Polymer Communication

Heterotactic poly(N-isopropylacrylamide) prepared via radical polymerization in the presence of fluorinated alcohols

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Abstract

Radical polymerization of N-isopropylacrylamide in toluene at $-40\,°C$ in the presence of fourfold amounts of fluorinated alcohols was investigated. The ^{13}C NMR analysis of the obtained polymers suggested that the addition of fluorinated alcohols induced heterotactic specificity in radical polymerization of NIPAAm, although syndiotactic poly(NIPAAm)s were obtained by adding alkyl alcohols as we have previously reported. To the best of our knowledge, this is the first synthesis of heterotactic poly(NIPAAm).
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Keywords: N-Isopropylacrylamide; Heterotactic polymer; Radical polymerization

1. Introduction

We have reported that hydrogen-bonding interaction between N-isopropylacrylamide (NIPAAm) and Lewis bases is available for stereocontrol in radical polymerization of NIPAAm. For instance, the addition of pyridine N-oxide into NIPAAm polymerization induced isotactic specificity [1], although the isotacticity of the obtained polymers (61%) was much lower than those by the Lewis acid-catalyzed radical polymerization [2–6]. On the other hand, the addition of phosphoric acid derivatives successfully induced syndiotactic specificity [7–9]. In particular, hexamethylphosphoramide (HMPA) afforded poly(NIPAAm) with *racemo* (*r*) dyad content = 72%, the highest syndiotacticity value of radically prepared poly(NIPAAm)s [7(c)].

Recently, we found that the addition of simple alkyl alcohols also induced syndiotactic specificity in NIPAAm polymerization, in which dyad syndiotacticity reached up to 71% with the addition of 3-methyl-3-pentanol [10]. NMR analysis revealed that alkyl alcohols also form hydrogen bond-assisted complex with NIPAAm monomer. The syndiotactic specificity is comparable to that of radical

polymerization in the presence of HMPA [7(c)], but behind that (*r* = 83%) of anionic polymerization of protected NIPAAm monomer [11].

Fluorinated alcohols play efficient roles in controlling the stereospecificity of radical polymerizations of vinyl monomers [12–17]. Significant increase in syndiotacticity was observed in radical polymerization of vinyl acetate (VAc) [12] or methyl methacrylate (MMA) [13,15]. Thus, we examined fluorinated alcohols (1–3) to improve the alcohol-mediated syndiotactic specificity of NIPAAm polymerization, and found that not syndiotactic but heterotactic poly(NIPAAm)s were successfully obtained. Heterotactic polymer is the third stereoregular polymer composed of an alternating sequence of *meso* (*m*) dyad and *r* dyad, and there are limited reports on the preparation of heterotactic polymers by radical polymerization [12,17–19]. To the best of our knowledge, this is the first synthesis of heterotactic poly(NIPAAm). Thus, we report here the preliminary results of the heterotactic-specific radical polymerization of NIPAAm.

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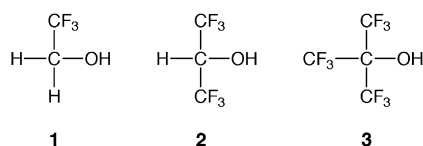
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2. Experimental

2.1. Materials

NIPAAm (Tokyo Kasei Kogyo Co.) was recrystallized from hexane−benzene mixture. Toluene was purified through washing with sulfuric acid, water, and 5% aqueous NaOH, this was followed by fractional distillation. Tri-n-butylborane (n-Bu$_3$B) as a tetrahydrofuran (THF) solution (1.0 M), 2,2,2-trifluoroethanol (**1**) (Aldrich Chemical Co.), 1,1,1,3,3,3-hexafluoroisopropanol (**2**), and nonafluoro-$tert$-butanol (**3**) (Tokyo Kasei Kogyo Co.) were used without further purification for polymerization reaction.

2.2. Polymerization

Typical polymerization procedure is as follows: NIPAAm (0.314 g, 2.8 mmol) was dissolved in toluene to prepare a 5 ml solution (0.56 mol/l). Four milliliters of the solution was transferred to the glass ampoule and cooled at −40 °C. Polymerization was initiated by adding n-Bu$_3$B solution (0.22 ml) into the monomer solution in the presence of O$_2$ [20]. After 24 h, the reaction was terminated with a small amount of THF solution of 2,6-di-$tert$-butyl-4-methylphenol at −40 °C. The polymerization mixture was poured into a large amount of diethyl ether, and the precipitated polymer was collected by centrifugation and dried in $vacuo$. The polymer yield was determined gravimetrically.

2.3. Measurement

The ^{1}H and ^{13}C NMR spectra of poly(NIPAAm)s were measured in deuterated dimethyl sulfoxide (DMSO-d_6) on an EX-400 spectrometer (JEOL, Ltd.) operated at 400 MHz at 150 °C for ^{1}H and at 100 MHz at 100 °C for ^{13}C. The dyad tacticities of the poly(NIPAAm)s were determined from ^{1}H NMR signals due to methylene group in chain and triad tacticities from ^{13}C NMR signals due to methine group in chain. The molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC) (HLC 8220 instrument (Tosoh Co.)) equipped with TSK gels (SuperHM-M and SuperHM-H (Tosoh Co.)) using dimethylformamide (LiBr 10 mmol/l) as an eluent at 40 °C

([polymer] = 1.0 mg/ml, flow rate = 0.35 ml/min). The SEC chromatogram was calibrated with standard polystyrene samples.

3. Results and discussion

We conducted radical polymerization of NIPAAm with n-Bu$_3$B under air in toluene at −40 °C in the absence or presence of fourfold amounts of fluorinated alcohols (**1**−**3**) (Table 1). In all cases, polymers were precipitated during the polymerization. The addition of fluorinated alcohols increased the molecular weight of the obtained polymers. Similar increases in molecular weight were observed in the presence of alkyl alcohols [10].

Fig. 1 demonstrates ^{1}H NMR spectra of methylene and methine groups in chain of the obtained poly(NIPAAm)s. The addition of **1** or **3** slightly increased r dyad content and, on the contrary, the addition of **2** slightly increased m dyad content ($cf.$ Table 1). These results contrast with the facts that significant increase in r dyad content was observed with the addition of alkyl alcohols and that the magnitude simply increased with an increase in bulkiness of the added alkyl alcohols [10]. However, the signals due to methine groups of the poly(NIPAAm)s obtained with fluorinated alcohols, in particular **3**, became sharper than that without fluorinated alcohols. This result suggests that the poly(NIPAAm)s prepared in the presence of fluorinated alcohols have some regularity other than simple stereosequences, such as isotactic and syndiotactic ones.

The stereospecificity induced by fluorinated alcohols strongly depends on the structure of the monomer used. Heterotactic specificity was induced in the radical polymerization of vinyl pivalate (VPi) [12] or N-vinylacetamide (NVA) [17], whereas syndiotactic specificity was enhanced in VAc [12] or MMA [13,15] polymerization. Thus, it is assumed that fluorinated alcohols induced heterotactic specificity in NIPAAm polymerization and, as a result, only slight changes were observed in dyad tacticity, because ideal heterotactic polymer has 50% contents of r and m dyads.

Thus, we conducted ^{13}C NMR measurement of poly(NIPAAm) prepared at −40 °C without fluorinated alcohols [Fig. 2(a)]. The signal due to main-chain methine carbon split into three broad peaks. Fig. 2(b) and (c) displays ^{13}C NMR

Table 1
Radical polymerization of NIPAAm in toluene at −40 °C for 24 h in the absence or presence of a fourfold amount of fluorinated alcohol

Run	Added alcohol	Yield/%	Dyad tacticity/%[a]		Triad tacticity/%[b]				$M_n^{[d]}$ (×10^4)	$M_w/M_n^{[d]}$
			m	r	(mm)	(mr)	(rr)	$r^{*[c]}$		
1	None	89	46	54	28	53	19	46	2.7	1.8
2	**1**	96	42	58	15	64	21	53	4.3	1.4
3	**2**	93	50	50	27	56	17	45	5.0	1.3
4	**3**	86	42	58	14	75	11	49	7.2	3.1

[NIPAAm]$_0$ = 0.5 mol/l, [fluorinated alcohol] = 2.0 mol/l, [n-Bu$_3$B] = 0.05 mol/l.

[a] Determined by ^{1}H NMR signals due to methylene group.

[b] Determined by ^{13}C NMR signals due to main-chain methine group.

[c] Calculated by $r^* = (rr) + 1/2$ (mr).

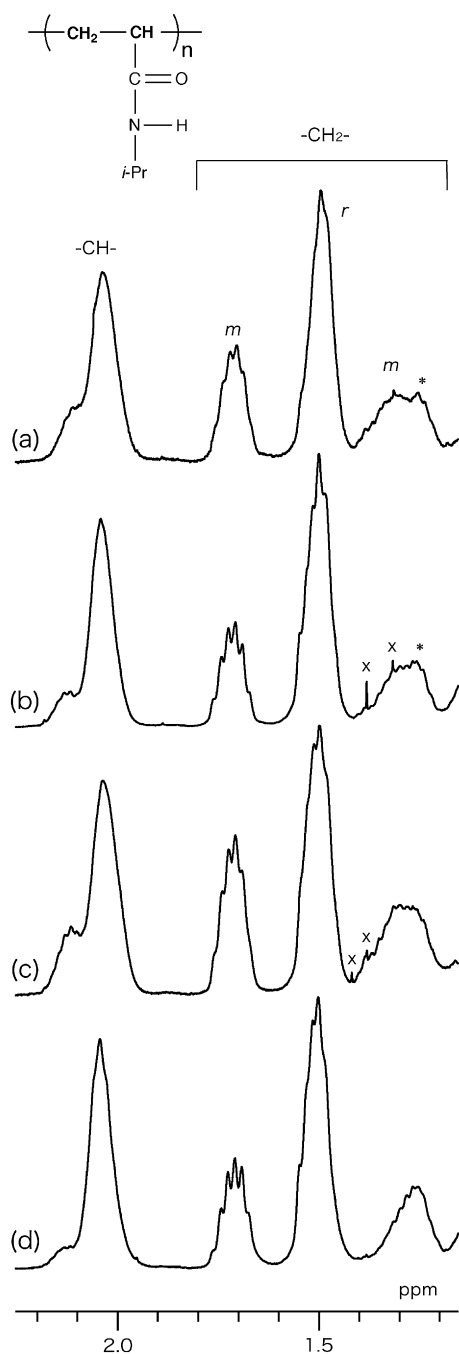[d] Determined by SEC (polystyrene standards).

Fig. 1. ^{1}H NMR spectra of methylene and methine protons in chain of poly-(NIPAAm)s prepared in toluene at $-40\,^{\circ}$C in the absence or presence of fluorinated alcohols: (a) none, (b) **1**, (c) **2**, and (d) **3**. (The asterisk indicates ^{13}C satellite peak of $(CH_3)_2$CH– and × denotes impurities.)

Fig. 2. ^{13}C NMR spectra of main-chain methine carbons of (a) atactic, (b) syndiotactic, and (c) isotactic poly(NIPAAm)s.

spectra of syndiotactic and isotactic poly(NIPAAm)s prepared in toluene at $-40\,^{\circ}$C in the presence of 3-methyl-3-pentanol [10] and in chloroform at $-60\,^{\circ}$C in the presence of 3,5-dimethylpyridine *N*-oxide [1,21], respectively. The peak at lower magnetic field increased in the spectrum of syndiotactic poly-(NIPAAm) and that at higher magnetic field increased in the spectrum of isotactic poly(NIPAAm). Thus, we roughly assigned the three peaks to the splittings due to triad tacticity, as shown in Fig. 2(a).
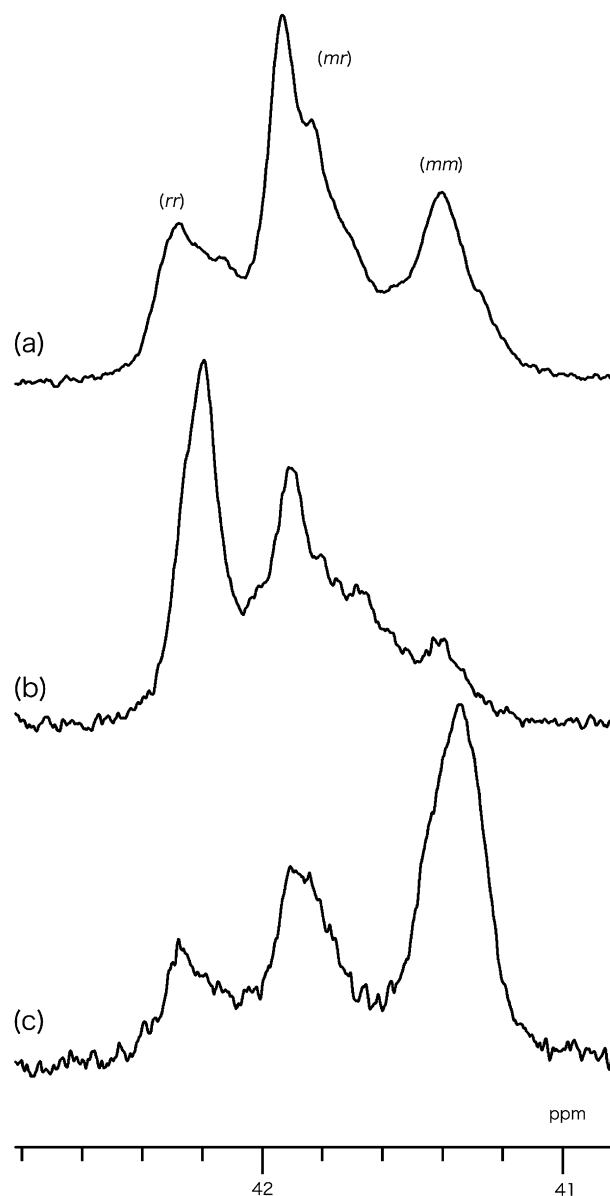
Fig. 3 shows ^{13}C NMR spectra of poly(NIPAAm)s prepared at $-40\,^{\circ}$C in the presence of fluorinated alcohols. The peak assigned to heterotactic triad stereosequence (*mr*) significantly increased in all the spectra and the stereoregularity seems to increase as the number of fluorine atoms in the added alcohol compounds increases [22]. These results suggest that fluorinated alcohols induced heterotactic specificity in NIPAAm polymerization as well as in VPi and NVA polymerizations, as expected.

Then, we tried to determine tacticities at triad level from the ^{13}C NMR signals. The determined triad tacticity is summarized in Table 1 along with dyad syndiotacticity (*r**) calculated from the obtained triad tacticity with the equation [*r** = (*rr*) + 1/2 (*mr*)]. In all cases, the calculated values (*r**) were smaller than the values (*r*) determined from ^{1}H NMR signals due to methylene protons. These results suggest that the assignment due to triad tacticities shown in Figs. 2 and 3 is
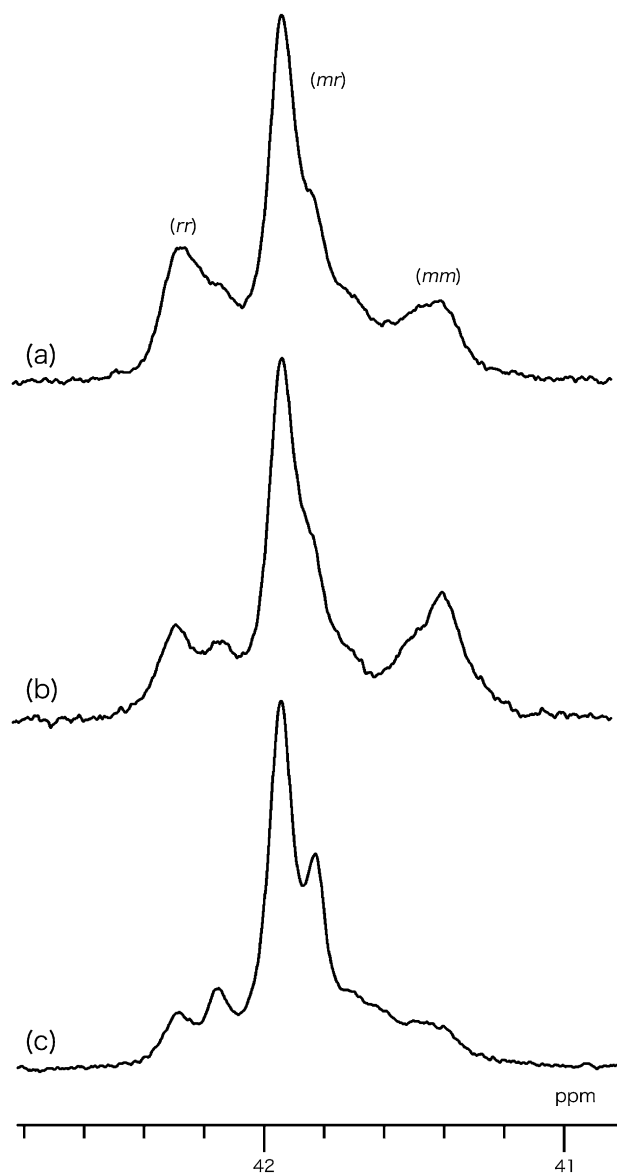
Fig. 3. ^{13}C NMR spectra of main-chain methine carbons of poly(NIPAAm)s prepared at −40 °C in the presence of (a) **1**, (b) **2**, and (c) **3**.

although quantitative analysis is difficult because of low resolution of ^{13}C NMR signals due to main-chain methine carbons. This result means that proper selection of the added agents, such as Lewis bases and alcohols, allows us to directly synthesize three kinds of stereoregular poly(NIPAAm)s [isotactic, syndiotactic and heterotactic poly(NIPAAm)s] even via radical polymerization mechanism. Further work is now under way to investigate the fluoroalcohol-mediated heterotactic-specific radical polymerization of NIPAAm in more detail, to accurately assign the splitting of the main-chain methine carbon resonances, and to examine the effect of heterotacticity on the solution properties of poly(NIPAAm)s, since it has been reported that isotacticity and syndiotacticity significantly influence the phase transition temperature of aqueous solution of poly(NIPAAm)s [10,23].

Acknowledgements

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not accurately correct, because of low resolution of the resonances due to the methine carbons. Based on the sharpness of the peak at middle magnetic field, however, we can conclude at least that the introduction of fluorine atoms to the added alcohol compounds significantly affected the stereospecificity of NIPAAm polymerization, and heterotactic poly(NIPAAm)s were successfully obtained for the first time.

The mechanism of heterotactic propagation induced by fluorinated alcohols is not clear at this time. However, it is assumed that the introduction of fluorine affected the structure of the hydrogen bond-assisted NIPAAm complex and, as a result, the heterotactic specificity was induced.

4. Conclusions

We succeeded in an induction of heterotactic specificity in NIPAAm polymerization by adding fluorinated alcohols,

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