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Structural Confirmation of *Exo*-Olefin-Coupled Polyisobutylene *via* Model Compound Synthesis and Characterization

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We report the synthesis and characterization of a model compound representing *exo*-olefin coupled polyisobutylene (PIB). Under certain conditions during the *in situ* quenching of quasiliving PIB with hindered bases to yield *exo*-olefin-terminated PIB, remaining PIB carbocations can undergo addition to *exo*-olefin PIB to yield coupled PIB with a molecular weight approximately double that of the primary chains. Characterization of the signals that arise in ^{1}H-NMR from the presence of coupled product has not yet been properly performed; the accurate chemical shifts of these products, specifically the *exo*-olefin product, have been in debate recently. Therefore, we carried out the synthesis of a model compound which mimics the *exo*-olefin coupled product, and through variations in the synthetic method were able to produce a range of *exo*- and *endo*-olefin coupled product mixtures. The model compounds have been fully characterized using NMR techniques, and we herein conclusively report the proton shift (for 500 MHz ^{1}H-NMR in $CDCl_3$) of 4.82 ppm for the *exo*-coupled product and that of 5.11 ppm for the *endo*-coupled product.

Keywords: polyisobutylene; exo-olefin-terminated polyisobutylene; coupled polyisobutylene; exo-olefin coupled polyisobutylene

1 Introduction

We recently reported the *in situ* quenching of quasiliving cationic polymerization of isobutylene with hindered bases to yield *exo*-olefin (methyl vinylidene)-terminated polyisobutylene (PIB) (1, 2). Under certain reaction conditions, notably when quenching is relatively slow, we observed that remaining PIB carbocations can undergo addition to *exo*-olefin PIB to yield a coupled species, *exo*-olefin-coupled PIB (Scheme 1) with a molecular weight approximately double that of the primary chains. Coupling of PIB has also been observed by others. Ivan et al. (3) reported a minor fraction of coupled products when quasiliving PIB was quenched with methallyltrimethylsilane (MATMS) to yield *exo*-olefin PIB. Ivan et al. (4) also reported coupling in $TiCl_4$-co-initiated isobutylene (IB) polymerizations that were reacted for long times in the presence of proton trap, 2,6-di-*tert*-butylpyridine (DTBP), and they concluded that DTBP was creating *exo*-olefin by β-proton abstraction at the PIB carbocation. Bae and Faust (5) also observed coupling with DTBP, but these authors attributed β-proton abstraction to a hindered-base impurity contained within the DTBP. Storey et al. (6) reported coupling of PIB caused by olefin formation at relatively high temperatures (−40°C).

The presence of coupled PIB is easily revealed by GPC. It can also be detected by ^{1}H-NMR spectroscopy; however, positive assignment of the signals that arise in ^{1}H-NMR due to coupling has been complicated due to the fact that coupling is often accompanied by other anomalous chain-end structures. Figure 1 shows PIB with a mixed chain-end composition including some coupled product. In a previous paper, we assigned the vinylidene protons of the coupled product to the signal (f) that appears at 4.82 ppm; however, both concurring (7) and conflicting (4) signal assignments have appeared in the literature. In an effort to fully understand and characterize the *in situ* quenching reaction products, we report in this work the synthesis of model compounds that mimic coupled PIB (Scheme 2). The model compounds have been fully characterized using NMR techniques, and this work conclusively shows the proper NMR assignments for the coupled PIB products.

2 Experimental

2.1 Materials

2,5-Dimethylpyrrole (2,5-DMP, 98%), methanol (MeOH, 99+%), hexane (95%, anhydrous), and titanium tetrachloride ($TiCl_4$, 99.9%, packaged in SureSeal bottles under nitrogen) were purchased and used as received from Sigma-Aldrich Co. Ammonia (Sigma-Aldrich Co., 2 M in methanol) was

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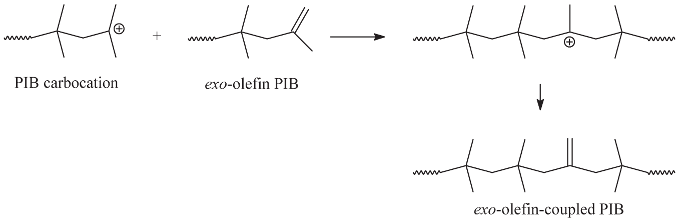


Sch. 1. *Exo*-olefin-coupled PIB formed by the addition of PIB carbocation to *exo*-olefin-terminated PIB.

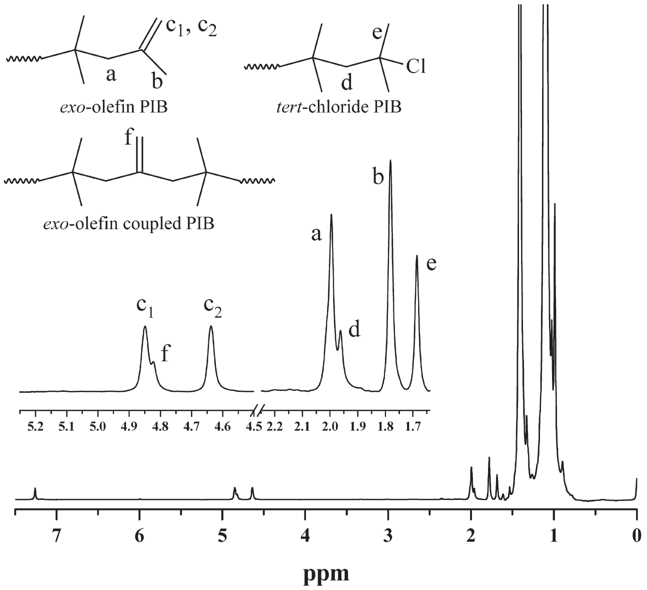


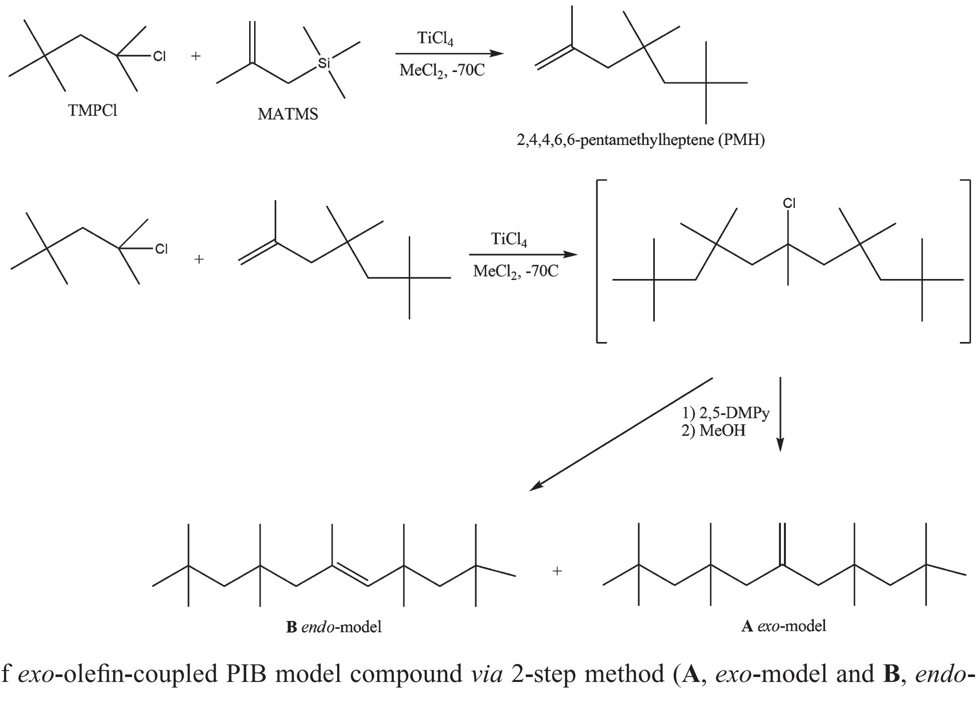
Fig. 1. ^{1}H-NMR spectrum of quenched PIB showing mixed products (*tert*-chloride, *exo*-olefin, and *endo*-olefin, and *exo*-olefin-coupled PIB). Figure adapted from Simison et al. (1).

diluted with an equal volume of de-ionized water prior to use. Celite 545®, diatomaceous Earth, was purchased and used as received from Fisher Chemicals. 2-Methylpropenyltrimethylsilane (methallyltrimethylsilane, MATMS) was purchased and used as received from Gelest, Inc. Isobutylene (IB) and methyl chloride (MeCl) (both BOC gases) were dried with $CaSO_4$ and $CaSO_4$/molecular sieves, respectively, and were then condensed at the specified reaction temperature immediately prior to use. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was synthesized as described previously (8).

2 Instrumentation

Solution NMR spectra were obtained using 5 mm o.d. tubes on a Varian Unity (500 MHz) or a Bruker AC-300 (300 Hz) spectrometer at 25°C. All solutions were at a concentration of 10% (w/w) in deuterated chloroform ($CDCl_3$) (Aldrich Chemical Co.) containing tetramethylsilane as an internal reference. Chemical shifts were referenced from the solvent resonance signals (^{1}H 7.26 and ^{13}C 77.0). All spectra were processed using Varian 6.0 software. All 1D and 2D-NMR technique parameters were set according to the standard Varian ChemPack macros, with modifications listed accordingly. ^{1}H-spin-lattice relaxation times (T_1) were determined using an inversion-recovery pulse sequence ($180°-\tau-90°$) with a delay of 20 sec between scans.

A ^{13}C-NMR spectrum using the Attached Proton Test (APT) technique was obtained in order to differentiate between C, CH, CH_2, and CH_3 groups. The pulse sequence parameters were set to a delay time of 4.0 sec with a 1st pulse of 45° and a 2nd pulse consisting of a composite 180° (45–90–45) and an acquisition time of 1.3 sec.



Sch. 2. Synthesis of *exo*-olefin-coupled PIB model compound *via* 2-step method (**A**, *exo*-model and **B**, *endo*-model).

Heteronuclear Single Quantum Coherence Spectroscopy (HSQC) experiments were performed using a delay time of $5 \times T_1$, obtaining 200 increments and 16 scans per increment, within spectral widths of 7530 and 3988 Hz and operating at 125.7 and 499.7 MHz in the ^{13}C and ^{1}H domains, respectively.

2.1 *Synthesis of 2,4,4,6,6-Pentamethylheptene (PMH)*

PMH was synthesized by reacting TMPCl with methallyltrimethylsilane (MATMS) within a dry N_2 atmosphere glovebox as shown in Scheme 2. A typical procedure, adapted from Roth and Mayr, (9) was as follows: to a 500 mL three-neck round bottom flask equipped with a mechanical stirrer and submerged within a −70°C bath were added 3.0 g (0.020 mole) TMPCl and 300 mL methylene chloride ($MeCl_2$). MATMS (7.7 g, 0.060 mole) was then added to the flask, and the resulting homogeneous solution was activated by the addition of 0.55 mL (5.0×10^{-3} mole) $TiCl_4$ in 20 mL $MeCl_2$. The mixture was allowed to react for approximately 5 h and then removed from the glovebox and allowed to warm to room temperature in a fume hood. Ammonia (60 mL of 1 N solution in 50/50, v/v, methanol/water) was added, and the reaction mixture was filtered over Celite. The aqueous layer was extracted with $MeCl_2$, and the combined extracts were dried over $MgSO_4$. The $MgSO_4$ was removed by filtration and the crude PMH isolated by rotary evaporation. A small portion of the crude PMH was distilled via bulb to bulb distillation using a Kugelrohr glassware oven (BÜCHI Labortechnik AG, Switzerland) under vacuum (17 mmHg) at 85°C oven temperature.

2.2 *Synthesis of 2,2,4,4,8,8,10,10-Octamethyl-6-methyleneundecane (Exo-Model) from PMH*

A 250 mL four-neck round-bottom flask, equipped with an overhead mechanical stirrer, was submerged in a –70°C constant-temperature hexane/heptane bath contained within a dry N_2 atmosphere glove box. $MeCl_2$ (250 mL) was charged to the flask and allowed to achieve thermal equilibrium. Next, 1.06 g PMH (6.3×10^{-3} mol) and 0.94 g TMPCl (6.3×10^{-3} mol) were added, and the system was activated with 0.55 mL $TiCl_4$ (5.0×10^{-3} mol) in 20 mL $MeCl_2$. The reaction was allowed to proceed for 5 min and then quenched with 1.05 mL 2,5-DMPy (1.0×10^{-2} mol). The reaction was then allowed to run for an additional 50 min, at which time it was terminated with an excess of MeOH (~5 mL). The volatiles from the reaction mixture were allowed to evaporate overnight in a fume hood. The product that remained was diluted with hexane and washed several times each with methanol, 0.1 N aqueous HCl, and deionized water. The hexane phase was then dried by stirring overnight with $MgSO_4$; the $MgSO_4$ was then removed by filtration, and the hexane was removed by rotary vacuum. The final product was analyzed by NMR spectroscopy.

2.3 *Synthesis of Exo-Model in One Step*

A representative synthesis was as follows: to a 250 mL round bottomed flask contained within a dry N_2 atmosphere glove box were charged 100.8 mL hexane, 67.2 mL MeCl, 20.0 mL TMPCl (1.2×10^{-1} mol), and 10.0 mL MATMS (5.7×10^{-2} mol). The mixture was allowed to stir and reach thermal equilibrium at –60°C, at which time reaction was initiated by addition of 1.91 mL $TiCl_4$ (neat and at room temp). After 3 min, 8.4 mL 2,5-DMPy (8.3×10^{-2} mol) was added to begin the quenching reaction. Aliquots were taken periodically during the course of the quenching reaction, and after 22 min total quenching time, excess prechilled MeOH was added to terminate the reaction. The volatiles from the reaction mixture were allowed to evaporate overnight in a fume hood, and the subsequent product isolation procedure was identical to that used for the two-step procedure.

2.4 *Synthesis of Exo-Model in One Step with Quencher Present at Initiation*

A representative synthesis was as follows: to a 250 mL round bottomed flask contained within a dry N_2 atmosphere glove box were charged 50.4 mL hexane, 33.6 mL MeCl, 10.0 mL TMPCl (5.9×10^{-2} mol), 5.0 mL MATMS (2.8×10^{-2} mol), and 4.2 mL 2,5-DMP (4.1×10^{-2} mol). The mixture was allowed to stir and reach thermal equilibrium at −60°C, at which time reaction was initiated by addition of 0.48 mL $TiCl_4$ (4.4×10^{-3} mol, neat and at room temp). Aliquots were taken periodically throughout the duration of the reaction, and after 30 min total reaction time, excess prechilled MeOH was added to terminate the reaction. The volatiles from the reaction mixture were allowed to evaporate overnight in a fume hood, and the subsequent product isolation procedure was identical to that used for the two-step procedure.

3 Results and Discussion

3.1 *Synthesis of PMH*

The PMH synthesis reaction was successful with a crude yield of 99.3%. A small portion of the crude PMH was distilled via bulb-to-bulb distillation using a Kugelrohr glassware oven; the ^{1}H-NMR spectrum of the purified product is shown in Figure 2.

3.2 *Synthesis of Exo-Model from PMH*

In the second step, PMH was reacted with TMPCl as shown in Scheme 2, to yield the coupled PIB model. The crude reaction product (86.5% yield) revealed only two signals in the olefinic region of the ^{1}H-NMR spectrum (Figure 3). The upfield signal at 4.82 ppm was assigned to the two identical protons of the vinylidene group in structure A (Scheme 2). The downfield signal at

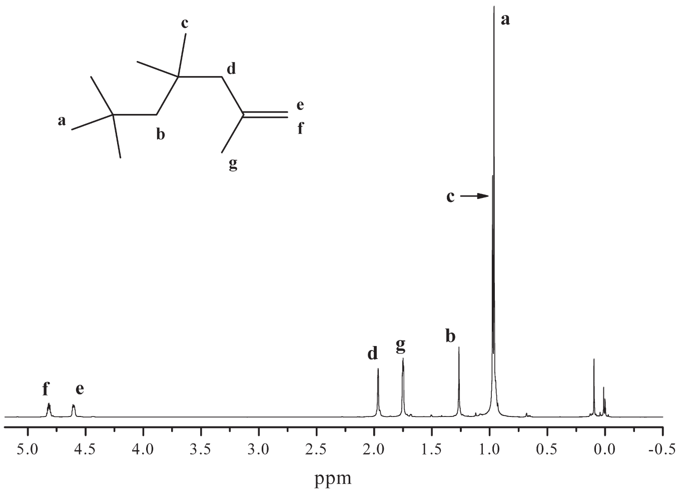


Fig. 2. ^{1}H-NMR spectrum of final PMH after purification by distillation.

5.11 ppm was assigned to the single proton of the trisubstituted olefin in structure B. Regarding the latter, apparently only one of two possible geometrical isomers is formed, but we cannot specify whether it is the *cis* or *trans* isomer based on the available data. Integration revealed that the isomer molar ratio A/B was approximately 1/2. An unsuccessful attempt was made to separate the two isomers using bulb-to-bulb distillation; apparently the two isomers have nearly identical boiling points. Several reaction parameters such as quencher addition time, quencher amount, and $TiCl_4$ concentration were adjusted in an attempt to increase the proportion of the *exo*-model, but these were unsuccessful.

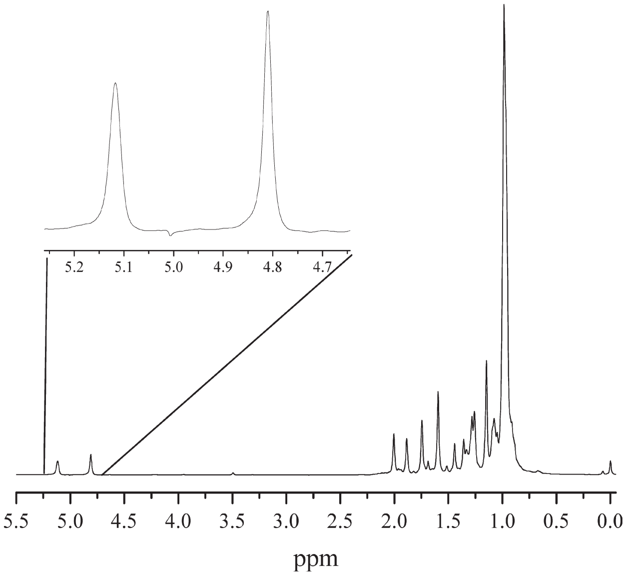


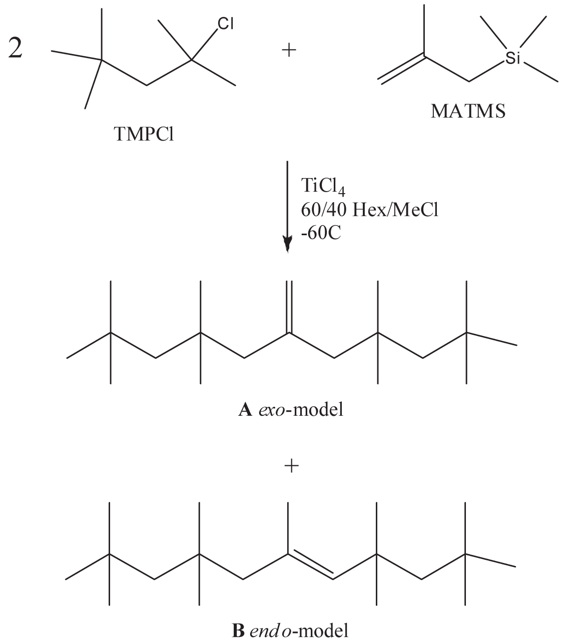
Fig. 3. ^{1}H-NMR spectrum of mixed *exo*- and *endo*-models produced from PMH.

3.3 Synthesis of Exo-Model in One Step

It occurred to us that synthesis of the coupled model compound could be simplified by utilizing a one-step reaction in which PMH was generated *in situ* (Scheme 3). This proved to be a viable approach, and the mixed isomers were obtained in 61.5% yield after purification by distillation. Once again, distillation was ineffective at separating the two isomers. In addition to being easier, the one-step synthesis had the unanticipated effect of yielding a higher proportion of the *exo*-model (57 mol%, molar ratio $A/B = 1.33$) and a cleaner crude product prior to distillation. Figure 4 shows the ^{1}H-NMR spectrum of the purified product, demonstrating the higher fraction of *exo*-model.

3.4 Synthesis of Exo-Model in One Step with Quencher Present at Initiation

Although the one-step, *in situ* procedure yielded a higher fraction of the *exo*-model, we remained interested in isolating the *exo*-model as a pure compound to facilitate structural characterization. We reasoned that an earlier introduction of the 2,5-DMP quencher would increase the proportion of the *exo*-model. We understood that the overall yield of the reaction might be significantly reduced since the quencher would also tend to cause elimination of TMPCl cation to its respective *exo*-olefin. With this in mind, we simply introduced the quencher to the reaction mixture prior to initiation with $TiCl_4$. Indeed, the yield for this reaction was quite low (crude product yield = 10.9%); however, the proportion of *exo*-model in the crude product mixture was approximately 85 mol% as seen in Figure 5. The data in Figure 5 were



Sch. 3. Synthesis of *exo*-model *via* one step reaction.

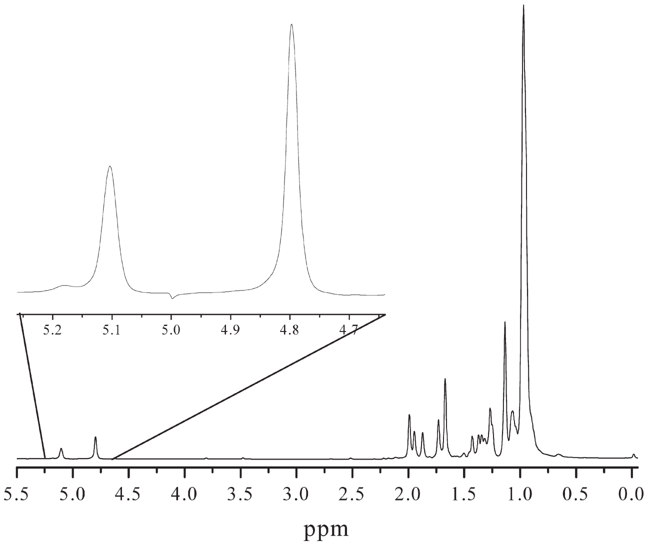


Fig. 4. ^{1}H-NMR spectrum of mixed *exo*- and *endo*-models synthesized using the one-step synthesis (Scheme 3).

useful in distinguishing the signals due to the *exo*- vs. the *endo*-model in the aliphatic region of the ^{1}H-NMR spectrum of the mixed isomers.

3.5 Structural Elucidation of Endo- and Exo-Model Compounds

A sample of mixed isomer models was prepared using the one-step method, with the quencher added after co-initiation with $TiCl_4$. This sample was purified using bulb-to-bulb distillation and subjected to detailed NMR analysis. The ^{1}H and ^{13}C-NMR spectra of the mixed isomer models (molar ratio 0.95:1, *exo*:*endo*) with peak assignments are depicted in Figures 6a and 6b, respectively.

To substantiate the assignments of the proton and carbon resonances as illustrated in Figures 6a and 6b, HSQC was utilized as shown in Figures 7 (olefinic region) and 8 (aliphatic region). HSQC provides critical information regarding ^{1}H-^{13}C connectivity and proton multiplicities (even or odd number of protons on a given carbon). The multiplicities are identified by (+) and (−) on the HSQC spectra and represent CH or CH_3 (+) and CH_2 (−). As indicated in Figure 7, the *exo*-model proton resonance (H_e) is connected to the carbon resonance C_1 and the *endo*-model proton resonance (H_g) is connected to the carbon resonance C_9. Multiplicity

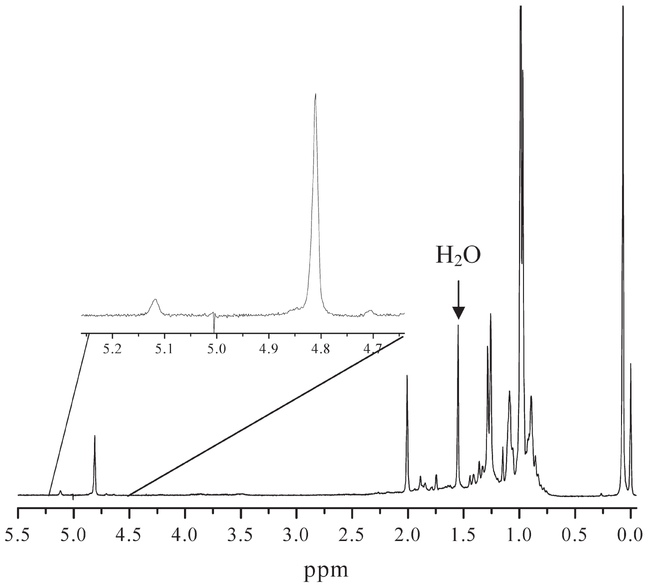
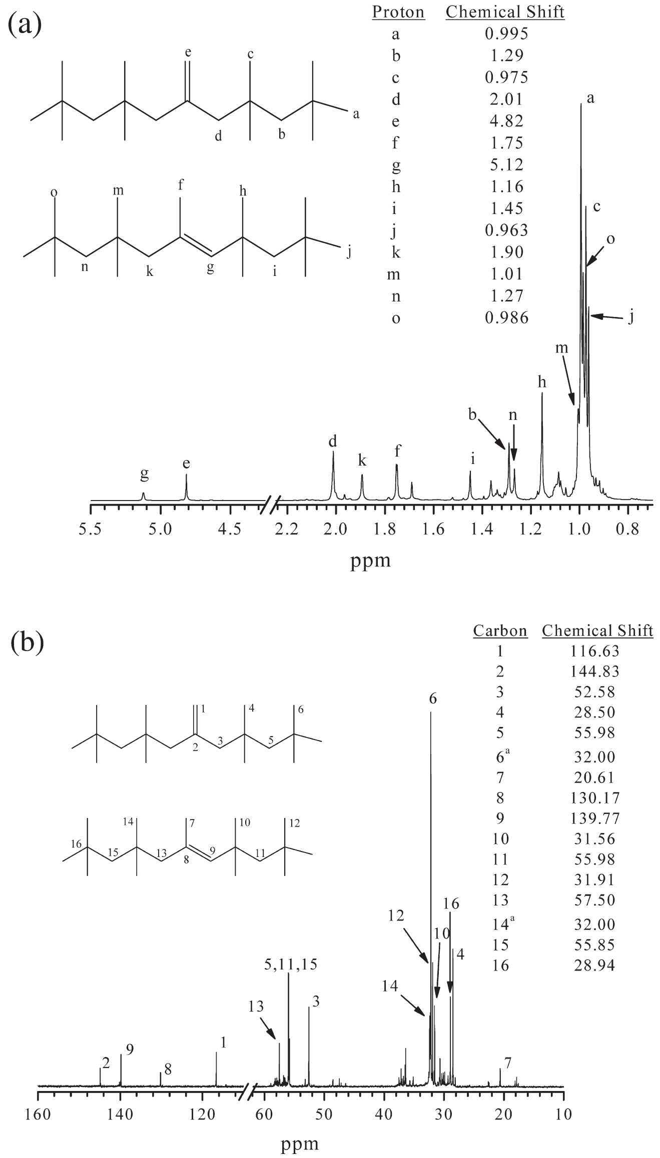


Fig. 5. ^{1}H-NMR spectrum of products from one-step synthesis with quencher present at initiation.



Proton	Chemical Shift
a	0.995
b	1.29
c	0.975
d	2.01
e	4.82
f	1.75
g	5.12
h	1.16
i	1.45
j	0.963
k	1.90
m	1.01
n	1.27
o	0.986

Carbon	Chemical Shift
1	116.63
2	144.83
3	52.58
4	28.50
5	55.98
6[a]	32.00
7	20.61
8	130.17
9	139.77
10	31.56
11	55.98
12	31.91
13	57.50
14[a]	32.00
15	55.85
16	28.94

Fig. 6. (a) ^{1}H-NMR spectrum of mixed *exo*- and *endo*-model compounds. (b) ^{13}C-NMR spectrum of *exo*- and *endo*-model compounds. [a]Carbons centered at 32.00 ppm cannot be fully resolved with a 500 MHz spectrometer.

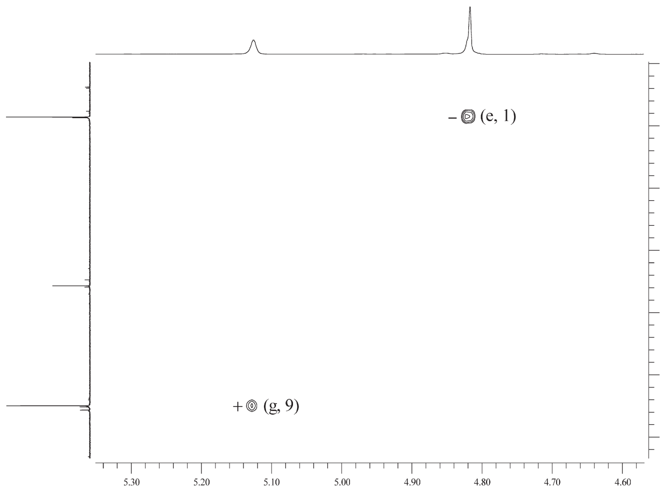


Fig. 7. HSQC spectrum displaying ^{1}H-^{13}C connectivities of olefinic protons of *exo*- and *endo*-model compounds.

data indicate that the former is CH_2 and the latter is CH. In Figure 8, we were able to positively confirm all of the aliphatic methylene protons H_b, H_d, H_i, H_k, and H_n of both models. Among the six methyl protons, H_a, H_c, and H_h were positively assigned by comparing the integrated peak intensities to the theoretical intensities predicted from the proposed structures. Of the remaining methyl protons, H_m was assigned with a fair degree of confidence, but the assignment of H_o and Hj remain less certain.

Because HSQC can only provide information about multiplicities, APT was utilized to obtain information concerning quaternary carbon atoms. The olefinic region of the APT spectrum in Figure 9 allows one to clearly identify the quaternary carbon resonances, C_2, and C_8 centered at 144.83 and 130.17 ppm, respectively.

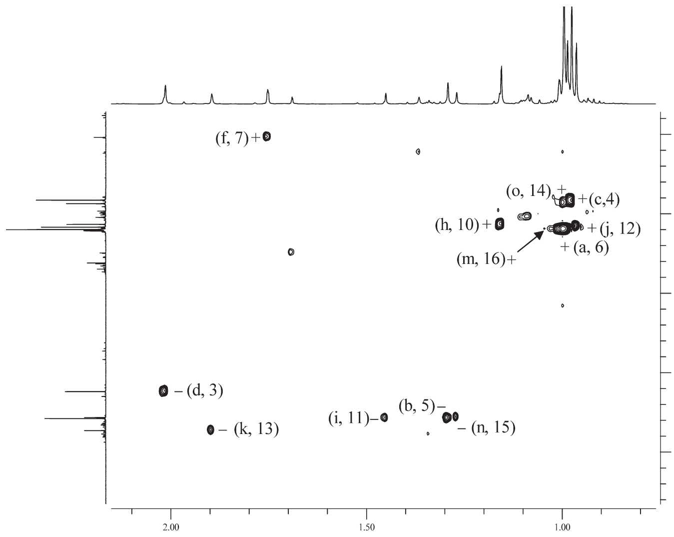


Fig. 8. HSQC spectrum displaying ^{1}H-^{13}C connectivities of methylene and methyl protons of *exo*- and *endo*-model compounds.

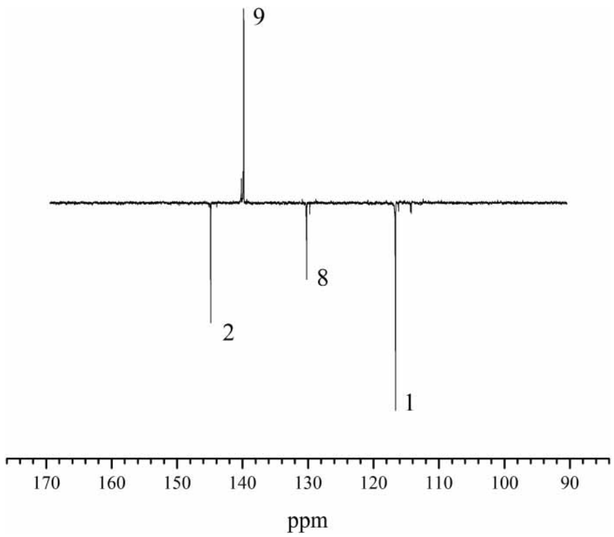


Fig. 9. APT spectrum showing proton multiplicities: CH and CH_3, up; and CH_2 and C (quaternary), down.

4 Conclusions

In this work, we report the synthesis and characterization of a model compound representing *exo*-olefin coupled PIB. Thorough NMR characterization of the 2,2,4,4,8,8,10,10-octamethyl-6-methyleneundecane (*exo*-model) and 2,2,4,4,6,8,8,10,10-nonamethylundec-5-ene (*endo*-model) mixture has allowed us to differentiate between the *endo*- and *exo*-olefin coupled PIB signals in the ^{1}H-NMR. We conclusively report the proton shift (for 500 MHz ^{1}H-NMR in $CDCl_3$) of 4.82 ppm for the *exo*-coupled product and that of 5.11 ppm for the *endo*-coupled product. Further assignments of peaks in the ^{1}H and ^{13}C-NMR are also reported.

5 Acknowledgements

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