser. The reaction was conducted at a given temperature with magnetic stirring. After 24 h, the reaction mixture was poured into a large amount of diethyl ether. The polymer precipitate was collected by centrifugation and dried *in vacuo*. In the experiments to examine the effect of temperature, poly(TBNPAAm) (169

mg, 1.0 mmol of the monomeric unit) and $\text{Sc}(\text{OTf})_3$ (98 mg, 2.0×10^{-1} mmol) were used. The reaction mixture was dialyzed against CH_3OH (Spectra/Por 3, molecular mass cutoff 3.5 kDa, Spectrum Laboratories Inc., Shiga, Japan). The dialysate was evaporated to dryness under reduced pressure to give a residue, which was further dried *in vacuo*. The conversion was calculated using the following equation:

$$\text{Conversion (\%)} = \left(1 - \frac{I_{a+c+e+a'+e'} - I_{f+f'} \times 4/3}{3 \times I_{f+f'}} \right) \times 100$$

where $I_{a+c+e+a'+e'}$ and $I_{f+f'}$ denote the integral intensities of the ^1H signals of the (co)polymers (FIGURE 1).

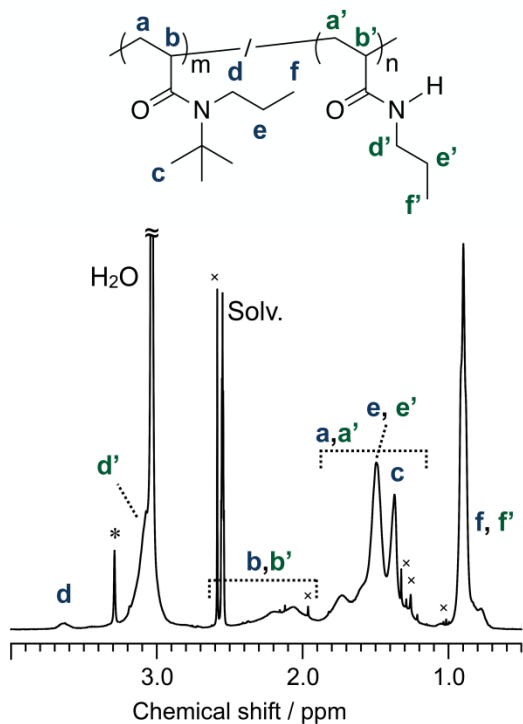


FIGURE 1 ^1H NMR spectrum of poly(TBNPAAm-co-NNPAAm) prepared by de-*tert*-butylation of poly(TBNPAAm) in a mixed solvent of CH_3CN and 1,4-dioxane at 80°C for 24 h, measured in a mixed solvent ($\text{CDCl}_3/\text{DMSO}-d_6 = 2.0/1.0$ vol/vol, 55°C). * and x denote the signals of the methyl group of CH_3OH used as a dialysis solvent and impurities, respectively.

RESULTS AND DISCUSSION

Polymerization of TBNPAAm

TBNPAAm was chosen as the *N,N*-disubstituted acrylamide monomer having a *tert*-butyl group at the nitrogen atom, because TBNPAAm has been reported to radically polymerize well.²⁷ Radical polymerization of TBNPAAm (1.0 mol/L) was carried out with AIBN (5.0×10^{-2} mol/L) in toluene at 60°C for 6 h. The polymerization mixture was poured into a large amount of CH_3OH . The polymer precipitate was collected by centrifugation and dried *in vacuo*. The polymer ($M_n = 3.2 \times 10^4$, $M_w/M_n = 2.1$) was obtained in 82% yield. FIGURE 2 shows the ^1H NMR spectrum of poly(TBNPAAm). The signals were broadened, likely because the two bulky *N*-substituents slowed down the molecular motion of the poly(TBNPAAm) polymer. As a result, insufficient resolution, even for diad tacticity determination, was observed. A similar tendency has been observed with poly(*N,N*-diphenylacrylamide)s.¹⁹

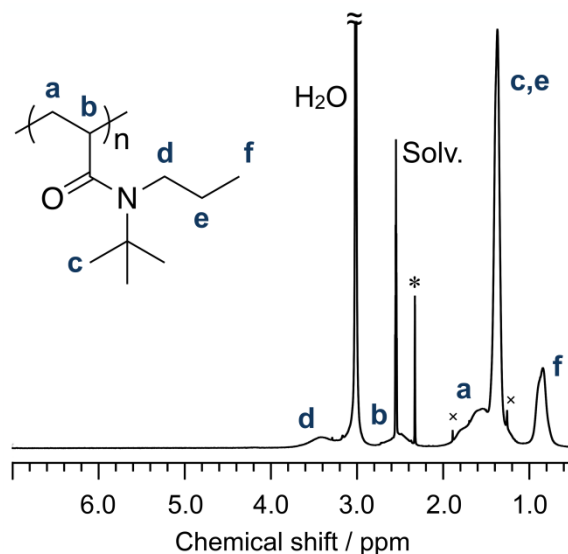


FIGURE 2 ^1H NMR spectrum of poly(TBNPAAm) prepared in toluene at 60°C with AIBN, measured in a mixed solvent ($\text{CDCl}_3/\text{DMSO}-d_6 = 2.0/1.0$ vol/vol, 55°C). * and x denote the signals of the methyl group of toluene used as a polymerization solvent and impurities, respectively.

De-*tert*-butylation of poly(TBNPAAm)

The de-*tert*-butylation reaction was carried out in CH₂Cl₂ in the presence of Sc(OTf)₃ (10 mol% relative to the monomeric units) for 24 h (TABLE 1), because a lot of organic compounds are almost quantitatively de-*tert*-butylated in CH₂Cl₂ at room temperature. However, the polymer was precipitated during the reaction. The conversion was determined to be 45%. To increase the reaction temperature, the reaction was conducted in CCl₂=CCl₂ at 100 °C, but the polymer was still precipitated, although a slight increase in conversion (58%) was observed. The polymer did not precipitate in toluene and acetone, but no de-*tert*-butylation was observed. The use of CH₃CN increased the conversion to 88%, and the conversion reached 96% by adding 1,4-dioxane to improve the solubility of the resulting poly(NNPAAm).

TABLE 1 Effect of the solvent on the de-*tert*-butylation of poly(TBNPAAm) with Sc(OTf)₃.

Solvent	Temperature / °C	Conversion ^b / %
CH ₂ Cl ₂ ^a	30	45
CCl ₂ =CCl ₂ ^a	100	58
toluene	80	n.r. ^b
acetone	40	n.r. ^b
CH ₃ CN	70	88
CH ₃ CN/1,4-dioxane (5.0/1.5 vol/vol)	80	96

^a Polymer was precipitated during the reaction. ^b No reaction.

To examine effect of temperature on the de-*tert*-butylation, the reactions were conducted in a mixed solvent of CH₃CN/1,4-dioxane at 50, 80 and 110 °C in the presence of Sc(OTf)₃ (20 mol% relative to the monomeric units). The conversion was increased with an increase in the reaction temperature, when the reactions were quenched after 12 h (FIGURE 3). The conversion gradually increased with the reaction time. Quantitative conversions were observed after 72

h regardless of the temperature. The M_n and M_w/M_n values of the transformed poly(NNPAAm)s were comparable to each other, regardless of the reaction temperature (50 °C: $M_n = 1.6 \times 10^4$, $M_w/M_n = 1.6$; 80 °C: 1.4×10^4 , 1.6; 110 °C: 1.3×10^4 , 1.4). It was therefore assumed that no side reactions, such as chain scission and cross-linking, occurred during the reaction.

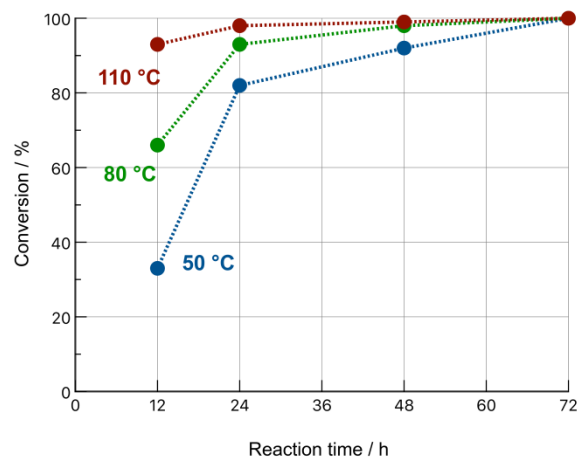


FIGURE 3 Effect of the reaction temperature on the de-*tert*-butylation of poly(TBNPAAm)

If inversion of configuration takes place during the reaction, atactic polymers would be obtained. However, this de-*tert*-butylation can extend to chiral amino acids.²⁶ It is therefore expected that the configurational sequences in polymers are retained during the reaction. FIGURE 4 shows the ¹³C NMR spectra of the main-chain methine groups of the poly(NNPAAm)s quantitatively transformed at 50 and 110 °C. Atactic polymers were not obtained, but polymers rich in *mr* triads were obtained. In addition, the triad tacticity was similar regardless of the reaction temperature. It was therefore assumed that the de-*tert*-butylation proceeded with retention of the configurational sequences in the original polymer. Furthermore, it should be noted that the *mr* triad contents were considerably greater than 50%. Heterotactic polymers cannot be characterized from the diad tacticity, because both a completely atactic polymer and a

completely heterotactic polymer have a *m* diad content of 50%. Consequently, it was not until poly(TBNPAAm) was transformed into poly(NNPAAm) that the actual stereochemical sequences in poly(TBNPAAm) were able to be characterized.

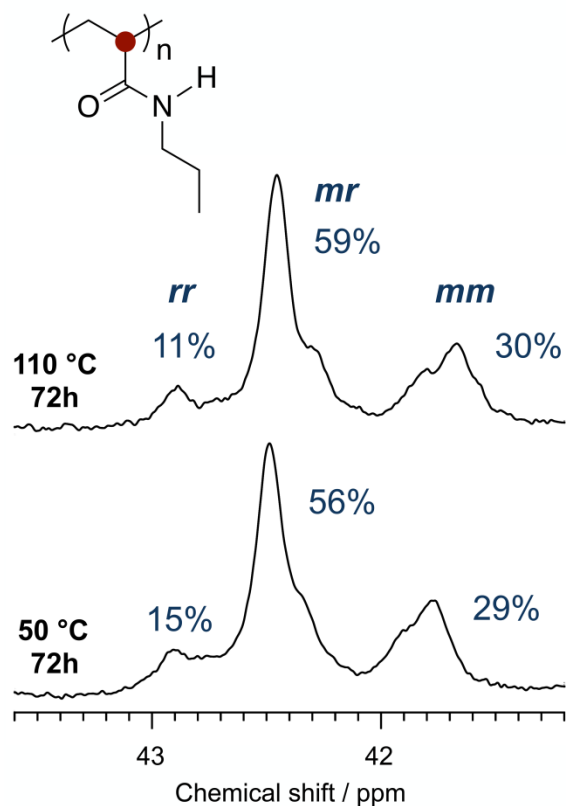


FIGURE 4 Expanded ^{13}C NMR spectra of the main-chain methine groups of the poly(NNPAAm)s transformed from poly(TBNPAAm) at 50 and 110 °C.

Polymerization of TBIPAAm

If TBIPAAm is used as a monomer, de-*tert*-butylation of the resulting polymer can afford poly(NIPAAm), which is the most typical thermosensitive polymer.²⁸⁻³¹ The phase transition behavior of an aqueous solution of poly(NIPAAm)s is strongly influenced by the stereochemical sequences.^{7,8,32,33} Therefore, the radical polymerization of TBIPAAm, instead of the TBNPAAm monomer, was conducted in toluene at 60 °C. However, no polymerization was observed. We have previously reported that

the addition of LiNTf_2 considerably accelerated the radical polymerization of (meth)acrylamides.^{12,13} Therefore, the radical polymerization of TBIPAAm was carried out in CH_3CN at -40, 0 and 60 °C in the presence of LiNTf_2 . However, unreacted monomers were recovered, regardless of the temperature.

The chemical shift difference between the α - and β -carbons in vinyl groups is a measure of the radical polymerizability: the difference increases with a decrease in the *Q*-values of the vinyl monomers.³⁴ FIGURE 5 shows the ^{13}C NMR signals of the α - and β -carbons in the vinyl groups of TBIPAAm, TBNPAAm, and DMAAm. The chemical shift difference in TBIPAAm is somewhat larger than in TBNPAAm or DMAAm. This result suggests that the *Q*-value of TBIPAAm is considerably smaller than the values of the other two monomers. Taking into account the fact that *N,N*-diisopropylacrylamide (DIPAAm) can be polymerized via radical, anionic, and coordination mechanisms,^{16,35} the slight increase in the steric repulsion induced by the *tert*-butyl group in TBIPAAm resulted in a loss of coplanarity between the vinyl and carbonyl groups. Similar phenomena have been observed for *N,N*-disubstituted methacrylamides,³⁶⁻⁴¹ which do not show polymerizability via any mechanisms unless the *N*-substituents are small and highly strained ring structures, such as aziridine and azetidine.⁴²⁻⁴⁴

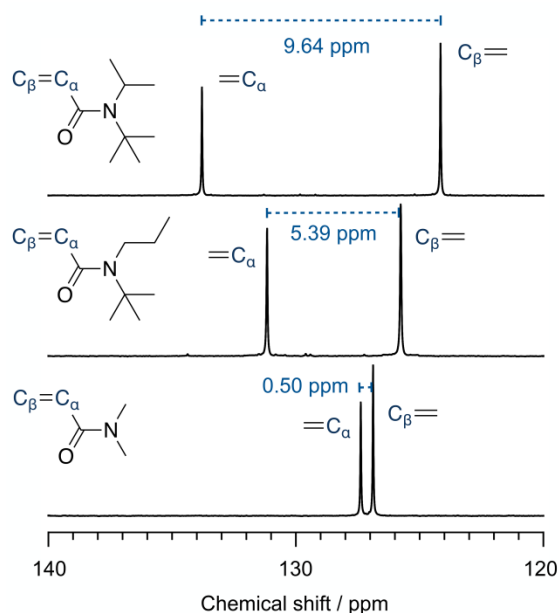


FIGURE 5 Expanded ^{13}C NMR spectra of the vinyl groups of TBIPAAm, TBNPAAm, and DMAAm, measured in CDCl_3 at 25°C .

CONCLUSIONS

Poly(TBNPAAm) was prepared by radical polymerization with AIBN in toluene at 60°C . De-*tert*-butylation of poly(TBNPAAm) was investigated by treatment with $\text{Sc}(\text{OTf})_3$. The reaction was strongly influenced by the solvent used. A mixed solvent of CH_3CN and 1,4-dioxane was found to be a suitable solvent, likely because the polymer remained dissolved throughout the reaction.

Quantitative conversions were observed after 72 h, regardless of the reaction temperature (50 to 110°C). ^{13}C NMR analysis revealed that the configurational sequences were retained during the reaction. As a result, the triad tacticity was successfully determined from the ^{13}C signals of the main-chain methine groups of the transformed polymers. Therefore, de-*tert*-butylation as a polymer reaction is a promising method to conduct the stereochemical analysis of *N,N*-disubstituted polyacrylamides at the triad level.

TBIPAAm was also found not to exhibit polymerizability, probably because of the loss of coplanarity between the vinyl and carbonyl groups. Based on the fact that TBNPAAm and DIPAAm can afford polymers via various mechanisms, a delicate steric balance between the vinyl group and the two *N*-substituents may play an important role in determining the polymerizability of *N,N*-disubstituted acrylamides.

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REFERENCES AND NOTES

- Hatada, K.; Kitayama, T.; Ute, K. *Prog Polym Sci* 1988, 13, 189-276.
- Okamoto, Y.; Habaue, S.; Isobe, Y.; Nakano, T. *Macromolecular Symposia* 2002, 183, 83-88.
- Satoh, K.; Kamigaito, M. *Chem Rev* 2009, 109, 5120-5156.
- Bovey, F. A.; Tiers, G. V. D. *Journal of Polymer Science* 1960, 44, 173-182.
- Nishioka, A.; Watanabe, H.; Yamaguchi, I.; Shimizu, H. *Journal of Polymer Science* 1960, 45, 232-234.
- Johnsen, U.; Tessmar, K. *Kolloid-Z* 1960, 168, 160-161.
- Hirano, T.; Okumura, Y.; Kitajima, H.; Seno, M.; Sato, T. *J Polym Sci, Part A: Polym Chem* 2006, 44, 4450-4460.
- Hirano, T.; Kamikubo, T.; Okumura, Y.; Bando, Y.; Yamaoka, R.; Mori, T.; Ute, K. *J Polym Sci, Part A: Polym Chem* 2009, 47, 2539-2550.
- Hirano, T.; Masuda, S.; Nasu, S.; Ute, K.; Sato, T. *J Polym Sci, Part A: Polym Chem* 2009, 47, 1192-1203.
- Hirano, T.; Miki, H.; Seno, M.; Sato, T. *Polymer* 2005, 46, 3693-3699.
- Hirano, T.; Ishizu, H.; Sato, T. *Polymer* 2008, 49, 438-445.

- 12 Hirano, T.; Saito, T.; Kurano, Y.; Miwa, Y.; Oshimura, M.; Ute, K. *Polymer Chemistry* 2015, 6, 2054-2064.
- 13 Hirano, T.; Segata, T.; Hashimoto, J.; Miwa, Y.; Oshimura, M.; Ute, K. *Polymer Chemistry* 2015, 6, 4927-4939.
- 14 Saito, R.; Saito, Y.; Kamoshita, H.; Tokubuchi, Y. *J Polym Sci, Part A: Polym Chem* 2012, 50, 3444-3451.
- 15 Huynh, B. G.; McGrath, J. E. *Polym Bull* 1980, 2, 837-840.
- 16 Butler, K.; Thomas, P. R.; Tyler, G. J. *Journal of Polymer Science* 1960, 48, 357-366.
- 17 Xie, X.; Hogen-Esch, T. E. *Macromolecules* 1996, 29, 1746-1752.
- 18 Kobayashi, M.; Okuyama, S.; Ishizone, T.; Nakahama, S. *Macromolecules* 1999, 32, 6466-6477.
- 19 Liu, W.; Nakano, T.; Okamoto, Y. *Polym J* 2000, 32, 771-777.
- 20 Habaue, S.; Isobe, Y.; Okamoto, Y. *Tetrahedron* 2002, 58, 8205-8209.
- 21 Isobe, Y.; Fujioka, D.; Habaue, S.; Okamoto, Y. *Journal of the American Chemical Society* 2001, 123, 7180-7181.
- 22 Kobayashi, M.; Ishizone, T.; Nakahama, S. *Macromolecules* 2000, 33, 4411-4416.
- 23 Kobayashi, M.; Ishizone, T.; Nakahama, S. *J Polym Sci, Part A: Polym Chem* 2000, 38, 4677-4685.
- 24 Okamoto, Y.; Habaue, S.; Isobe, Y.; Suito, Y. *Macromolecular Symposia* 2003, 195, 75-80.
- 25 Hirano, T.; Anmoto, T.; Umezawa, N.; Momose, H.; Katsumoto, Y.; Oshimura, M.; Ute, K. *Polym J* 2012, 44, 815-820.
- 26 Evans, V.; Mahon, M. F.; Webster, R. L. *Tetrahedron* 2014, 70, 7593-7597.
- 27 Fukuda, W.; Suzuki, Y.; Kakiuchi, H. *Journal of Polymer Science Part C: Polymer Letters* 1988, 26, 305-311.
- 28 Heskins, M.; Guillet, J. E. *Journal of Macromolecular Science, Part A* 1968, 2, 1441 - 1455.
- 29 Fujishige, S.; Kubota, K.; Ando, I. *The Journal of Physical Chemistry* 1989, 93, 3311-3313.
- 30 Schild, H. G. *Prog Polym Sci* 1992, 17, 163-249.
- 31 Halperin, A.; Kröger, M.; Winnik, F. M. *Angew Chem Int Ed* 2015, 54, 15342-15367.
- 32 Ray, B.; Okamoto, Y.; Kamigaito, M.; Sawamoto, M.; Seno, K.-i.; Kanaoka, S.; Aoshima, S. *Polym J* 2005, 37, 234-237.
- 33 Hirano, T.; Miki, H.; Seno, M.; Sato, T. *Polymer* 2005, 46, 5501-5505.
- 34 Hatada, K.; Kitayama, T.; Nishiura, T.; Shibuya, W. *Curr Org Chem* 2002, 6, 121-153.
- 35 Miyake, G. M.; Chen, E. Y. X. *Macromolecules* 2008, 41, 3405-3416.
- 36 Yokota, K.; Oda, J. *Kogyo Kagaku Zasshi* 1970, 73, 224-228.
- 37 Otsu, T.; Inoue, M.; Yamada, B.; Mori, T. *Journal of Polymer Science: Polymer Letters Edition* 1975, 13, 505-510.
- 38 Butler, G. B.; Myers, G. R. *Journal of Macromolecular Science: Part A - Chemistry* 1971, 5, 135-166.
- 39 Kodaira, T.; Aoyama, F. *Journal of Polymer Science: Polymer Chemistry Edition* 1974, 12, 897-910.
- 40 Otsu, T.; Yamada, B.; Mori, T.; Inoue, M. *Journal of Polymer Science: Polymer Letters Edition* 1976, 14, 283-285.
- 41 Záborský, J.; Houska, M.; Kálal, J. *Die Makromolekulare Chemie* 1985, 186, 247-253.
- 42 Watanabe, N.; Sakakibara, Y.; Uchino, N. *Kogyo Kagaku Zasshi* 1969, 72, 1349-1352.
- 43 Okamoto, Y.; Yuki, H. *Journal of Polymer Science: Polymer Chemistry Edition* 1981, 19, 2647-2650.
- 44 Suzuki, T.; Kusakabe, J.-i.; Kitazawa, K.; Nakagawa, T.; Kawachi, S.; Ishizone, T. *Macromolecules* 2010, 43, 107-116.