



Isotactic-specific anionic polymerization of *N*-isopropylacrylamide with dilithium tetra-*tert*-butylzincate in the presence of a fluorinated alcohol or Lewis acid

Tomohiro Hirano*, Takahiro Furutani, Tatsuya Saito, Tadashi Segata, Miyuki Oshimura, Koichi Ute

Department of Chemical Science and Technology, Institute of Technology and Science, The University of Tokushima, 2-1 Minamijosanjima, Tokushima 770-8506, Japan

ARTICLE INFO

Article history:

Received 30 June 2012

Received in revised form

28 August 2012

Accepted 1 September 2012

Available online 7 September 2012

Keywords:

Anionic polymerization

N-Isopropylacrylamide

Isotactic

ABSTRACT

The polymerization of *N*-isopropylacrylamide (NIPAAm) with dilithium tetra-*tert*-butylzincate (TBZL) has been investigated in toluene at low temperatures in the presence of alkyl and fluorinated alcohols. Of the alcohols examined, 1,1,1,3,3,3-hexafluoro-2-propanol induced isotactic specificity and accelerated the polymerization process, affording the corresponding poly(NIPAAm)s with *meso* (*m*) diad contents of 82% in relatively high yields. It is worthy of note that the introduction of a fluorinated alcohol, which is typically used as an inhibitor in conventional anionic polymerization processes, enabled control over the stereospecificity and rate of the anionic polymerization of NIPAAm when TBZL was used as an initiator. Yttrium trifluoromethanesulfonate also induced isotactic specificity in the NIPAAm polymerization process in methanol and gave poly(NIPAAm) with an *m* diad content of 88% in high yield.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

N-Isopropylacrylamide (NIPAAm) does not undergo vinyl polymerization *via* a conventional anionic mechanism, because of the acidic proton of its amide group. Protection of the acidic proton is therefore required together with deprotection step following polymerization to provide poly(NIPAAm)s. In fact, there are reports in the literature describing the anionic polymerizations of protected NIPAAm monomers, followed by deprotection [1,2]. In these reports, stereocontrol of the anionic polymerization can be achieved, depending on the protecting group, initiator system and polymerization conditions, including the solvent and the temperature of the process. For instance, the polymerization of a trimethylsilyl-protected NIPAAm with a mixture of *tert*-BuLi and *n*-Bu₃Al in toluene at –40 °C gave a highly isotactic poly(NIPAAm) with a *meso* (*m*) diad content of 97.3% [1]. Furthermore, the polymerization of a methoxymethyl-protected NIPAAm with a mixture of 1,1-diphenyl-3-methylpentyllithium and diethylzinc in tetrahydrofuran (THF) at –78 °C gave a syndiotactic poly(NIPAAm) with a *racemo* (*r*) diad content of 83%, whereas an isotactic polymer with an *m* diad content of 85% was obtained when lithium chloride (LiCl) was used instead of diethylzinc [2].

Recently, dilithium tetra-*tert*-butylzincate (TBZL), which has been reported as a bulky 'ate' complex, provided poly(NIPAAm)s directly *via* the anionic polymerization of unprotected NIPAAm monomers [3,4]. The direct anionic polymerization of unprotected

NIPAAm monomers in these cases was attributed to the soft nucleophilicity and weak basicity of TBZL. Unfortunately, however, no information regarding the stereoregularities of the poly(NIPAAm) products formed according to these processes have been reported.

In contrast to direct anionic polymerization, a wide range of stereoregular poly(NIPAAm) materials are prepared by the radical polymerization of unprotected NIPAAm monomers. For instance, the addition of alkyl [5,6] and fluorinated alcohols [7,8] to NIPAAm polymerizations in toluene at low temperatures gave syndiotactic and heterotactic polymers, respectively. Furthermore, the introduction of a catalytic amount of a Lewis acid, such as yttrium trifluoromethanesulfonate [Y(OTf)₃], gave isotactic polymers in the polymerization of NIPAAm in methanol (MeOH) [9,10].

In the present paper, the anionic polymerization of NIPAAm with TBZL was investigated at low temperatures in the presence of alkyl alcohols, fluorinated alcohols, and Y(OTf)₃. These conditions effectively induced syndiotactic, heterotactic and isotactic specificity *via* radical mechanisms. It is therefore assumed that these additives significantly influence the stereosepecificity of the anionic polymerization of NIPAAm with TBZL. In fact, the induction of significant isotactic specificity was also successfully achieved in the anionic polymerization of unprotected NIPAAm monomers.

2. Experimental

2.1. Materials

NIPAAm (Tokyo Chemical Industry, Tokyo, Japan) was recrystallized from a hexane-toluene mixture prior to use. Toluene was

* Corresponding author. Tel.: +81 88 656 7403; fax: +81 88 656 7404.

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

purified by washing with sulfuric acid, water and 5% aqueous sodium hydroxide (NaOH) solution, followed by fractional distillation. MeOH (Kanto Chemical, Tokyo, Japan) was fractionally distilled. The TBZL solution in THF (supplied by Tosoh Finechem Corp., Yamaguchi, Japan), anhydrous ethanol (EtOH) (Wako Pure Chemical Industries, Osaka, Japan), 3-methyl-3-pentanol (3Me3PenOH), 2,2,2-trifluoroethanol (TFE), (Sigma–Aldrich Japan, Tokyo, Japan), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (supplied by Daikin Industries, Osaka, Japan), 2-propanol (*i*PrOH), nonafluoro-*tert*-butanol (NFTB), and Y(OTf)₃ (Tokyo Chemical Industry) were used as received.

The concentration of the *tert*-butyl group in the TBZL solution was determined to be 3.5 mol/L by hydrolysis with an excess of 0.1 N hydrogen chloride (HCl) solution and subsequent back-titration with a 0.1 N NaOH solution using phenolphthalein as an indicator. The concentrations of Zn²⁺ and Li⁺ were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (OPTIMA 3000, PerkinElmer Japan Co., Ltd., Yokohama, Japan) to be 0.84 and 3.0 mol/L, respectively. These values were consistent with a 1:2 molar mixture of *tert*-Bu₄ZnLi₂ and LiCl, with the latter being formed as a by-product of the reaction of *tert*-butyllithium and zinc chloride (ZnCl₂) during the preparation of TBZL. The concentration of TBZL was calculated as being one-fourth the concentration of the *tert*-butyl group, based on the assumption that only one of the four *tert*-butyl groups on Zn participates in the initiating reaction.

2.2. Polymerization

A typical polymerization procedure was as follows. NIPAAm (0.28 g, 2.5 mmol) and HFIP (1.68 g, 10.0 mmol) were dissolved in toluene to a total volume of 5.0 mL. A portion (4.0 mL) of the resulting solution was transferred to a glass ampoule and cooled to –60 °C. The glass ampoule was degassed and filled with nitrogen six times. The polymerization was initiated by the addition of an aliquot of TBZL (2.0 mol% relative to the monomer; 0.047 mL, 0.86 mol/L) in THF to the solution. The reaction was subsequently terminated after 16 h by the addition of methanolic solution of 2 N HCl at the polymerization temperature. The resulting mixture was then poured into diethyl ether (400 mL) and the precipitated polymer was collected by centrifugation and dried *in vacuo*. The polymer yield was determined gravimetrically.

2.3. Measurements

¹H NMR spectra (400 MHz) were obtained using an EX-400 or ECX-400 spectrometer (JEOL Ltd., Tokyo, Japan). Deuterated dimethyl sulfoxide (DMSO-*d*₆) was used as a solvent for NMR analysis. The diad tacticity of the poly(NIPAAm)s was determined from the ¹H NMR signals of the methine and methylene groups in the main chain at 150 °C.

3. Results and discussion

3.1. The polymerization of NIPAAm with TBZL in toluene and in MeOH

The polymerization of NIPAAm with TBZL was investigated in both toluene and MeOH at a variety of different temperatures over a 16 h period (Table 1). Polymer yields for the polymerizations in MeOH at higher temperatures tended to be higher than the corresponding yields when the process was conducted in toluene. These results were consistent with reports from the literature [3] in which the use of protic solvents was found to accelerate the polymerization of NIPAAm. Polymers rich in *m* diad were obtained in

Table 1
Polymerization of NIPAAm with TBZL in toluene and MeOH for 16 h period.

Run	Solvent	Temp.	Yield	Diad/% ^a		$M_n(\text{Obsd})^b$	$M_n(\text{Calcd})^c$	f^d
		°C		%	<i>m</i>	<i>r</i>	10 ³	
1	Toluene	40	22	59	41	6.7	1.3	0.19
2	Toluene	20	20	58	42	5.6	1.2	0.21
3	Toluene	0	23	56	44	7.0	1.3	0.19
4	Toluene	–20	11	59	41	3.4	0.7	0.20
5	Toluene	–40	13	60	40	4.0	0.8	0.20
6	Toluene	–60	9	57	43	3.5	0.6	0.16
7	MeOH	40	>99	47	53	16.0	5.7	0.36
8	MeOH	20	33	47	53	16.9	1.9	0.11
9	MeOH	0	83	46	54	24.8	4.8	0.19
10	MeOH	–20	85	45	55	22.7	4.9	0.22
11	MeOH	–40	23	48	52	5.4	1.4	0.25
12	MeOH	–60	16	50	50	4.0	1.0	0.25
13	MeOH	–80	10	51	49	3.9	0.6	0.15

[NIPAAm]₀ = 0.5 mol/L, [TBZL]₀ = 2.0 mol%.

^a Determined from the ¹H NMR signals of the methine and methylene groups in the main chain.

^b Determined from the ¹H NMR signals of the –NCH(CH₃)₂ and *tert*-butyl groups.

^c Calculated with the following equation: $M_n(\text{Calcd}) = 113.16 (MW_{\text{NIPAAm}}) \times 50 ([\text{NIPAAm}]_0 / [\text{TBZL}]_0) \times \text{yield} / 100 + 58.12 (MW_{\text{tert-Bu-H}})$.

^d Initiator efficiency.

toluene, regardless of temperature used (Table 1, runs 1–6). In contrast, the *m* diad content of the polymers formed in MeOH increased gradually with decreasing temperature, and provided almost atactic polymers (Table 1, runs 7–13). This result corresponded well with the solvent-dependency of the stereospecificity typically observed in the anionic polymerizations of (meth)acrylates, in which the isotactic specificity increases in non-polar solvents such as toluene [11,12].

The molecular weights of the poly(NIPAAm)s were difficult to determine by size-exclusion chromatography because the polymers were adsorbed on the stationary phase. In particular, no elution peaks were detected for the poly(NIPAAm)s with high *m* diad contents even under the same conditions as reported previously [5–8]. The chain-end structures of the poly(NIPAAm)s prepared with TBZL were reported to be composed of *tert*-butyl group at the initiating chain-end and hydrogen at the terminating chain-end [3]. The ¹H NMR spectrum of poly(NIPAAm) prepared with TBZL in MeOH at –60 °C (Table 1, run 12) is shown in Fig. 1. As expected, a resonance corresponding to the *tert*-butyl group derived from TBZL was clearly present in the spectrum. The molecular weights of the polymers were subsequently estimated by end-group analysis of the *tert*-butyl proton signals and the signals

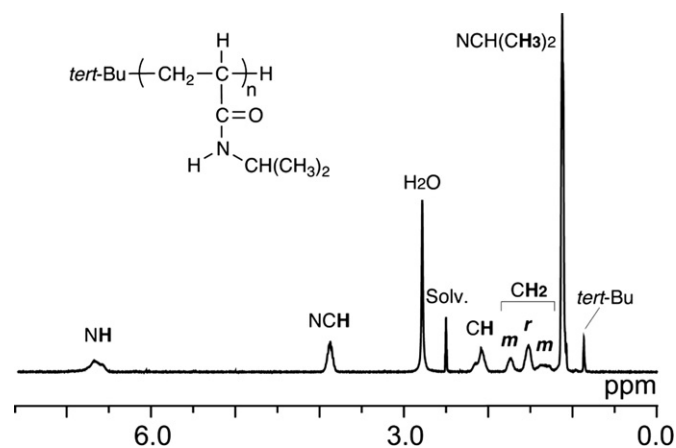


Fig. 1. ¹H NMR spectrum of poly(NIPAAm) prepared with TBZL in MeOH at –60 °C (Table 1, run 12).

Download English Version:

<https://daneshyari.com/en/article/5183256>

Download Persian Version:

<https://daneshyari.com/article/5183256>

[Daneshyari.com](https://daneshyari.com)