Stereospecific Anionic Polymerization of α -(Alkylthiomethyl)acrylates and α -(2-Thienylmethyl)acrylate

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(Received April 9, 1999)

ABSTRACT: Novel α -substituted acrylates having various functional groups containing a sulfur atom at the α -position, such as benzyl α -(butylthiomethyl)acrylate, benzyl α -(*t*-butylthiomethyl)acrylate, benzyl α -(benzylthiomethyl)acrylate, benzyl α -(triphenylmethylthiomethyl)acrylate, ethyl α -(2-thienylmethyl)acrylate, benzyl α -(benzylsulfinylmethyl)acrylate, and benzyl α -(benzylsulfonylmethyl)acrylate, were synthesized, and polymerizability and stereoregularity of the obtained polymers using lithium reagents were investigated. In the anionic polymerization of α -(alkylthiomethyl)acrylates and ethyl α -(2-thienylmethyl)acrylate in toluene, highly isotactic polymers were obtained in good yields. A bulky α -substituent, triphenylmethylthiomethyl group, prevents polymerization. The anionic polymerization of α -(alkylthiomethyl)acrylates in tetrahydrofuran (THF) resulted in low yields and isotacticities, ethyl α -(2-thienylmethyl)acrylate gave an isotactic polymer in a good yield. A side reaction, the elimination of alkylthiolate anion from the propagating end, seems to take place in the polymerization of α -(alkylthiomethyl)acrylates in THF.

KEY WORDS Stereospecific Polymerization / Anionic Polymerization / Isotactic Polymer / α -(Alkylthiomethyl)acrylate / α -(2-Thienylmethyl)acrylate / Chain Transfer /

Allylic sulfides produce SH2' substitution products in radical reactions.¹ Therefore, α -(alkylthiomethyl)acrylates (**1**), alkoxycarbonyl substituted allylic sulfides, can be utilized as chain-transfer agents based on the addition-fragmentation mechanism (Scheme 1) in the radical polymerization of styrene, methyl methacrylate, and acrylates.^{2,3} The addition of a propagating radical to the double bond of **1** followed by fragmentation generates the macromolecule with a double bond at the ω -end and the thiyl radical which initiates further polymerization. Therefore, the radical polymerization of **1** has been unsuccessful and its homopolymer has not yet been synthesized.

Methods for stereoregular arrangement of various functional groups along the main-chain are particularly important for designing novel functional polymers. Since sulfides are convenient for further transformation to other functional groups, stereoregular polymer bearing various alkylthio groups as side chains might provide a useful method for the construction of novel function. We recently found that the anionic polymerization of α -(alkoxymethyl)acrylates⁴ and α -(aminomethyl)acrylates,⁵ both of which have a polar substituent on the α -position of an acrylate, with lithium reagents gave

highly isotactic polymers. The radical polymerization of these monomers resulted in atactic polymers or no polymerization. In the present report, the investigation of anionic polymerization using series of benzyl α -(alkylthiomethyl)acrylates is reported. Effects of a variety of alkylthio groups on the reactivity and stereoregulation in the anionic polymerization of novel monomers, benzyl α -(butylthiomethyl)acrylate (**1a**), benzyl α -(*t*-butylthiomethyl)acrylate (**1b**), benzyl α -(benzylthiomethyl)acrylate (**1c**), and benzyl α -(triphenylmethylthiomethyl)acrylate (**1d**), were mainly examined.

Although thiophene and poly(thiophene) derivatives have received considerable attention due to their electronic conductivity in the partially oxidized state, little data are available on stereocontrolled polymers with pendant thiophene groups.⁶ Here, the stereospecific polymerization developed for α -(alkylthiomethyl)acrylates is expanded to a novel α -substituted acrylate having a functional group containing a sulfur atom, ethyl α -(2-thienylmethyl)acrylate (**2**).

Scheme 1.

EXPERIMENTAL

Measurements

¹H and ¹³C NMR spectra were measured on a Varian Gemini-2000 (400 MHz for ¹H) spectrometer in CDCl₃ or benzene-*d*₆ with tetramethylsilane as the internal standard. Infrared (IR) spectra were recorded on a

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JASCO FT/IR-550 spectrometer. Mass spectra were taken on a JEOL LMS-AX505HA mass spectrometer. Size exclusion chromatographic analysis (SEC) was performed on a JASCO 880-PU chromatograph equipped with a JASCO 875-UV ultraviolet detector or a JASCO 830-RI refractive index detector. Two commercial columns (TSK G5000H, 60×0.72 (i.d.) cm, Shodex AC 802.5 50×0.72 (i.d.) cm) were connected in series and chloroform was used as eluent. Calibration was performed using standard polystyrenes.

Materials

Solvents, toluene and tetrahydrofuran (THF), used in the polymerization were distilled from Na wire, and distilled again from butyllithium (*n*-BuLi) for toluene and LiAlH₄ for THF under high vacuum just before use. *n*-BuLi was prepared from 1-chlorobutane and lithium powder in heptane. A pentane solution of *t*-butyllithium (*t*-BuLi) was purchased from Aldrich. A radical initiator diisopropyl peroxydicarbonate [(*iso*-PrOCO₂)₂] was generously donated by NOF Co. and used as toluene solution. Monomers (**1a**–**d**) were synthesized from benzyl α -(bromomethyl)acrylate⁷ and the corresponding thiols using potassium carbonate in CH₂Cl₂.^{2b} Monomers, **3** and **4**, were prepared from **1c** using hydrogen peroxide in acetic acid.

Benzyl α -(butylthiomethyl)acrylate (**1a**): ¹H NMR (400 MHz, CDCl₃) δ 0.90 (t, 3H, *J* = 7.4 Hz, CH₃), 1.33–1.57 (m, 4H, CH₂), 2.45 (t, 2H, *J* = 7.6 Hz, SCH₂), 3.40 (s, 2H, SCH₂), 5.23 (s, 2H, CH₂Ph), 5.67 (s, 1H, vinyl), 6.25 (s, 1H, vinyl), 7.25–7.45 (m, 5H, aromatic); IR (neat, cm⁻¹) 1721, 1630, 1456, 1324, 1302, 1185, 1127. *Anal.* Calcd for C₁₅H₂₀SO₂: C, 68.15%; H, 7.62%. Found: C, 68.16%; H, 7.63%.

Benzyl α -(*t*-butylthiomethyl)acrylate (**1b**): ¹H NMR (400 MHz, CDCl₃) δ 1.33 (s, 9H, CH₃), 3.48 (s, 2H, SCH₂), 5.23 (s, 2H, CH₂Ph), 5.86 (s, 1H, vinyl), 6.30 (s, 1H, vinyl), 7.25–7.45 (m, 5H, aromatic); IR (neat, cm⁻¹) 1723, 1632, 1498, 1457, 1365, 1323, 1301, 1176, 1123. *Anal.* Calcd for C₁₅H₂₀SO₂: C, 68.15%; H, 7.62%. Found: C, 68.07%; H, 7.71%.

Benzyl α -(benzylthiomethyl)acrylate (**1c**): ¹H NMR (400 MHz, CDCl₃) δ 3.30 (s, 2H, SCH₂), 3.67 (s, 2H, SCH₂), 5.23 (s, 2H, OCH₂Ph), 5.63 (s, 1H, vinyl), 6.27 (s, 1H, vinyl), 7.20–7.40 (m, 10H, aromatic); IR (neat, cm⁻¹) 1722, 1630, 1495, 1454, 1324, 1302, 1186, 1124, 951; MS (EI) *m/z* 298 (M⁺). *Anal.* Calcd for C₁₈H₁₈SO₂: C, 72.45%; H, 6.08%. Found: C, 72.44%; H, 6.22%.

Benzyl α -(triphenylmethylthiomethyl)acrylate (**1d**): m.p. 81.0–82.0°C; ¹H NMR (400 MHz, CDCl₃) δ 3.09 (s, 2H, SCH₂), 5.20 (s, 2H, OCH₂Ph), 5.41 (s, 1H, vinyl), 6.14 (s, 1H, vinyl), 7.15–7.45 (m, 20H, aromatic); IR (neat, cm⁻¹) 1713, 1635, 1486, 1443, 1322, 1179, 1128, 940. *Anal.* Calcd for C₃₀H₂₆SO₂: C, 79.97%; H, 5.82%. Found: C, 79.98%; H, 5.82%.

rac-Benzyl α -(benzylsulfinylmethyl)acrylate (**3**): ¹H NMR (400 MHz, CDCl₃) δ 3.41 (d, 1H, *J* = 12.8 Hz, SCH₂), 3.79 (d, 1H, *J* = 12.8 Hz, SCH₂), 3.96 (d, 1H, *J* = 12.8 Hz, SCH₂), 5.19 (d, 1H, *J* = 12.8 Hz, SCH₂), 5.23 (d, 1H, *J* = 12.8 Hz, OCH₂Ph), 5.97 (s, 1H, vinyl), 6.55 (s, 1H, vinyl), 7.25–7.45 (m, 5H, aromatic); IR (neat, cm⁻¹) 1716, 1628, 1497, 1455, 1414, 1327, 1184, 1048, 968. *Anal.* Calcd for C₁₈H₁₈SO₃: C, 68.76%; H, 5.77%. Found: C, 68.76%; H, 5.85%.

Benzyl α -(benzylsulfonylmethyl)acrylate (**4**): m.p. 69.5–70.0°C; ¹H NMR (400 MHz, CDCl₃) δ 3.98 (s, 2H, SCH₂), 4.26 (s, 2H, SCH₂), 5.26 (s, 2H, OCH₂Ph), 6.11 (s, 1H, vinyl), 6.66 (s, 1H, vinyl), 7.30–7.45 (m, 5H, aromatic); IR (neat, cm⁻¹) 1713, 1631, 1449, 1410, 1331, 1302, 1182, 1118, 966. *Anal.* Calcd for C₁₈H₁₈SO₄: C, 65.44%; H, 5.49%. Found: C, 65.46%; H, 5.06%.

Ethyl α -(2-thienylmethyl)acrylate (**2**): To a solution of 2-bromothiophene (0.10 mol) in THF (85 mL) was added a hexane solution of *n*-BuLi (1.6 M, 68 mL) at –78°C. After stirring for 1 h, CuCl (0.052 mol) was added, and the mixture was stirred for 1 h at 0°C. A solution of ethyl α -(bromomethyl)acrylate⁷ (10 g, 0.052 mol) in THF (50 mL) was introduced to the mixture at –78°C. The reaction was continued at room temperature for 3 h. The crude product was separated as an organic phase by adding a large amount of water, and purified by column chromatography on silica gel (hexane/ethyl acetate = 10/1) (7.7 g, 76% yield); b.p. = 52–54°C/0.15 mmHg; ¹H NMR (400 MHz, CDCl₃) δ 1.28 (t, 3H, *J* = 7.2 Hz, CH₃), 3.83 (s, 2H, SCH₂), 4.21 (q, 2H, *J* = 7.2 Hz, OCH₂), 5.58 (s, 1H, vinyl), 6.25 (s, 1H, vinyl), 6.80–7.20 (m, 3H, aromatic); IR (neat, cm⁻¹) 2981, 1718, 1633, 1326, 1301, 1254, 1200, 1155, 1026, 696. *Anal.* Calcd for C₁₀H₁₂SO₂: C, 61.20%; H, 6.16%. Found: C, 61.15%; H, 6.31%.

Anionic Polymerization Procedure

Polymerization was carried out in a glass ampule equipped with a three-way stopcock. The purified reagents were transferred into an ampule with a syringe under a dry nitrogen atmosphere. The polymerization was initiated by adding an initiator solution to a monomer solution. Polymerization was typically carried out using a monomer (1.20 mmol), an initiator (0.12 mmol), and a solvent (1.5 mL). Termination of the polymerization was accomplished by adding a small amount of methanol and a polymer was precipitated in a large amount of methanol. The polymer was separated by centrifugation and dried *in vacuo*.

RESULTS AND DISCUSSION

The radical polymerizations of α -(alkylthiomethyl)acrylates (**1a**–**d**) using (*iso*-PrOCO₂)₂ in toluene at 30°C gave no polymers as expected from the allylic sulfide character of the monomers.^{1,2} The monomers were almost quantitatively recovered as hexane soluble parts. The results of the anionic polymerization of **1a**–**d** using alkyl lithium reagents in toluene and THF are listed in Table I.

The anionic polymerization of **1a** with *n*-BuLi in toluene gave a polymer in a good yield (72%) (entry 1). The ¹H NMR spectrum of the obtained polymer measured in benzene-*d*₆ at 80°C is shown in Figure 1(a).

Table I. Anionic polymerization of benzyl α -(alkylthiomethyl)acrylates^a

Entry	Monomer	Initiator	Solvent	Time	Yield ^b	DP ^c	M_w/M_n^c
				h	%		
1	1a	<i>n</i> -BuLi	Toluene	24	72	53	2.87
2		<i>t</i> -BuLi	THF	96	3	16	—
3	1b	<i>n</i> -BuLi	Toluene	24	64	28	18.9
4		<i>t</i> -BuLi	THF	96	15	18	—
5	1c	<i>n</i> -BuLi	Toluene	24	93	18	—
6		<i>t</i> -BuLi	THF	96	1	9 ^d	—
7		Li piperidide	THF	96	<1	—	—
8	1d^e	<i>n</i> -BuLi	Toluene	96	0	—	—
9		<i>n</i> -BuLi	THF	96	0	—	—

^a [Monomer]/[initiator] = 10, temp = -78°C . ^b Methanol insoluble part. ^c Determined by SEC (polystyrene standard). ^d Peak-top value. ^e [Monomer] = 0.4 M.

Figure 1. 400 MHz ^1H NMR spectra of poly(**1a**) (entry 1, Table I) (a), poly(**1b**) (entry 3, Table I) (b), and poly(**1c**) (entry 5, Table I) (c) obtained with *n*-BuLi in toluene at -78°C ((a) benzene-*d*₆, 80°C ; (b) and (c), CDCl₃, 60°C). $\times$ denotes a peak of CHCl₃.

The spectral pattern is simple and each peak is assigned to a vinyl polymer corresponding to poly(**1a**). The spectral pattern of the main chain methylene protons around 2.5 ppm shows a typical AB quartet with a coupling constant 15.4 Hz as shown in an expanded spectrum. These observations indicate that a highly isotactic polymer is produced in the anionic polymeriza-

tion of **1a** in toluene similarly to the anionic polymerization of α -(alkoxymethyl)acrylates⁴ and α -(*N,N*-dialkylaminomethyl)acrylates⁵ with lithium reagents.

Figure 2. 100 MHz ^{13}C NMR spectra of the carbonyl carbon in poly(**1a**) (entry 1, Table I) (a), poly(**1b**) (entry 3, Table I) (b), poly(**1c**) (entry 5, Table I) (c) obtained with *n*-BuLi in toluene, and poly(**1b**) with *t*-BuLi in THF (entry 4, Table I) (d) (CDCl₃, 60°C).

Figure 2(a) shows the ^{13}C NMR spectrum of the carbonyl carbon of poly(**1a**) obtained in toluene. A sharp singlet is observed, indicating that the anionic polymerization of **1a** proceeds in a highly isotactic-specific

Figure 3. 400 MHz ^1H NMR spectrum of poly(**1b**) (entry 4, Table I) obtained with $t\text{-BuLi}$ in THF at -78°C (CDCl_3 , 60°C).

manner.

The anionic polymerizations of monomers, **1b** and **1c**, using $n\text{-BuLi}$ in toluene afforded polymers in good yields (entries 3 and 5). The ^1H NMR spectra of the obtained poly(**1b**) and poly(**1c**) are depicted in Figures 1(b) and 1(c), respectively. AB quartet spectral patterns of β -methylene protons (2.1–2.5 ppm) are observed. The ^{13}C NMR spectra of the carbonyl carbon show sharp singlets for both polymers, although there are small shoulder peaks for poly(**1b**) [Figures 2(b) and 2(c)]. Thus, the anionic polymerization of α -(alkylthiomethyl)acrylates in toluene proceeds under isotactic-specific control.

The polymerizations of monomers, **1a–c**, using alkylolithium reagents in THF resulted in much lower yields and lower molecular weights (entries 2, 4, and 6) than those in toluene. The polymerization with lithium piperidide, an effective initiator for polymerization of α -(aminomethyl)acrylates,⁵ resulted in a trace yield (entry 7). Stereoregularity of the polymers was affected by the solvents. Figure 3 demonstrates the ^1H NMR spectrum of the poly(**1b**) obtained in THF. The spectral pattern of main chain methylene protons around 2.3 ppm is different from that of the poly(**1b**) obtained in toluene [Figure 1(b)]. The ^{13}C NMR spectrum of the carbonyl carbon shows multiplets, although the polymer appears to be still rich in isotacticity [Figure 2(d)]. The effect of THF for stereoregulation seems smaller than that in the anionic polymerization of α -(alkyl)acrylates,⁸ which usually affords polymers rich in syndiotacticity in polar solvents. However, in anionic polymerizations of α -(alkoxymethyl)acrylates⁴ and α -(N,N -dialkylamino-methyl)acrylates⁵ with lithium reagents, highly isotactic polymers are formed regardless of the polarity of solvents.

In the anionic polymerization of α -(alkylthiomethyl)acrylates in THF, a side reaction, elimination of alkylthiolate anion from the propagating end, must take place similarly to the anionic polymerization of methyl α -(phenoxymethyl)acrylate (MPMA) reported previously.^{5b} In the ^1H NMR spectrum of the poly(**1b**) obtained in THF (Figure 3), signals of the olefinic protons of the end group, generated by the elimination of t -butylthiolate anion (Scheme 2), were observed at around 5.6 and 6.0 ppm, and these chemical shifts are different from those of **1b**. The generation of the olefinic unit at the

Scheme 2.

ω -end was not observed in the polymerization in toluene (Figure 1). The generation of the olefinic group at the ω -end in the poly(**1b**) (entry 4) was estimated to be 73% from the integral ratio of the ^1H NMR spectrum (Figure 3) and the molecular weight measured by SEC. The eliminated alkylthiolate anion seems effective for reinitiation of the polymerization like a chain transfer reagent in radical polymerization, because the monomers were hardly recovered and the methanol-soluble oligomers were mainly obtained in the polymerization of **1s** in THF.

The polymerizations of **1d** in toluene and THF gave no polymer (entries 8 and 9), probably because the bulky α -substituent, triphenylmethylthiomethyl group, prevents polymerization as reported previously for α -(alkoxymethyl)acrylates^{4,9} and α -(N,N -dialkylamino-methyl)acrylates.^{5,10} In the methanol soluble part of the polymerization of **1d** in toluene, compound **5** corresponding to a dimer initiated by triphenylmethylthiolate anion followed by the elimination was formed in about 75% yield.¹¹ This suggests that the monomer **1d** seems an effective chain-transfer agent in anionic polymerization.

The radical and anionic polymerizabilities of monomers **3** and **4**, having sulfinyl and sulfonyl groups, respectively, were examined. The anionic polymerization of these monomers using $n\text{-BuLi}$, lithium piperidide, and cyclohexylmagnesium bromide in toluene at -78°C as well as the radical polymerization using $(\text{iso-PrOCO}_2)_2$ in toluene at 30°C did not proceed. Ethyl α -(phenylsulfonylmethyl)acrylate exhibits chain transfer reaction in the radical polymerization.^{2b}

The allylic sulfide character of α -(alkylthiomethyl)acrylates causes significant termination reaction, elimination of thiolate anion, in the anionic polymerization in THF as well as in the radical polymerization. Therefore, a novel monomer **2** was designed and synthesized. **2** has a thioether group at the homoallylic position. The results of the radical and anionic polymerizations of **2** in toluene and THF are summarized in Table II. Although the radical polymerization with $(\text{iso-PrOCO}_2)_2$ in toluene at 30°C did not proceed (entry 1), anionic polymerizations using lithium reagents in toluene and THF resulted in good yields (entries 2–4), indicating that no side reaction occurred in marked contrast to the anionic polymerization of α -(alkylthiomethyl)acrylates (**1**).

Figure 4 shows the ^1H NMR spectrum of the polymer obtained with $n\text{-BuLi}$ in toluene (entry 2). Each peak is sharp and assigned to a vinyl polymer corresponding to

Table II. Radical and anionic polymerization of **2**^a

Entry	Initiator	Solvent	Time	Yield ^b	DP ^c	M_w/M_n^c
			h	%		
1	(<i>iso</i> -PrOCO ₂) ₂	Toluene	48	0 ^d	—	—
2	<i>n</i> -BuLi	Toluene	15	78	31	48
3	TMEDA-DPEDALi ^e	Toluene	15	91	19	1.3
4	<i>n</i> -BuLi	THF	15	81	23	32

^a Radical polymerization: [monomer]/[initiator] = 30, temp = 30°C; anionic polymerization: [monomer]/[initiator] = 10, temp = -78°C.

^b Methanol insoluble part. ^c Determined by SEC (polystyrene standard). ^d Hexane insoluble part. ^e TMEDA: *N,N,N',N'*-tetramethylethylenediamine; DPEDALi: *N,N'*-diphenylethylenediamine monolithium amide.

Figure 4. 400 MHz ¹H NMR spectrum of poly(**2**) (entry 2, Table II) obtained with *n*-BuLi in toluene at -78°C (CDCl₃, 60°C).

poly(**2**) as shown in the figure. The spectral pattern was quite similar to that of the polymer obtained anionically in THF (entry 4). Sharp singlets with the same chemical shift were observed in the ¹³C NMR analysis of the carbonyl carbon of these polymers (Figures 5(a) and 5(c)), although there are small shoulder peaks for the polymer obtained in THF (entry 4). Therefore, the polymers obtained with *n*-BuLi must be highly isotactic regardless of the polarity of solvents as previously reported in the anionic polymerization of α -substituted acrylates with lithium reagents,^{4,5} although peak splitting of the main chain methylene protons in the ¹H NMR spectrum (Figure 4) was not observed in CDCl₃ at 60°C.¹²

The polymer prepared using the complex of DPEDALi (*N,N'*-diphenylethylenediamine monolithium amide) with TMEDA (*N,N,N',N'*-tetramethylethylenediamine) showed much lower stereoregularity than poly(**2**)s obtained with *n*-BuLi (Figure 5(b)). A basic diamine ligand should prevent the coordination of the polar

Figure 5. 100 MHz ¹³C NMR spectra of the carbonyl carbon in poly(**2**) obtained with *n*-BuLi (entry 2, Table II) (a), with DPEDALi-TMEDA in toluene (entry 3, Table II) (b), and with *n*-BuLi in THF (entry 4, Table II) (c) (CDCl₃, 60°C).

substituents of the growing polymer and **2** to the counter-cation (Li⁺), in addition to the weak coordination ability of the homoallylic sulfur atom in thiophene.

In conclusion, novel monomers, **1a–c** bearing alkylthiomethyl groups on the α -position of an acrylate, were anionically polymerized to the corresponding vinyl polymers, although α -(alkylthiomethyl)acrylates generally show chain transfer activity based on the addition-fragmentation reaction and has no homo-polymerizability in radical polymerization. The polymers obtained with *n*-BuLi in toluene were highly isotactic. The anionic polymerization of a novel monomer, **2** having 2-thienylmethyl group on the α -position of an acrylate, provided a polymer with high isotacticity regardless of the polarity of the solvent. New functional polymers with thioether and thiophene groups arranged on the main chain of a highly isotactic poly(acrylate) were synthesized.

Acknowledgments. This work was partially supported by a Grant-in-Aid for Scientific Research (No. 09750973) from the Ministry of Education, Science, Sports and Culture of Japan, and by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corporation (JST).

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11. ^1H NMR (400 MHz, CDCl_3) δ 2.26 (d, 2H, $J=11.2\text{ Hz}$, $-\text{SCH}-$), 2.49 (s, 2H, $-\text{CH}_2-$), 2.62 (d, 2H, $J=11.2\text{ Hz}$, $-\text{SCH}-$), 4.92 (s, 2H, $-\text{OCH}_2-$), 4.96 (s, 2H, $-\text{OCH}_2-$), 5.26 (s, 1H, vinyl), 5.91 (s, 1H, vinyl), 7.15–7.50 (m, 40H, aromatic); IR (neat, cm^{-1}) 3057, 3030, 2925, 1720, 1594, 1489, 1443, 1297, 1142, 742, 698; *Anal.* Calcd for $\text{C}_{60}\text{H}_{52}\text{S}_2\text{O}_4$: C, 79.97%; H, 5.82%. Found: C, 79.74%; H, 6.00%.
12. Although ^1H NMR analysis of poly(2) obtained with $n\text{-BuLi}$ in toluene was also carried out in nitrobenzene- d_5 at 180°C , peak splitting of the main chain methylene protons was not shown.