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Catalytic Synthesis of Polyethylene-*block*-Polynorbornene Copolymers Using a Living Polymerization Nickel Catalyst

Haiyang Gao*, Yong Liu, Guiliang Li, Zefan Xiao, Guodong Liang, and Qing Wu

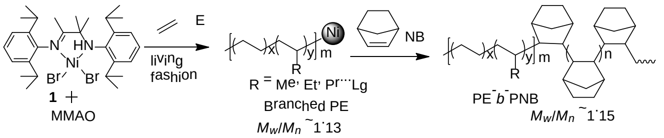
Polyethylene-*block*-polynorbornene (PE-*b*-PNB) copolymers were synthesized using an amine-imine nickel catalyst by sequential monomer addition in a living fashion. Norbornene homopolymerizations catalyzed by amine-imine nickel catalyst were firstly evaluated and the high-molecular-weight polynorbornenes (PNBs) with polydispersities of 1.9~3.0 were produced. Introduction of the PE building block can significantly slow down the insertion rate of norbornene monomer to afford low-molecular-weight PNB block. Well-defined PE-*b*-PNB block copolymers (M_w/M_n<1.16) were prepared by combination of living polymerization of ethylene for 15 min and sequential polymerization of norbornene. The block copolymer architecture was studied and confirmed by FT-IR, NMR, DSC, and transmission electron microscopy (TEM).

Introduction

Precise control over macromolecular structure including molecular weight, composition, and architecture of the polymer is a central goal in synthetic polymer chemistry. Copolymerization is an important process that usually allows the alteration of the macromolecular structure through adjustment of the ratio of individual components, and the obtained copolymers are expected to display unique material properties that have not been achieved by conventional homopolymers. New synthetic approaches for precise placement of the chemical functionality thus attract considerable attention, and transition metal catalyzed living polymerization is one of the best methods to prepare copolymers.[1] Recent advances in the design and synthesis of transition metal catalysts for olefin polymerization have resulted in the discovery and development of quite a few efficient and selective catalysts for living polymerizations of ethylene, α-olefin, and other olefins.[2] These catalysts have produced a wide array of living-polymerization-based polyolefins.[1a,3]

In comparison with poly(ethylene-*co*-α-olefin) copolymers, cyclic olefin copolymers (COC) consisting of a cyclic monomer such as norbornene (NB) and ethylene have received increasing interest over the past decade because they show good thermal properties, good chemical resistance, low water absorption, and excellent transparency.[4] These properties of COC can be tuned by comonomer composition, sequence distribution, and microstructure of copolymers.[5] Currently, poly(ethylene-*ran*-norbornene) random copolymers (NB incorporation >50 mol%) have been prepared by metallocene catalysts,[6] and poly(ethylene-*alt*-norbornene) alternating copolymers (NB incorporation <50 mol%) have also been synthesized by non-metallocene titanium,[7] α-diimine palladium catalysts,[8] and rare earth metal catalysts.[9] Several block copolymers consisted of polyethylene (PE) as crystalline segment and poly(ethylene-*alt*-norbornene) as amorphous segment have been synthesized by titanium based living systems.[10] To the best of our knowledge, no example of polyethylene-*block*-polynorbornene (PE-*b*-PNB) block copolymer is prepared to date though the block copolymer architecture is conventional. Main limitations for synthesis of well-defined PE-*b*-PNB block copolymer are rare transition metal based catalysts and vastly different monomer reactivities between ethylene and norbornene.[10,11] The current titanium and palladium based living systems of ethylene were reported to show practically no reactivity or very low catalytic activity toward NB homopolymerization,[7,8,10] synthesis of the PE-*b*-PNB block copolymer is thereby infeasible using these living systems. This prompted us to discover or develop new living systems from different metal centers point of view and this catalytic system is required to exhibit good activity toward norbornene.

Recently, a bulky amine-imine nickel catalyst precursor (**1** in Scheme 1) has been reported to afford the PE with narrow polydispersity (M_w/M_n < 1.10) in a living fashion in a wide temperature range.[12] It is known that nickel based catalysts are usually highly active for norbornene polymerization and can afford soluble polynorbornene (PNB) in aryl halide solvents.[4,13] Living polymerization nickel based catalyst seems to provide a viable access to precise synthesis of PE-*b*-PNB block copolymer.[14] In this contribution, PE-*b*-PNB block copolymers are first synthesized using an amine-imine nickel catalyst by sequential monomer addition in a living fashion (Scheme 1). Our study also discloses that PE block length has a decisive influence on chain propagation rate of sequential norbornene monomer, which provides an exciting opportunity for controlled incorporation of PNB block.



Scheme 1 Synthesis of PE-*b*-PNB block copolymer by sequential monomer addition.

Results and Discussion

By using sequential monomer addition in a living polymerization, PE-*b*-PNB block copolymers can be synthesized by two strategies. One is to synthesize well-defined PE block to incorporate norbornene monomer. The opposite approach is to precisely synthesize PNB block to incorporate ethylene. Firstly, norbornene polymerizations catalyzed by an amine-imine nickel complex **1** upon activation with MMAO were firstly evaluated.

Table 1 Norbornene homopolymerizations with an amine-imine nickel catalyst.

Run	Solvent	T_p (°C)	Al/Ni	Activity [a]	M_n [b]	PDI [b]
1	Tol	-20	200	97	386	1.97
2	Tol	-20	1000	141	374	1.99
3	Tol	20	200	78	148	2.65
4	CB	-40	200	44	492	2.62
5	CB	-20	200	328	586	1.97
6	CB	0	200	232	480	2.27
7	CB	20	200	192	212	2.92
8	CB	-20	100	65	601	1.50
9	CB	-20	500	563	548	2.36
10	CB	-20	1000	658	491	2.78

Polymerization conditions: addition of nickel complex: 10 μmol; cocatalyst: MMAO; norbornene addition: 2g; total volume: 20 mL; reaction time: t = 30 min for toluene and 10 min for chlorobenzene. [a] In units of kg PNB/(mol Ni h).[b] M_n (in unit of kg/mol) and M_w/M_n (PDI) were determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C.

Results of norbornene polymerizations in Table 1 demonstrate that nickel catalyst **1** exhibits a moderate activity toward norbornene polymerization in toluene (Tol). When toluene is replaced by chlorobenzene (CB) as the reaction medium for norbornene polymerization, the higher activity was achieved (runs 1 *vs* 5, 2 *vs* 10, 3 *vs* 7 in Table 1). This can be attributed to high polarity and good solubility of chlorobenzene for the obtained PNB. The norbornene polymerization results over the temperature range from -40 to 20 °C (runs 4-7) in chlorobenzene also show that the catalytic activity and molecular weight of the PNB reach the maximum values at -20 °C while molecular weight distribution (PDI) of the obtained PNB is the narrowest at -20 °C. When Al/Ni molar ratio increases from 100 to 1000 at a fixed temperature of -20 °C (runs 5, 8-10 in Table 1), catalytic activity increases but molecular weight of the obtained PNB with wide distribution reduces. Previous documents have addressed that β-H elimination cannot facilely undergo for norbornene addition polymerization because of special steric conditions of the *cis*-2,3-*exo* inserted norbornene.[10c,15] Broadened molecular weight distribution at high Al/Ni molar ratio should be a result of occurrence of chain transfer to aluminum cocatalyst.[13] Attempts to achieve living polymerization of norbornene with nickel catalyst **1** at very low Al/Ni molar ratio of 100 was unsuccessful (PDI = 1.5, run 8 in Table 1) from viewpoint of suppression of chain transfer to aluminum cocatalyst. This suggests that embedding of nickel species in the high-molecular-weight PNB probably occurs and broadens distribution of the polymer product. The norbornene polymerization using nickel catalyst **1** in the presence of ethylene was also performed, and low-molecular-weight polymer product (M_n = 6100, M_w/M_n = 2.19) possessing a vinyl end group, which is derived from a β-H transfer from the last-inserted ethylene unit, was produced (see Figure S3 in Supporting Information). This fact strongly indicates that ethylene plays a significant role of chain transfer agent for growing PNB chain.[15] On the basis of the behaviour of norbornene polymerization catalyzed by amine-imine nickel **1**, the first strategy is infeasible for synthesis of well-defined PE-*b*-PNB block copolymer.

Our previous study has addressed that living polymerization of ethylene can be achieved using amine-imine nickel catalyst **1**.[12] A great challenge is how to introduce well-defined PNB sequence using the second strategy for synthesis of PE-*b*-PNB block copolymer. The above results of norbornene homopolymerization suggest that the molecular weight distribution of the PNB can become narrow by lowering Al/Ni molar ratio and slowing down insertion rate of norbornene monomer to afford relative low-molecular-weight PNB. In theory, the molecular weight depends on the relation of chain growth to chain transfer and chain termination reactions. Usually, nickel catalysts can produce high-molecular-weight PNBs in short time with an extremely rapid chain propagation rate.[4,13] Therefore, a crucial issue is how to slow down insertion rate of norbornene for yielding relative low-molecular-weight PNB. Our previous study on copolymerizations of norbornene and styrene indicates that presence of styrene unit in propagation chain can obviously slow down insertion rate of norbornene, which seems to provide a viable access to reducing propagation rate of norbornene.[16] It can be anticipated that PE block can also slow down insertion rate of norbornene to afford relative low-molecular-weight PNB with a narrow distribution.

The influence of PE block length on insertion rate of sequential norbornene was herein studied. PE blocks with various molecular weights were prepared by changing polymerization time in chlorobenzene under the conditions of -20 °C and low Al/Ni molar ratio of 200. As expected, narrowly dispersed PEs (M_w/M_n <1.15) were also obtained in chlorobenzene (runs 1-4 in Table 2). When the ethylene polymerization was carried out for the desired time, ethylene gas was removed and then norbornene monomer was introduced. PE-*b*-PNB block copolymers were obtained after 15 min of sequential norbornene polymerization.

Comparison of polymerization results in entries 1-3 in Table 2 clearly demonstrates that PE block length has a decisive influence on sequential PNB block length and long PE block significantly reduces sequential PNB block length (PE-*b*-PNB: 12.1-125.9 *vs* 23.3-19.9 *vs* 45.2-1.6 kg/mol). The turnover frequency (TOF) values, which are calculated by the molar equivalents of monomer polymerized per molar equivalent of Ni per minute, also suggest that chain propagation rate of sequential PNB block is significantly retarded by PE sequence. This observation is contrast to a traditional chain end control mechanism for polymer propagation. The reasonable explanation is that coordination and insertion of bulky and strained norbornene monomer on nickel center is retarded by flexible PE block because nickel center is usually surrounded by coil PE chain in solution. The molecular weight distributions of the obtained PE-*b*-PNB block copolymers relative to the PNB homopolymers become narrow. PE-*b*-PNB block copolymers with narrow molecular weight distribution of ~1.15 were also successfully synthesized when molecular weight of PE block sequence is large enough (> 23.3 kg/mol). However, too long PE block leads to difficult incorporation of PNB sequence. Therefore, the PE block with M_n of 23.3 kg/mol obtained at 15 min living polymerization of ethylene was used to synthesize well-defined PE-*b*-PNB block copolymers with different PNB block sequence lengths. Polymerization results (runs 2, 5-7 in Table 2) show that the molecular weight of block copolymer increases with prolonging reaction time. GPC traces of the polymers shown in Figure 1 are symmetric without any tail or shoulder peaks in low-molecular-weight region and PDI values are below 1.16, suggesting occurrence of chain-extension reaction by a living fashion. To the best of our knowledge, it is the first report on synthesis of well-defined PE-*b*-PNB block copolymer. Our study reports the initial synthesis of PE-*b*-PNB diblock copolymers using an approach of slowing down propagation rate of sequential PNB by retard of PE block, which may open a way for synthesis of various PNB block copolymers by transition metal catalyzed living polymerization.

Table 2 Norbornene homopolymerizations with an amine-imine nickel catalyst

Run	t_E (min)	PE		t_{NB} (min)	Yield (g)	PE-*b*-PNB		TOF of NB[c]
		M_n[a]	PDI[a]			M_n[b]	PDI[b]	
1	8	12.1	1.08	15	0.366	138	1.63	21560
2	15	23.3	1.13	15	0.251	43.2	1.16	8439
3	30	45.2	1.15	15	0.325	46.8	1.15	5460
4	15	23.3	1.13	0	0.132	-	-	-
5	15	23.3	1.13	5	0.176	29.4	1.14	9362
6	15	23.3	1.13	10	0.219	38.8	1.15	9255
7	15	23.3	1.13	20	0.276	49.2	1.16	7659

Polymerization conditions: addition of nickel complex: 10 μmol; temperature: -20 °C; Al(MMAO)/Ni = 200; ethylene pressure: 1.2 atm; solvent: chlorobenzene; total volume: 20 mL; When the ethylene polymerization was carried out for the desired time, ethylene gas was removed and then 1g of norbornene in 2.5 mL chlorobenzene was introduced. [a] M_n (in unit of kg/mol) and M_w/M_n were determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C. [c] Turnover frequency (TOF) (in unit of mol NB/(mol Ni min)), which was calculated by the molar equivalents of monomer polymerized per molar equivalent of Ni per minute.

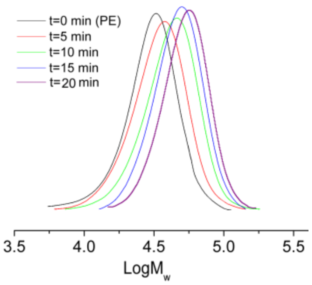


Figure 1 GPC traces of PE and PE-*b*-PNB block copolymers.

The obtained copolymer was characterized to elucidate the microstructure, and the spectra of each homopolymer were also shown for comparison. Figure 2 shows FT-IR spectra of the PNB (run 5 in Table 1), PE (run 4 in Table 2), and PE-*b*-PNB (run 2 in Table 2) block copolymer. FT-IR spectrum of PNB revealed no traces of double bond, which often appear at 1680-1620, 966, and 735 cm^{-1}, while the existence of a vibration band of bicyclics of norbornene at 941 cm^{-1}.[13] This proves that the obtained PNB is addition polymerization product. The characteristic vibration band of bicyclics is also observed in FT-IR spectrum of PE-*b*-PNB copolymer, ensuring the incorporation of norbornene in the copolymer. ^{13}C NMR analysis was further conducted to have an insight into microstructure of the polymers. ^{13}C NMR spectrum of the PNB obtained by amine-imine nickel catalyst **1** is nearly same to that produced by the previously reported nickel based catalysts.[4,13] The resonances of methenes and methines appear at 29.4~33.0 ppm for C5 and C6, 35.5~38.5 ppm for C7, 38.8~42.8 ppm for C1 and C4, and 46.1~54.0 ppm for C2 and C3 (Figure 3). The distribution of the stereotriad sequences of the PNB is determined from the C1 and C4 regions (mm at 38.8 ppm, mr at 39.8 ppm, and rr at 41.4 ppm) to be [mm] =59.6%, [mr]= 32.4%, and [rr]=8.0%. The PE obtained at -20 °C is branched polymer containing dominant methyl branch (39/1000C) (see Table S1 in Supporting Information). In the spectrum of the copolymer, all resonances of the PE and PNB homopolymer clearly appear, which is distinct from the previous spectra of the poly(ethylene-*ran*-norbornene)[6] and poly(ethylene-*alt*-norbornene) copolymers (see Table S2 in Supporting Information).[7-9] It is safely concluded that the copolymer is block architecture on the basis of ^{13}C NMR assignments and unimodal GPC results.

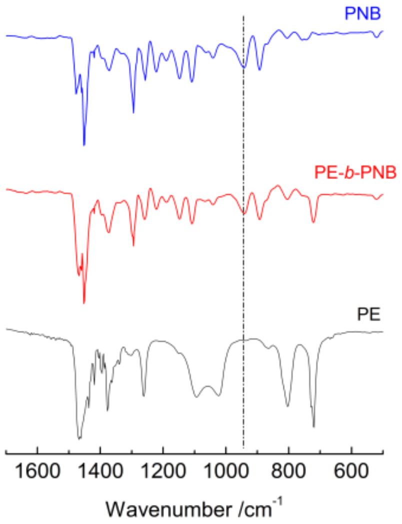


Figure 2 FT-IR spectra of the PNB, PE, and PE-*b*-PNB block copolymer.

More supports come from differential scanning calorimetry (DSC) analysis and wide-angle X-ray diffraction (WAXD) analysis of polymer samples. In the DSC curves (Figure 4), the semicrystallized PE displays broad melting endotherms at peak point of 89 °C while the amorphous PNB cannot exhibit any obvious endothermic signals upon heating to the decomposition temperature (450 °C). Similar melting endotherms are also observed for the PE-*b*-PNB copolymer whereas the intensity of melting peak decreases. The WAXD spectrum (Figure S5) of the PE-*b*-PNB copolymer is a simple superposition of the spectra of PE and PNB homopolymers, and characteristic peaks for the PE (2θ = 21.3°) and PNB (2θ = 9-11 and 17-19°) are observed, respectively.

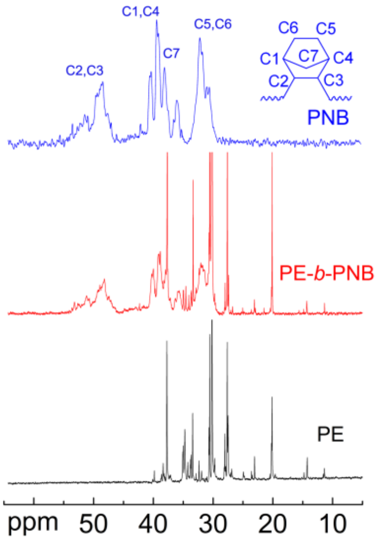


Figure 3 ^{13}C NMR spectra of the PNB, PE, and PE-*b*-PNB block copolymer.

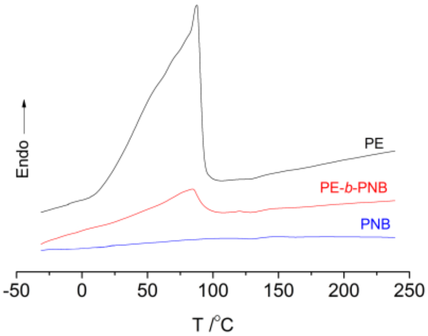


Figure 4 DSC curves of the PNB, PE, and PE-*b*-PNB block copolymer.

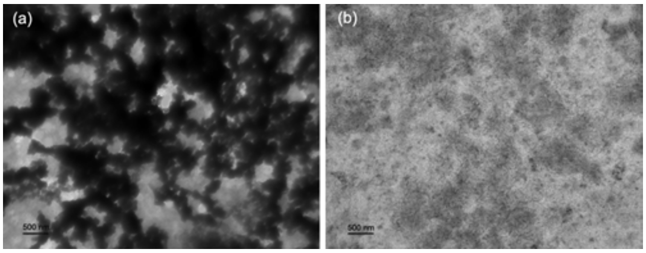


Figure 5 SEM micrographs of (a) PE/PNB blend polymer and (b) PE-*b*-PNB block copolymer stained with RuO_4.

Further information about the PE-*b*-PNB block copolymer is given by transmission electron microscopy (TEM). The TEM micrograph of the PE/PNB blend polymer (Figure 5a) shows obvious phase separation including black PE phase and gray PNB phase,[17] while conversely that of the PE-*b*-PNB (Figure 5b) displays considerable homogeneous structures. These results further confirm the formation of the desired block copolymer.

Conclusions

In summary, we report the initial synthesis and characterization of well-defined PE-*b*-PNB diblock copolymer using a living polymerization nickel catalyst by sequential monomer addition.

The achievement of the highly controlled copolymerization of ethylene and norbornene further expands the application of amine-imine nickel living system. The strategy we herein presented, slowing down chain propagation rate of sequential PNB by retard of the former PE building block, which may open a way for synthesis of various PNB block copolymers by transition metal catalyzed living polymerization. This novel block copolymer may be used to a broad spectrum of applications including compatibilizers, elastomers, and composite materials.

Experimental section

General Procedures

All manipulations involving air- and moisture sensitive compounds were carried out under an atmosphere of dried and purified nitrogen with standard vacuum-line, Schlenk, or glovebox techniques.

Materials

Toluene and hexane were dried over sodium metal and distilled under nitrogen. Dichloromethane and chlorobenzene was dried and distilled from calcium hydride. MMAO (7 wt. % Al in heptane) was purchased from Akzo-Nobel and used as received. Ethylene (99.99%) was purified by passing through Agilent moisture and oxygen traps. Norbornene (bicyclo-[2.2.1]hept-2-ene; Acros) was purified by distillation over potassium and used as a solution. Other commercially available reagents were purchased and used without purification. A amine-imine nickel complex **1** $Ar\text{-}N{=}C(Me)\text{-}(Me)_2C\text{-}NH\text{-}ArNiBr_2$ (Ar = 2,6-diisopropylphenyl)was prepared according to the reported methods.[12]

Measurements

^1H NMR and ^{13}C NMR spectra of the polymers in *o*-dichlorobenzene-d_4 were recorded on a Bruker 500 MHz spectrometer at 120 °C. GPC analyses of the molecular weight and molecular weight distribution (PDI) of the polymers were performed on a PL-GPC 220 instrument with standard polystyrene as the reference and with 1,2,4-trichlorobenzene (TCB) as the eluent at 150 °C. FT-IR spectra were recorded on a Nicolet Nexus 670 FTIR spectrometer. Differential scanning calorimetry (DSC) analysis was conducted with a Perkin-Elmer DCS-7 system. The DSC curve was recorded at a heating rate of 10 °C/min. The cooling rate was 10 °C/min. Wide-angle X-ray diffraction (WAXD) curve of the polymer powder was obtained using a D/Max-IIIA powder X-ray diffracrometer. The morphological observations of the copolymer and blend polymer were performed on a transmission electron microscope (TEM) (Philips TECNAI) with an accelerating voltage of 120 kV. The specimens were obtained by frozen-section with a diamond knife at low temperature and stained with RuO_4.[17]

Typical ethylene polymerization procedure

In a typical procedure, a round-bottom Schlenk flask with stirring bar was heated to 150 °C under vacuum for 3 h and then cooled to room temperature. The flask was pressurized to 1.2 atm of ethylene and vented three times. The appropriate MMAO solution was introduced into the glass reactor. The system was maintained by continuously stirring for 5 min, and then chlorobenzene and 2 mL solution of nickel complex were syringed into the well-stirred solution in order, and the total reaction volume was kept at 20 mL. The ethylene pressure was kept constant value of 1.2 atm by continuous feeding of gaseous ethylene throughout the reaction. The reaction temperature of -20 °C was maintained with a cooler in polymerization experiments. The polymerizations were terminated by the addition of 200 mL of acidic methanol (95:5 ethanol/HCl) after continuously stirring for an appropriate period. The resulting precipitated polymers were collected and treated by filtration, washing with methanol several times, and drying in vacuum at 40 °C to a constant weight.

Typical norbornene polymerization procedure

In a typical procedure, the appropriate MMAO solution was introduced into a chlorobenzene solution of norbornene in a 50 mL round-bottom glass flask. Chlorobenzene and nickel complex solution were syringed into the well-stirred solution in order, and the total reaction volume kept 20 mL. The reaction was continuously stirred for an appropriate period at polymerization temperature. Polymerizations were terminated by addition of the acidic methanol (methanol-HCl, 95:5). The resulting precipitated polymers were collected and treated by filtering, washing with methanol several times, and drying in vacuum at 40 °C to a constant weight.

Synthesis of PE-*b*-PNB block copolymer

A round-bottom Schlenk flask with stirring bar was heated to 150 °C under vacuum for 3 h and then cooled to room temperature in a typical procedure. The flask was pressurized to 1.2 atm of ethylene and vented three times. The appropriate MMAO solution was introduced into the glass reactor. The system was maintained by continuously stirring for 5 minutes at -20 °C, and then chlorobenzene and 2 mL solution of nickel complex were syringed into the well-stirred solution in order, and the total reaction volume was kept at 20 mL. The ethylene pressure was kept constant value of 1.2 atm. After ethylene polymerization of the desired time, the ethylene feed was stopped, and ethylene gas was removed under vacuum and the reaction flask was charged with N_2. Then norbornene solution was introduced and sequential norbornene polymerization was carried out at -20 °C. The polymerization was terminated by the addition of 200 mL of acidic methanol (95:5 ethanol/HCl) after continuously stirring for an appropriate period. The resulting precipitated polymer was collected and treated by filtration, washing with methanol several times, and drying in vacuum at 40 °C to a constant weight.

Preparation of PE/PNB blend sample for TEM measurement

A mixture of PE (46.6 mg, entry 4 in Table 2), PNB polymer (31.0 mg, entry 5 in Table 1) and chlorobenzene (40 mL) was stirred well under nitrogen at room temperature for 5 minutes. The mixture was heated at reflux temperature for 1 h with stirring. The resulting solution was poured into methanol (200 mL) at room temperature. The precipitated polymer was collected by filtration, washed with methanol several times, and dried in vacuum at 40 °C to a constant weight.

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DSAPM Lab, PCFM Lab, Institute of Polymer Science, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China. E-mail: gaohy@mail.sysu.edu.cn; Fax: 86-20-84114033; Tel: 86-20-84113250.

† Electronic Supplementary Information (ESI) available: [Detailed experimental procedures, NMR characterization and assignment of polymers.]. See DOI: 10.1039/b000000x/.

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