

The effect of controlled degradation on the molecular characteristics of heterophasic ethylene–propylene copolymers

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ABSTRACT: A commercial heterophasic ethylene–propylene copolymer (HEPC) produced by Sasol Polymers using a Ziegler–Natta catalysed gas-phase process was vis-broken (controlled degradation) to various degrees by making use of an organic peroxide. The effects of the amount of vis-breaking on the molecular characteristics and physical properties were subsequently studied by making use of preparative Temperature Rising Elution Fractionation (p-TREF), Nuclear Magnetic Resonance (NMR), Differential Scanning Calorimetry (DSC), High Temperature Size Exclusion Chromatography (HT-SEC), and deposition of the SEC fractions via the LC Transform Interface (SEC-FTIR). It was found that by increasing the amount of organic peroxide, the molecular characteristics of the heterophasic copolymer are severely affected and hence influence the physical characteristics of the polymer dramatically. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41783.

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INTRODUCTION

Heterophasic ethylene–propylene copolymers (HEPCs), also known as impact copolymers (ICPs), are widely known to have superior low temperature impact resistance properties over conventional polypropylene (PP).^{1–3} As a result of these superior properties, coupled with the good mechanical performance, heat resistance, and versatility of conventional polypropylene, HEPCs have seen a growing demand in the market in recent times. The most common commercial method to produce these polymers is a sequential two stage polymerization of (first) propylene and then copolymerization of propylene and ethylene in the second reactor. The result of this two stage polymerization process is a highly complex mixture of amorphous, random, and blocky ethylene–propylene copolymers with different chemical composition distributions as well as different molar mass distributions, together with highly isotactic polypropylene and some polyethylene homopolymer.^{3–6} It has been proposed that in this complex mixture of morphologies, the ethylene–propylene segmented or blocky copolymers can act as compatibilizers whereby they enhance the interfacial adhesion between random rubbery copolymers and the polypropylene homopolymer. This interaction can be related to the enhancement of impact strength at low temperatures.^{7,8}

Vis-breaking or controlled rheology (CR) is a process used during the manufacturing of polypropylene and propylene copoly-

mers to decrease the average molecular weight of the polymer. By decreasing the average molecular weight of the polymer a higher melt flow rate (MFR) as well as a decrease in the molecular weight distribution (MWD) is achieved. This should result in a polymer that is less prone to warpage and exhibits more uniform shrinkage. In addition, higher extrusion rates for fibres and films and significantly increased elongation at break should be achieved. The effect of vis-breaking on the molecular characteristics of HEPCs is still largely unexplored.⁹ This is significant, as it is generally accepted that the properties of these HEPCs are dependent on the microstructure of the polymers.¹⁰ Whether or not the microstructure of the HEPC is affected by the vis-breaking process is the focus of this study. A fundamental understanding of the way the peroxide affects the molecular structure of these complex polymers could be useful in predicting the properties of the vis-broken products.

In this study, three HEPCs with equal ethylene content were vis-broken to varying degrees by making use of an organic peroxide. The effects of the amount of vis-breaking on the molecular characteristics and physical properties were subsequently studied by first fractionating the polymer according to crystallizability by making use of preparative temperature rising elution fractionation (p-TREF). The molecular composition and properties were then determined by ¹³C-NMR spectroscopy, DSC, high temperature size exclusion chromatography

Table I. Properties of Prepared Samples^a

Sample	Peroxide added (wt %)	Ethylene content (wt %)	Melt flow rate (g/10 min)	Tensile modulus (MPa)	Yield stress (MPa)	Charpy notched impact		
						23°C	0°C	-20°C
MS001	0.000	6.90	1.48	1419	26.8	81.0	12.3	7.26
MS002	0.025	6.90	3.67	1403	26.4	17.1	7.95	5.47
MS005	0.200	6.90	42.1	1300	16.2	14.7	7.58	5.57

^a According to ASTM standards for testing.

(HT-SEC), coupling FTIR, and SEC by deposition the SEC fractions via a LC Transform Interface (SEC-FTIR).

EXPERIMENTAL

Sample Preparation

The heterophasic copolymers used in this study were all prepared from a commercial reactor grade sample (denoted “base polymer”) produced and sold by Sasol Polymers (South Africa). The base polymer powder was compounded with the processing stabilizers Irganox® 1010 (1 000 ppm) and Irgafos® 168 (1 000 ppm) (BASF, Ludwigshafen, Germany) in a twin screw ZSK 18 Coparion Extruder at 500 rpm and barrel zone temperatures from 80 to 210°C. Increasing amounts of the vis-breaking peroxide Trigonox 301® (3,6,9-Triethyl-3,6,9-trimethyl-1,4,7-triperoxonane, Akzo Nobel Polymer Chemicals, Amersfoort, Netherlands) were added (premixed before extrusion as a 20 wt % masterbatch) in order to achieve different vis-breaking steps. Table I shows a summary of the main characteristics of the various samples.

Preparative Temperature Rising Elution Fractionation

A preparative TREF instrument built in-house was used for this part of the study.¹¹ Typically 3 g of a sample (Table I) was dissolved in 300 mL of xylene (stabilised with a mixture of Irganox 1010 and Irgafos 168, 0.1 wt % in total) at a temperature of 130°C. To the hot solution, in a glass reactor, preheated sea sand (Aldrich, South Africa) was added, ensuring that the sand covered the solution completely. The sand/polymer solution mixture was then cooled in a controlled fashion at 1°C/h. When the mixture reached room temperature, the sand support and residual solvent was transferred to an elution column, and placed in a modified oven. Elution with xylene (stabilized with 0.025 wt % beta-hydroxytoluene, Ciba Switzerland) at set temperature intervals and subsequent evaporation of the xylene and precipitation with acetone lead to fractions of the polymer being isolated. These fractions were dried under vacuum to constant weight.

Size Exclusion Chromatography and Size Exclusion Chromatography Coupled to Fourier-Transform Infrared Spectroscopy

The method used here (with small adaptations) followed that reported by Pasch *et al.*¹² SEC was conducted using a PL220 Chromatograph (Polymer Laboratories, Varian, Church Stretton, Shropshire, England). Analysis was done at 150°C using with three 300 mm × 7.5 mm PLgel Olexis columns, a PLgel Olexis Guard and a refractive index detector. Samples were prepared by dissolution in trichlorobenzene (TCB, Sigma-Aldrich South

Africa, refluxed over sodium and freshly distilled and filtered) at 160°C. Sample concentration was 2 mg mL⁻¹ for the SEC-FTIR experiments and 0.5 mg mL⁻¹ for the SEC analyses. An automated sample injection system was used with TCB as the mobile phase. The mobile phase flow rate was 1.0 mL min⁻¹. Sample injection volume was always 200 μL. For SEC experiments, calibration was done by using polystyrene standards (PSS GmbH, Mainz, Germany).

For the SEC-FTIR experiments, the column outlet was connected to a LC Transform (solvent evaporation FTIR interface, Series 300, Lab Connections, Carrboro, USA). The deposition stage was at 165°C and the spray nozzle at 150°C. The line connecting the nebulization compartment and the high temperature chromatograph was kept at 150°C. Overheating of the nozzle was prevented by a constant flow of compressed air. Deposition of the solutes onto a heated germanium disk was followed by FTIR analysis [Nicolet iS10 Spectrometer, (Thermo Electron, Waltham, USA)]. Data analysis was done with the Omnic software package (Thermo Electron).

NMR Spectroscopy

A standard procedure developed for polyolefins at the NMR laboratories at the University of Stellenbosch was used to obtain high resolution ¹³C-NMR spectra on a 600 MHz Varian^{Unity} INOVA NMR Spectrometer. Samples were prepared at a concentration of about 6 wt % in deuterated tetrachloroethane (Aldrich, South Africa). As has been previously reported,⁹ spectra were obtained by making use of a 90° flip angle of about 6μs with continuous proton decoupling. The method utilized an acquisition time of 1.8 s. The pulse delay was 15 s. According to literature¹³ spectra obtained with this method should be quantitative, as long as only those carbon atoms with relaxation delays of less than 3 s used for calculations.

RESULTS AND DISCUSSION

Fractionation Results

Fractions were collected at predetermined temperatures of 30, 60, 80, 90, 100, 110, 120, and 130°C. The weight % of the fractions as a function of elution temperature is shown in Figure 1, which shows both the weight fraction per temperature increment ($W_i\%/\Delta T$) and the % weight fraction ($W_i\%$). It can be seen that all three samples elutes over a broad range of temperatures indicating heterogeneity in both isotacticity and chemical composition. Three main fractions can be identified, namely those eluting at 30, 110, and 120°C. These fractions constitute approximately two thirds of the total sample weight and will therefore influence the bulk of the polymer to a large extent.

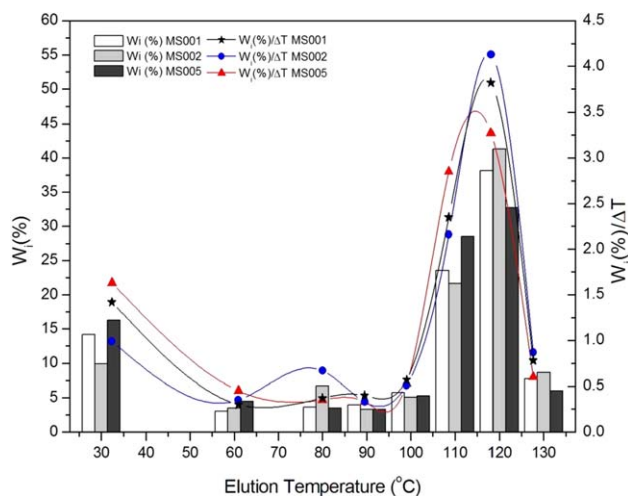


Figure 1. TREF elution curve comparison for MS001, MS002, and MS005. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As TREF fractionates according to crystallinity the 30°C fraction is expected to be amorphous whereas the higher temperature fractions (110°C and up) will be highly crystalline. The smaller fractions in between will be semi-crystalline.^{6,12} Figure 1 clearly illustrates that there are quite significant changes that occur in the three main fractions when increasing the vis-breaking step.

From Figure 1 it is clear that there are three main fractions that make up these copolymers. The majority of the sample is made up of the crystalline fractions (those that elute in the preparative TREF at 110, 120, and 130°C), and the “rubbery” or mostly amorphous phase (the 30°C fraction). The remainder of the material is comprised of the crystalline copolymer fraction (the part that elutes at 60, 80, 90, and 100°C in the prep-TREF experiment). The prep-TREF profiles of the three HEPCs clearly show that an increase in the extent of vis-breaking does alter the crystallization behavior of the polymers in question.

First, it is clear that the composition of the crystalline fractions (those that elute at 110–130°C) change as the extent of vis-breaking increases. For example, the most vis-broken sample (MS005) has more material eluting in the 110°C fraction than the nonvis-broken material (MS001), and correspondingly the MS005 sample has less material eluting in the 120°C fraction compared with MS001. In comparison, the less vis-broken MS002 sample has roughly the same amount as MS001 eluting at 110°C while it has slightly more material eluting at 120°C compared with MS001. Overall therefore, it is clear that increasing vis-breaking increasingly changes the solution crystallization behavior of the samples.

The copolymer fractions (eluting at 60, 80, 90, and 100°C) are quite interesting. The amounts of the fractions eluting at 90 and 100°C (which is believed to be the more crystalline copolymers present in this fraction) are roughly similar for all three samples. At the 80 and 60°C fractions, differences are observed. There is a notable increase in the amount of material of the MS002 sample that elutes at 80°C compared with the other two samples. Overall, the amount of material that elutes at 60°C increases slightly as the extent of vis-breaking is increased.

The rubbery phase (the 30°C or soluble fraction) appears to be larger for the most vis-broken material (MS005). This is quite clear from the amount of material present in the 30°C or soluble fraction of MS005 (Figure 1).

It is clear that vis-breaking does affect the crystallization profile of the HEPCs. In order to help explain the change in crystallizability, we investigated the chemical composition distribution of the three HEPCs.

NMR Analysis

Initially we used ¹³C-NMR to determine comonomer (ethylene) content and monomer sequence distributions on all the TREF fractions. Comonomer content and sequence distributions were calculated according to relationships developed by Ray *et al.*¹⁴ and Randall.¹⁵ Isotacticity data was also calculated according to the method of Viville *et al.*¹⁶ Selected relationships are shown in Figures 2–5. We plotted the diad concentrations relating to ethylene–propylene (EP) junctions (Figure 2), as well as the triad concentrations relating to continuous ethylene sequences (EEE) (Figure 3), propylene sequences (PPP) (Figure 4) and the “blocky” copolymer sequences (EEP, PEE, PPE, and EPP) [Figure 5(a,b)]. The triads relating to the isolated E and P units (PEP and EPE) were also investigated but are not shown here. These values, taken in conjunction with the profile changes resulting from the prep-TREF experiments are very interesting.

As could be expected we see (Figure 2) no EP junctions in the 110, 120, or 130°C fractions, although we do see some blocky P units in the 120°C fractions (Figure 4). In the 110°C fraction the EEE triads (Figure 3) decrease sharply after the first vis-breaking step, similar to what was seen in the 100°C fraction. We see no blocky E or P units. The amount of PPP triads (Figure 4) increase in the 110°C fraction as the vis-breaking steps increase. This is due to molecular weight (chain end) effects as crystalline PP is broken down by the peroxide. This is reflected by the decrease in PPP triads in the 120°C fraction as vis-breaking increases. Then we also see the appearance of some EEE triads in the 120°C fraction. We postulate that this is due

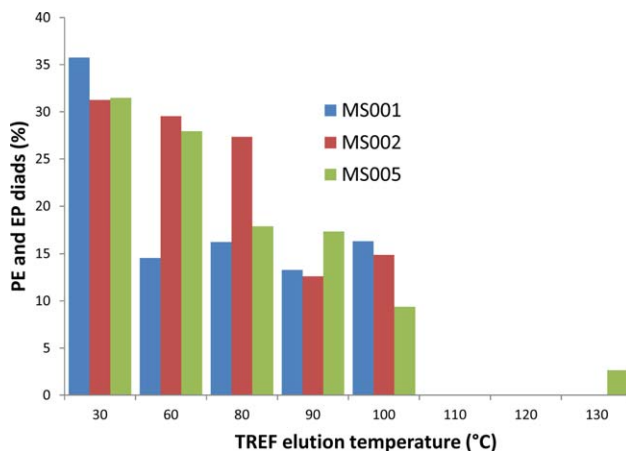


Figure 2. The relative concentrations of EP diads of the TREF fractions as determined by ¹³C-NMR. The legends represent the samples obtained by vis-breaking experiments (see Table I). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

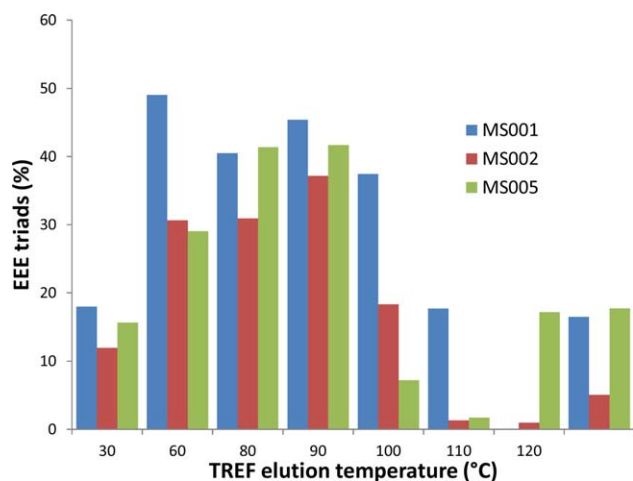


Figure 3. The concentration of EEE triads in the TREF fractions of vis-broken samples as determined by ^{13}C -NMR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the breakdown, at the EP junctions, of ethylene rich copolymers with the resultant formation of highly crystalline PE, or true “block” copolymers (as reflected by the appearance of blocky P sequences in the 120°C fraction. Interestingly we see the presence of apparently ethylene homopolymer (as represented by the EEE triads present) in the 130°C fraction, together with some apparently less isotactic PP. We have observed this phenomenon before, and believe this to be an artifact caused by molecular weight effects during the initial crystallization onto a support. This material appears to decrease after the first vis-breaking step, and reappears when the material is highly vis-broken.

In the copolymer fractions we see some significant changes. The prep-TREF profiles show that increasing vis-breaking results in an increase in the material that is sparingly crystalline (elutes at 60°C). Here it is clear that the chemical composition changes significantly after the first vis-breaking step, with the EP junctions doubling in concentration (Figure 2). This increase

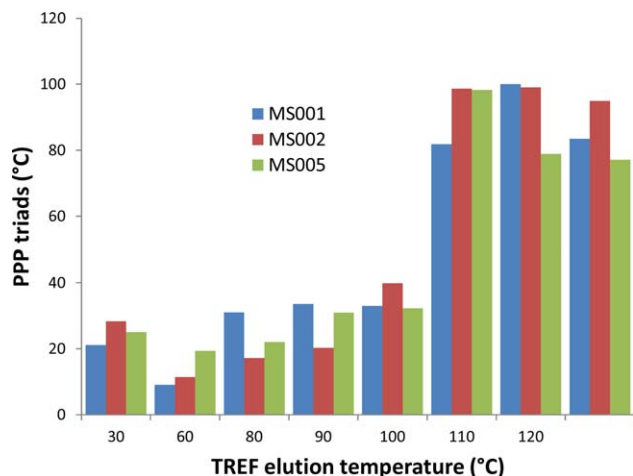


Figure 4. The concentration of PPP triads in the TREF fractions of visbroken samples as determined by ^{13}C NMR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coincides exactly with an increase in the blocky E and P sequences [Figure 5(a,b)]. This is accompanied with a decrease in the EEE triads and a slight increase in the PPP triads (Figures 3 and 4). It can be postulated that the materials crystallizing in this fraction of TREF originates from the first step vis-breaking of more crystalline blocky copolymers.

In the fraction that elutes at 80°C we observe an initial increase in the EP junctions (Figure 2) (as opposed to a decrease that was observed for the 60°C fractions) after vis-breaking, while further vis-breaking leads to a decrease back to the original level. The change is also reflected in the Blocky E units and the Blocky P units, and is also reflected in the amount of polymer eluting at this step (Figure 1). It appears that the first vis-breaking step results in blocky copolymers, possibly those that originally eluted in the 90 to 110°C fractions being broken down and crystallizing at lower temperatures. The EEE and PPP triads (Figures 3 and 4) concentration reflects the inverse behavior, an initial decrease followed by an increase.

Around 90°C the EP junctions are reasonably constant over all the HEPCs, although a slight increase is observed for the MS005 sample. This behavior is mirrored in the concentration of the EEE and PPP triads. What is interesting though, is that

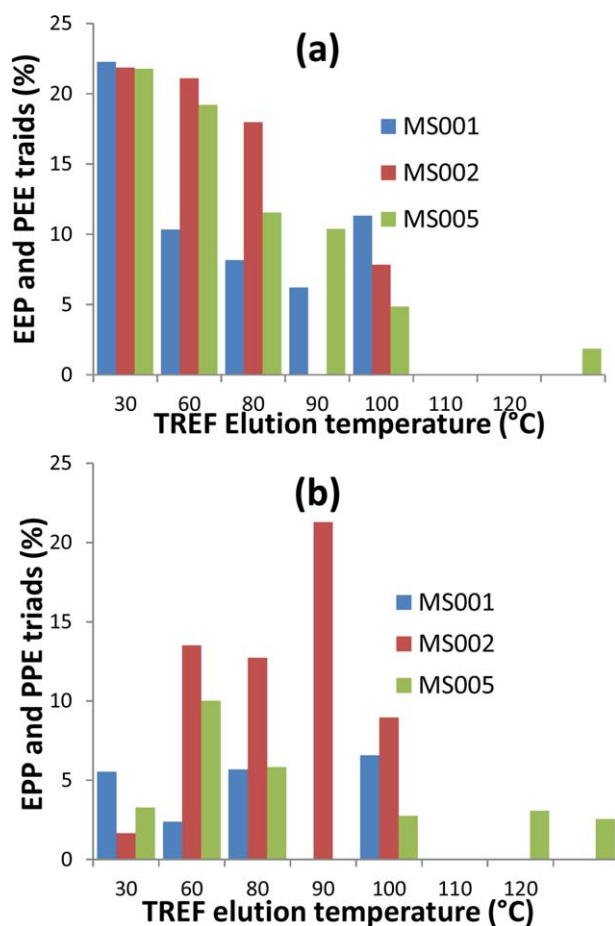


Figure 5. The concentration of (a) EEP and PEE and (b) EPP and PPE triads in the TREF fractions of vis-broken samples as determined by ^{13}C -NMR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

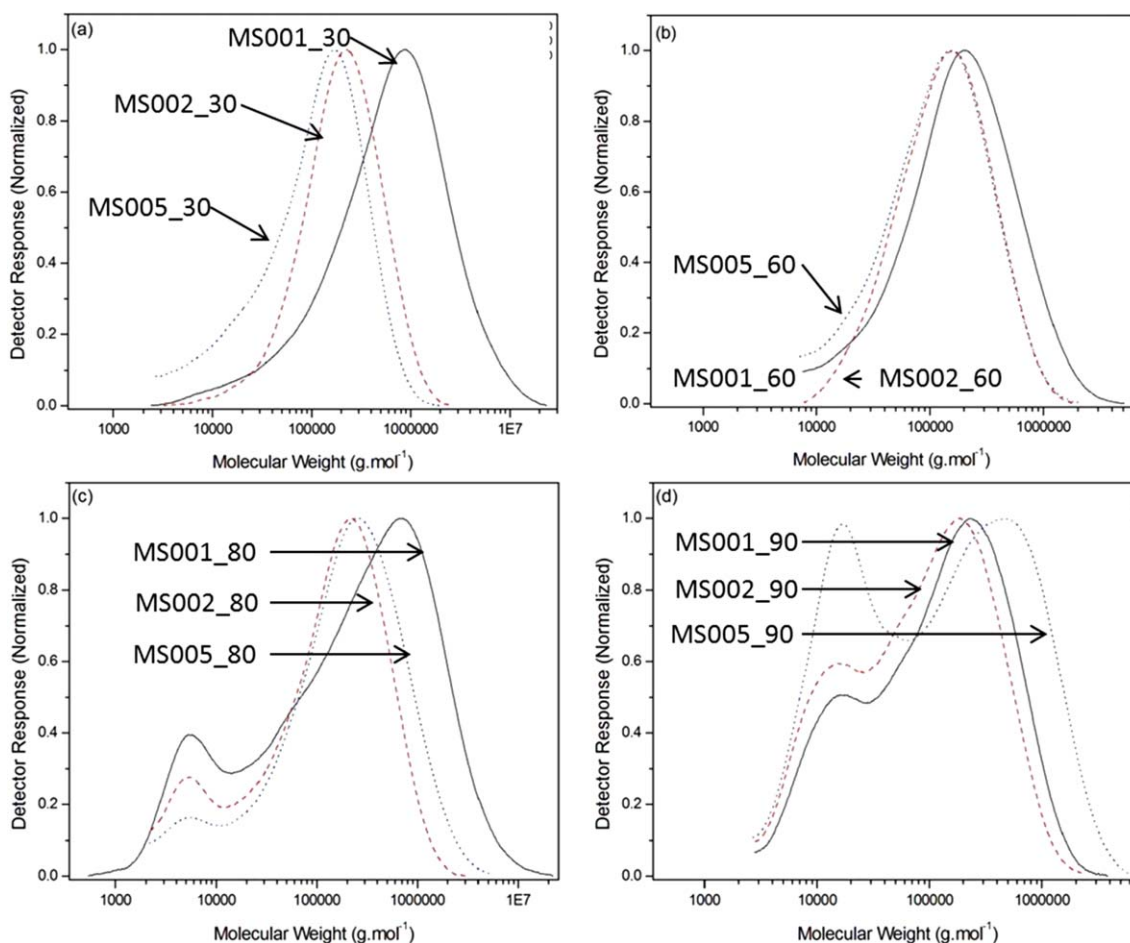


Figure 6. SEC curves comparing the molecular weight distributions for the lower temperature TREF fractions of the three bulk samples (a–d represent 30–90°C fractions). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the Blocky E sequences disappear completely after the first vis-breaking step, and correspondingly, Blocky P sequences appear. The TREF data shows little or no change in the amount of material that elutes here, yet the NMR data shows some changes. As stated before, it is thought that the blocky copolymers that now elute at lower temperatures were originally part of this fraction in MS001.

In the more crystalline copolymer fractions we see large changes. EP junctions decrease steadily as the number of vis-breaking steps increase (100°C fraction), while the EEE triads decrease sharply. The number of Blocky E sequences decrease steadily. This decrease shows that vis-breaking affects the ethylene rich copolymers which, after reaction and chain scission could crystallize as blocky copolymers at lower temperatures, and are as such found in these TREF fractions. Alternatively, chain scission at or near the EP junctions in these copolymers could, as was shown earlier, “release” more highly crystallizable “polyethylene-like” materials which could crystallize at higher temperatures (and as such be present in those TREF fractions). Segmented ethylene–propylene copolymers with long ethylene sequences act as compatibilizers that will enhance interfacial adhesion between random copolymer regions and propylene homopolymer regions and enhancing impact strengths.^{7,8,21}

Breaking down of these copolymers will therefore affect the low temperature impact properties of the HEPCs. The concentration of the PPP triads remains constant, but the amount of blocky P units decrease sharply with more vis-breaking steps.

In the rubbery phase (which contains mostly EPR, while some atactic PP and ethylene homopolymer may also form part of this fraction¹⁷) we see that the concentration of the diads representing the EP junctions remains quite stable for the 30°C fractions, after a slight decrease during the first vis-breaking step. The “blocky” E (EEP and PEE triads) or P (PPE and EPP triads) in the rubbery phase are largely unchanged by vis-breaking. It does appear as if the PPP sequences increase slightly and the EEE sequence decrease.

HT-SEC Analysis

Fractionation by crystallization gives only molecular information of the material based on crystallization, and the effect of the molecular weight changes during the vis-breaking step is not addressed. The molecular weight distributions of the TREF fractions for the three bulk samples are shown in Figures 6(a–d) and 7(e–h). Note that the labels are omitted for graph (f), Figure 7, as all the plots are on top of each other. Similar to what was shown by Pasch *et al.*,^{6,12} the TREF fractions of all three samples

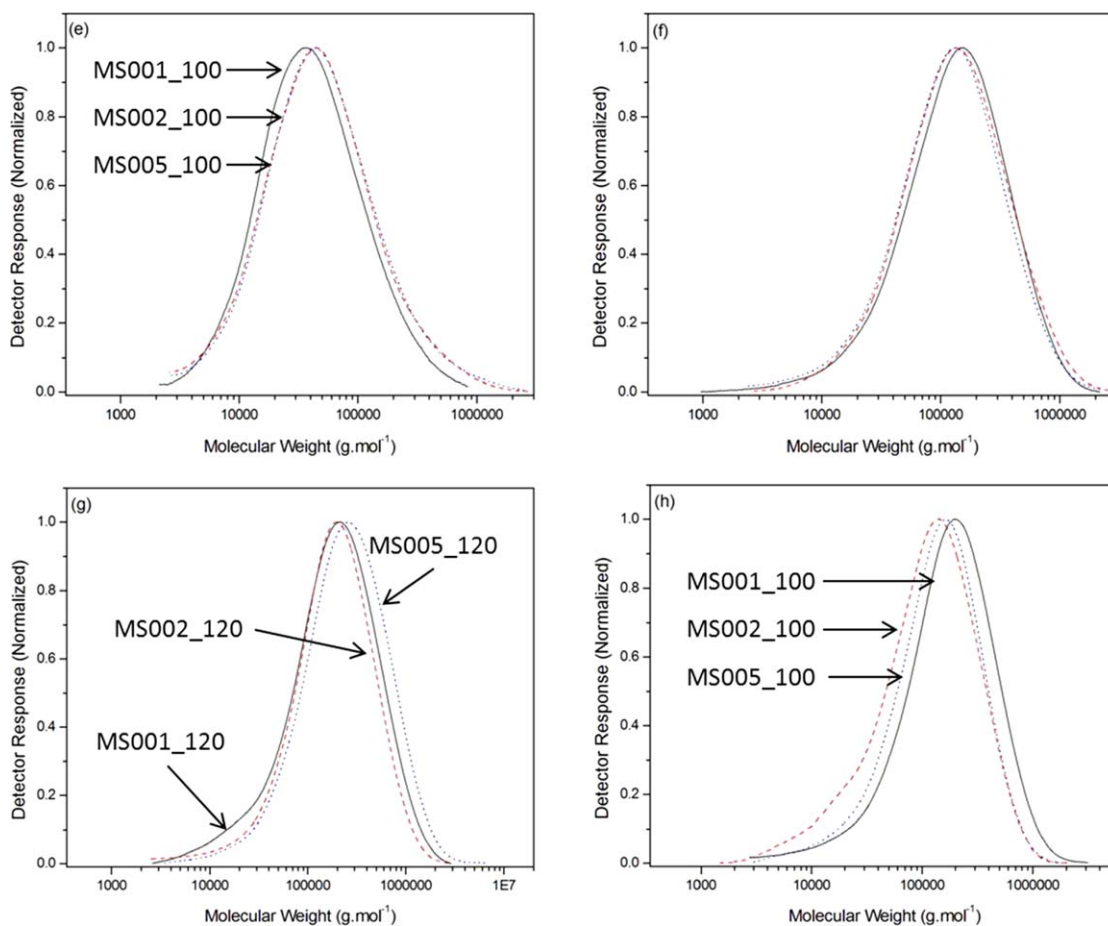


Figure 7. SEC curves comparing the molecular weight distributions for the higher temperature TREF fractions of the three bulk samples (e–h represent 100–120°C fractions). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

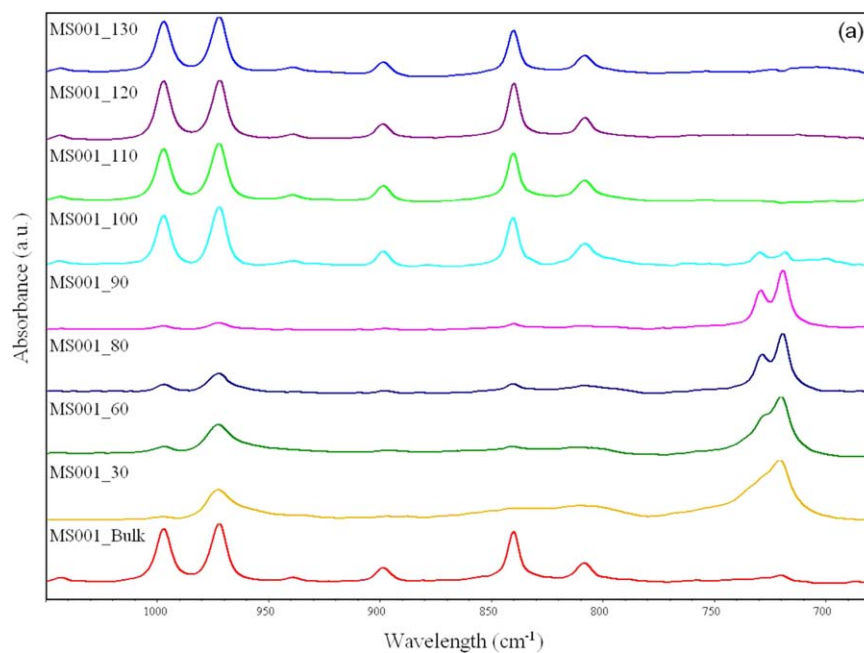


Figure 8. FTIR spectra for the bulk MS001 sample and its TREF fractions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

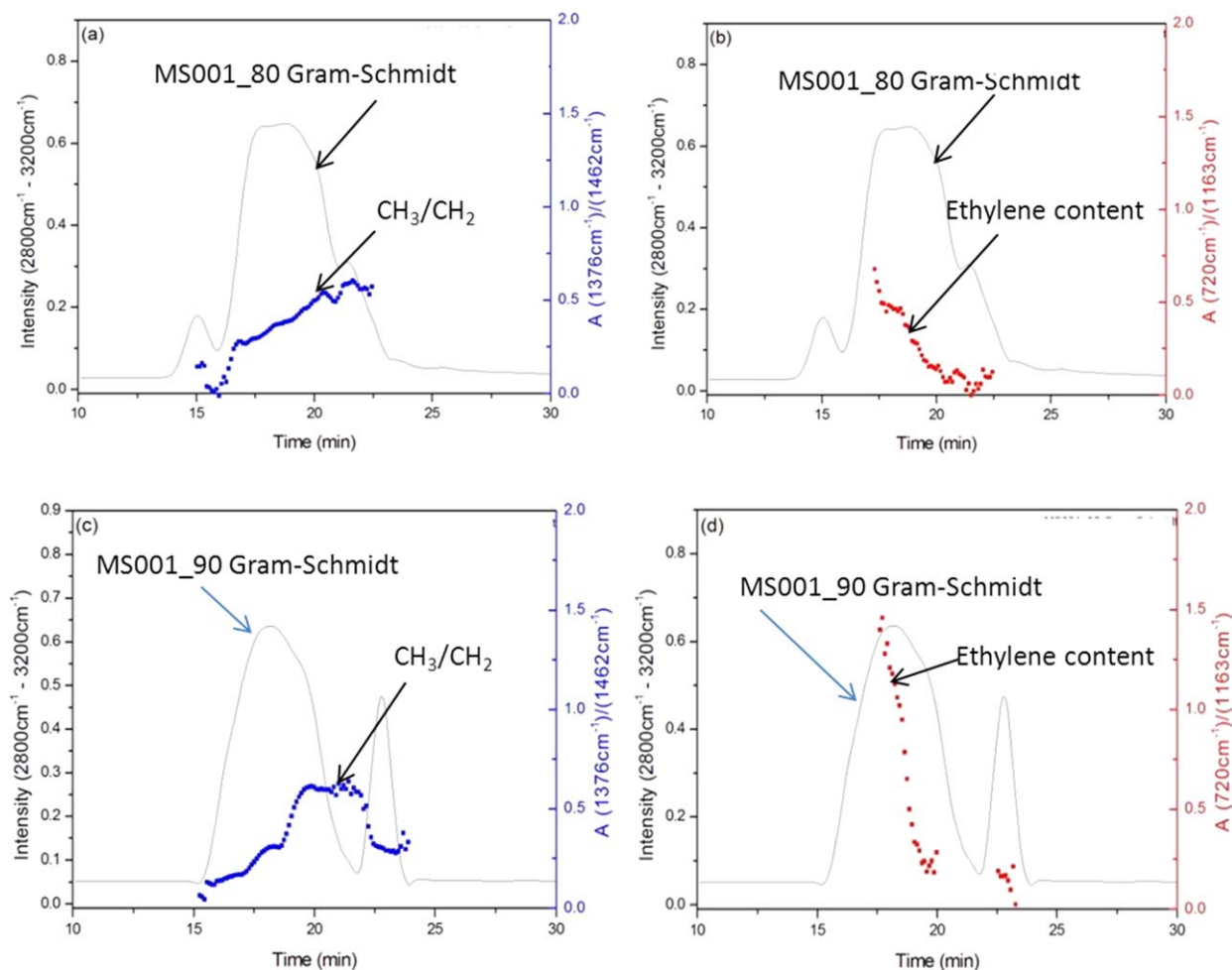


Figure 9. SEC-FTIR analysis of MS001 illustrating the propylene content (a and c) and the ethylene content (b and d) as a function of molecular weight for the 80 and 90°C fractions, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

generally exhibit the characteristic ethylene–propylene heterophasic copolymer molecular weight distributions. The high temperature fractions (100–130°C) exhibit mono-modal molecular weight curves, whereas the mid temperature fractions (80 and 90°C) have clear bi-modal distributions. The 30 and 60°C fractions shows a very slight shoulder at the higher molecular weight side. Bi-modal molecular weight distributions are indicative of compositional heterogeneity and has been found in the mid-temperature elution fractions of heterophasic copolymers.^{6,18,19}

When we compare the molecular weight curves of selected fractions over the range of samples (nonvis-broken and vis-broken) we can see the following:

In the “soluble” or 30°C fraction the two vis-broken samples have not only narrower molecular weight distributions but that the molecular weight distribution has also shifted to significantly lower molecular weights with increasing vis-breaking. This clearly indicates that the organic peroxide has a dramatic effect on the ethylene–propylene rubber (EPR) and atactic components of the heterophasic copolymer.

With the 80 and 90°C fractions the bimodal distributions remain present for all three samples, but the composition is

altered, with the lower molecular weight component of the 80°C fraction decreasing with increasing vis-breaking, whereas this increases in the case of the 90°C fraction.

As it was established with NMR that these fractions contain ethylene and propylene sequences that are linked,^{6,12} more information is required before drawing a conclusion as to why these specific regions are influenced by the organic peroxide. This can be addressed with SEC-FTIR.

FTIR Analysis

FTIR analyses were performed on all three bulk samples and their respective TREF fractions. The results of the data obtained for the nonvis-broken MS001 sample are shown in Figure 8. MS002 and MS005 show similar profiles. The exception is the spectrum for the 100°C fraction of MS001 which shows a doublet peak at 720–740 cm^{-1} , indicative of the presence of a crystalline polyethylene sequence. This doublet is not seen for samples MS002 and MS005 (this corresponds to the NMR analysis which show a decrease in the long EEE sequences). From literature^{20,21} assignments can be made for most if not all the absorption peaks. The absorption peaks at 998 cm^{-1} and 841 cm^{-1} are caused by methyl-rocking vibrations associated

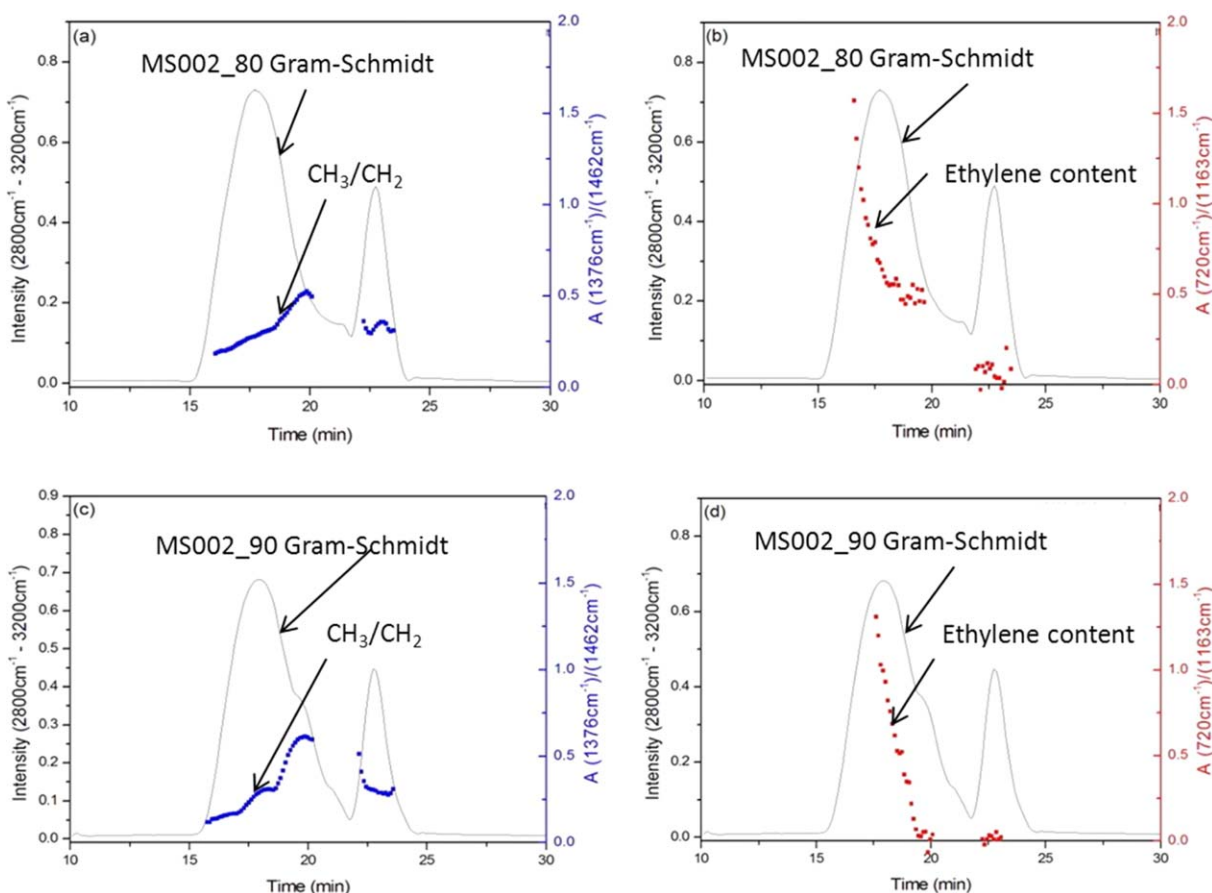


Figure 10. SEC-FTIR analysis of MS002 illustrating the propylene content (a and c) and the ethylene content (b and d) as a function of molecular weight for the 80 and 90°C fractions, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with isotactic (crystalline) polypropylene, whereas the peak at 973 cm⁻¹ can be associated with the methyl rocking vibrations of atactic (amorphous) polypropylene. The band at 720 cm⁻¹ is indicative of rocking vibrations of CH₂ sequence lengths greater than 5. Sparingly crystalline polyethylene will cause the doublet at 730 cm⁻¹ to exhibit a shoulder at 720 cm⁻¹.²¹

From the spectra presented in Figure 8 it can therefore be concluded that the 30°C fractions consist mainly out of ethylene-propylene random copolymer (EPR) due to the single band at 720 cm⁻¹ and the absence or very weak bands at 998 cm⁻¹ and 841 cm⁻¹. When looking at the mid-temperature fractions (those that elute at 60, 80, and 90°C) it can be seen that there is a steady increase in the weak band at 998 cm⁻¹ as well as the doublet at 730 cm⁻¹ indicating that propylene sequences has begun crystallising and that there is an increase in crystallisable ethylene segments. These fractions therefore consist mainly of propylene-ethylene segmented copolymers, as confirmed by NMR analysis. For the high temperature fractions (those that elute >100°C) the bands at 720 cm⁻¹ and 730 cm⁻¹ are completely invisible (except for MS001 as discussed above), indicating that these fractions are nearly pure polypropylene. NMR analyses however, does indicate that very small amounts of EEE sequences do exist in some of these fractions.

SEC-FTIR Analysis

As TREF-SEC does not supply any information on the chemical heterogeneity of these TREF fractions, coupling the TREF-SEC via a LC transform interface to FTIR provides information on the propylene and ethylene content as well as their respective crystallinity distributions as a function of molecular weight. Of interest to us were the fractions eluting at 80 and 90°C. The SEC-FTIR analyses of these fractions are shown in Figures 9–11.

Both 80 and 90°C fractions for nonvis-broken and vis-broken samples show a steady increase in the CH₃/CH₂ ratio with increasing time and thus elution volumes (decreasing molecular weight). A slight decrease in the ratio is seen at ~23 min (23 mL). Correspondingly, it is found that at high molecular weights (low elution volumes) these fractions are rich in ethylene, which steadily decreases to zero with decreasing molecular weight. It can therefore be concluded that the lower molecular weight component of the bi-modal distribution in these fraction consists mainly out of propylene homopolymer, whereas the higher molecular weight component of these fractions consist of ethylene-propylene copolymer. According to literature⁶ crystalline polypropylene is found in the low molecular weight components of these heterophasic copolymers, while crystalline polyethylene or polyethylene segments of ethylene-propylene copolymers are found at high molecular weights.

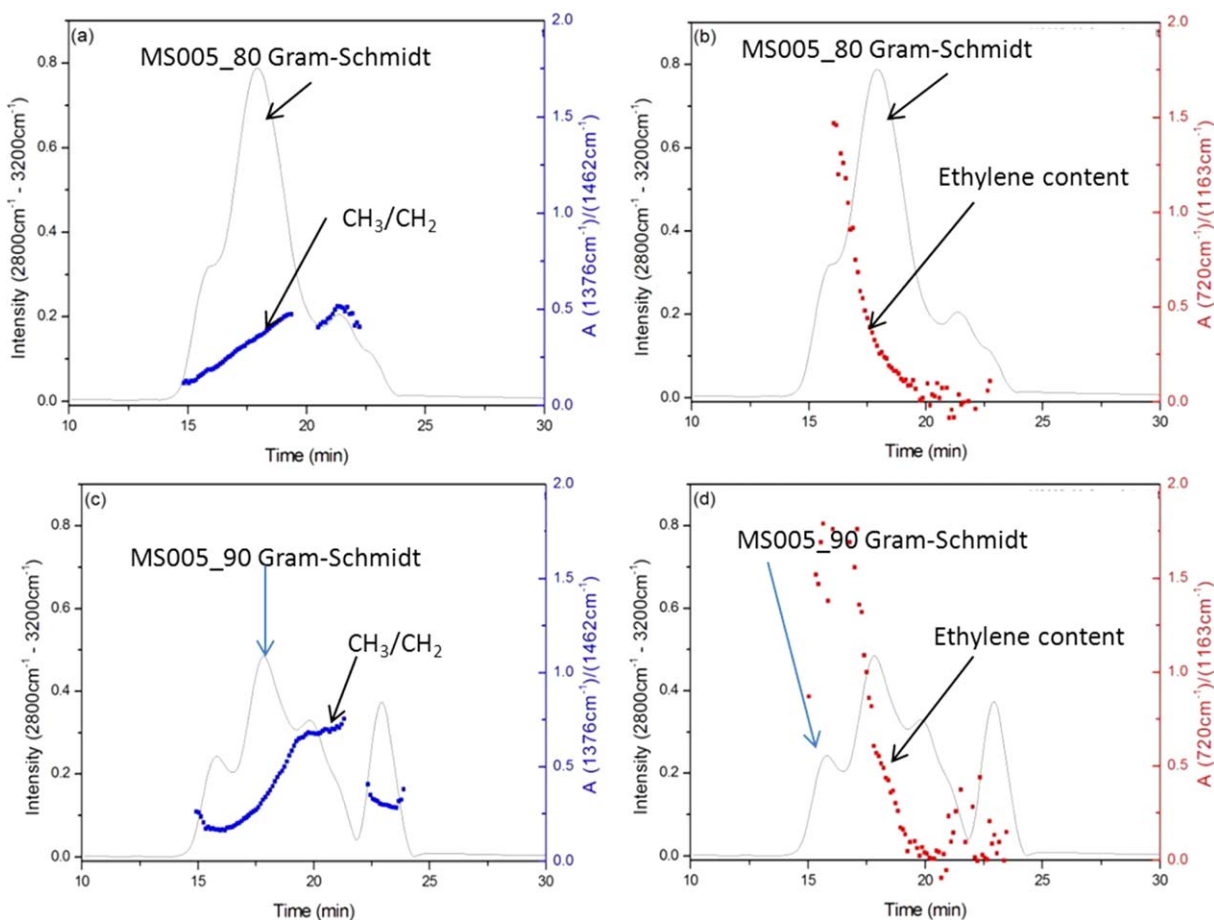


Figure 11. SEC-FTIR analysis of MS005 illustrating the propylene content (a and c) and the ethylene content (b and d) as a function of molecular weight for the 80 and 90°C fractions respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

It is clearly evident that the already complex structure and characteristics (see Table I) of propylene–ethylene heterophasic copolymers are further influenced by the use of an organic peroxide to induce vis-breaking. Increasing the amount of peroxide added not only increased the MFR but also dramatically affects the physical properties of the polymer. With an increase in peroxide concentration, there is a marked decrease in tensile modulus, stress at yield as well as impact strengths.

Increased vis-breaking leads to a change in the crystallization behaviour of HEPCs, and this can be related to a change in the chemical composition distribution of these complex copolymers.

Significantly, it can be shown that vis-breaking affects the segmented ethylene–propylene copolymers with long sequences of ethylene. This leads to a significant decrease in low temperature impact strength as these copolymers act as compatibilizer between the rubbery domains and the isotactic polypropylene matrix. The compositional heterogeneity present in the TREF fractions representing the segmented copolymer fractions was shown by SEC-FTIR to be significantly altered by vis-breaking.

In order to fully understand the way that the peroxide interacts with the various molecular components of the HEPCs, a study on the reaction of the peroxide with the individual components

needs to be done. This work is at present under way and will be reported on in the near future.

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