Hydrogen-Bond-Assisted Asymmetric Radical Cyclopolymerization of *N*-allyl-*N*-*tert*-butylacrylamide in the Presence of Chiral Tartrates

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Abstract:

Low-temperature radical polymerization of achiral *N*-allyl-*N*-*tert*-butylacrylamide (AltBAAm) was conducted in toluene in the presence of chiral tartrates, such as diethyl L-tartrate (L-EtTar) and di-*n*-butyl L-tartrate. The ^{1}H NMR spectra of the polymers obtained indicated progress of cyclopolymerization at low temperatures such as –80 °C. Optical properties of the poly(AltBAAm)s examined by optical rotation and circular dichroism measurements indicated asymmetric induction in the cyclopolymerization of achiral AltBAAm. For example, addition of L-EtTar at –80 °C provided the polymer with specific rotation of –4.8°. The *tert*-butyl groups of poly(AltBAAm)s were removed by treatment with CF_3SO_3H, transforming into poly(*N*-allylacrylamide)s [poly(AlAAm)s]. Then, stereochemistry in the stereorepeating unit was investigated by comparing ^{1}H NMR signals of the poly(AlAAm)s with those of model compounds, *cis*- and *trans*-3-ethyl-4-methyl-2-pyrrolidones. Taking the negative specific rotation values of the poly(AltBAAm)s obtained with L-tartrates into account, it was revealed that (3*S*,4*S*)-*trans*-unit was predominantly formed through the hydrogen-bond-assisted complex formation of AltBAAm with L-tartrates.

1. Introduction

Radical cyclopolymerization has been well established for numerous nonconjugated diene monomers, including 1,6-diene monomers [1-9]. In radical polymerizations of the 1,6-diene monomers with two vinyl groups of different polymerizing tendencies, more reactive vinyl group is preferentially consumed more than the other one. For example, radical polymerization of allyl methacrylate in the presence of chain transfer agents gives soluble polymers having pendant allyl groups [10]. Furthermore, chemoselective radical polymerization of *N*-allylmethacrylamide has been achieved with an aid of complexation with Li^+ cation, resulting in formation of linear polymer having pendant allyl groups [11]. However, of the asymmetric 1,6-diene monomers, *N*-allyl-*N*-*tert*-butylacrylamide (AltBAAm) has been reported to give almost completely cyclized polymers with a 5-membered ring [12, 13]. In the polymerization system, radical species attack the acryloyl double bond to form the corresponding radical and subsequent intramolecular radical addition produces *exo* radical with a 5-membered ring (Scheme 1) [12, 14, 15]. Such a high cyclization selectivity arises from the monomer conformation; AltBAAm favors completely *s-cis* form over *s-trans* one, likely owing to the steric hindrance of the *tert*-butyl group [14, 16].
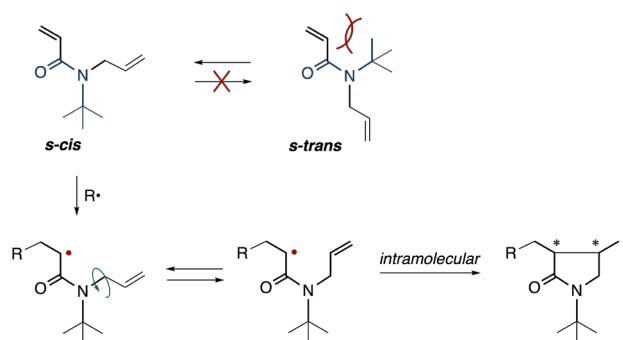
Scheme 1 Propagating reaction in the radical cyclopolymerization of AltBAAm in *s-cis* form.

As a result of formation of the 5-membered ring, two asymmetric carbons are generated per the repeating monomeric unit; four kinds of monomeric units with different stereochemical structures are formed (Scheme 2). Of the four stereorepeating units, a preferential formation of a certain monomeric unit leads to formation of optically active polymer. Indeed, optically active polymers were prepared by radical cyclopolymerization of AltBAAm in the presence of β-cyclodextrin as a chiral inducer [13].
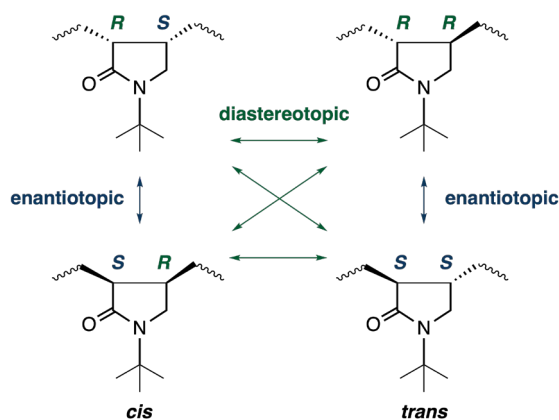
Scheme 2 Four kinds of stereorepeating units in poly(AltBAAm).

We have reported stereospecific radical polymerizations of amide-containing vinyl monomers with an aid of hydrogen bonding interaction [17-21]. For example, chiral tartrates induced syndiotactic specificity in radical polymerization of *N,N*-dimethylacrylamide (DMAAm) in toluene at low temperatures, whereas isotactic-rich polymers were obtained in the absence of tartrates [20]. In addition, tartrates enhanced polymer yield and molecular weight of the polymers obtained. DMAAm forms a 1:1 complex with tartrates with double hydrogen bonds, because chiral tartrates favor the *trans* conformation, in which two hydroxy groups are oriented at the same side, even in solution [22-24]. It is therefore concluded that the complex formation causes the induction of the syndiotactic specificity and the enhancement of the polymerization.

Racemic tartrates exhibited almost the same effect to the chiral tartrates in the DMAAm polymerizations at –40 °C to 0 °C [20]. However, optical purity of the added tartrates significantly influenced the polymerization behaviors at –60 and –80 °C: both the *racemo* diad content and molecular weight of the polymers decreased with a decrease in the optical purity. This suggests that the chirality of the tartrates involved in the complex formation becomes an increasingly important factor at lower temperatures. Accordingly, we investigated the effect of tartrates, such as diethyl L-tartrate (L-EtTar) and di-*n*-butyl L-tartrate (L-BuTar), on the radical cyclopolymerization of AltBAAm in

toluene at low temperatures. This paper describes asymmetric induction in the radical cyclopolymerization of achiral AltBAAm complexed with chiral tartrates through hydrogen bonding interaction.

2. Experimental

2.1. Materials

AltBAAm was prepared by the reaction of acryloyl chloride with *N*-allyl-*N*-*tert*-butylamine according to the literature procedures [12, 16, 25]. Dimethyl 2,2′-azobisisobutyrate (MAIB) (supplied by Otsuka Chemical Co., Ltd., Osaka, Japan) was recrystallized from methanol (MeOH). MeOH and toluene (Kanto Chemical Co., Inc.) was fractionally distilled. L-EtTar, diethyl D-tartrate (D-EtTar), L-BuTar, acryloyl chloride, *N*-allyl-*N*-*tert*-butylamine, 3-ethyl-4-methyl-3-pyrrolin-2-one, 10% Pd/C (Tokyo Chemical Industry, Tokyo, Japan), tetrahydrofuran (THF), potassium *tert*-butoxide/THF solution, diethyl ether (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan), ethanol (Junsei Chemical Co., Ltd, Tokyo, Japan) and trifluoromethanesulfonic acid (CF$_3$SO$_3$H, Kishida Chemical Co., Ltd, Osaka, Japan) were used as received.

2.2 Polymerization

The typical polymerization procedure was as follows. AltBAAm (0.4704 g, 2.8

mmol) and L-BuTar (1.4754 g, 5.6 mmol) were dissolved in toluene to prepare 5 mL of solution. MAIB (0.0414 g, 0.18mmol) was dissolved in toluene to prepare 1 mL of solution. The former solution (4 mL) and latter solution (0.5 mL) were added to a glass ampoule to give the following final concentrations: $[AltBAAm]_0 = 0.5$ mol L^{-1}, $[L\text{-}BuTar]_0 = 1.0$ mol L^{-1} and $[MAIB]_0 = 0.2 \times 10^{-2}$ mol L^{-1}. The glass ampoule was degassed and filled with nitrogen six times at $-50\ °C$ before being set at the required polymerization temperature. The mixture was irradiated at a distance of *ca*. 5 cm from a UV-LED lamp (LED-41UV375N100VF, $\lambda = 375$ nm, 410 mW, Optocode Co., Tokyo, Japan) to initiate polymerization. After 24 h, the reaction mixture was dialyzed against MeOH (Spectra/Por 3, molecular mass cutoff 3.5 kDa, Spectrum Laboratories Inc., Shiga, Japan). The resulting dialysate was evaporated to dryness under reduced pressure to give a residue, which was dissolved in benzene and freeze-dried to give the polymer product. The polymer yield was determined gravimetrically.

2.3 Synthesis of 3-ethyl-4-methyl-2-pyrrolidone (EMP)

A model compound, *cis*-3-ethyl-4-methyl-2-pyrrolidone (*cis*-EMP), was prepared by a slightly modified literature method [26]. To a stirred solution of 3-ethyl-4-methyl-3-pyrrolin-2-one (57.6 mg, 0.46 mmol) in ethanol (10 mL) was added 10% Pd/C

catalyst (49.0 mg), and the resulting mixture was stirred under H_2 atmosphere at 0 °C.

After 24 h, the catalyst was filtered off by celite, and the filtrate was evaporated to give

cis-EMP (177.9 mg, 77.0 %) as a white powder.

To a stirred solution of cis-EMP (10.0 mg, 0.0786 mmol) in THF (9 mL) was

added a 0.78 mL THF solution of potassium tert-butoxide (1.0 mol L^{-1}), and the resulting

mixture was stirred under reflux. After 3 h, the solvent was evaporated. The residue was

dissolved in diethyl ether, and insoluble fraction was removed by centrifugation. The

solvent was evaporated to give trans-EMP (11.2 mg, 40.5 %) as a brown oil.

2.4 Measurements

The molecular weights and molecular weight distributions of poly(AltBAAm)s

were determined by size exclusion chromatography (SEC); the chromatograph was

calibrated with standard polystyrene samples. SEC was performed on an HLC 8220

chromatograph (Tosoh Corp., Tokyo, Japan) equipped with TSK gel columns [SuperHM-

M (150 × 6.5 mm, i.d) and SuperHM-H (150 × 6.5 mm, i.d)] (Tosoh Corp.). THF was

used as the eluent at 40 °C with a flow rate of 0.35 mL min^{-1}. The initial polymer

concentration was set at 3.0 mg mL^{-1}.

^1H magnetic nuclear resonance (NMR) spectra were measured in $CDCl_3$ at

55 °C or in a mixed solvent of DMSO-d_6 and CF_3SO_3H at 120 °C using ECZ-400

spectrometer (JEOL Ltd., Tokyo, Japan). The ^{1}H chemical shifts were referenced to

internal tetramethylsilane ($\delta = 0.00$ ppm) in $CDCl_3$ or the residual solvent signal ($\delta = 2.50$

ppm) in the mixed solvent. Specific rotation and circular dichroism (CD) spectra of

poly(AltBAAm)s were measured on polarimeter (P-1030, JASCO, Tokyo, Japan) and

spectropolarimeter (J-820, JASCO), respectively. Thickness of a cast film was

determined using surface measurement system based on white interferometer (Profilm3D,

Filmetrics, Kanagawa, Japan).

2.5 Computational method

The initial lowest energy conformations of four stereoisomers of *N-tert*-butyl-

3,4-dimethyl-2-pyrrolidones were calculated using the molecular mechanics (MM2)

force field in Chem3D (ver. 19.1), followed by the semiempirical quantum chemical PM6

method in Gaussian 09 [27]. All the PM6 conformers were further optimized by a density

functional theory (DFT) at the B3LYP/6-31G(d) level of theory in Gaussian 09. Then,

CD spectra was calculated with time-dependent self-consistent field (TD-SCF) method

using DFT at the B3LYP/6-31G(d) level of theory in Gaussian 09.

3. Results and Discussion

3.1 Radical polymerization of AltBAAm in toluene at low temperatures

Radical polymerization of AltBAAm was carried out in toluene at low temperatures (Table 1). A two-fold amount of L-BuTar (1.0 mol L^{-1}) was added relative to the monomer (0.5 mol L^{-1}), because DMAAm formed the complex with L-BuTar quantitatively at −80 °C under the same conditions [20]. Polymers were obtained in moderate yields, regardless of the presence of L-BuTar (Table 1, runs 1, 5, 9-10). Fig. 1 shows ^{1}H NMR spectrum of the polymer obtained at −80 °C in the presence of L-BuTar (Table 1, run 5). Degree of cyclization (DC) was calculated by the following equation:

$$\text{DC (\%)} = \left(\frac{I_e}{I_e + I_{d'+d''}} \right) \times 100$$

where I_e and $I_{d'+d''}$ denote the integral intensities of the ^{1}H signals of the methylene groups in the cyclic and non-cyclic units, respectively. The DC values were close to 100%, regardless of the temperature (Table 1, runs 1-5, 9-10). It is therefore suggested progress of cyclopolymerization of AltBAAm even at low temperatures, as reported for the polymerization at elevated temperatures [12, 13].

Table 1 Radical polymerization of AltBAAm with MAIB in toluene in the presence or absence of tartrates[a]

Run	Temp. / °C	Additive	Yield / %	$M_n \times 10^{-4}$ [b]	M_w/M_n [b]	DC[c] / %	$[\alpha]_D^{20}$ [d]
1	0	L-BuTar	65	0.41	2.7	98.7	+0.0 ±0.1
2	−20	L-BuTar	71	0.59	2.6	99.9	+0.2 ±0.1
3	−40	L-BuTar	73	1.2	1.8	99.5	+0.5 ±0.2
4	−60	L-BuTar	67	1.8	1.7	99.5	−1.2 ±0.1
5	−80	L-BuTar	43	2.3	2.0	99.1	−2.8 ±0.1
6	−80	L-EtTar	53	1.3	1.8	99.4	−4.8 ±0.1
7	−80	D-EtTar	44	1.3	2.1	99.4	+4.2 ±0.2
8	60	None	65	2.1	2.0	99.7	−0.2 ±0.1
9	0	None	74	0.53	2.8	99.9	−0.3 ±0.1
10	−80	None	50	1.8	2.0	99.3	−0.5 ±0.2

[a] $[AltBAAm]_0 = 0.5$ mol L^{-1}, $[Additive]_0 = 1.0$ or 0.0 mol L^{-1}, $[MAIB]_0 = 2.0 \times 10^{-2}$ mol L^{-1}. [b] Determined by SEC (polystyrene standards). [c] Degree of cyclization. Determined by ^{1}H NMR. [d] $c = 1.00$.
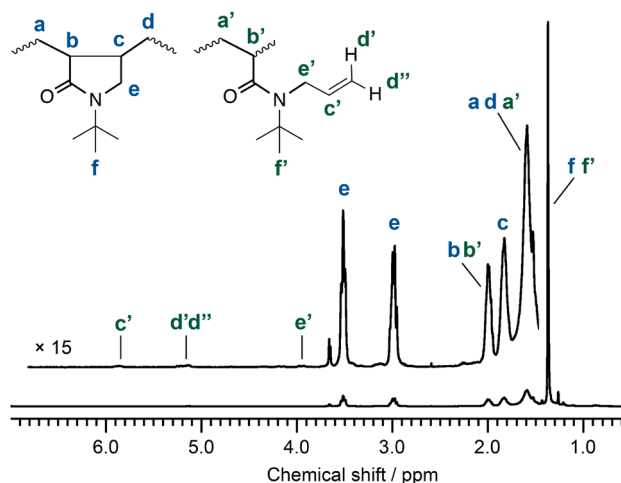
Fig. 1 ^{1}H NMR spectrum of the poly(AltBAAm) prepared at −80 °C in the presence of L-BuTar (CDCl₃, 55 °C).

The polymers obtained at −60 and −80 °C in the presence of L-BuTar showed levorotatory (Table 1, runs 4-5), whereas the polymers obtained above −40°C exhibited no optical activity within experimental error. It should be noted that the levorotation was induced, even though the dextrorotatory L-BuTar was added. The absolute value in $[\alpha]_D^{20}$
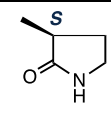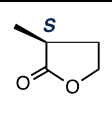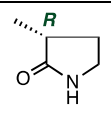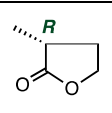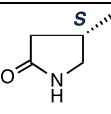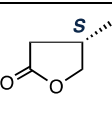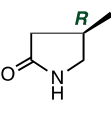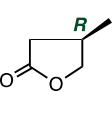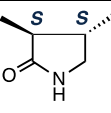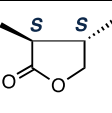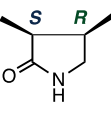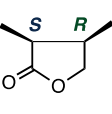
increased by decreasing the polymerization temperature. The addition of L-EtTar instead

of L-BuTar increased the specific rotation up to –4.8° (Table 1, run 6). Furthermore, the

addition of D-EtTar provided the polymer with specific rotation opposite in sign (+4.2°)

(Table 1, run 7). Consequently, the hydrogen-bond-assisted complex formation of

AltBAAm with the chiral tartrates successfully provided optically active polymers at low
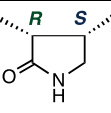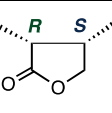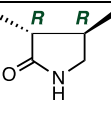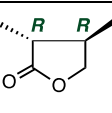
temperatures.

The values of $[\alpha]_D^{20}$ do not seem to be very high, likely because asymmetric

induction is essentially difficult *via* radical mechanism. For example, radical cyclization

of *N*-allyl-2-bromo-*N*-phenylpropanamide with tri-*n*-butyltin hydride in CH_2Cl_2 at –

78 °C gave the corresponding 5-membered lactam in enantiomeric excess (*ee*) of 5 %,

even though not only a chiral diol, TADDOL, but also Ti(O*i*-Pr)$_4$ were added [28]. The

radical cyclopolymerization of *N*-allyl-*N*-phenylmethacrylamide in the presence of

SnCl$_4$/(−)-menthol gave an optically active polymer with $[\alpha]_D$ of −5.6° [29]. Tacticities

of polystyrene, poly(methyl acrylate) and poly(methyl methacrylate) were not controlled

by chiral ruthenium complexes, whereas asymmetric addition reactions proceeded in

relatively high optical yields (10–30% *ee*) for the corresponding monomers [30].

Furthermore, radical polymerization of *N*-cyclohexylmaleimide with chiral cobalt

complex gave an optically active polymer with $[\alpha]_D$ of +7° [31]. It is therefore assumed

that the optical activity was significantly induced in the present system, taking into account that only hydrogen bonding interaction was utilized.

Table 2 summarizes specific rotations of 2-pyrrolidone and dihydro-2(3*H*)-furanone derivatives [32-41]. The monomethyl isomers having the *S* configuration at the α or β position of the carbonyl group showed levorotatory, regardless of the parent structure. Specific rotations of dimethyl 2-pyrrolidones have not been reported so far, but those of some dimethyl derivatives of dihydro-2(3*H*)-furanone have been reported. The (3*S*,4*S*)- and (3*R*,4*S*)-dihydro-3,4-dimethyl-2(3*H*)-furanones show levorotatory, whereas the (3*S*,4*R*)-isomer shows dextrorotatory. Accordingly, the specific rotation of the 5-membered lactams and lactones is suggested to depend on the absolute configuration at the β position more than the α position. It is therefore assumed that the (3*S*,4*S*)- and/or (3*R*,4*S*)-stereorepeating units were preferentially formed during the AltBAAm polymerization in the presence of L-tartrates.

Table 2 Reported $[\alpha]_D$ values for mono- and dimethyl 2-pyrrolidones and dihydro-2(3H)-furanones

2-Pyrrolidones	$[\alpha]_D$	Dihydro-2(3H)-furanones	$[\alpha]_D$
(S) 2-pyrrolidone	−71.2° (c 1.4, benzene, 22 °C)[32]	(S) dihydrofuranone	−21.5° (c 5.5, EtOH, 15 °C)[33]
(R) 2-pyrrolidone	+68.6° (c 1.4, benzene, 22 °C)[32]	(R) dihydrofuranone	+23.1° (c 9.7, EtOH, 23 °C)[34]
(S) 2-pyrrolidone	−20.3° (c 1.2, CHCl$_3$)[35]	(S) dihydrofuranone	−23° (c 4, MeOH)[36]
(R) 2-pyrrolidone	+30.0° (c 1.08, CHCl$_3$)[37]	(R) dihydrofuranone	+23.1° (c 5.0, CHCl$_3$, 20 °C)[38]
(S, S) 2-pyrrolidone	not reported	(S, S) dihydrofuranone	−50.9° (c 0.9, CHCl$_3$, 20 °C)[39]
(S, R) 2-pyrrolidone	not reported	(S, R) dihydrofuranone	+39.9° (c 1, CHCl$_3$, 20 °C)[40]
(R, S) 2-pyrrolidone	not reported	(R, S) dihydrofuranone	−35.5° (c 0.74, CHCl$_3$, 23 °C)[41]
(R, R) 2-pyrrolidone	not reported	(R, R) dihydrofuranone	not reported

To investigate the absolute configurations in the stereorepeating unit in more detail, CD measurement was conducted. Unfortunately, CD measurements in a solution state failed, probably because of strong absorption of the solvents such as MeOH and acetonitrile. Therefore, a cast film was prepared by dropping a 3.0 wt% MeOH solution of the poly(AltBAAm) prepared at −80 °C in the presence of L-EtTar onto a quartz plate

(φ: 30mm × t: 1 mm). A transparent film with a thickness of *ca*. 6 μm was successfully

formed. The quartz plate was placed on a handmade adaptor perpendicular to the light

path. The spectra taken at 45°-intervals showed almost the same spectral patterns,

indicating the formation of isotropic film. Fig. 2 shows an average spectrum of the four

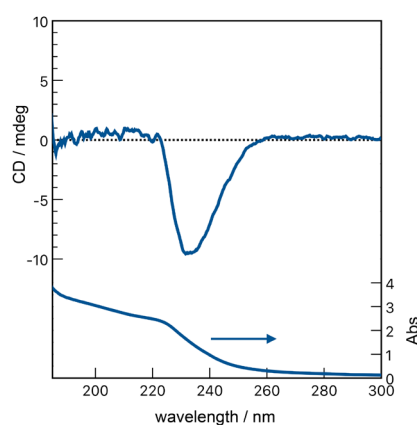CD spectra. Negative Cotton effect was clearly observed.

Fig. 2 CD and absorption spectra of the cast film of poly(AltBAAm) prepared at –80 °C in the presence of L-EtTar.

Fig. 3 shows predicted CD spectra of four stereoisomers of model compounds,

N-tert-butyl-3,4-dimethyl-2-pyrrolidones, obtained by TD-DFT calculation. Negative

Cotton effects were expected to be observed in the CD spectra of the (3*S*,4*S*)- and (3*R*,4*S*)-

isomers. This result confirms again that the (3*S*,4*S*)- and/or (3*R*,4*S*)-stereorepeating units

were preferentially formed during the AltBAAm polymerization in the presence of L-
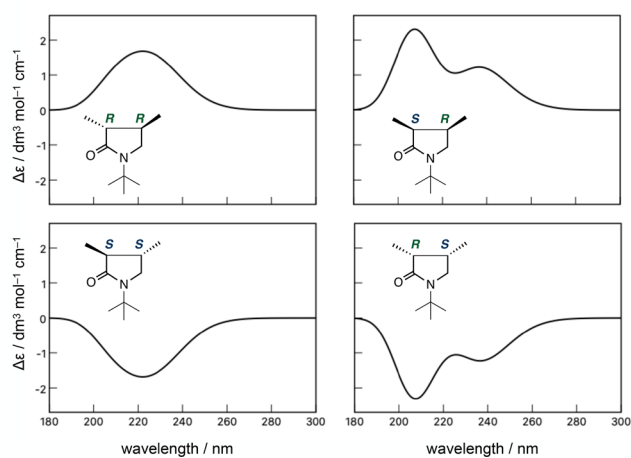
tartrates.

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Fig. 3 Calculated CD spectra of four stereoisomers of *N-tert*-butyl-3,4-dimethyl-2-pyrrolidones.

3.2 Determination of cis-trans configuration in the stereorepeating unit

The strong singlet signal of the *tert*-butyl group makes structural investigation of poly(AltBAAm) difficult by NMR (*cf*. Fig. 1). We have reported successful de-*tert*-butylation of poly(*N-tert*-butyl-*N-n*-propylacrylamide)s by treatment with scandium triflate in a mixed solvent of acetonitrile and 1,4-dioxane [42]. However, this catalytic reaction is insufficient for *N-tert*-butyl lactams [25]. Therefore, we decided to adopt other methods.

The cumyl group attached to nitrogen atom of lactams can be deprotected in trifluoroacetic acid (TFA) [43, 44]. Furthermore, stereochemical configuration at the α position of the carbonyl group is retained during the reaction even under reflux for 3 h.

Therefore, poly(AltBAAm) was dissolved in TFA, and stirred at 70 °C for 24 h. However, ^{1}H NMR spectral pattern of the recovered polymer was scarcely changed. The conversion was calculated to be *ca*. 6% from the integral intensities of the signal of the remaining *N*-*tert*-butyl group.

The *tert*-butyl group at the nitrogen atom of lactams can be removed by treatment with H_2SO_4 at 50 °C, with retention of stereochemical configuration [45]. However, treatment of isotactic poly(*N,N*-diphenylacrylamide) with H_2SO_4 containing 10 vol% H_2O at 90 °C leads to hydrolysis reaction accompanied with racemization of the main chain, resulting in formation of atactic poly(acrylic acid) [46]. Furthermore, the use of concentrated H_2SO_4 fails recovering poly(acrylic acid), probably because the polymer is decomposed due to oxidizing properties of the concentrated H_2SO_4 [46].

Therefore, we used CF_3SO_3H instead of H_2SO_4, because CF_3SO_3H and its conjugate base have resistance to both reductive and oxidative cleavage [47]. The 76 mg of poly(AltBAAm) was dissolved in 9 ml of CF_3SO_3H, and stirred at 50 °C for 6 days. Fig. 4 shows ^{1}H NMR spectrum of the resulting polymer, measured in DMSO-d_6 at 120 °C. Disappearance of the *N-tert*-butyl signal indicated successful de-*tert*-butylation. Furthermore, the signal of O=C–N–H was observed at 7.0 ppm, whereas no signal of COOH was observed. This means that no side reactions such as hydrolysis reaction

occurred during the reaction. Consequently, poly(AltBAAm) was successfully transformed into the polymer corresponding with poly(N-allylacrylamide) [poly(AlAAm)] formed by cyclopolymerization of N-allylacrylamide (Scheme 3).

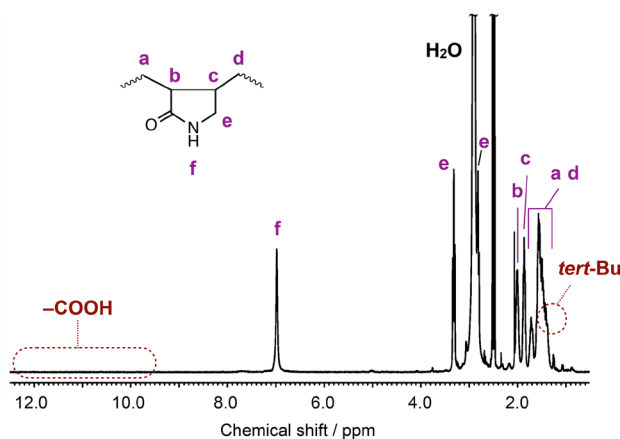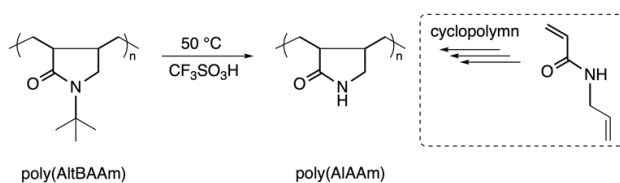**Fig. 4** ^{1}H NMR spectrum of the polymer prepared by de-tert-butylation of poly(AltBAAm) (DMSO-d_6, 120 °C).

Scheme 3 Transformation of poly(AltBAAm) to poly(AlAAm) *via* de-tert-butylation.

The signal of H_2O was overlapped with the signal **e** as long as DMSO-d_6 was used as a solvent (*cf*. Fig. 4). Therefore, a mixed solvent of DMSO-d_6 (5.0 ml) and CF_3SO_3H (0.5 ml) was used as a measurement solvent (Fig. 5a) in order to make the signal of H_2O down-field shift. The signals of the polymer were clearly observed, and the

integral intensities almost agreed well with those expected for poly(AlAAm) having the cyclic units. Small signals (**b'**, **c'** and **e'**) were clearly observed in the spectrum (Fig. 5b) of the poly(AlAAm) derived from the poly(AltBAAm) formed at 60 °C in the absence of additives (Table 1, run 8)   This suggests that the stereochemical configurations at the stereorepeating units are retained during the de-*tert*-butylation reaction, and the polymer prepared at –80 °C has well defined structure with regard to *cis-trans* configuration in the cyclic monomeric unit more than the polymer prepared at 60 °C.
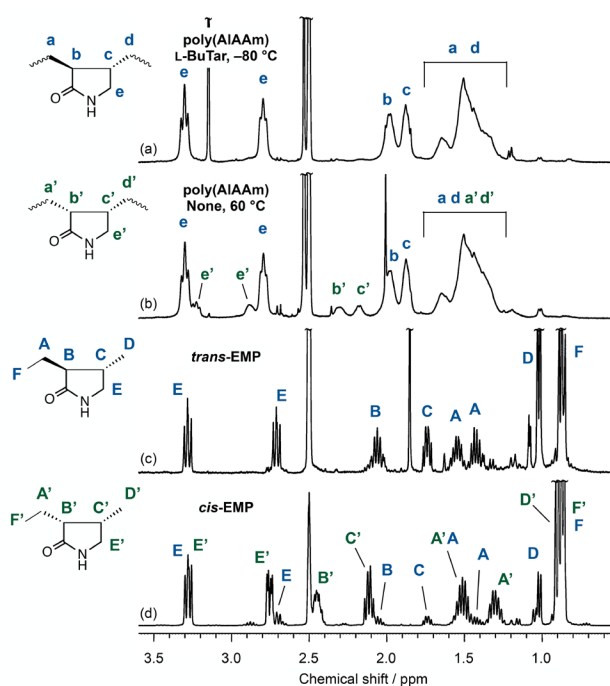

Fig. 5 ^{1}H NMR spectra of poly(AlAAm)s transformed by de-*tert*-butylation of poly(AltBAAm)s prepared by radical cyclopolymerization of AltBAAm (a) at –80 °C in the presence of L-BuTar and (b) at 60 °C in the absence of additives, respectively, and (c) *trans*-EMP and (d) *cis*-EMP (a mixed solvent of DMSO-d_6 and CF$_3$SO$_3$H , 120 °C).

To assign the *cis-trans* configuration in the predominant stereorepeating units of the polymer prepared at –80 °C, model compounds (*cis*-EMP and *trans*-EMP) were prepared as shown in Scheme 4. The ^{1}H NMR spectra of the model compounds were shown in Fig. 5c and d. The chemical structures of (3*S*,4*S*)- and (3*R*,4*S*)-isomers were shown as representative examples, because specific rotation and CD experiments suggested that the absolute configuration at the β position of the carbonyl group in the stereorepeating unit would be *S*. All the signals were assigned as shown in the figure. Note that the diastereotopic hydrogens in the methylene groups attached to the chiral carbons provided signals at different chemical shifts (**A, A', E** and **E'**). In principle, hydrogenation with Pd/C proceeds in *syn* fashion to produce *cis*-EMP. However, the *cis*/*trans* ratio was calculated to be 85/15 from the integral intensities of the signals **E+E'** (lower magnetic field) and **C** (Fig. 5d). This suggests that partial epimerization occurred during work-up, because *trans*-EMP is thermodynamically stable more than *cis*-EMP.
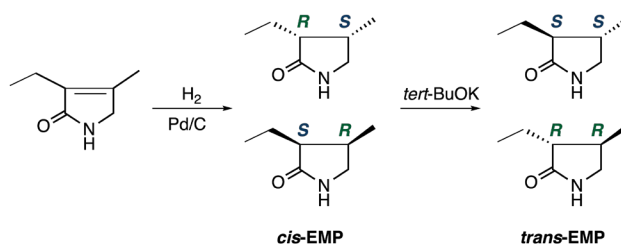

Scheme 4 Synthesis of model compounds by hydrogenation of 3-ethyl-4-methyl-3-pyrrolin-2-one, followed by epimerization with *tert*-BuOK.

The signals **B'** and **C'** in *cis*-EMP exhibited significant down-field shifts as compared to the signals **B** and **C** in *trans*-EMP. Furthermore, difference in chemical shifts of the signals **E'** in *cis*-EMP was smaller than that of the signals **E** in *trans*-EMP. On the basis of the assignments for the model compounds, the signals of the poly(AlAAm) were assigned as shown in the figure. The *trans* unit was found to be formed in a preferential manner. The *cis*/*trans* ratio in the stereorepeating unit was roughly calculated from the integral intensities of the signals **e+e'** (lower magnetic field) and **c'**. The *trans* fraction increased from 80 % to 97 % by lowering the polymerization temperature from 60 °C to –80 °C.

The configurations in the stereorepeating units are determined at the intramolecular addition (*cf*. Scheme 1). The planar radical derived from acrylamides should be slightly twisted for the acryloyl radical to attack the allyl double bond. To form optically active poly(AltBAAm)s, the chiral tartrates binding to the carbonyl group in the acryloyl radical must induce a bias toward one direction. The mechanism is not clear at this time, but one possible explanation is steric repulsions of the ester groups in the chiral tartrates with both the growing polymer chain and *N-tert*-butyl group at the chain-end unit (Scheme 5). Consequently, it appeared that chiral tartrates exhibited asymmetric

induction in *trans*-selective radical cyclopolymerization of AltBAAm, in which (3*S*,4*S*)-

trans-unit was predominantly formed through the complex formation of AltBAAm with

L-tartrates by hydrogen bonding interaction. The addition of less bulky tartrate increased

the specific rotation value of the polymers obtained (*cf.* Table 1, runs 5-7). This is

probably because a decrease in the bulkiness of the ester groups enhanced the complex

formation through the weak hydrogen bonding interaction.
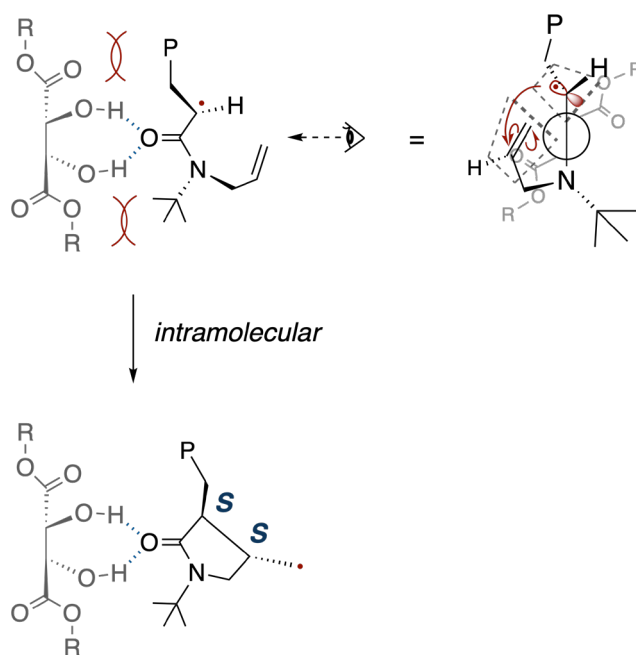
Scheme 5 Possible mechanism for the intramolecular addition to produce the (3*S*,4*S*)-
trans-unit.

4. Conclusions

Low-temperature radical polymerization of AltBAAm was investigated in toluene in the

presence or absence of chiral tartrates, such as L-EtTar and L-BuTar. The ^{1}H NMR spectra of the polymers obtained indicated the progress of the cyclopolymerization at low temperatures such as –80 °C.

The polymers obtained at –80 °C exhibited levorotatory, although dextrorotatory L-tartrates were added. This indicates asymmetric induction in the cyclopolymerization of AltBAAm. The specific rotation values so far reported for 2-pyrrolidones and dihydro-2(3*H*)-furanones suggested that the (3*S*,4*S*)- and/or (3*R*,4*S*)-stereorepeating units were preferentially formed in the presence of L-tartrates. In addition, negative Cotton effect was observed in the CD spectrum of the polymer obtained at –80 °C in the presence of L-EtTar. The CD spectra of model compounds, *N-tert*-butyl-3,4-dimethyl-2-pyrrolidones, obtained by TD-DFT calculation also suggested the preferential formation of the (3*S*,4*S*)- and/or (3*R*,4*S*)-stereorepeating units.

The *N-tert*-butyl groups were removed to facilitate NMR analysis. Then, it was revealed that the *trans* configuration was preferentially formed in the stereorepeating unit by comparing the ^{1}H NMR spectra of the transformed polymers with those of the model compounds, *cis*- and *trans*-EMPs. Consequently, L-tartrates exhibited asymmetric induction in radical cyclopolymerization of achiral AltBAAm, in which the (3*S*,4*S*)-*trans*-unit was predominantly formed through the complexation by hydrogen bonding

interaction, and the preferential formation of the (3*S*,4*S*)-*trans*-unit was responsible for the levorotation of the poly(AltBAAm) prepared in the presence of L-tartrates.

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