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Ring-opening metathesis polymerization (ROMP) of norbornene macromonomer using $Mo(CHCMe_2Ph)(NAr)(OR)_2$ as the initiator

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Abstract

Efficient polymerization of norbornene macromonomer bearing a ring-opened poly(norbornene) substituent has been accomplished by the ring-opening metathesis polymerization by the well-defined Schrock-type molybdenum initiator, $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(OCMe(CF_3)_2)$. The key steps for the macromonomer synthesis are: (i) selective end capping of ring-opened poly(norbornene) with *p*-$Me_3SiOC_6H_4CHO$; (ii) exclusive hydrolysis of the $SiMe_3$ group; and (iii) esterification of OH group produced at the end of preformed polymer chain with norbornene carboxylic acid chloride. $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(OCMe(CF_3)_2)$ was found to be an effective initiator in order for this polymerization to proceed to the complete conversion. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Ring-opening metathesis polymerization; Norbornene macromonomer; Molybdenum

1. Introduction

Polymacromonomers represent an important class of branched polymers whose main characteristic is an axisymmetric distribution of branching points along the central backbone contour [1,2]. Upon polymerization of macromonomers, polymers of extremely high branch density and uniform branch length can be obtained, which would not be the case when using other synthetic strategies such as star-polymer syntheses. Interest in polymacromonomers arises from their unique properties in solution and in bulk [3,4]. However, little attention has been paid to the efficient synthesis of these multibranched systems in contrast to the case of star polymers. One major limitation associated with the homopolymerization of macromonomers is the difficulty of obtaining complete conversion and precise size control of the branched structure formed.

Molybdenum alkylidene complexes of the type $Mo(CHR')(NAr)(OR)_2$ ($Ar = 2,6\text{-}{}^iPr_2C_6H_3$, $2,6\text{-}Me_2C_6H_3$; $OR = O^tBu$, $OCMe(CF_3)_2$ etc.; $R' = CMe_3$ or CMe_2Ph) are useful initiators for the living ring-opening metathesis polymerization (ROMP) of cyclic olefins, especially norbornenes and disubstituted norbornadienes [5–11]. The absence of chain-transfer and termination reactions in such polymerizations allows the production of homopolymers and block copolymers of low molecular dispersity, and allows the control of terminal group in the initiation site and in the termination site. The fact that a wide variety of non-protic functionalities are also tolerated by this catalyst allows architectural and functional possibilities for ROMP polymers [12,13].

It has already been reported by Gnanou et al. and Feast et al. that macromonomers can be polymerized without chain-transfer and termination reactions via ring-opening metathesis mechanism using the molybdenum-alkylidene initiator [14–19]. These reports indicate that the ROMP is one of the most efficient ways to prepare polymacromonomer with complete conversion as well as with a uniform molecular weight distribution. However, the results presented there was only the case of living anionic polymerization, and several limitations still exist in preparing various kinds of polymacromonomers. In this report, we wish to present our preliminary results on the preparation of new type of polymacromonomers by ROMP with the molybdenum initiators.

2. Results and discussion

2.1. Preparation of macromonomer

$Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(O^tBu)_2$ (Catalyst A) was chosen as the initiator, because this catalyst is the most widely used in this type of polymerization. The polymerization was performed in toluene by adding norbornene

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Table 1
$Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(O^tBu)_2$-catalyzed ROMP of norbornene (reaction conditions: toluene, room temperature (see Section 3))

Run	Equiv.[a]	Time (h)	M_w[b] ($\times 10^{-4}$)	M_w/M_n[b]	Yield (%)
1	25	0.5	0.80	1.17	>98
2	25	0.5	0.77	1.14	90
3	25	0.5	0.65	1.16	90
4	50	0.5	1.31	1.12	>98
5	50	0.5	1.28	1.10	>98
6	50	0.5	1.14	1.09	90
7	50	0.5	1.20	1.11	>98
8	50	0.5	1.14	1.09	98
9	50	0.5	1.19	1.11	90
10	100	0.5	1.90	1.12	>98
11	100	0.5	2.23	1.06	>98
12	100	0.5	2.23	1.09	>98
13	200	1.0	5.21	1.03	>98
14	400	1.0	11.9	1.04	>98

[a] Molar ratio of norbornene/Mo.

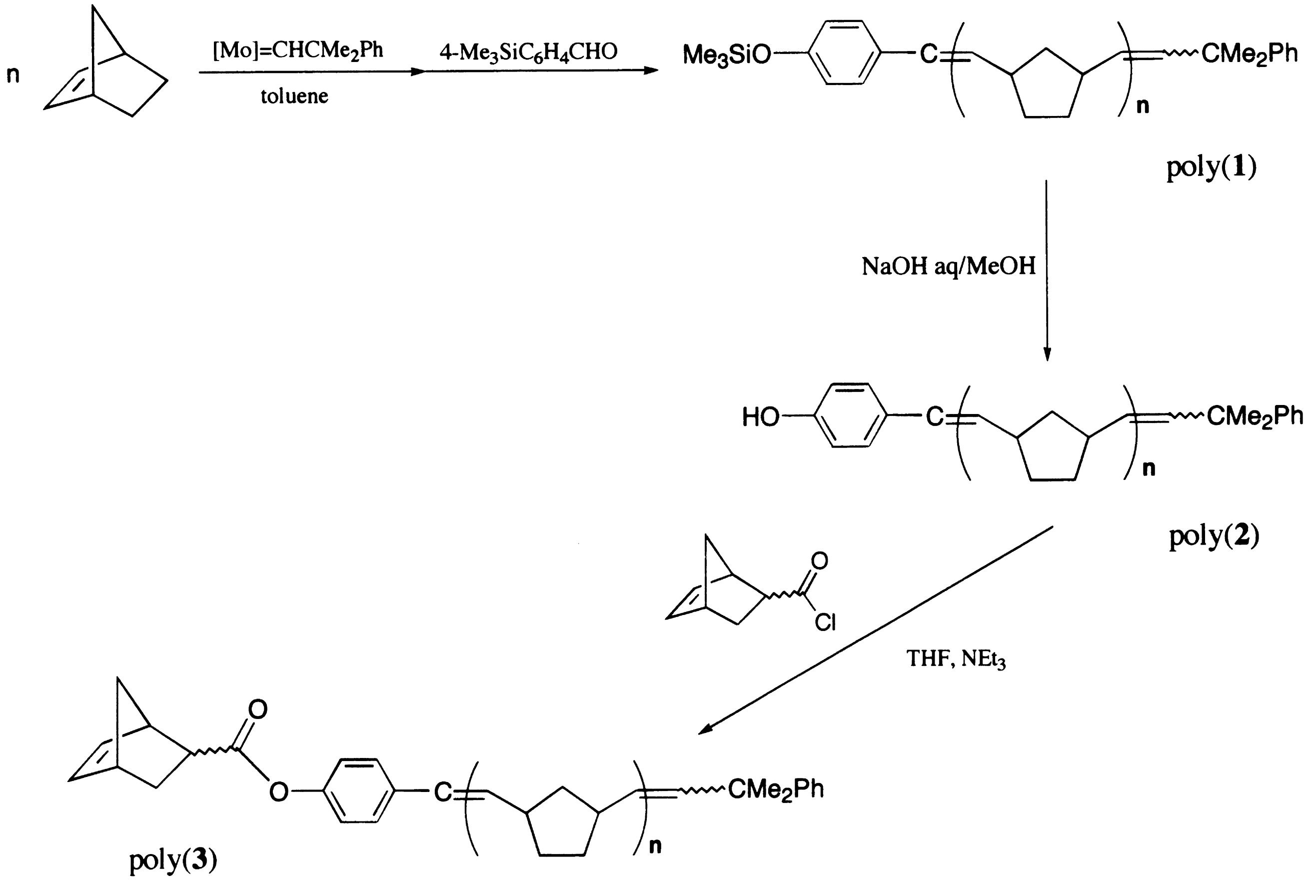
[b] GPC in THF vs polystyrene standard.

of 25–400 molar equivalent to the initiator, and the resultant polymers were cleaved from the initiator fragment metal in a Wittig-like reaction with p-$Me_3SiC_6H_4CHO$. This is the established method of cleaving ROMP polymer–metal bond of this type, and the polymer yield exceeded 90% in all cases. The molecular weight and its distribution of purified homopolymers [poly(**1**)] were characterized by gel permeation chromatography (GPC), and the results are summarized in Table 1.

^1H NMR spectra of the resultant polymer, poly(**1**), showed relatively broad signals at 5.2 and 5.3 ppm due to olefinic protons and broad signals between 0.9 and 2.0 ppm and between 2.4 and 2.8 ppm characteristic to ring-opened polymers of norbornene. In addition, a signal characteristic to $SiMe_3$ group was observed at 0.3 ppm, and a number of signals characteristic to vinyl protons at the polymer chain end group were also observed [20]. The resultant polymer was a mixture of *cis*-and *trans*-isomers (64% *trans*-form, run 6).

The average M_w of polymer increased with increasing molar ratio of monomer against initiator, and the molecular weight distribution of poly(**1**) was fairly sharp ($PDI = 1.03 - 1.17$). These results might indicate that this polymerization is a living polymerization.

The preparation of macromonomer in this study is depicted in Scheme 1. Hydrolysis of trimethylsilyl group in poly(**1**) was performed in a mixed solvent consisting of 5 N NaOH and MeOH at room temperature, and the ^1H NMR signal at 0.3 ppm due to $SiMe_3$ group disappeared after the hydrolysis reaction [poly(**2**)]. The yield was almost quantitative in all cases (Table 2).



Scheme 1.

Table 2
Preparation of macromonomer poly(**3**) by deprotection of trimethylsilyl group and esterification with norbornene carboxylic acid chloride (for reaction conditions, see Section 3)

Run	Equiv.[a]	Poly(**1**)		Poly(**2**)		Yield (%)	Poly(**3**)		Yield (%)
		M_w[b] ($\times 10^{-4}$)	M_w/M_n[b]	M_w[b] ($\times 10^{-4}$)	M_w/M_n[b]		M_w[b] ($\times 10^{-4}$)	M_w/M_n[b]	
1	25	0.80	1.17	0.86	1.12	>98	0.85	1.21	95
3	25	0.65	1.16	0.67	1.15	95	0.74	1.16	90
4	50	1.31	1.12	1.34	1.12	>98	1.28	1.11	98
6	50	1.14	1.09	1.14	1.10	>98			
7	50	1.20	1.11	1.35	1.11	>98			
8	50	1.14	1.09	1.13	1.11	95	1.29	1.11	90
10	100	1.90	1.12	2.00	1.13	>98			

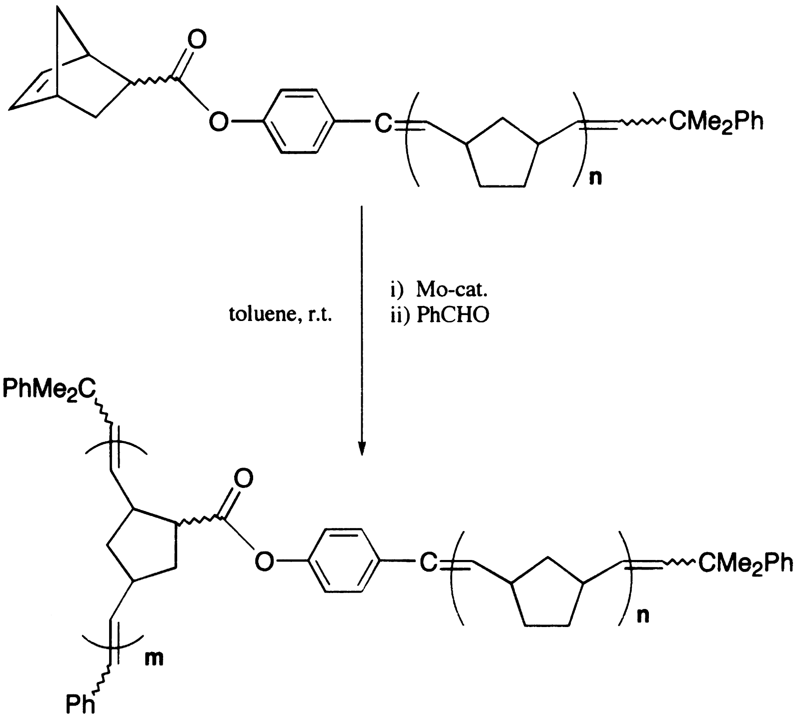
[a] Molar ratio of norbornene/Mo (Table 1).
[b] GPC in THF vs polystyrene standard.

The macromonomer was then prepared by the reaction of poly(**2**) with norbornene carboxylic acid chloride in THF containing NEt_3. Slightly excess amount [1.5 equiv. to poly(**2**)] of the chloride was necessary to attain the complete conversion of poly(**2**) to the macromonomer (**3**) in high yield (Table 2), and the chloride remaining unreacted in solution was removed by pouring the reaction mixture into MeOH in which the product, the methyl ester, is soluble.

2.2. Polymerization of macromonomer

Two types of catalysts [$Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(O^tBu)_2$ (catalyst A), and $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(OCMe(CF_3)_2)_2$ (catalyst B)] were chosen for the polymerization. The polymerization was performed in toluene, and the reaction was terminated by adding benzaldehyde (Scheme 2). The results are summarized in Table 3.

^1H NMR spectrum of the resultant polymer did not show signals (6.02–6.19 ppm) due to the olefinic proton of the norbornene skeleton (Fig. 1), indicating that the polymerization took place in the ring-opening fashion under these conditions. The disappearance of norbornene olefinic carbon was also seen in the ^{13}C NMR spectrum. In addition, the resultant polymer prepared by the catalyst B has an unimodal molecular weight distribution ($M_w/M_n = 1.19$ and 1.20), and the observed M_w value was in fair agreement with the calculated value [M_w of poly(**3**) times 10]. On the other hand, the polymer prepared by the catalyst A showed a



Scheme 2.

Table 3
Polymerization of macromonomer poly(**3**) (for reaction conditions, see Section 3)

Run	Poly(**3**)		Catalyst	Equiv.[a]	Polymacromonomer		Yield (%)
	M_w[b] ($\times 10^{-4}$)	M_w/M_n[b]			M_w[b] ($\times 10^{-4}$)	M_w/M_n[b]	
3	0.74	1.16	A	10	8.74	1.40	95
3	0.74	1.16	B	10	8.54	1.20	96
8	1.29	1.11	B	10	12.7	1.19	96

[a] Molar ratio of poly(**3**)/Mo.
[b] GPC in THF vs polystyrene standard.

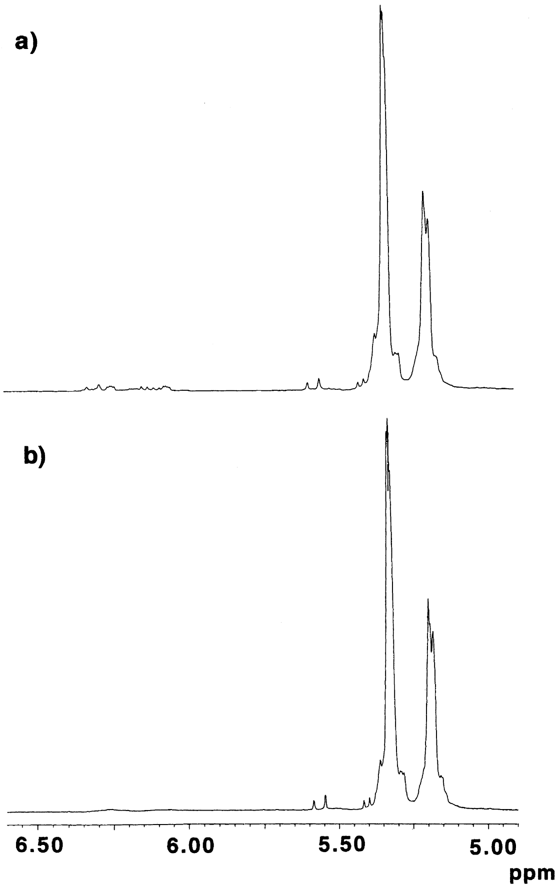


Fig. 1. ^{1}H NMR spectra of: (a) macromonomer poly(**3**); and (b) polymacromonomer ($CDCl_3$).

broad molecular weight distribution. It thus turned out that the catalyst B is a more suitable initiator for this polymerization than the catalyst A, affording the polymacromonomer in high conversion.[1] The difference observed between the catalyst A and B would be due to different propagation rates and different reactivities of molybdenum-alkylidene species.

We have shown that polymacromonomer can be prepared by ring-opening metathesis polymerization in a high yield. Since the present transition metal complex initiator is very useful for preparing block copolymers by using the nature of living ROMP [21], our next target on this project is to prepare various polymacromonomers carrying amphiphilic block copolymers in the side chain. In addition, since a wide variety of non-protic functionalities are tolerated by this initiator, the method presented here would introduce the possibility to prepare polymacromonomers containing various functions in the side chain.

3. Experimental section

3.1. General procedure

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. All chemicals used were reagent grade and were purified by the standard purification procedures. Polymerization grade toluene was distilled from sodium and benzophenone, stored over sodium/potassium alloy, and passed through alumina prior to use. Tetrahydrofuran (THF) for monomer synthesis was distilled from sodium and benzophenone under nitrogen atmosphere. All chemicals used were reagent grade and purified by the standard procedures. p-$Me_3SiOC_6H_4CHO$ was prepared by the reaction of p-hydroxybenzaldehyde with Me_3SiCl in THF containing NEt_3. $Me_3SiOC_6H_4CHO$ was then distilled in the presence of molecular sieves under nitrogen atmosphere, and was stored in the drybox at −30°C. Preparation of $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_4)(OCMe(CF_3)_2)_2$ and $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_4)(O^tBu)_2$ were according to the literature [22–24]. Norbornene carboxylic acid chloride was prepared according to the literature [25].

All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^{1}H; 100.40 MHz, ^{13}C), and all chemical shifts are given in ppm and are referenced to tetramethylsilane. Obvious multiplicities and routine coupling constants are usually not listed, and all

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[1] The polymerization by the catalyst B with the macromonomer similar to run 3 (poly(**3**), $M_w = 0.71 \times 10^4$) was also carried out under the same conditions (10 equiv.). M_w and M_w/M_n values for the resultant polymacromonomer were 6.88×10^4 and 1.11, respectively (95.7% yield). This result strongly indicates that the results presented here are reproducible.

spectra were obtained in the solvent indicated at 25°C unless otherwise noted. HPLC grade THF were used for GPC and were degassed prior to use. GPC were performed at 40°C on a Shimazu SCL-10A using a RID-10A detector (Shimazu Co. Ltd) in THF (containing 0.03 wt% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 ml/min). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm)∅ were calibrated vs polystyrene standard samples.

3.2. General procedure for the polymerization of macromonomer

*3.2.1. Synthesis of homopolymers [poly(**1**)]*

A toluene solution of Mo(CHCMe$_2$Ph)(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (80 μmol in toluene 1.0 g) was added in one portion to a rapidly stirred toluene solution (4.0 g) containing prescribed amount of norbornene at room temperature, and the reaction mixture was stirred for 30 min. The polymerization was quenched by *p*-Me$_3$SiOC$_6$H$_4$CHO in excess amount after the consumption of monomers, stirred for 1 h for completion. The resultant solution was poured dropwise to stirred cold methanol (~200 ml), affording white–pale yellow precipitates. The polymer was collected by filtration, and was then dried in vacuo. ^{1}H NMR (CDCl$_3$): δ 5.22 and 5.35 (br.m, 2H olefinic), 2.80 and 2.37 (br.s, 2H), 1.85 and 1.08 (m, 2H), 1.81 and 1.36 (m, 4H), and 0.26 (s, Si(C*H*$_3$)$_3$). Peaks corresponding to the polymer chain end could also be observed: δ 6.26 (d, PhC*H*=CH–), 6.04 (dd, PhCH=C*H*–), 5.56 (d, PhMe$_2$CC*H*=CH–), and 5.39 (m, PhMe$_2$CCH=C*H*–). Other resonances corresponding to phenyl group were also observed. ^{13}C NMR (CDCl$_3$): δ 134.0, 133.9, 133.8, 133.7, and 133.1, 133.0 and 132.8 (olefinic), 128.0, 126.9, 126.1, 125.5, and 120.1 (aromatic carbon), 68.0, 50.8, 43.4, 43.2, 42.7, 42.1, 41.3, 38.6, 38.4, 33.1, 32.9, 32.3, 32.2, 25.6, 21.3, and 0.2 [Si(*C*H$_3$)$_3$].

*3.2.2. Hydrolysis of poly(**1**)*

Poly(**1**) (368 mg) prepared by the above procedure was dissolved in a minimum amount of THF, and the solution was then poured into a mixed solution consisting of methanol (20 ml) and 5 N NaOH aqueous solution (5 ml) at room temperature. The reaction mixture was stirred overnight and the resultant precipitate was collected by filtration, washed with water and then dried in vacuo. The resultant precipitate was dissolved in minimum amount of THF, and then poured into cold methanol. ^{1}H NMR (CDCl$_3$): δ 5.32 and 5.19 (br.m, 2H olefinic), 2.77 and 2.41 (br.s, 2H), 1.854 and 1.05 (m, 2H), 1.75 and 1.33 (m, 4H). Peaks corresponding to the polymer chain end could also be observed.

3.2.3. Preparation of macromonomer

The deprotected polymer, poly(**2**), and NEt$_3$ (ca. 1.1 equiv. to the polymer) were dissolved in THF, and norbornene carboxylic acid chloride (1.5 equiv.) was then added dropwise. The reaction mixture was stirred for 2 h at room temperature, and was then refluxed for 5 h. After these procedures, the mixture was dropwise poured into a cold methanol solution. The resultant precipitate was collected by filtration, was then dried in vacuo. The prepared macromonomer was further purified by passing through alumina column (as a toluene solution) in the drybox until the polymerization results kept constant. ^{1}H NMR (CDCl$_3$): δ 6.32 and 6.07 (m, olefinic, norbornene), 5.37 and 5.18 (br.m, olefinic), 3.36–2.96 (m, norbornene non-olefinic), 2.78 and 2.41 (br.s), 1.85 and 1.03 (m), 1.77 and 1.34 (m). Other peaks corresponding to norbornene non-olefinic protons were covered with the polymer resonances, and peaks corresponding to the polymer chain end could also be observed. ^{13}C NMR (CDCl$_3$): δ 173.3 (C=O), 149.7 (phenoxy), 138.5, 138.3, 138.1, 135.7, 135.6 (norbornene olefinic), 133.9–134.1, 133.5, 133.3, 132.8–133.1, 131.2, 129.6, 128.1, 126.7–127.1, 126.3, 125.7, 121.6, 121.3 (olefinic and aromatic), 49.9, 46.9, 46.1, 43.5, 43.3, 42.9, 42.2, 41.5, 41.3, 40.2, 38.8, 38.5, 33.2, 33.1, 32.5, 32.3, 32.2, 29.1–29.5 (non-olefinic).

3.2.4. Polymerization of macromonomer

The typical example is as follows. The macromonomer (80 mg, 10 equiv. to the catalyst B) was dissolved in toluene (2.0 g), and the catalyst solution (toluene 0.5 g) was added in one portion at room temperature. The mixture was stirred for 30 min, and the polymerization was terminated by the addition of benzaldehyde. The solution was stirred for 1 h for completion, and the solution was poured into cold methanol to isolate the polymer as a white precipitate. Yield 96%. ^{1}H NMR (CDCl$_3$): δ 5.27 and 5.14 (br.m, 2H olefinic), 2.70 and 2.37 (br.s, 2H), 1.78 and 0.97 (m, 2H), 1.48 and 1.30 (m, 4H). ^{13}C NMR (CDCl$_3$): δ 167.3, 149.4, 144.0, 137.9, 133.5–133.8, 132.8–133.0, 131.4, 131.0, 130.0, 127.9, 126.0, 125.5, 42.8–43.4, 42.0–42.1, 41.4, 40.2, 38.7, 38.5, 38.4, 33.2, 33.0, 32.4, 32.3, 30.1, 29.1.

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