Macromolecules

ARTICLE

pubs.acs.org/Macromolecules

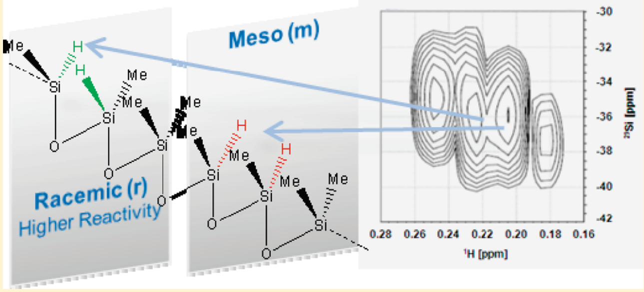
A Systematic Approach To Decipher the Microstructure of Methyl Hydrosiloxane Copolymers and Its Impact on Their Reactivity Trends

Anubhav Saxena,*[†] Meghna Markanday,[†] Alok Sarkar,[†] Vinod K. Yadav,[‡] and Ajaib S. Brar[‡]

[†]GE India Technology Centre, 122, EPIP, Phase 2, Hoodi Village, Whitefield Road, Bangalore 560066, India

[‡]Department of Chemistry, Indian Institute of Technology, New Delhi 110016, India

ABSTRACT: A thorough comprehensive microstructure analysis of poly(dimethylsiloxane-*co*-hydromethylsiloxane) copolymers (PDMS-*co*-PHMS) was achieved using high resolution two-dimensional NMR ($^{29}Si/^{1}H$) techniques viz. heteronuclear multiple bond coherence (HMBC) and total correlation spectroscopy (TOCSY) in conjunction with 1D ^{29}Si and ^{1}H NMR spectroscopy. A rigorous analysis of the splitting patterns along ^{29}Si NMR axes of hydromethylsiloxane, [$-$OSi(H)Me$-$]/"D^{H}" units and dimethylsiloxane, [$-OSi(Me)_2-$]/"D"units in PDMS-*co*-PHMS revealed sensitivity of their chemical shifts to variation in copolymer composition. Interestingly, ^{1}H NMR signals of hydromethylsiloxane, [$-$OSi(H)Me$-$] units showed an additional sensitivity to tacticity (meso, racemic) effects. With aid of 2D HMBC ($^{29}Si/^{1}H$) NMR spectra, we could resolve unambiguously the highly complex and overlapped $-Si-CH_3$ region in ^{1}H NMR spectrum into the respective compositionally and configurationally sensitive D/D^{H} triads. Further, the reactivity trend of Si$-$H groups was studied by hydrosilylation reaction of these copolymers (PDMS-*co*-PHMS) with model molecules like α-methylstyrene and 1-octene. An intriguing trend toward preference for racemic (r) orientation of Si$-$H on PDMS-*co*-PHMS backbone during hydrosilylation reactions resulting in syndiotactically enriched products was observed. This observation signifies a crucial fact of possible scientific interest that the Si$-$H dyads with the racemic configurations were more available for complexation with Pt catalyst during hydrosilylation than the meso dyads. The authors attribute these not-so-obvious experimental observations to the role of conformation of the polymeric chains. The interpretation of these peculiar findings and the reactivity patterns observed has been documented in this article.



INTRODUCTION

Methylhydrosiloxane containing polymers and oligomers are essential building blocks for the preparation of many organic/inorganic hybrid materials.[1,2] They have attracted a significant amount of academic attention[3] because of their unique usefulness in novel engineered material, and in catalyst design including catalytically active metal-nanoparticle synthesis,[4−6] development of novel molecular catalysts,[7−15] synthesis of mesogen-jacketed liquid crystalline polymers,[16] controlled reduction of amines,[17,18] and surface tailoring of biomaterials.[19] The Si$-$H bonds on them serve as chemical hooks for attaching the desired functionality. In fact, research shows presence of vicinal Si$-$H as even more viable. Therefore, a considerable amount of attention is required for the microstructure analysis of polymethylhydrosiloxane (PHMS) polymer—a key precursor to a plethora of functional polymers—in view of designing stereoregular polymers for enhanced performance. The available reports describing the elucidation of microstructure of polymethylhydrosiloxane copolymers are only based on 1D-NMR analysis and are useful to precisely determine the sequence distribution of methylhydrosiloxane units [$-$OSi(H)Me$-$] along the polymer backbone. Though the valuable role of various 1D and 2D-NMR techniques in decoding the stereoregular configurations is well-established in organic homopolymers like PMMA,[20] polypropylene (isotactic, syndiotactic),[21] polystyrene,[22] and polyvinyl chloride[23] and their copolymers,[24] there is no detailed work on configurational analysis of polymethylhydrosiloxane and its copolymers to the best of our knowledge. Interestingly, in the case of Si-containing polymers (e.g., polysilane and polysiloxane) despite the stereochemistry being analogous to that of vinyl polymers with alternating stereogenic and nonstereogenic centers, there were numerous issues like much longer relaxation times of Si vs C, broader line widths and insufficient dispersion of resonances which enhanced the difficulties of deducing microstructure of Si-based polymers using NMR.

^{29}Si NMR spectroscopy has been utilized as one of the tools to understand and analyze the structural features of silicon-based polymers.[25−28] Researchers including West et al[26] have analyzed the microstructure of polysilane homopolymers like $[PhMeSi]_n$ by studying the ^{29}Si NMR spectra of sterically defined samples. Jones et al[27] extended these analyses further and thus, strengthened the assignments of earlier researchers by showing that estimates of microtacticity through peak deconvolution agreed

Received: May 27, 2011
Revised: July 14, 2011
Published: July 26, 2011

well with Bernoullian statistical model. However, they also mentioned that integrals of the overlapping peaks in ^{29}Si NMR spectra may not be considered totally reliable measures of tacticity. The stereochemical aspects of methylhydrosiloxane-based polymers were first realized when a triplet peak was observed at −34.88 ppm in the ^{29}Si NMR spectra.[28] Harris and co-workers assigned the 1:2:1 triplet as representing an atactic polymer wherein the central peak was assigned as heterotactic (mr) sequences.[28] More recently, Pratt and co-workers synthesized an identical polyhydromethylsiloxane system at very low temperature that showed a triplet in the ratio of 6.25:1.00:1.08, which was explained in terms of “mm” sequences being thermodynamically more preferred over “mr” and “rr” sequences.[28] However, the direct assignments of the isotactic and syndiotactic triad sequences are not known. In order to entirely rule out any ambiguity in assignments for Si-based polymers, we need to resort to high resolution 2D NMR analogous to the way it is used for clear-cut configurational analysis of various organic polymers.[20−24] The biggest advantage is that the information obtained from 2D-NMR allows resolution and assignment of the resonances from the mm, mr/rm, and rr triad sequences in polymers without resorting to the actual synthesis of a stereoregular polymer with known relative configuration.[25]

Unlike the homopolymers [e.g., poly[MePhSi]s, PDMS, or PHMS], the copolymers like PDMS-*co*-PHMS have additional splitting patterns due to compositional variations as well. This makes the microstructure analysis of copolymers even more challenging as compared to their homo counterparts. Cancouet[27] et al, have established the position of “D” and “D^H” centered compositional triads in ^{29}Si{^{1}H} NMR and Si−H and Si-CH_3 regions in ^{1}H NMR spectra by studying the signal intensity trends in polymers with varying compositions. However, there is no mention of the tacticity analysis of these PDMS-*co*-PHMS copolymers. To the best of our knowledge, 2D NMR, viz. heteronuclear multiple bond coherence (HMBC), total correlation spectroscopy (TOCSY), etc., has not been utilized for a detailed microstructural analysis of Si-based polymers.

Here we report an in-depth compositional and configurational analysis of poly(hydromethylsiloxane-*co*-dimethylsiloxane)s using high resolution NMR [^{1}H, ^{29}Si, HMBC (^{1}H, ^{29}Si), TOCSY (^{1}H, ^{1}H)] techniques. We demonstrated an intriguing trend in terms of the preferred microstructural patterns during the hydrosilylation reaction of these copolymers with different substituents and directed efforts to studying the effect on microstructure of PDMS-*co*-PHMS before and after hydrosilylation reaction to decipher the rationale behind these not-so-obvious observations.

■ EXPERIMENTAL SECTION

Materials. Octamethylcyclotetrasiloxane (Momentive), 1,1,1,3,3,3-hexamethyldisiloxane (Momentive), acid-treated bentonite clay (Ace Chemicals), 1,3,5,7-tetramethylcyclotetrasiloxane (Gelest),1-octene (Aldrich) and α-methylstyrene (AMS, Aldrich) were used as supplied. Karstedt’s catalyst was purchased from Aldrich as solution of 3−3.5% Pt in vinyl-capped polydimethylsiloxane.

Measurements. The 1D and 2D NMR spectra were recorded on Bruker DPX-400 spectrometer in $CDCl_3$ (t, 7.24 ppm). ^{1}H and ^{29}Si measurements were made at frequencies of 400.13 and 79.49 MHz, respectively, and calibrated with respect to the solvent signal. Gradient HMBC experiments were recorded using the pulse sequence inv4gplplrnd of the Bruker software. The spectra were acquired with 512 increments in the F1 dimension and 2048 data points in the F2 dimension. Total correlation spectroscopy (TOCSY) experiment was performed using standard pulse sequence. A total of 32 scans were accumulated for 512 experiments with 2 s delay time.

Geometry Optimization Calculations. The geometry optimizations of the (MD^HD^HDM) (Table 1) in the gas phase were done by using the Forcite module of Accelrys. For each conformer, the polymer chain consisted of three repeat units. The packing model with a density of 1 g/cm^3 containing five chains was constructed by the Amorphous Cell module. The resulting structures were subsequently optimized by the following procedure. A 2000- step energy minimization (using geometry optimization method) was adopted; however, all the structures were energy converged before 1000 steps. “Smart” algorithm was used in the geometry optimization calculation at a room temperature with a fine quality cutoff criteria of 1×10^{-4} kcal/mol for energy and of 0.005 kcal mol^{-1} A^{-1} for force. The Smart algorithm is a cascade of the steepest descent, ABNR, and quasi-Newton methods for geometry optimization.

Preparation of $MD^H{}_{20}D_{10}M$ Copolymer. A 200 mL three-necked flask was charged with acidic IER (ion exchange resin, 1.3 g), 1,1,1,3,3,3-hexamethyldisiloxane (30.8 mmol, 5.0 g), octamethylcyclotetrasiloxane (77.2 mmol, 22.8 g), and 1,3,5,7-tetramethylcyclotetrasiloxane (154.3 mmol, 37.0 g). The resulting mixture was stirred at 65−70 °C under an argon atmosphere for 10 h. To stop the polymerization, the mixture was cooled and the solid catalyst was removed by filtration on a 0.5 cm Celite bed. The volatile oligomers were distilled under reduced pressure (0.5 Torr), at 150 °C during 30 min.

Preparation of $MD^H{}_{10}D_{20}M$ Copolymer. A 200 mL three-necked flask was charged with acidic IER (1.3 g), 1,1,1,3,3,3-hexamethyldisiloxane (30.8 mmol, 5.0 g), octamethylcyclotetrasiloxane (154.3 mmol, 45.2 g) and 1,3,5,7-tetramethylcyclotetrasiloxane (77.1 mmol, 18.5 g). The resulting mixture was stirred at 65−70 °C under an argon atmosphere for 10 h. To stop the polymerization, the mixture was cooled and the solid catalyst was removed by filtration on a 0.5 cm Celite bed. The volatile oligomers were distilled under reduced pressure (0.5 Torr), at 150 °C during 30 min.

Hydrosilylation of $MD^H{}_{20}D_{10}M$ Copolymers with 1-Octene/α-Methylstyrene. $MD^H{}_{15}D^{Oct}{}_5D_{10}$. A 200 mL three-necked flask was charged with Karstedt’s catalyst (2 ppm of platinum), $MD^H{}_{20}D_{10}M$ (7.5 mmol, 60.0 g), and 1-octene (1.9 mmol, 0.21 g). The resulting mixture was stirred at 25 °C under an argon atmosphere until all the olefin was consumed (12 h). The homogeneous mixture was cooled and the catalyst was removed by filtration on a 0.5 cm Celite bed.

Table 1. Notations and Abbreviations Used for the Representation of Various Poly(methylhydrosiloxane) Copolymers

notation	D^H/ D/D^{Oct}/D^{AMS} content	abbreviations
$MD^H{}_{20}D_{10}M$	D^H = 20; D = 10	M = −$OSiMe_3$
$MD^H{}_{10}D_{20}M$	D^H = 10; D = 20	D^H = −OSiMeH−
$MD^H{}_{15}D^{Oct}{}_5D_{10}M$	D^H = 15; D = 10; D^{Oct} = 5	D = −$OSiMe_2$−
$MD^H{}_{10}D^{Oct}{}_{10}D_{10}M$	D^H = 10; D = 10; D^{Oct} = 10	D^{Oct} = −OSiMe(*n*-octyl)−
$MD^H{}_{15}D^{AMS}{}_5D_{10}M$	D^H = 15; D = 10; D^{AMS} = 10	D^{AMS} = −OSiMe(α-methylstyryl)−

$MD^{H}{}_{10}D^{Oct}{}_{10}D_{10}$. A 200 mL three-necked flask was charged with Karstedt's catalyst (2 ppm of platinum), $MD^{H}{}_{20}D_{10}M$ (7.5 mmol, 60.0 g), 1-octene (3.8 mmol, 0.42 g). The resulting mixture was stirred at 25 °C under an argon atmosphere until all the olefin was consumed (12 h). The homogeneous mixture was cooled and the catalyst was removed by filtration on a 0.5 cm Celite bed.

$MD^{H}{}_{15}D^{AMS}{}_{5}D_{10}$. A 200 mL three-necked flask was charged with Karstedt's catalyst (10 ppm of platinum), $MD^{H}{}_{20}D_{10}M$ (7.5 mmol, 60.0 g), α-methylstyrene (1.9 mmol, 0.22 g). The resulting mixture was stirred at 25 °C under an argon atmosphere until all the olefin was consumed (24 h). The homogeneous mixture was cooled and the catalyst was removed by filtration on a 0.5 cm Celite bed.

^{1}H NMR Chemical Shifts for $MD^{H}{}_{x}D_{y}M$ Copolymers. $D{-}D^{H}$ (ppm from TMS): $-Si(CH_3)_2{-}O{-}$, 0.095 (DDD); 0.120 (DDD^H); 0.145 (D^HDD^H).

$-Si(CH_3)H{-}O{-}$, 0.175 (DD^HD); 0.195 (D^HD^HD); 0.220 ($D^HD^HD^H$). $-Si{-}H$, 4.64 (DD^HD); 4.715 (D^HD^HD); 4.735 ($D^HD^HD^H$).

^{29}Si NMR Chemical Shifts for Dimethylsilyl Groups D (ppm) of $MD^{H}{}_{x}D_{y}M$ Copolymers. ^{29}Si NMR chemical shifts of pentad centered in *DDD* triad, D*DDD*D (−21.6), D*DDD*D^H (−21.3), D^H*DDD*D^H (−21.1). Pentad centered in DDD^H triad, $DDDD^HD$ (−20.3), $DDDD^HD^H$ and D^HDDD^HD (−20.0), $D^HDDD^HD^H$ (−19.7). Pentad centered on triad D^HDD^H: DD^HDD^HD (−18.9), $DD^HDD^HD^H$ (−18.6), $D^HD^HDD^HD^H$ (−18.3).

^{29}Si NMR Chemical Shifts for Methylhydrosilyl Groups D^H (ppm) of $MD^{H}{}_{x}D_{y}M$ Copolymers. ^{29}Si NMR chemical shifts of pentad centered in DD^HD triad: DDD^HDD (−37.3), DDD^HDD^H (−37.0), $D^HDD^HDD^H$ (−36.7). Pentad centered in DD^HD^H triad, DDD^HD^HD (−36.2), $DDD^HD^HD^H$ and $D^HDD^HD^HD$ (−35.9), $D^HDD^HD^HD^H$ (−35.6). Pentad centered on triad $D^HD^HD^H$: $DD^HD^HD^HD$ (−35.0), $DD^HD^HD^HD^H$ (−34.8), $D^HD^HD^HD^HD^H$ (−34.5).

^{1}H NMR $MD^{H}{}_{15}D^{Oct}{}_{5}D_{10}M$. (ppm) 0.05−0.25 (m, 138H), 0.55 (m, 10H), 0.90 (m, 10H), 1.30 (m, 65H), 4.75 (m, 15H).

^{1}H NMR $MD^{H}{}_{10}D^{Oct}{}_{10}D_{10}M$. (ppm) 0.05−0.25 (m, 138H), 0.55 (m, 20H), 0.90 (m, 20H), 1.30 (m, 130H), 4.75 (m, 10H).

^{1}H NMR $MD^{H}{}_{15}D^{AMS}{}_{5}D_{10}M$. (ppm) 0.05−0.25 (m, 138H), 1.00 (m, 10H), 1.30 (d, 15H), 3.00 (m, 5H), 7.25 (m, 25H).

RESULTS AND DISCUSSION

Various possible orientations in space of "Si−*H*" and "Si−*CH*$_3$" on siloxane backbone can be typically categorized into "isotactic" (mm), "syndiotactic" (rr), and "heterotactic" (mr) triads.

As mentioned earlier, tacticity analysis in Si-based polymers has been mainly done for homopolymers. In the case of copolymers, there are additional peaks due to the compositional changes arising from varying monomer ratios. This is because there is influence of the neighbor units on the chemical shift of a given silicon atom up to several units. We have assigned Si−*H* and Si−*CH*$_3$ regions in ^{1}H NMR and the position of resonances from "D" and "D^{H}" centered pentad and heptad units in the ^{29}Si{^{1}H} NMR spectrum by studying the signal intensity trends in two copolymers with different compositions ($MD^{H}{}_{10}D_{20}M$ and $MD^{H}{}_{20}D_{10}M$). Two distinct resonance domains in ^{29}Si NMR are observed, corresponding to D units (between −18.5 and −22 ppm) and D^{H} units (between −34.7 and −37.5 ppm). These domains were further assigned to various triads, pentads and heptads.[27] A representative ^{29}Si and ^{1}H NMR spectrum of $MD^{H}{}_{20}D_{20}M$ and $MD^{H}{}_{10}D_{20}M$ is shown in Figure 1 with the respective triads and pentad resonances marked.

Utilizing these assignments as a reference point, we have examined in detail the configurational sensitivity (seen as finer splitting of ^{29}Si NMR spectra) of PDMS-*co*-PHMS with the aid of spectroscopic evidence in the form of 1D and 2D (^{1}H, ^{29}Si) NMR experiments. Resorting to 2D NMR was an obvious choice, as it is known to render much better sensitivity and resolution than that obtained by direct detection of ^{29}Si resonances in a 1D experiment. In this analysis, 2D HMBC (^{29}Si, ^{1}H) was preferred over other available 2D NMR techniques like HMQC/HSQC, due to its ability to capture the correlations between ^{29}Si and ^{1}H resonances that are two to three bonds away. This enabled us to deeply examine the stereoregular sensitivity/orientations of Si−H and Si-CH$_3$ on PDMS-*co*-PHMS backbone (Figure 2).

Two different extreme compositions of PDMS-*co*-PHMS, viz. $MD^{H}{}_{10}D_{20}M$ and $MD^{H}{}_{20}D_{10}M$, were examined in this work. The two main resonance domains of interest to us are D units (between −18.5 and −22 ppm) and D^{H} units (between −34.7 and −37.5 ppm). The end-groups −SiMe$_3$ give rise to few cross-peaks between 7 and 9 ppm on ^{29}Si axis in 2D HMBC spectra (Figure 2). As they do not seem to contribute any significant revelation on understanding the microstructure of these copolymers, we chose to defer from any further discussion about them in this article. Seven cross-peaks (1−5, 7, 8) were observed, which corresponded to the D-region (−18.5 to −22.5 ppm) on the ^{29}Si axis in 2D HMBC spectra (Figure 2). The positions of these cross peaks matched well with the position of compositionally sensitive D-centered triads/pentads on ^{29}Si NMR axis.[27] Any splitting of contours along the ^{1}H axis while keeping the position along ^{29}Si axis almost fixed (±0.2 ppm)[25] was not observed in the D-region and hence the inference can be drawn that "D" region seem to experience only compositional sensitivity and no configurational sensitivity in the two studied compositions of PDMS-*co*-PHMS. Furthermore, a few of the cross peaks (7, 8) in $MD^{H}{}_{10}D_{20}M$ are missing in the HMBC spectrum of $MD^{H}{}_{20}D_{10}M$, which further confirms these peaks to result from composition variations. Each cross-peak position (1−5, 7, 8) on ^{29}Si NMR axis correlated with a position on ^{1}H NMR axis in the range 0.11−0.17 ppm (Table 2). The Si−*CH*$_3$ region (0.05−0.25 ppm) in ^{1}H NMR spectra appears as complex series of overlapped resonances due to peaks from both "D" and "D^{H}" units. The correlations of ^{29}Si peak positions with ^{1}H NMR positions from 2D HMBC spectra enabled an unambiguous assignment of the peaks from "D" units of PDMS-*co*-PHMS.

However, six cross peaks (10−14, 15) are seen in the D^{H} region (between −34.7 and −37.5 ppm) and are present in the spectra of polymers with both compositions. These cross peaks differed from those seen in the D region since they show two to three cross-peaks resolved along the ^{1}H axis which occur at almost same position on the ^{29}Si axis (Table 3, Figure 2). A closer scrutiny indicates cross-peaks (10, 11, 12) corresponding to −34.5 ppm on the ^{29}Si axis and cross peaks (13, 14) seen as two separate contours on ^{1}H axis matched to −36.0 ppm on the ^{29}Si axis. The contours 10−12 centered around −34.5 ppm on the ^{29}Si axis appear from 0.20 to 0.25 ppm on the ^{1}H axis. Such pattern of 2−3 separate cross-peaks along the ^{1}H axis corresponding to almost the same position on the ^{29}Si axis is believed by authors to be a sign of possible configurational sensitivity of D^{H} region.

The question arises of analyzing the different configurations viz. "mm", "mr", or "rr". Delving deeper into the impact of "mm",

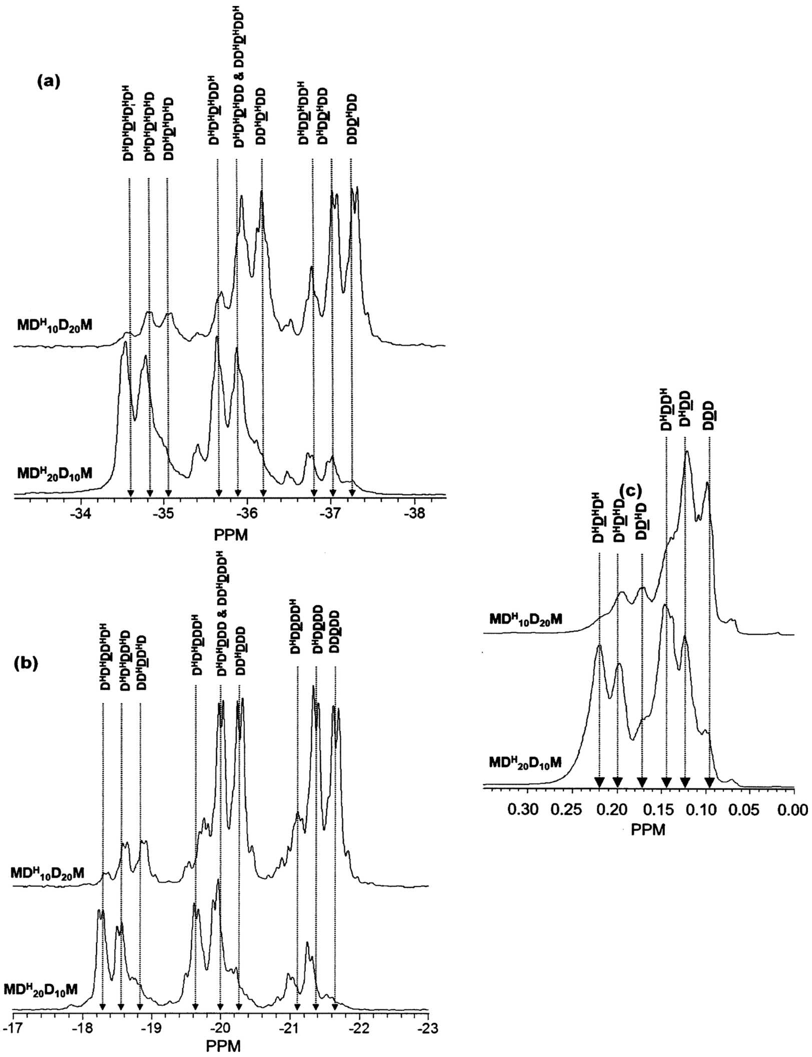


Figure 1. ^{29}Si NMR spectra of PDMS-*co*-PHMS (a) D^H and (b) D- region and ^{1}H NMR spectra (c) −Me region.

"mr", or "rr" sequences on the Si−CH_3 chemical shifts a few things can be realized. If the polymer backbone is drawn in the planar zigzag conformation, then the Si−CH_3 in "mm" triads see two −CH_3 groups on neighboring Si atoms (Scheme 1), while the Si−CH_3 in "rr" triad sees two "H" on its neighboring Si atoms. Comparing the ^{1}H chemical shifts of Si−CH_3 for both of them due to the influence of neighboring groups, it can be predicted that methyl protons in "rr" triads (0.25 ppm) will be most deshielded followed by those in "mr" triads (0.22 ppm) and then those in, "mm" triads (0.20 ppm) (Table 3).[24]

The peaks due to monomer stereosequences (m, r) could be resolved from those owing to compositional effect (D or D^H) on the basis of the chemical shifts along the ^{1}H NMR axis while analyzing the cross-peaks in 2D NMR spectra from "D" and "D^H" regions. The regions, 0.11−0.17 ppm and 0.20−0.25 ppm on ^{1}H NMR axis result from "D" and "D^H" regions, respectively. Thus, the compositional sensitivity could be distinguished based on these regions. Further, splitting within each region indicated changes due to monomer sequences.

Having achieved a thorough analysis of stereoregularity of PDMS-*co*-PHMS by 2D HMBC (^{29}Si, ^{1}H), the assignments could be translated to Si−CH_3 region in ^{1}H 1D-NMR spectra (Figure 3).

Further evidence of tacticity seen in D^H region was given by studying the correlation of the Si−*H* region (4.64 to 4.76 ppm) with the Si−CH_3 (0.08 to 0.24 ppm) in 2D TOCSY (^{1}H, ^{1}H) NMR spectrum (Figure 4). The cross peaks in TOCSY are absent for the D region in the ^{1}H NMR spectrum. The cross-peaks in this region of TOCSY spectrum are mainly arising from three-bond H−H coupling in H−Si−CH_3 fragments. It is observed that instead of a single contour expected in this region due to a direct correlation of Si−H with Si-CH_3 in H−Si−CH_3 fragments, we see splitting of this contour into further cross-peaks corresponding to configurationally sensitive D^H regions along the ^{1}H NMR axis. This finer splitting is an indication of the presence of stereochemical effect in the Si−H region.

Having thoroughly analyzed and confirmed the stereoregularity of PDMS-*co*-PHMS with varying compositions, we extended our investigation towards knowing how the reactivity of $-[-OSi(H)Me-]_n-$ microstructures vary depending upon their configurational sensitivity. Earlier, Lewis et al. investigated the reactivity of various hydrosilanes containing multiple Si−H groups to understand the steric and electronic effects of the neighboring groups in the hydrosilylation reaction.[29] Adopting this approach ensured a better understanding of the preferred

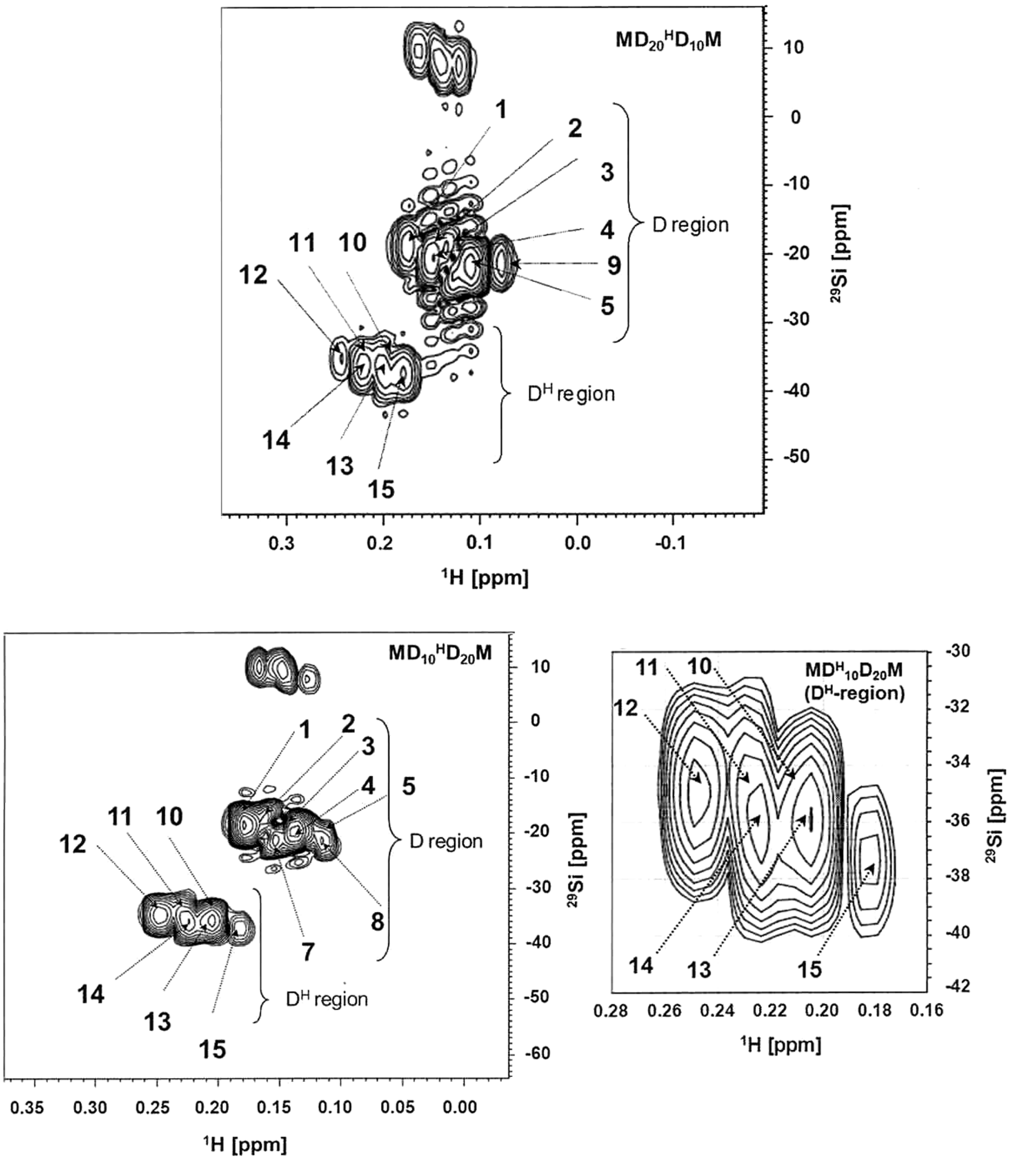


Figure 2. 2D HBMC (^{29}Si, ^{1}H) NMR spectra of varying compositions of PDMS-*co*-PHMS viz. $\mathrm{MD^{H}{}_{20}D_{10}M}$, and $\mathrm{MD^{H}{}_{10}D_{20}M}$.

Table 2. Spectral Assignment of D-Region Based on ^{29}Si NMR and 2D HMBC (^{29}Si, ^{1}H) Spectra

triad	peak label	pentad	^{29}Si NMR	^{29}Si/ ^{1}H (ppm)
$\mathrm{D^{H}}D\mathrm{D^{H}}$	1	$\mathrm{D^{H}D^{H}}D\mathrm{D^{H}D^{H}}$	−18.2	−18.2/0.17
	2	$\mathrm{D^{H}D^{H}}D\mathrm{D^{H}D}$	−18.4	−18.6/0.16
	3	$\mathrm{DD^{H}}D\mathrm{D^{H}D}$	−18.8	−18.8/0.14
$\mathrm{D^{H}}D\mathrm{D}$	4	$\mathrm{D^{H}D^{H}}D\mathrm{DD^{H}}$	−19.6	−19.6/0.14
	5	$\mathrm{D^{H}D^{H}}D\mathrm{DD}$	−19.9	−19.9/0.11
	6	$\mathrm{DD^{H}}D\mathrm{DD}$	-	-
$\mathrm{D}D\mathrm{D}$	7	$\mathrm{D^{H}D}D\mathrm{DD^{H}}$	−21.4	−21.4/0.15
	8	$\mathrm{D^{H}D}D\mathrm{DD}$	−21.8	−21.8/0.10
	9	$\mathrm{DD}D\mathrm{DD}$	-	-

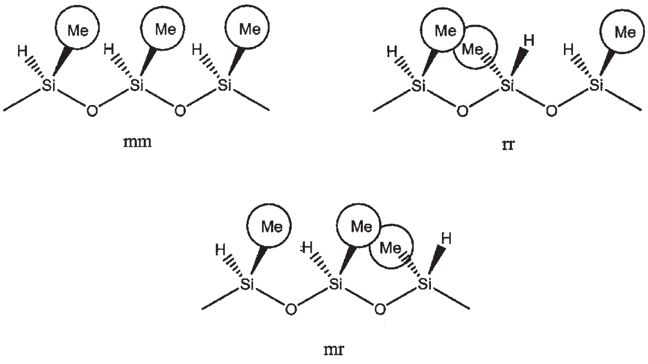
Table 3. Spectral Assignment of $\mathrm{D^{H}}$-Region Based on ^{29}Si NMR and 2D HMBC (^{29}Si, ^{1}H) Spectra

triad	peak label	triad	29 Si NMR	^{29}Si/ ^{1}H (ppm)
$\mathrm{D^{H}}D^{\mathrm{H}}\mathrm{D^{H}}$	10	$\mathrm{D^{H}{}_{m}}D^{\mathrm{H}}{}_{m}\mathrm{D^{H}}$	−34.5	−34.5/0.20
	11	$\mathrm{D^{H}{}_{m}}D^{\mathrm{H}}{}_{r}\mathrm{D^{H}}$	−34.5	−34.5/0.22
	12	$\mathrm{D^{H}{}_{r}}D^{\mathrm{H}}{}_{r}\mathrm{D^{H}}$	−34.5	−34.5/0.25
$\mathrm{D^{H}}D^{\mathrm{H}}\mathrm{D}$	13	$\mathrm{D^{H}{}_{m}}D^{\mathrm{H}}\mathrm{D}$	−36.0	−36.0/0.20
	14	$\mathrm{D^{H}{}_{r}}D^{\mathrm{H}}\mathrm{D}$	−36.0	−36.0/0.22
$\mathrm{D}D^{\mathrm{H}}\mathrm{D}$	15	$\mathrm{D}D^{\mathrm{H}}\mathrm{D}$	−37.2	−37.2/0.18

trend in configurational orientation of functionalities during the hydrosilylation reaction. Thus, a model study was conducted by performing hydrosilylation reactions with two different functionalities viz. α-methylstyrene (AMS with branching at the α position with aromatic functionality) and 1-octene (a linear aliphatic chain).

From studying the variation in peak intensities in the proton region ("Si−CH_3") in ^{1}H and ^{29}Si 1D-NMR spectra of different hydrosilylation products (5 and 10% AMS or 1-octene grafted onto PDMS-*co*-PHMS), it was determined (Figure 5) that there

Scheme 1. Various Stereoregular Orientations of Si−*H* and Si−*C*H_3 in PDMS-*co*-PHMS



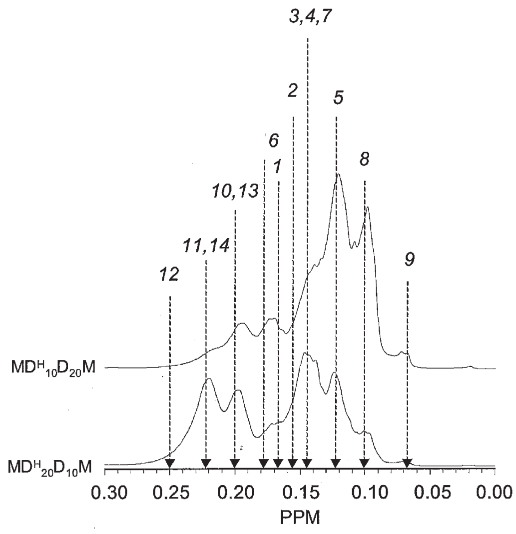


Figure 3. ^{1}H NMR spectra of Si−*C*H_3 region in PDMS-*co*-PHMS copolymers of two compositions viz. $MD_{20}{}^{H}D_{10}M$ and $MD_{10}{}^{H}D_{20}M$.

is a typical pattern of faster consumption of "rr/mr" (syndiotactic) "Si−*H*" on PDMS-*co*-PHMS than "mm" (isotactic) Si−H. Surprisingly, this preference is quite evident for reactions with both α-methylstyrene and 1-octene, irrespective of their individual differences in steric hindrance.

This interesting observation is a possible indication of a mechanism during hydrosilylation favoring reaction with syndiotactic ("rr"/"mr") over isotactic ("mm") "Si−*H*" fractions on PDMS-*co*-PHMS − probably for minimizing the steric interactions/hindrance. The preference of "racemic" Si−H over "meso" Si−H to undergo hydrosilylation reaction was a very intriguing observation as it meant that the Si−H dyads placed opposite to each other in space (racemic) are more available for complexation with Pt catalyst during hydrosilylation than the meso dyads. Analyzing further, we realized that it may not be only configuration but also conformation[30,31] which plays a role in determining the exact orientation of Si−H triads in space and, thus, dictating the final tacticity achieved after hydrosilylation.

It is well-known that the Si−O backbone is very flexible and thus, easily allows existence of polymeric siloxane chains in various conformations. An analogy could be drawn to prevalent conformers for various organic polymers like polypropylene, polysilanes etc.[30,31] Possible favorable sawhorse and Newman conformations were proposed and sketched (Scheme 2) for "m" and "r" configurations assuming a preference toward "trans" conformations due to their minimum energy. The geometry optimization calculations of the two isomer of MD^HD^HDM in the gas phase using the Forcite module of Accelrys has also supported the fact that in the most stable conformations of "m" and "r"dyads, the "r" dyad was the one which brings two −Si−H bonds in the closest proximity.

We do not claim these conformations to be absolute, but believe them to be a possible manner of polymer chains orienting themselves so that the two "−Si−H" groups on racemic (r)

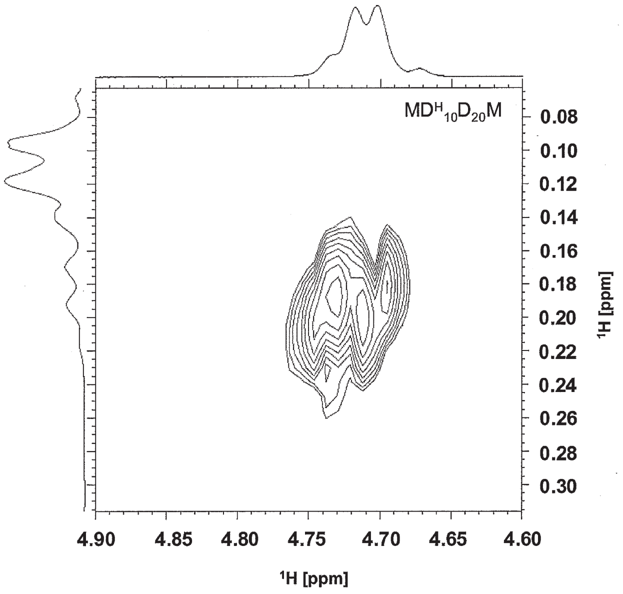


Figure 4. 2D TOCSY (^{1}H, ^{1}H) NMR spectrum showing the correlation of Si−*H* region with Si−*C*H_3.

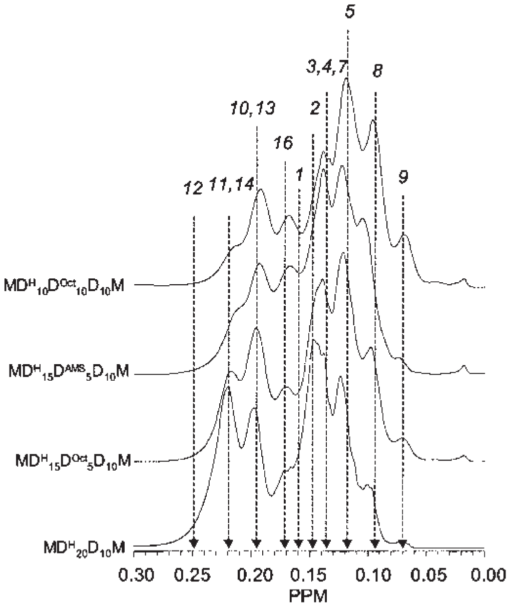
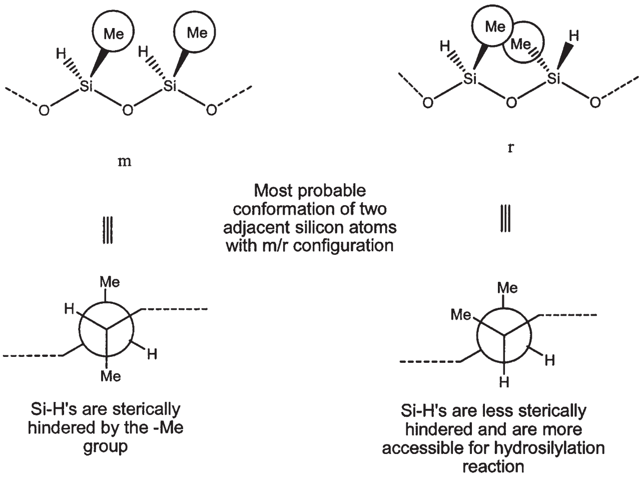


Figure 5. ^{1}H NMR spectra of PDMS−PHMS-Oct/AMS copolymers obtained after hydrosilylation of PDMS-*co*-PHMS with AMS/octene.

Scheme 2. Possible Conformations of "m" and "r" Configurations of PDMS-*co*-PHMS during the Hydrosilylation Reaction with 1-Octene/AMS



triads land up being closer to each other as compared to the isotactic (m) triad. Recently, numerous researchers[3] have confirmed the role of dual Si—H synergistic effect in driving the hydrosilylation mechanism to an extent that it becomes a deciding factor for the success or failure of the reaction. It is strongly evident that presence of a vicinal "Si—H" in most cases is very crucial in ensuring the complexation of the platinum catalyst in hydrosilylation reactions. It implies that the platinum-catalyzed hydrosilylation reactions are accelerated manifold when two "Si—H" are present vicinal/in close proximity to each other as it greatly helps in the platinum—alkene/alkyne complex formation. The effect is seen to an extent that, if a second Si—H is not present close the one reacting, then the chance is the reaction may not happen at all. Keeping these reports in mind,[3] it may be reasonable to conclude that, "r" triad Si—H groups are relatively closer to each other in space compared to the corresponding groups in the "m" triad. This conformational effect may lead to its faster reaction during the hydrosilylation. Although it is not obvious if the hydrosilylation proceeds with retention or inversion of the Si stereochemistry, it is reasonable to infer that a polymer rich in syndiotacticity is obtained.

CONCLUSIONS

A thorough comprehensive microstructure analysis of Polydimethylsiloxane/Polyhydromethylsiloxane copolymers (PDMS-*co*-PHMS) was achieved using high resolution two-dimensional NMR (^{29}Si/^{1}H) techniques viz. heteronuclear multiple bond coherence (HMBC) and total correlation spectroscopy (TOCSY) in conjunction with 1D ^{29}Si and ^{1}H NMR spectroscopy. With the aid of 2D HMBC (^{29}Si/^{1}H) NMR, we could resolve unambiguously the highly complex and overlapped resonances in the $-\mathrm{Si}-CH_3$ region in ^{1}H NMR into the respective compositionally and configurationally sensitive D/D$^{\mathrm{H}}$ triads. Studying the variation in the peak patterns of $-\mathrm{Si}-CH_3$ region in ^{1}H NMR, before and after hydrosilylation reactions, revealed a very unique microstructural pattern. The final copolymers formed by hydrosilylation reaction of "AMS" and "1-octene" with PDMS-*co*-PHMS showed a clear preference for reaction of triads with syndiotactic orientation (rr/mr) over those with isotactic (mm), orientation. This preference was attributed to close proximity of Si—H groups in dyads with the racemic configurations to those with meso orientation, making them more available for complexation with Pt catalyst during hydrosilylation than in the meso dyad. Thus, the entire analysis in current work gives us strong ground to believe that the conformation of the Si—H also plays a critical role along with configuration in deciding the reactivity of Si—H. Future work may be directed toward introducing chiral side-chains and studying the resulting effects.

AUTHOR INFORMATION

Corresponding Author

*E-mail: anubhav.saxena@ge.com. Telephone: +91-80-40882303. Fax: +91-80-28412111.

ACKNOWLEDGMENT

The authors thank Dr. Khijar Sarnaik and Dr. Pradeep Nadkarni for their support and encouragement. Authors also acknowledge assistance from Dr. Raja Roy, Dr. Pratima Tripathi, and Dr. Vivek Karambelkar in recording NMR and Dr. Amjad M. Basha in geometry optimization for various isomers.

REFERENCES

(1) Corey, J. *Chem. Rev.* **2011**, *111*, 863.

(2) (a) Chauhan, B. P. S.; Rathore, J. S. *J. Am. Chem. Soc.* **2005**, *127*, 5790. (b) Amro, K.; Clément, S.; Déjardin, P.; Douglas, W. E.; Gerbier, P.; Janot, J.-M.; Thami, T. *J. Mater. Chem.* **2010**, *20*, 7100.

(3) (a) Tsutsumi, H.; Sunada, Y.; Nagashima, H. *Organometallics* **2011**, *30*, 68. (b) Uchimaru, Y.; Sayed, A-M.; Tanaka, M. *Organometallics* **1993**, *12*, 2065. (c) Sunada, Y.; Fujimura, Y.; Nagashima, H. *Organometallics* **2008**, *27*, 3502.

(4) Fu, B.; Missanghi, M. N.; Downing, C. M.; Kung, M. C.; Kumg, H. H.; Xiao, G. *Chem. Mater.* **2010**, *22*, 2181.

(5) Dumont, M. F.; Moisan, S.; Aymonier, C.; Marty, J.-D.; Mingotaud, C. *Macromolecules* **2009**, *42*, 4937.

(6) Rahaim, R., Jr; Maleczka, R. *Org. Lett.* **2011**, *13*, 584.

(7) Motoyama, Y.; Kamo, K.; Nagashima, H. *Org. Lett.* **2009**, *11*, 1345.

(8) Motoyama, Y.; Mitsui, K.; Ishida, T.; Nagashima, H. *J. Am. Chem. Soc.* **2005**, *127*, 13150.

(9) Motoyama, Y.; Abe, M.; Kamo, K.; Kosako, Y.; Nagashima, Y. *Chem. Commun.* **2008**, 5321.

(10) Vankelecom, I. F. J.; Tas, D.; Parton, R. F.; Van de Vyver, V.; Jacobs, P. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1346.

(11) Parton, R. F.; Vankelecom, I. F. J.; Tas, D.; Janssen, K. B. M.; Knops-Gerrits, P.-P.; Jacobs, P. A. *J. Mol. Catal. A: Chem.* **1996**, *113*, 283.

(12) Wolfson, A.; Janssens, S.; Vankelecom, I.; Geresh, S.; Gottlieb, M.; Herskowitz, M. *Chem. Commun.* **2002**, 388.

(13) Mwangi, M. T.; Runge, M. B.; Bowden, N. B. *J. Am. Chem. Soc.* **2006**, *128*, 14434.

(14) Runge, M. B.; Mwangi, M. T.; Bowden, N. D. *J. Organomet. Chem.* **2006**, *691*, 5287.

(15) Guedes, D. F. C.; Leod, T. C. O.; Gotardo, M. C. A. F.; Schiavon, M. A.; Yoshida, I. V. P.; Ciuffi, K. J.; Assis, M. D. *Appl. Catal., A* **2005**, *296*, 120.

(16) Zhang, L.; Chen, S.; Zhao, H.; Shen, Z.; Chen, X.; Fan, X.; Zhou, Q. *Macromolecules* **2010**, *43*, 6024.

(17) Hanada, S.; Ishida, T.; Motoyama, Y.; Nagashima, H. *J. Org. Chem.* **2007**, *72*, 7551.

(18) Hanada, S.; Tsutsumi, E.; Motoyama, Y.; Nagashima, H. *J. Am. Chem. Soc.* **2009**, *131*, 15032.

(19) Xu, J.-P.; Ji, J.; Shen, J.-C. *Biomed. Mater.* **2009**, *4*, 1.

(20) (a) White, A.; Filisko, F. *J. Polym. Sci: Polym. Lett. Ed.* **1982**, *10*, 525. (b) Huggett, R.; Brooks, S.; Sadler, I. *Biomaterials* **1984**, *5*, 118.

(21) (a) Cheng, N.; Lee, G. *Polym. Bull.* **1985**, *13*, 549. (b) Suzuki, S.; Nakamura, Y.; Hasan, A. T. M.; Liu, B.; Terano, M.; Nakatani, H. *Polym. Bull.* **2005**, *54*, 311. (c) Asakura, T.; Nishiyama, Y.; Doi, Y. *Macromolecules* **1987**, *20*, 616.

(22) (a) Kawamura, T.; Toshima, N.; Matsuzaki, K. *Macromol. Rapid Commun.* **1994**, *15*, 479. (b) Pasch, H.; Hiller, W.; Haner, R. *Polymer* **1998**, *39*, 1515.

(23) (a) Crowther, M.; Szeverenyi, N.; Levy, G. *Macromolecules* **1986**, *19*, 1333. (b) Tincher, W. *J. Polym. Sci.* **1962**, *62*, S148.

(24) (a) Brar, A. S.; Dutta, K. *Macromolecules* **1998**, *31*, 4695. (b) Mukherjee, M.; Chatterjee, S. K.; Brar, A. S.; Dutta, K. *Macromolecules* **1998**, *31*, 8455. (c) Brar, A. S.; Kaur, S. *J. Polym. Sci. Chem., Part A: Polym. Chem.* **2005**, *43*, 1100. (d) Brar, A. S.; Singh, G.; Shankar, R. *Polymer* **2005**, *46*, 7164. (e) Brar, A. S.; Markanday, M. *Polymer* **2005**, *46*, 11527. (f) Brar, A. S.; Kaur, M. *Eur. Polym. J.* **2003**, *39*, 705. (g) Brar, A. S.; Kumar, R. *J. Mol. Struct.* **2002**, *616*, 37–47.

(25) (a) Saxena, A.; Rajaraman, S.; Leatherman, M. *Macromolecules* **2007**, *40*, 752. (b) Saxena, A.; Okoshi, K.; Fujiki, M.; Naito, M.; Guo, G.; Hagihara, T.; Ishikawa, M. *Macromolecules* **2004**, *37*, 367. (c) Shankar, R.; Saxena, A.; Brar, A. S. *J. Organomet. Chem.* **2002**, *650*, 223. (d) Chai, M.; Saito, T.; Pi, Z.; Tessier, C.; Rinaldi, P. *Macromolecules* **1997**, *30*, 1240. (e) Dioumaev, V.; Rahimian, K.; Gauvin, F.; Harrod, J. *Organometallics* **1999**, *18*, 2249. (f) Kawakami, Y.; Takeyama, K.; Komuro, K.; Ooi, O. *Macromolecules* **1998**, *31*, 551.

(26) Woolf, A.-R.; Nozue, I.; Maxka, J.; West, R. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 701.

(27) (a) Jones, R.; Benfield, R.; Evans, P.; Holder, S.; Locke, J. *J. Organomet. Chem.* **1996**, *521*, 171. (b) Cancouet, P.; Daudet, E.; Helary, G.; Moreau, M.; Sauvet, G. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 826.

(28) (a) Harris, R. K.; Kimber, J. K. *J. Chem. Soc., Chem. Commun.* **1974**, 559. (b) Pratt, L. M.; Smid, J.; Khan, I. M. *Polym. Prepr.* **1994**, *35*, 643. (c) Saam, J. C. *J. Inorg. Organomet. Polym.* **1999**, *9*, 3.

(29) (a) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998. (b) Stein, J.; Lewis, L. N.; Smith, K. A.; Lettko, K. X. *J. Inorg. Organomet. Polym.* **1991**, *1*, 325.

(30) (a) Natta, G.; Corradini, P.; Ganis, P. *Makromol.Chem.* **1960**, *39*, 238. (b) Yoon, D.; Sundararajan, P.; Flory, P.-J. *Macromolecules* **1975**, *8*, 776.

(31) Freire, J.; Pierola, I.; Horta, A. *Macromolecules* **1996**, *29*, 514.