Structural Determination of Ethylene-Propylene-Diene Rubber (EPDM) Containing High Degree of Controlled Long-Chain Branching

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ABSTRACT: This work highlights an attempt to characterize the degree and nature of long-chain branching (LCB) in an unknown sample of ethylene-propylene-diene rubber (EPDM). Two EPDM rubbers selected for this study were comparable in comonomer compositions but significantly different with respect to molar mass and the presence of LCB. Both rubbers contained 5-ethylidene-2-norbornene (ENB) as diene. Solution cast films of pure EPDM samples were used for different characterization techniques. ^{1}H-NMR, and ^{13}C-NMR were used for assessing the comonomer ratios and LCB. Size exclusion chromatography (SEC) equipped with triple detector system was used to determine the molar mass (both absolute and relative) and polydispersity index (PDI). Presence of branching was also detected using sec-viscometry. Rheological analysis has also been used for characterizing LCB. Finally, on the basis of the experimental findings and the available theories, an attempt was made to identify the chemical nature and degree of LCB. This study reveals the possibility of detailed characterization of molecular architecture of EPDM containing LCB by comparing with an essentially linear EPDM in light of an existing theory. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2962–2972, 2009

Key words: elastomers; EPDM; long chain branching; NMR; polymers; rheology; size exclusion chromatography

INTRODUCTION

Ethylene-propylene-diene rubbers (EPDM) are used for several outdoors applications e.g., in the building, construction, engineering, and automotive sectors by virtue of their resistance to oxygen, ozone, heat, and UV because of the saturated hydrocarbon backbone.[1] One of the most important grades of EPDM is with 5-ethylidene-2-norborene (ENB) as a diene and the typical chemical structure is shown in Scheme 1.

With metallocene catalysts, it possible to synthesize ethylene, propylene, and other higher α-olefine copolymers with narrow and unimodal chemical composition distribution (CCD) compared to bimodal and nonuniform CCD obtained by Ziegler-Natta catalysts.[2,3] Moreover, metallocene catalyst can also be used to synthesize a copolymer containing long-chain branching (LCB). The term LCB attributes to the configuration of a polymer molecule possessing side chains with a degree of polymerization, which are capable to entangle with each other (i.e., molar mass of the side chain is above the entanglement molar mass of the polymer). LCB introduction in polymer using metallocene catalysts increases the shear thinning and melt elasticity, while keeping the molar mass distribution (MWD) or PDI typically between 2.0 and 2.5.[2,3] Rubbers made with metallocene catalysts combine the excellent mechanical properties and good processability.[4–6] Therefore, LCB containing rubber results in excellent filler dispersion, smooth surface finishes, and form stability along with consistent mechanical properties. Several new grades of EPDM are commercially available, which contain controlled LCB with narrow PDI and higher molar mass.[4–6] It is also claimed that some of these new grades having high molar mass and controlled LCB could behave as a high ENB content EPDM (which is one of the costly grades of EPDM).[5,6] This could result in higher state of curing
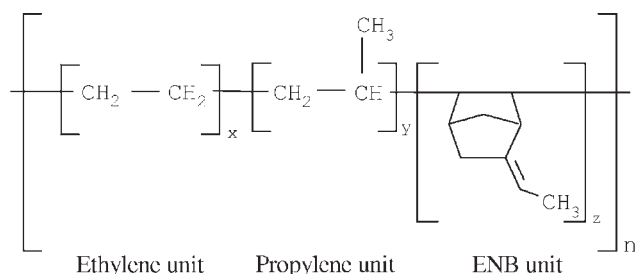
Scheme 1 Representative chemical structure of EPDM containing ENB as a diene.

at a relatively low level of unsaturations and make possible to develop a cost efficient formulation with enabled properties.[5,6]

Unfortunately, the information on the degree and chemical nature of LCB in EPDM is not available from the manufacturer because of trade secrecy. Interestingly, several methods are reported in the literatures for characterizing vis-à-vis quantifying the degree and nature of LCB in polyolefins.[2,3] However, limited information on quantifying LCB of EPDM using rheology, ^{13}C-NMR, and SEC study are available.[7–11] In most of these cases either LCB is well defined as the polymer is synthesized in a controlled lab scale or several known model polymers are considered to quantify the nature and degree of LCB[7–10] and establish the structure property.[12–14] However, it is really challenging to characterize the LCB of a pure rubber without having knowledge on the chemistry of branching (and without having a model system) and thus often forces to rely on the available data.

The objective of this present study is to characterize and quantify the LCB of a pure EPDM rubber. This is accomplished by the help of an essentially linear EPDM containing no or insignificant branching and that too from different manufacturer with different molar mass but having similar comonomer compositions and PDI. This resembles with a typical problem of quantifying LCB vis-à-vis branching architecture without knowing much about the underlying chemistry with regard to LCB.

EXPERIMENTAL

Materials

The details of the EPDM types used in this study are given in Table I. E-1 was Nordel® IP 4520 from The Dow Chemical Company,[15] and E-2 was Keltan®8340A from DSM Elastomer, Netherland.[16] AVK Gummi A/S, Denmark, provided EPDM samples.

Thin films of EPDM were prepared by dissolving E-1 and E-2 in n-heptane (concentrations ~0.05g/mL) at room temperature. Solution cast films were made on glass Petri dishes by pipetting 50 mL and allowed to dry at room temperature for 3 days. The films were peeled off and rinsed with methanol. The film thicknesses were 1.0–1.2 mm. These films were used for characterization.

Table II shows the details of Engage® 8400 (ethylene-octene copolymer) obtained from The Dow Chemical Company (Midland, MI).[17] It was included in this study to compare and contrast the rheology and NMR data, as it contains a known amount of well-defined hexyl branching. This is to support our assumption on the essentially linear structure of E-1 and establish our postulations on branching.

Size exclusion chromatography

The absolute molar mass (mass average, M_w; and number average, M_n) and polydispersity index (M_w/M_n, PDI) of the EPDM were measured using SEC. EPDM films were dissolved in tetrahydrofuran (THF) at room temperature for 24 h for SEC study. Before SEC experiments, samples were heated to 50°C for 4 h. The sample solutions were filtered through 13 mm Whatman GD/X filters (0.45 μm pore size). One hundred microliters of the sample solution (concentration of approximately 2 mg/mL) was injected onto the chromatographic system consisting of a precolumn, a Waters Styragel HT 6E 7.8 × 300 mm and a PL gel Mixed-D 7.5 × 300 mm, operated at room temperature. Differential refractive index (DRI), viscometry and light scattering (LS)

TABLE I
Characterization of the EPDM Rubbers Used in the Study

EPDM type	Ethylene[a] (wt %)	ENB[a] (wt %)	Branching[b]	Molar mass[c] M_w (kg/mol)	M_w/M_n[c]	Molar mass[d] M_w (kg/mol)
E-1	50	5.0 ± 0.5	–	202	2.74	133
E-2	55	5.0 ± 0.5	Long chain	376	2.80	258

[a] Verified by ^{1}H-NMR study.
[b] Verified by rheology experiments (frequency sweep) using parallel-plate geometry.
[c] Based on calibration with narrow molar mass distribution polystyrene standards.
[d] Absolute value measured by size exclusion chromatography (SEC) using a calculated $dn/dc = 0.077$ for EPDM in tetrahydrofuran at 20°C.

TABLE II
Material Properties of Engage® 8400[17]

Engage 8400	Octene content[a]	Density (g/cm^3)	Melting point[b] (°C)	T_g[b] (°C)	% Total crystallinity
Ethylene-octene copolymer	~40 wt %	0.870	60	−55	21

[a] Verified by NMR study.
[b] Verified by DSC (rate of heating 10°C/min).

signals were obtained by using a Viscotek 200 DRI-detector, a Viscotek LD-600 and RALLS-detector, respectively, at room temperature. A calibration curve for the column was also determined based on the analysis of a narrow molar mass distribution polystyrene standards having molar masses between 2,050,000 and 3250. THF was used as eluent with a flow rate of 1 mL/min. The pump used was Shimadzu LC-10AD type and the auto injector employed was Shimadzu SIL-10 Advp.

NMR spectroscopy

The relative diene (ENB), ethylene (e), and propylene (p) content of each EPDM were determined by ^{1}H-NMR using a Bruker 250 MHz spectrometer at room temperature. The measurements were performed using 10% (w/v) solutions of rubber films dissolved in 1,2-dichlorobenzene-d_4 (Deutero GmbH, Germany). Sixteen scans were averaged for each of the ^{1}H experiments. Similarly, the characterizations for comonomer compositions and LCB were determined by ^{13}C-NMR on the same instrument at 75 MHz. [13]C spectra were run as 10% solutions in 1,2-dichlorobenzene-d_4 (Deutero GmbH, Germany). Scans of 1024 were averaged for the ^{13}C experiments. To increase the signal to noise ratio, the ^{13}C spectrum of E-2 was rerun for longer time, where 51,200 scans were averaged.

Rheology

LCB for rubber films was characterized by running the frequency sweep Rheology experiments. A Rheometrics RMS-800 spectrometer were used employing parallel plate (diameter 25 mm) geometry at 2% strain over the temperature range of 40–100°C with an interval of 20°C within a frequency range of 0.01–100 rad/s. To check possible degradation effects during experiments, measurements were repeated several times. In all cases variations among measurements were negligible. Storage (G') and loss moduli (G'') were determined for the various temperatures over the entire frequency ranges for each sample. The zero-shear viscosity (η^o) and the loss angle ($\delta°$) were measured for each samples at 100°C.

RESULTS AND DISCUSSION

Size exclusion chromatography

The results of the SEC characterization are summarized in Table I. Conventional calibration was used for SEC to estimate molar mass and the width of the molar mass distribution or PDI. An absolute value of M_w was obtained by using simultaneous LS and DRI detection. The dn/dc (mL/g) for the EPDM-THF system necessary to calculate the absolute molar mass was estimated to be 0.077.[18] The M_w and M_w/M_n values obtained agree well with the reported values.[4–6,15,16] M_w of E-2 is found approximately 1.9 times higher than that of E-1. However, no significant difference in PDI (M_w/M_n) of E-1 and E-2 is observed.

The linear intrinsic viscosity/molar mass relationships are obtained from Visometry/SEC analysis and Mark-Houwink (MH) plots for E-1 and E-2 are shown in Figure 1. MH constants e.g., α for E-1 (0.69) agrees with the value reported for the linear EPDM[18] and α for E-2 (0.475) reveals a dense structure in solution due to presence of high degree of LCB. It is quite interesting to note from Figure 1 that at molar mass of around 100 kg/mol, the intrinsic viscosity of E-1 is lower than the E-2. This indicates that the degree of LCB increases with the increase in molar mass of E-2 that, however, does not affect the PDI to a significant extent. This could also attribute
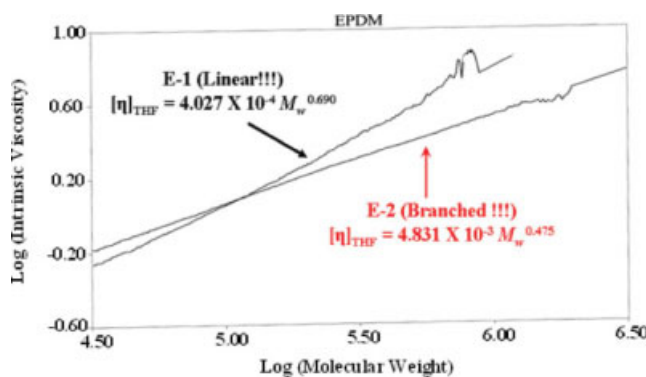

Figure 1 Mark-Houwink plot of E-1 and E-2 as obtained from SEC/viscometry. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
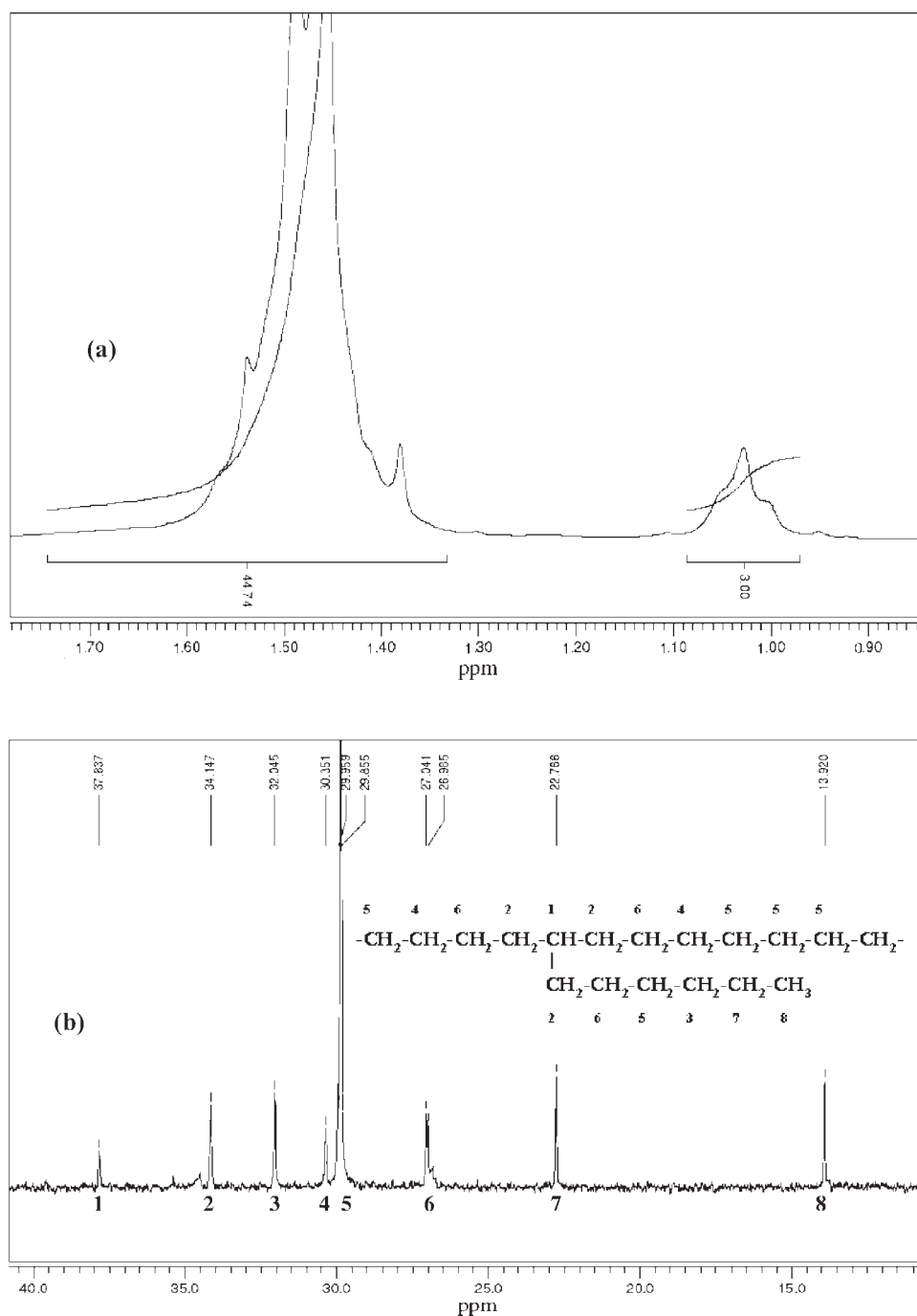
Figure 2 NMR spectra of Engage® 8400 (a) ¹H and (b) ¹³C.

to a substantial difference in the ethylene to propylene ratio either by original comonomer compositions of E-1 and E-2 or by presence of LCB in E-2. Significance of this observation is elaborated later.

NMR spectroscopy

The ¹H-NMR spectra of Engage 8400 is shown in Figure 2(a). Assuming Engage 8400 is a copolymer of ethylene and 1-octene, the terminal methyl (CH₃) resonance of the octene unit appears around 1.04 ppm. Because the terminal CH_3 peak represents three protons, the methylene (CH_2) groups in the pendant hexyl group account for 10 protons. This leaves ~35 protons in the main chain. In other words, there are about 17 CH_2 groups plus 1 methine (CH) group in the main chain for each hexyl side chain. Because each octene unit contributes three protons (1 CH_2 and 1 CH) in the main chain, there are 16 CH_2 groups per octene unit, giving a mole ratio of 8 : 1 (ethylene : octane). This agrees with product data sheet (Table II).[17] The ¹³C-
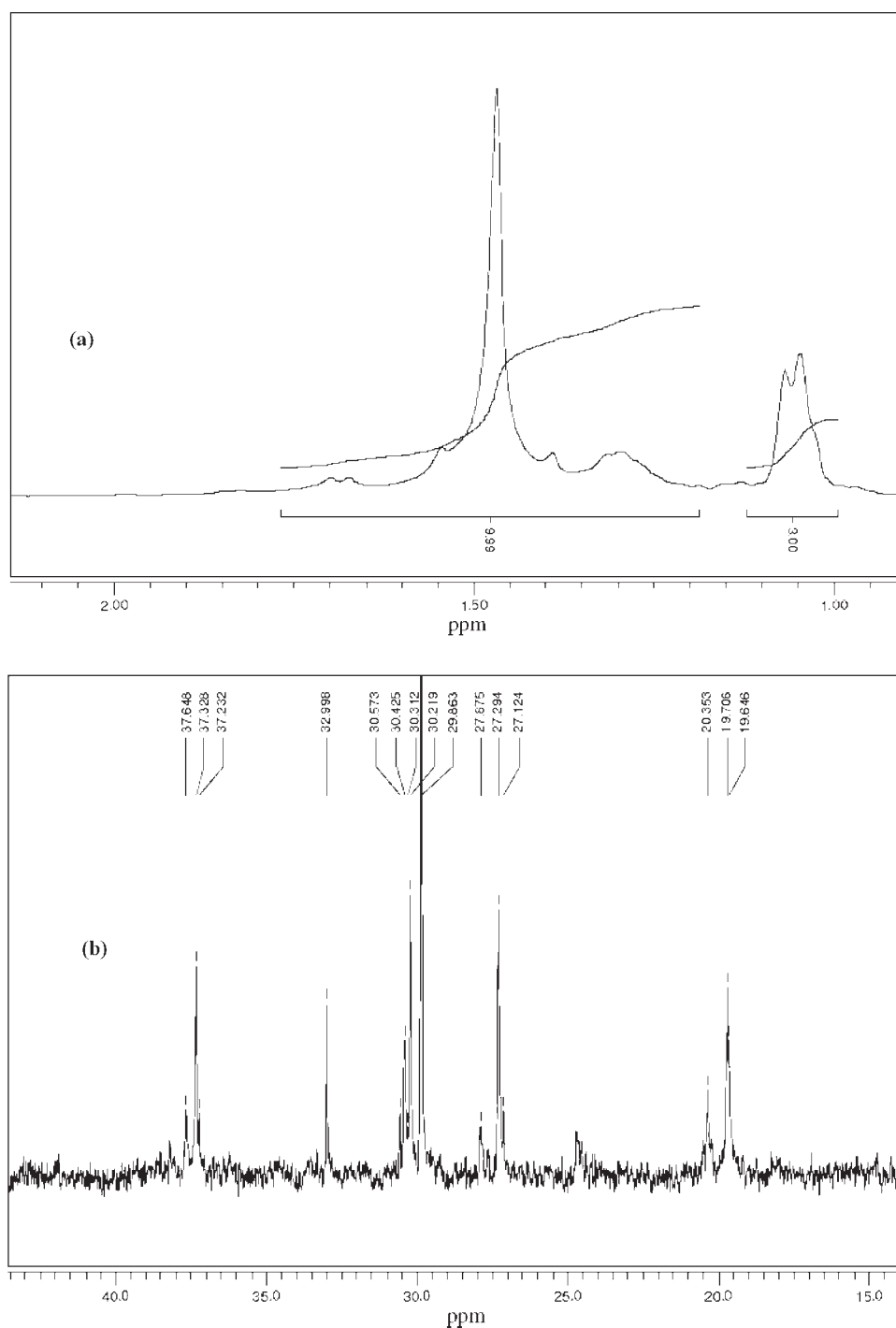
Figure 3 NMR spectra of E-1 (a) ^{1}H and (b) ^{13}C.

NMR spectrum is in accordance with such a structure [Fig. 2(b)]. The large peak at 30 ppm represents the CH$_2$ groups in the main chain, whereas the side chains give rise to peaks at 13.9, 22.8, 27, 30.4, 32.1, 34.1, and 37.8 ppm. The CH protons at the branch points yield the small peak at 30.35 ppm. The most diagnostic peak is the one at 13.9 ppm originating from the CH$_3$ protons at the end of the hexyl/longer side chains.[19] All the ^{13}C resonances have been assigned in Figure 2(b).[20,21]

The ^{1}H-NMR spectrum of E-1 is very similar to the Engage 8400, shown in Figure 3(a). The doublet at 1.1 ppm is due to the methyl groups in the propylene units while the large singlet centred around 1.5 ppm are due to all of the methylene groups plus 1 methine group at branch point. The intensity of the methylene protons compared with the methyl protons is much less in E-1. The integrals indicate 4–5 methylene groups per methyl groups. Each propylene unit takes out two of these methylenes leaving
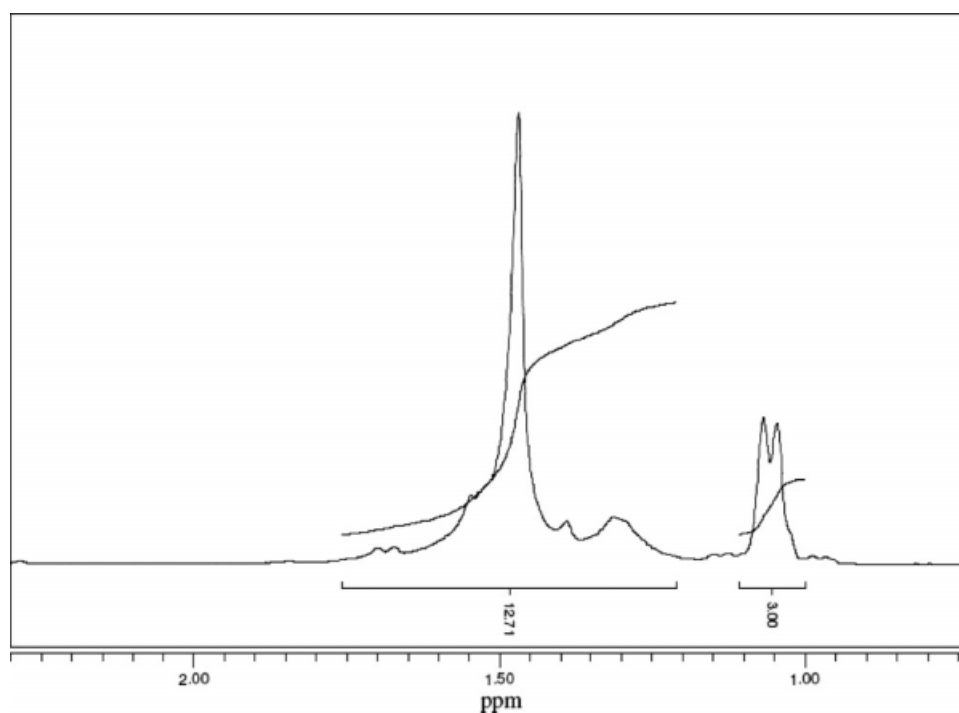
Figure 4 ^{1}H-NMR spectra of E-2.

2–3 for the ethylene groups. A rough estimate would then be 1–2 ethylene units per propylene group. ^{13}C spectrum of E-1 [Fig. 3(b)] is a combination of the Engage 8400 and a typical ethylene-propylene copolymer. In Figure 3(b) no resonance is observed around 14 ppm, which signifies the absence of any terminal methyl from a long- and short-chain branches. This also indicates that the terminal methyl from the ENB units is absent probably because of very low concentration (less than 2 mole %) of the ENB units in the studied EPDM.

The ^{1}H-NMR of E-2 is given in Figure 4 is very similar to that of E-1. The integrals indicate $\sim$ 6 methylene groups per methyl group. The ^{13}C spectrum of E-2 shown in Figure 5 is also similar to that of E-1 with some additional peaks. The spectrum shown in Figure 5 was run for a much longer time (51,200 scans were averaged). The small peak around 13.8 ppm is due to the presence of terminal CH$_3$ protons in a hexyl or longer side chain, which is only possible if the polymer had a significant fraction of hexyl or longer pendant groups. The CH$_3$ peak of the ENB unit appears also at the same position. The peak from the pendant CH$_3$ group of propylene unit appears at 19.9 ppm. It is important to note that the intensity of the CH$_3$ peak of propylene unit is much more than that of terminal CH$_3$ from a pendant hexyl (or longer) unit, which signifies that only a fraction of side chains are long units. For LCB, the carbons at the branch point and at α and β positions with respect to the branch point can also be identified from the ^{13}C spectrum. The peaks at

33.3 and 37.3 ppm are due to the methine branch point, and α carbon with respect to the branch point, respectively. The most striking feature of this spectrum is the low intensity of the signal from the main chain (CH$_2$) repeat units ($\delta^+\delta^+$) at 29.9 ppm. This is due to extensive branching of the main chain (both short and long chain), which is further supported by rheology study. The major peaks were assigned in Figure 5. Note that due to the presence of both methyl and LCB, two different sets of chemical shift arises, which are shown in two structures in Figure 5.[20,21] Because the methyl branch is predominating, the high intensity peaks are due to this kind of branch units. The type of branching has no influence on the carbons that are three or more bonds away from the branch points and that is why the chemical shift of $\gamma/\gamma\delta^+$ carbons are identical in both type of branch structures. The ^{1}H spectrum of E-2 is not interpreted in a quantitative manner (as in case of E-1) due to this extensive branching.

The concentration of ENB estimated from ^{1}H-NMR study[22] agrees well with the value reported by the manufacturers[15,16] for E-1 and E-2 (Table I). The amount of ENB present in E-1 and E-2 is found comparable within the limit of experimental error.

An idealized structure of ethylene (e) propylene (p) rubber (4 : 2) in a regular e-e-p pattern is shown below in Figure 6(a). The chemical shift values and assignments were made with the program Chem-Draw® Ultra. If we change the structure to a block type with the propylene groups together the idealized spectrum changes dramatically [Fig. 6(b)]. The
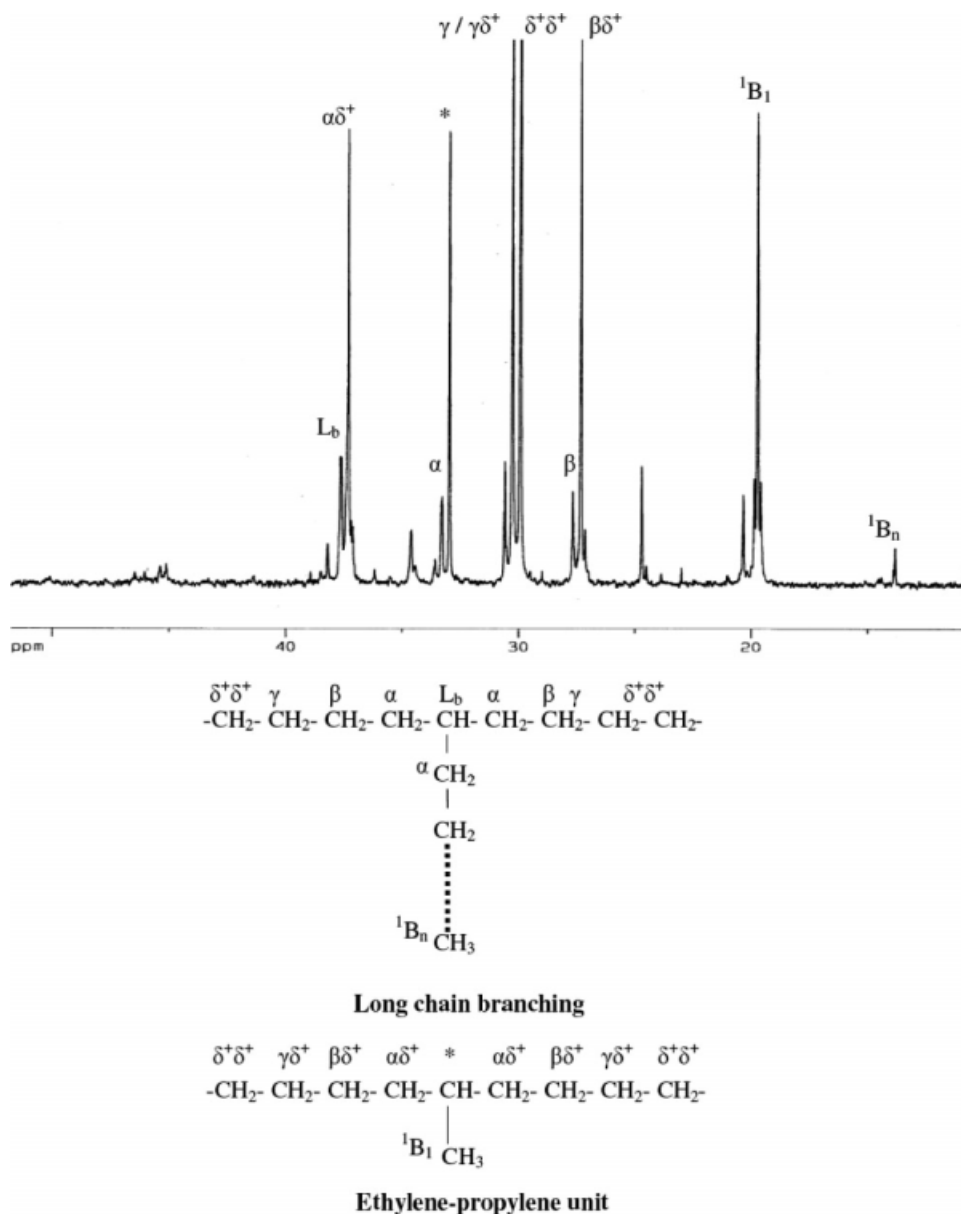
Figure 5 ^{13}C-NMR spectra of E-2 and assignment of LCB and EPDM.

actual EPDM ^{13}C spectra are more plausibly in accordance with the regular e-e-p structure [Fig. 6(a)]. Otherwise, we could have noticed the peak at 44.1 ppm due to methylene groups in between two methine carbons. This grouping only occurs with propylene–propylene pairs situated next to each other. But, that signal is not observed in the two EPDM spectra [Figs. 3(b) and 5] ruling out the possibility of p-p type pairs in the structure.

Rheology

The zero shear viscosity ($\eta°$) values obtained from the rheology experiments (viscosity vs. apparent shear rate) conducted at 100°C for Engage 8400, E-1 and E-2 are shown in Figure 7(a). For polymeric liquids, viscosity dependence on shear rate can, in general, be described by such "viscosity" curves shown in Figure 7(a). For sufficiently low shear rate values, viscosity becomes independent of shear rate, i.e., the material exhibits Newtonian behavior. This limiting viscosity is called the zero shear viscosity (η_0). At this zone, the polymer behaves as linear viscous where any alignment is destroyed by random thermal motion. With increasing the shear rate, significant alignment results in a decrease in viscosity where the steady state alignment is achieved and with more alignment the material flows faster. With further increase in shear rate the viscosity curve levels out, and the material tends toward Newtonian behavior again. However, for most polymeric liquids, it is impossible to determine experimentally
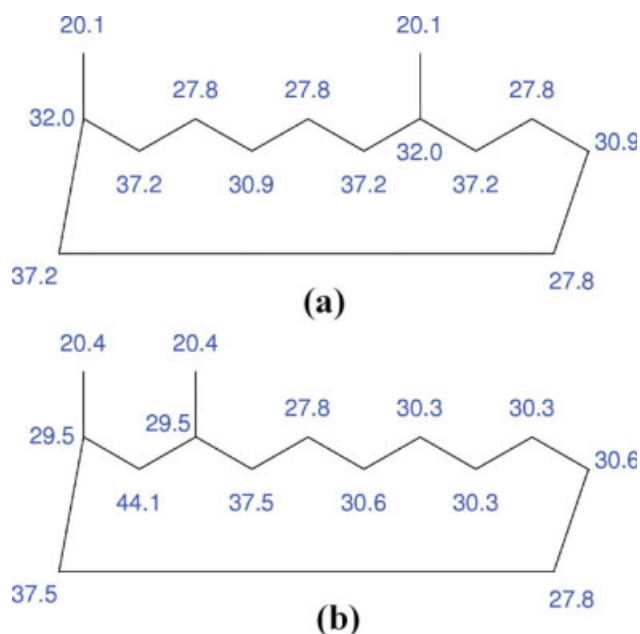
Figure 6 Idealized EPDM structure predicted from ^{13}C-NMR: (a) regular e-e-p structure and (b) block p-p structure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

such zone due to polymer degradation occurs at high shear rates.

Engage 8400 is found to be a typical thermo-rheologically simple material in Figure 7(a). At 100°C, η_0 of E-2 (6.07 × 10^6 Pa s) is almost 18 times higher than that of E-1 (3.45 × 10^5 Pa s). Since E-1 and E-2 have molecular masses much above their entanglement molar mass (M_e of EPDM ∼1860 g mol^{-1}),[23] it is reasonable to assume that they are in the regime of $\eta° \sim M_w^{3.4-3.6}$. We can, therefore, hypothesize that LCB enhances the zero shear viscosity of E-2 to a considerable extent. Otherwise, with 1.9 times higher molar mass, zero shear viscosity of E-2 would have been approximately 9 times higher than that of E-1 (considering, $\eta° \sim M_w^{3.4}$). Moreover, intense shear thinning behavior of E-2 compared to E-1 is also evident in Figure 7(a) due to the presence of LCB.

One of the common ways to look into the presence of LCB and its effect on the rheological properties is to plot loss angle ($\delta°$) over the frequency ranges of experiment at a particular temperature.[4–6] Such typical plot for E-2, E-1 and Engage 8400 is shown in Figure 7(b). E-2 shows enhanced elastic character (lower values of $\delta°$) and a broader transition between the terminal ($\delta = 90°$) and plateau zones ($\delta = 0°$) compared to E-1. The loss angle ($\delta°$) for E-2 remains almost unchanged over a specific frequency range and shows the gel-like rheological behavior. This shows clearly that considerable amount of LCB is present in E-2 compared to E-1, whereas, Engage 8400 appears to be a thermo rheologically simple material despite the presence of the

significant amount of short-chain branching. As a consequence, crossover of G'' (viscous moduli) and G' (elastic moduli) has not been observed for E-2 over the entire frequency ranges of the experiment even at 100°C [Fig. 8(a)].[24] Further increase in temperature to 200 and 250°C did not alter such observation (not shown). Such crossover for E-1 and Engage 8400 was well observed at 100°C [Figs. 8(b) and 9]. All these evidences clearly reveal that E-2 is a thermorheologically complex rubber, which can also be observed through a modified Cole–Cole plot (Fig. 10). Typically, log G'' is plotted against log G' at different temperature. Superimposition of log G'' vs. log G' at different temperature for E-1 indicates the thermorheological simplicity. In comparison, E-2 shows a clear deviation from the superimposition at different temperature. All the above observations prove that compared to E-2, E-1 is an essentially linear EPDM and E-2 contains a significant amount of LCB.

We also attempted to estimate the flow activation energy for E-1 and E-2 to observe the effect of LCB. For E-1, the flow activation energy is estimated as 35
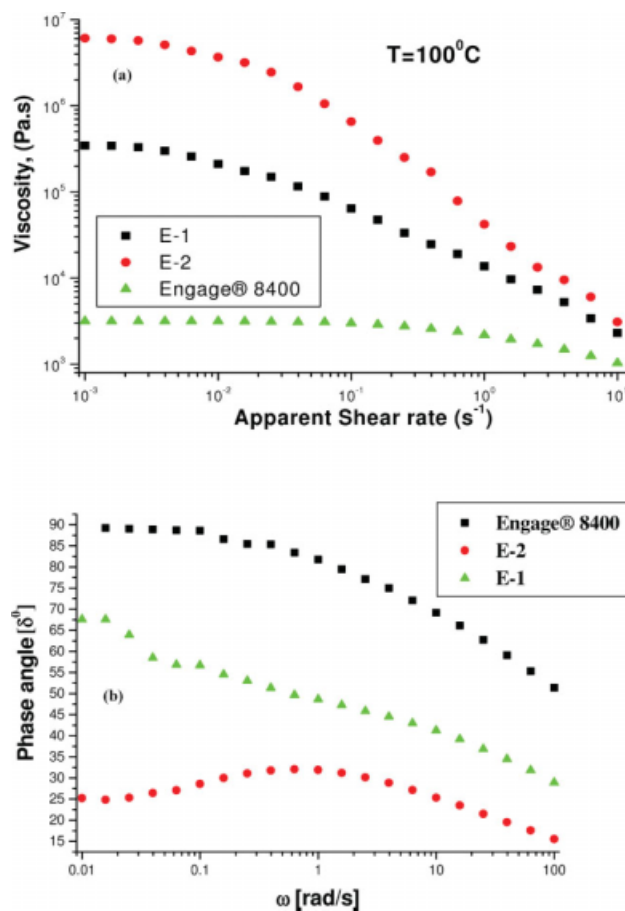

Figure 7 (a) Viscosity vs. apparent shear rate and (b) phase angle ($\delta°$) vs. frequency of Engage® 8400, E-1 and E-2 at 100°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
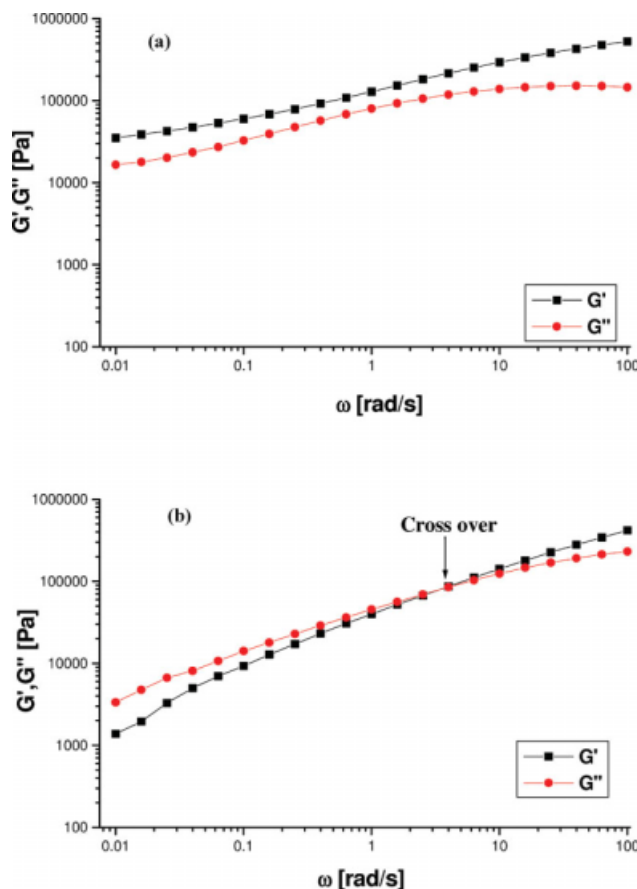
Figure 8 Storage (G') and loss (G'') moduli from frequency sweep at 100°C: (a) E-2 and (b) E-1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

kJ/mole (agrees well with cited value in the literature) using time–temperature superposition. Because of thermorheological complexity owing to the presence of extensive LCB in E-2, the time–temperature superposition did not exist and hence could not estimate the flow activation energy of E-2.

LCB estimation

The MH equations from the Viscometry/SEC for the E-1 is $[\eta]_{THF} = 4.027 \times 10^{-4} \, M_w^{0.690}$ and for E-2 is $[\eta]_{THF} = 4.831 \times 10^{-3} \, M_w^{0.475}$. Interestingly, Groto and Grasseley[23] proposed $[\eta]_{THF} = 3.88 \times 10^{-4} \, M_w^{0.686}$ for a linear hydrogenated polyisoprene (i.e., equivalent to an alternating ethylene propylene rubber of $\sim 1 : 1$ e : p having an essentially linear structure) which is very close to the value we obtained for E-1. This, therefore, indicates that Groto and Grassley's findings[23] for linear hydrogenated polyisoprene rubber is applicable to E-1. Furthermore, their proposed relation on zero shear viscosity and molar mass at 100°C i.e., $[\eta]_0 = 4.86 \times 10^{-4} \, M_w^{3.48}$ could also be applied for E-1.[23] Using M_w of E-1 estimated from the SEC the above equation yields $\eta_0 =$
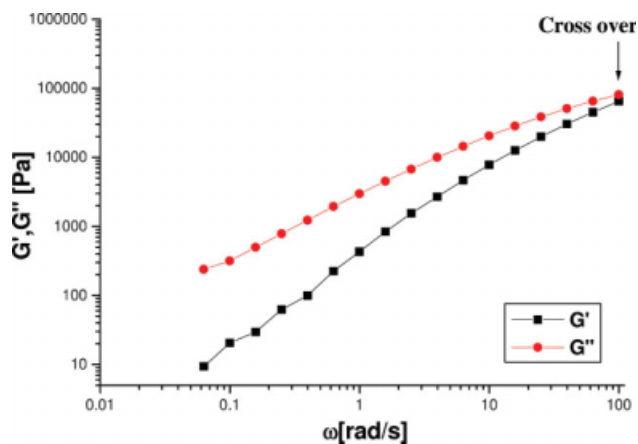
Figure 9 Storage (G') and loss (G'') moduli from frequency sweep at 100°C of Engage® 8400. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

3.29×10^5 Pa s. The experimental value for E-1 at 100°C obtained from the rheology experiment is 3.45×10^5 Pa s, which is very close and thus validates our hypothesis on the essential linear nature of E-1.

To quantify the degree of LCB in E-2, following assumptions are made, which seems reasonable considering all the results:

  I. E-1 is an essential linear polymer
 II. The comonomer composition (e/p/ENB) is practically identical for E-1 and E-2 and major differences are in molar mass and LCB

When compared in the same environment (temperature and solvent), a branched polymer has a higher segment density and a lower hydrodynamic volume than that of a linear polymer of equal molar
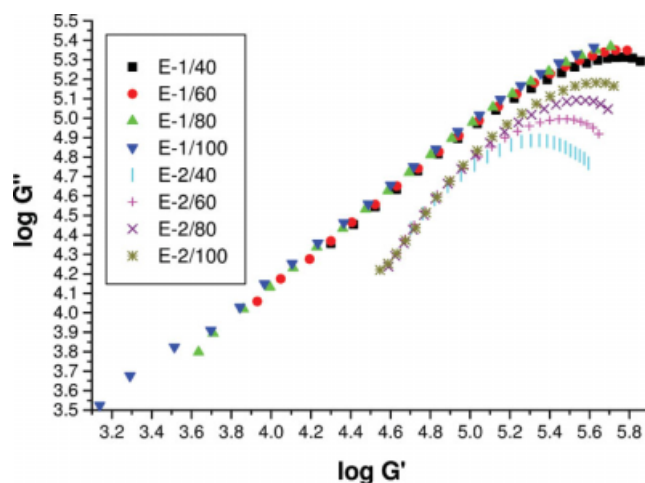

Figure 10 Modified Cole–Cole plot of E-1 (solid symbols) and E-2 (open symbols) at different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mass. The mean square radius of gyration is a measure of a polymer's hydrodynamic volume. Consequently, the ratio of mean square radius of gyration of a branched polymer to that of a linear polymer of the same molar mass in the identical environment expresses the degree of branching. The ratio g is referred to as the index of branching or contraction factor. Similarly, the ratio of the intrinsic viscosity of a branched polymer to a linear polymer of equal molar mass is conventionally denoted as g'. However, quantifying the LCB frequency (number of branches per chain/molecule) using g-ratio methods requires several theoretical considerations.[25] The other traditional approach to LCB characterization is through counting branch points by means of ^{13}C NMR in solution. This approach has a sensitivity limitation.[25] Several other methods for LCB quantification for polymers are also available and many are being proposed in literatures.[25,26] However, none of them are really straightforward and most of them require several model polymers or parameters to estimate the branching density especially for a polymer with unknown chemistry of LCB. So, the g-ratio method is chosen to quantify the density of LCB of E-2 in this study.

MH equation obtained for E-1 could be used to calculate the intrinsic viscosity of a hypothetical "essentially linear" E-2 of identical M_w and PDI which is $[\eta]_L = 2.19$ dL/g. Since, E-2 actually contains significant amount of LCB, we obtained $[\eta]_B = 1.55$ dL/g from SEC/viscometry. From $g' = [\eta]_B/[\eta]_L$, we get $g' = 0.7078$. As per literature, g' is related to g by an exponent factor b, $g' = g^b$. It is necessary to mention that much work has focus to understand the theoretical basis that relates g' to molecular parameters but still the dependence of g' and g is not clearly understood.[27] Moreover, the contraction factor g is also dependent on molar mass and degree of LCB (Fig. 1). But for simplicity and LCB frequency calculation, we ignore such dependence within the ranges of mass average molar mass of E-1 and E-2 (1.33×10^5 – 2.58×10^5). The value of b is reported to vary between 0.5 to 1.5 depending upon the nature, type, and degree of branching as well as molar mass and PDI.[28] Generally, b is equal to 0.5 for low levels of branching or for star polymers, whereas b is closer to 1.5 for comb-shaped polymers (very high degree of branching). Rheology and SEC study revealed the presence of very high degree of LCB in E-2. ^{13}C-NMR study shows that LCBs are predominantly trifunctional in nature. So, $b = 1.5$ is a good approximation for our case.[28] Hence, we get $g = 0.7942$. Now, we can use the following equation for trifunctional ($f = 3$) branching, $g = [(1 + m/7)^{1/2} + 4m/9\pi]^{-1/2}$.[29] Solving for m (the number of branch unit per molecule which is the LCB frequency), we get approximately 27 branches per rubber molecule.

However, if we consider $g' = g^b$, where $b = (2 - \varepsilon)$ and ε is the exponential from the MH equation for the linear analogue[29] a total of 28 branches are estimated per rubber molecule. Hence, approximately 27–28 branches (for b $\approx$ 1.31 to 1.5) per rubber molecule are present in E-2 sample assuming only trifunctional branching is randomly distributed.

This, therefore, indicates the presence of a comb type branching architecture (highly branched) in E-2 where branches are long enough to entangle with each other. Considering approximately 27–28 branches on an average per rubber molecule, the average molar mass of the rubber chain between two successive branching points would be well above the entanglement molar mass of EPDM. Thus, the rubber chain in between two branch points can also play a major role in entanglement to enhance the viscosity. The α-value obtained from MH equation for E-2 indicates highly dense structure.[27–31] Highly branched type molecules at lower molar mass acquire higher intrinsic viscosity than their corresponding linear counterpart with same molar mass (Fig. 1).[27–31] With higher conversion during polymerization, degree of branching increases with molar mass yet PDI remains unaffected because of the controlled nature of LCB introduced by the catalysts.[31,32] Moreover, ^{13}C-NMR did not show a high intensity peak for the main chain of E-2 even after signal averaging for a long time (51,200 scans were averaged for the ^{13}C spectrum of E-2 in Fig. 5). This is only possible if there are very small numbers of methylene units (compared with E-1), which are 3 or more carbons away from the branch point. Therefore, we can conclude that E-2 has a very high degree of branching (possibly both short and long chain). As a consequence of high degree of LCB along with high molar mass, several types of entanglements e.g., between LCBs, between main chains and among LCBs to main chains exist in E-2, which can act as physical crosslinks. This could be a reason for E-2 to behave like a lightly crosslink rubber or microgel, which is manifested by the dominance of elastic moduli (G') over viscous moduli (G'') throughout the frequency ranges in rheology experiments even at 250°C (not shown).[24,32]

Another point we would like to specify with regard to its behavior like high ENB grades leading to higher state of crosslinking as claimed by E-2 datasheet. Our previous work on the crosslinked E-1 and E-2 confirm this to be true.[33,34] Approximately, 60% higher crosslinking density (both in sulphur and peroxide curing using the identical formulations and conditions) is observed in E-2 compared to that in E-1 despite the similar ENB content (~5 ± 0.5 wt %). This is also attributed to the highly dense branched structure of E-2. High degree of LCB increases the probabilities of both inter and intra

molecular crosslinking that leads to increasing the overall crosslinking density.

In a long-chain branched high molar mass polymer, well-entangled LCB suppress longitudinal motion at low frequencies since the terminal relaxation involves the movement of the entire molecule. Moreover, a further mechanism at higher frequencies is also needed to allow translation of a branched molecule. Long chain branch retraction to a more compact structure has been proposed as such a mechanism.[35–40] These mechanisms were further explored and the whole viscoelastic response was found to depend, not only on the LCB content, but also on LCB structure and topology.[40] The combination of high molar mass together with high degree of LCB makes E-2 a thermorhelogically complex and quite unique with regard to both melt and solution properties.

CONCLUSIONS

This work has clearly demonstrated that in-depth understanding on molecular architecture of an unknown EPDM rubber containing high degree of LCB is possible even though the chemistry of branching is not known. Structural information on LCB containing EPDM is elucidated using SEC, NMR, and Rheology by the help of an essentially linear EPDM with similar comonomer compositions but with different molar mass. Both the studied EPDM was found to have a regular e-e-p type backbone as revealed by NMR study. E-1 is found to be thermorheologically simple rubber compared to E-2. On the basis of our experimental observations and theoretical considerations, we predicted the presence of high degree of LCB in E-2 and the branching architecture was more likely to be a comb type. For E-2, α of MH equation estimated from SEC/viscometry matches with the reported values for other polymers containing high degree of LCB. The quantification of degree of LCB using semiempirical equations supports our notion while NMR validates our postulation. With some reasonable assumption, this work furnishes the structural information of EPDM containing high degree of LCB without prior information on the chemistry of branching vis-à-vis its reason for behaving as a high ENB content rubber.

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