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The effect of different structure parameters on the crosslinking behaviour and network performance of LDPE

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Abstract

In the present study, we investigate the crosslinking behaviour of 6 ordinary low density polyethylenes, and the effect of relatively modest changes in the polyethylene structure on the properties of the resulting network. The observed variations in gel formation are mainly explained by differences in molecular weight, where both $\bar{M}_n$ and $\bar{M}_w$ affect the results. The presence of long chain branches (LCB) present on the polymer main chain is shown to have a significant effect on the network quality. The occurrence of LCB affects the ability in making effective entanglements, a behaviour which is largely dependent on the length of the branches. At high LCB frequencies, the long chain branches are relatively short and therefore more prone to disentangle. The frequency and the amount of LCB, together with the molecular weight, have a large impact on the coil size. The coil size is believed to be an important parameter for the crosslinking behaviour, as a large coil size facilitates interconnections between adjacent polymer coils. In addition, LCB increases the probability of creating intramolecular crosslinks. However, this study shows that a very high amount of LCB is needed in order to obtain any significant effect on the network quality originating from intramolecular crosslinks.

Keywords: Polyethylene; Long chain branching; Crosslinking

1. Introduction

Polyethylene (PE) is the most widely used thermoplastic polymer in the world, with a big versatility of application possibilities. Several desirable application properties can be obtained by choosing one of a large variety of polyethylene grades. To achieve a better dimension stability during heat exposure, crosslinks are introduced between the polyethylene chains in order to create a three dimensional network. The network not only improves the heat resistance, but also makes the material more resistant towards chemicals and stress-cracking which makes it a very durable material [1]. Crosslinked polyethylene, XLPE, has further extended the application fields for PE. The material is commonly used as insulation for electrical wires and cables, as hot water pipes, and in other applications where high demands are put on the durability of the polymer [2,3]. In addition, crosslinked materials also exhibit a memory effect which makes them very useful for the production of heat shrinking products [4].

There are several possible ways of introducing crosslinks into polyethylene [5], but the most commonly used method in industrial settings today is peroxide crosslinking. A number of peroxides are suitable crosslinking agents, but dicumylperoxide (DCP) is most frequently used for the crosslinking of low density polyethylene (LDPE). The decomposition temperature for DCP is high enough to keep the pre-curing during processing at a low level, and sufficiently low to allow an efficient and rapid crosslinking at a relatively moderate temperature where unnecessary degradation is avoided. The peroxide decomposes into radicals, which abstracts hydrogen from the polymer. The crosslinking reaction is then described as a combination of macroradicals. For a more detailed description, see references [5,6].

Various factors affect the crosslinking process. Besides external aspects, such as crosslinking temperature and time, a number of structural characteristics of the polymer strongly influence both the crosslinking ability and the resulting network. For example, the presence of vinyl groups on the LDPE chain has a large impact on the crosslinking efficiency [7–10]. The introduction of vinyl groups into LDPE gives higher amounts of gel at shorter crosslinking times at a specific peroxide concentration. Furthermore, a high $\bar{M}_n$-value is important, since short polymer chains are more difficult to incorporate into a crosslinked matrix, and therefore decrease

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the potential for obtaining a high gel-content. Also, the possibility of trapping the entanglements, physical crosslinks, greatly affects the resulting network density of a crosslinked polymer. High $\bar{M}_n$-values have been proven to increase the network density as long chains (and thereby fewer chain ends) increase the importance of trapped entanglements on the network formation [11,12]. Two recent studies by Smedberg et al. [13,14], discuss the influence of long chain branches (LCB) on the crosslinking efficiency for LDPE. Their findings are based upon that a polymer coil with long chain branches occupies a smaller volume than a linear polymer of the same molecular weight. They suggest that this difference in size leads to a difference in 'network efficiency' of the crosslinked polymer; the long chain branched polymer with its smaller coil size would be more inclined to make intramolecular crosslinks, i.e. within its own coil, than a more expanded coil which could more easily form crosslinks with adjacent polymer coils. The intramolecular crosslinks do not contribute to the effective network as they do not tie together two polymer molecules, which thereby impair the network strength of the crosslinked polymer. A recent quantitative analysis supports these findings [15].

In this work, we have chosen to work with 6 'ordinary' LDPEs in order to investigate potential differences in crosslinking behaviour and/or network properties. The previous studies mentioned above [13–15] included samples of a somewhat more extreme character, especially regarding the MFR_2 (melt flow rate) values and in amount of long chain branches. As numerous factors affect the crosslinking, we have chosen to investigate a more 'normal' selection of LDPEs, which can all be used in the production of XLPE. The main goal of this study is to further analyse the importance of LCB for the crosslinking and network formation of LDPE. Size Exclusion Chromatography in combination with Multi Angle Laser Light Scattering (SEC-MALLS) was used as an important tool in the determination of LCB. The original polyethylenes, the subsequent crosslinking, and the network formation and resulting quality of the network were evaluated using SEC, FTIR, gel content determinations, swelling measurements, dynamic mechanical analyses, and uniaxial strain experiments.

2. Experimental

2.1. Materials

This work is based on a study of 6 LDPEs, provided by BOREALIS AB, Stenungsund. The polymers were chosen to constitute a selection of normal LDPEs, covering a range of different MFR values and densities. The range was kept quite narrow as we wanted to avoid extreme values in molecular weight and branching content. All samples were taken during the production of commercially available LDPE qualities. However, to avoid unwanted interactions from potential additives such as stabilizers, all LDPEs, except PE F, were taken manually from the production line prior to the addition of additives. Since PE F was purchased at a later time, ordinary commercial grade was used. All samples were delivered as pellets. It should be mentioned that despite the precautions made when selecting the materials, sample PE B showed signs of being inhomogeneous. We decided to keep the material in the investigation, bearing in mind that the results might be affected.

2.2. MFR measurements

Melt Flow Rate (MFR) measurements, according to ISO1133:1997, give an estimation of the melt viscosity of the material. A certain weight is used to force polyethylene at 190 °C through a standard die and the amount of polyethylene that flows through the die during 10 min is measured. In this study, the MFR_2 value was measured, meaning that a weight of 2.16 kg was used.

2.3. FTIR

To investigate the presence of double bonds, FTIR was performed on all non-crosslinked samples. Thin films were made as described below and the FTIR-spectra were recorded on a Perkin-Elmer FTIR Spectrum 1000 using 20 scans and a resolution of $4\,\mathrm{cm}^{-1}$. Different unsaturated groups such as vinyl, vinylidene, and *trans*-vinylene can be detected by FTIR. Only vinyl bonds were investigated here, as they most strongly affect the crosslinking. The vinyl group absorbs at both 909 and $990\,\mathrm{cm}^{-1}$, but only the peak at $909\,\mathrm{cm}^{-1}$ is used here, due to its stronger absorption. The number of double bonds/1000 C was calculated using the peak at $2020\,\mathrm{cm}^{-1}$ as an internal standard, and the extinction coefficients reported by Haslam et al. [16].

2.4. Crosslinking

The polyethylenes were crosslinked in the melt using dicumylperoxide (DCP) as a crosslinking agent. Three different concentrations were used: 0.5, 1, and 2% (w/w). To ensure a more homogenous impregnation of DCP, and to facilitate the penetration of the crosslinking agent into the material, the pellets were cooled in liquid nitrogen and thereafter ground to a powder. A suitable amount of DCP was dissolved in methanol and added to the powder at a ratio of 1 ml DCP-solution/1 g of LDPE. The impregnation lasted for 1 h at ambient temperature and pressure, with agitation every 15 min. The powder was then dried under vacuum for 5 h at 20 °C to reach a complete evaporation of the solvent. This mode of procedure ensures a complete uptake of the peroxide into the polymer.

Crosslinking was performed at 180 °C. A pressure of approximately 25 bar was applied for 10 min when the curing was considered as completed [17,10]. The samples were then removed from the press and left to cool, still with a certain weight applied to avoid bubble formation during cooling. Prior to crosslinking, the polymers were allowed to melt for 2 min at 125 °C with no pressure applied, allowing a homogeneous distribution of the peroxide. In all experiments, except for the hot set test, thin films of approx. 0.5 mm were made from 1 g of impregnated polymer. For the hot set test, 10 g of the polymer was used giving square, 1-mm thick samples, from which the hot set test specimens were punched out.

2.5. Molecular weight measurements

The molecular weights and molecular weight distributions were determined using Size Exclusion Chromatography (SEC) on a Waters 150 CV equipped with a refractive index (RI) detector, an on-line viscosimeter and a Wyatt Dawn F Multi Angle Light Scattering (MALLS) detector. The samples (2 mg/ml) were dissolved over night in 1,2,4-trichlorobenzene (TCB) at 135 °C and thereafter filtered on a 0.5 μm Waters original metal net filter to remove undissolved particles and gels. A stabilizer, Santonox R from Monsanto, was added to avoid degradation of the polyethylenes. The experiments were performed with a flow rate of 1.07 ml/min at 135 °C with TCB as the eluant, and the separation was performed on three polystyrene-divinylbenzene columns. An injection volume of 206 μl was employed. The calibration was made using 11 standard polystyrenes with molecular weights ranging from 1800 to 2,700,000, and calculations were performed according to the principle of universal calibration [18] using $K=0.000392$ and $\alpha=0.725$ [19].

The MALLS measurements were performed using a He–Ne laser working at a wavelength of 632.8 nm. The detector was calibrated with toluene and normalised using a monodisperse polystyrene standard with a molecular weight of 4000. A constant d*n*/d*c* of −0.104 ml/g was used in the calculations. Theoretically, d*n*/d*c* changes with the molecular weight but according to Margerison et al. [20], d*n*/d*c* for most polymers can be considered constant above a molecular weight of approximately 10,000.

The data was collected and processed with the Waters Millennium program (RI, visc.) and the ASTRA software from Wyatt Technology Corp. (MALLS). The absolute molecular weights and *z*-average root mean square (RMS) radius, $R_{g,z}$, obtained from the MALLS measurements are calculated using the mathematical formalism by Debye [21–23].

2.6. Gel-content

The gel-content of the crosslinked thin films was determined using a solvent extraction method. Approximately, 0.3 g of each LDPE sample was placed in a pre-weighed 100 mesh stainless steel basket and extracted in 1.1 dm^3 of refluxing 1,1,1-decahydronaphtalene containing 10 g of a hindered phenol antioxidant (Irganox 1076) to prevent degradation. After 6 h, the solvent was replaced with another 0.9 dm^3 of preheated 1,1,1-decahydronaphtalene and the extraction continued for another 1 h. The samples were then dried under vacuum at 80 °C for 5 h whereupon a constant weight was reached. The weight of the non-soluble, crosslinked fraction that remained in the baskets was calculated, yielding the gel-content of the original crosslinked film.

2.7. Swelling measurements

The density of the network was determined by measuring the uptake of *p*-xylene of the crosslinked gel obtained in the gel-content experiment. The samples, still in their stainless steel baskets, were placed in 0.25 dm^3 of boiling *p*-xylene (b.p. = 138 °C) and left to reflux for a minimum of 2 h, when equilibrium swelling is achieved. The uptake of *p*-xylene was measured by immediately weighing the samples when removed from the boiling *p*-xylene The molecular weight between the crosslinks ($M_{c,swell},$) is calculated according to the Flory–Rhener equation [24], in the same way as described in Ref. [13]. The correction for loose chain ends is done according to Ref. [26].

2.8. Hot set tests

Uniaxial strain tests were performed on the crosslinked samples at temperatures above the melting temperature. An oven equipped with a special frame designed for this purpose was used. Dumbbell-shaped specimens with a total length of 75 mm were punched out and a reference length of 20 mm, L_0, was marked out. The samples were loaded with different weights giving stresses, σ, ranging from 0.015 to 0.32 MPa depending on the material, and then placed in the oven at 200 °C. After 15 min, the new length between the reference marks, L_1, was measured and the load was removed from the specimen. The sample was left to relax for 5 min at 200 °C and thereafter allowed to cool to room temperature. The distance between the reference marks was then measured again, giving L_2. The elongation, $\lambda_1=L_1/L_0$, was calculated for all samples. Due to the expansion and density change of the material at 200 °C, L_0 and σ had to be corrected. L_0 increases to 21.40 mm ($L_{0,\mathrm{corr}}$) and λ_1 is thus replaced with $\lambda_{1,\mathrm{corr}}$. The area expansions caused by the temperature causes σ to decrease by a factor 1.14. Thereafter, σ is further corrected with respect to the elongation of the sample, giving σ_{corr}.

The molecular weight between the crosslinks can also be calculated based on the uniaxial strain test, giving $M_{c,\mathrm{hotset}}$. The calculations are based on the statistical mechanical theory of rubber elasticity [27], assuming an affine network model and performed as shown in Eq. (1):

$$M_{c,\mathrm{hot-set}}=\frac{1}{\left(\frac{2}{M_n}+\frac{\sigma_{\mathrm{corr}}}{\rho_{200}RT\left(\lambda_{1,\mathrm{corr}}-\frac{1}{\lambda^2_{1,\mathrm{corr}}}\right)}\right)} \tag{1}$$

where

σ_{corr} is the corrected stress
λ_{corr} $L_1/L_{0,\mathrm{corr}}$
ρ_{200} is the density of the polymer at 200 °C (here 753.6 kg/m^3 [28])
R 8.3144 J/mol K
T is the temperature in K (here 473 K)

$\bar{M}_n$ is the number average molecular weight prior to crosslinking

The so-called hot set elongation, $\lambda_{\text{hotset}}=(L_1-L_0)/L_0$ was calculated for the samples that were subjected to a nominal stress of 0.2 MPa. The permanent deformation, $\lambda_2=(L_2-L_0)/L_0$, was also calculated for all samples. The corrected values are not used in these cases as λ_{hotset} is mostly used industrially as an approximate measure of the network strength, and $\lambda_{2?}$is measured at room temperature.

2.9. Dynamic mechanical analyses

The torque, as a function of curing time at 180 °C, was measured at a constant frequency of 2.3 rad/s in a Rheometrics RDA II, using two parallel plates. Since it was difficult to ensure that the torque was measured on the bulk material and not only at the surface, a constant pressure of 4 N was applied on the material and ridged plates were used. Normal planar plates were not used due to irreproducible results. The DMA samples were prepared by using impregnated polyethylene powder which was allowed to melt at 125 °C for 2 min with no pressure applied and then for 30 s with a pressure of approximately 40 bar. This resulted in circular samples with a diameter of 20 mm and a thickness of 1.5 mm. The total melting time of 2.5 min was sufficient to get homogenous samples and the samples could still be considered as being uncured. Due to technical reasons, only samples PE A-D could be analysed in the rheometer.

2.10. Calculation of Long Chain Branches (LCB)

The branching ratio, g, is defined as the ratio between R_g^2 of a branched polymer and that of a linear polymer with the same molecular weight:

$$g=\frac{\left\langle R_{g,\theta}^2\right\rangle_{\text{br}}}{\left\langle R_{g,\theta}^2\right\rangle_{\text{lin}}} \tag{2}$$

Theoretically, this expression implies theta conditions which cannot be used in practice. Lately, with the development of MALLS and SEC-MALLS, and the relative ease by which R_g can be obtained, it has become more common to calculate the branching ratio in a good solvent. These calculations are based on the assumption that the relative change in swelling when going from theta conditions to a good solvent, is approximately the same for a branched and a linear polymer. In several studies, the potential difference in swelling has been ignored [29,30] or claimed to be of minor importance [31–33]. However, the validity of this assumption has been questioned by others [34,35].

The discussion regarding the swelling performance can be avoided by instead calculating another branching ratio, g', which compares the intrinsic viscosities of a branched and linear polymer of the same molecular weight (Eq. (3)):

$$g'=\frac{[\eta]_{\text{br}}}{[\eta]_{\text{lin}}} \tag{3}$$

η_{lin} is calculated according to the Mark–Houwink equation, $\eta_{\text{lin}}=KM^{\alpha}$ with $K=0.000392$ and $\alpha=0.725$ [19]. $\bar{M}_{w,\text{MALLS}}$ is used as the molecular weight in the equation. The ratios g and g' are related through the ratio, B, as follows:

$$g^B=g' \tag{4}$$

The value of the branching ratio, g, calculated in this way, is thus converted to theta conditions. B normally lies between 0.8 and 1.0 for randomly branched polyethylenes in a good solvent [36]. Remember, however, that B varies with the molecular weight and thus within the molecular weight distribution [29,30]. In this work, we only study average values of the molecular weight and have chosen to use $B=0.9$ [34]. The number of LCBs can thereafter be calculated according to the theory developed by Zimm and Stockmeyer [37]. For polydisperse polymers having trifunctional branching points, Eq. (5) is used in the determination of n_w, the weight average number of branched points per molecule.

$$g=\frac{6}{n_w}\left[\frac{1}{2}\frac{\left(2+n_w\right)^{1/2}}{n_w^{1/2}}\ln\left(\frac{\left(2+n_w\right)^{1/2}+\left(n_w\right)^{1/2}}{\left(2+n_w\right)^{1/2}-\left(n_w\right)^{1/2}}\right)-1\right] \tag{5}$$

The number of long chain branches/1000C is then calculated according to Eq. (6):

$$\text{LCB}/1000C=\frac{n_w\times 14{,}000}{\bar{M}_{w,\text{MALLS}}} \tag{6}$$

Calculations of LCB/1000C were performed as an overall value, based on an average of the entire distribution of the polymer.

3. Results

3.1. Analyses of the non-crosslinked samples

The results from the FTIR, SEC, and MFR measurements are presented in Table 1, together with the densities provided by the supplier. The densities and MFR values of the samples are a representative mix of different MFR-density combinations. The weight average molecular weights given are those obtained by universal calibration ($\bar{M}_{w,\text{RI}}$) and light scattering ($\bar{M}_{w,\text{MALLS}}$). The $\bar{M}_w$-results differ markedly depending on the method used, and it should be noted that the results obtained with the RI detector are only relative, based on the hydrodynamic volume of the sample and calibrated with linear polymers, while the MALLS method gives absolute molecular weights of the samples. Samples PE D and PE F exhibit the highest $\bar{M}_{w,\text{MALLS}}$-values. Most $\bar{M}_n$-values fall within a narrow range, with the exception of the $\bar{M}_n$-values for PE A and PE C. FTIR shows that the amount of vinyl groups is below 0.2/1000C for all samples, which means that the vinyl groups only marginally affect the crosslinking. Smedberg et al. [10] have shown that a constant level of approximately 0.1 vinyls/1000C is always present even after complete

Table 1
Results from analyses of the non-crosslinked PE samples

Sample	MFR_2 (g/10 min)	FTIR (vinyls/ 1000C)	Density (g/cm^3)	$\bar{M}_{n\text{-RI}}$ (10^{-3})	$\bar{M}_{w\text{-RI}}$ (10^{-3})	$\bar{M}_{w\text{-MALLS}}$ (10^{-3})
PE A	4.7	0.18	0.920	12.7	81.7	153.9
PE B	0.9	0.094	0.926	16.2	76.2	116.6
PE C	0.3	0.081	0.927	20.0	81.1	122.3
PE D	0.1	0.16	0.920	16.8	118.5	247.7
PE E	1.8	0.13	0.923	14.5	74.5	122.9
PE F	0.3	0.15	0.918	15.8	110.7	212.6

crosslinking, meaning that this level must be exceeded for vinyl groups to influence the crosslinking reactions. The MFR-values are all quite low, except that for PE A. A low MFR-value normally indicates a high molecular weight, and vice versa, but in samples containing long chain branches, this is not always the case as the branching also affects the melt viscosity.

3.2. Crosslinking

Upon crosslinking, the gel-content and the network quality was determined for all samples. The development of gel as a function of peroxide content is shown in Fig. 1. The samples show different crosslinking behaviour. Samples PE B, PE C, PE D and PE F all arrive at a final gel-content of approximately 90–92%, while samples PE A and PE E do not exceed 80% even upon addition of 2% peroxide. At lower peroxide contents, the difference in gel-content between PE D and PE F and the other samples is even larger, 65% compared to 30–40%. Obviously, PE D and PE F readily produce substantial amounts of gel even at low concentrations of peroxide.

3.3. Network density

The density of the obtained network was calculated using two experimental techniques; swelling and uniaxial strain test (hot set). The two methods gave different values of the crosslinking density, here denoted $M_{c,\text{swell}}$ and $M_{c,\text{hotset}}$. M_c is defined as the molecular weight between two crosslinks which means that a high network or crosslinking density implies a low M_c-value. Fig. 2a and b show the crosslinking density plotted versus peroxide concentration and Fig. 2c and d the crosslinking density versus the gel-content for the two methods, respectively.

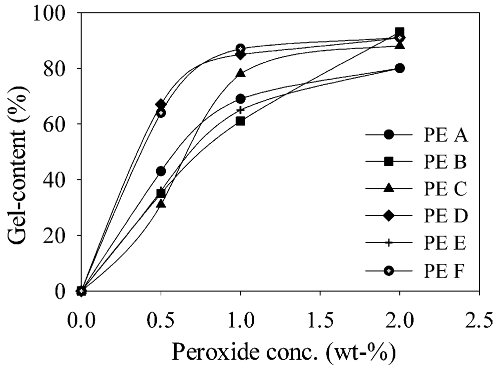

Fig. 1. Gel-content as a function of peroxide content for all samples cured at 180 °C.

The figures show that PE C has a markedly looser network than the other samples, and that the same qualitative result is obtained regardless of whether we look at the amount of added peroxide or at the obtained gel-content. The network density for PE A does not change much as a function of added DCP and the network can be characterised as 'medium dense'. However, when plotted as a function of gel-content, the network is apparently dense. It is also evident that the network density calculated from the hot set experiment in general gave a looser calculated network than obtained from the swelling measurement. The most dramatic effect is found in PE B with 2% DCP where the network appears almost 70% more dense based on the results from the swelling experiment. However, many measurements on PE B were problematic and suffered from relatively large experimental errors and results that were difficult to reproduce (see above). Fig. 2c and d show that all samples approach the same M_c when a gel-content of approximately 90–95% is reached.

The uniaxial strain tests were also utilised for studying the stress-strain relationship by measuring the elongation response to different loads. The stress-strain curves for all samples at 2% DCP are shown in Fig. 3 upon correcting the stress for the area changes due to the elongation. All samples were subjected to approximately the same set of loads. However, as some samples could withstand higher loads, the maximum load varies for the samples, as does the minimum load. In Fig. 3, the samples exhibiting the steepest slope, i.e. the highest modulus, are the samples that could be subjected to the highest nominal stress. The initial modulus, shown in Table 2, varies by a factor of 7 from the softest (PE B) to the stiffest (PE F) material. PE D and PE F, together with PE C show the highest initial modulus.

Table 3 shows the hot set elongation for all samples (see Experimental). The method is used in industry as a quality control of the network strength, and the network is considered strong enough when the hot set elongation is below 100% for a nominal load of 0.2 MPa. None of the sample crosslinked in the presence of 0.5% DCP could endure a load of 0.2 MPa and they are therefore not presented in the table. At 2% DCP, samples PE A and PE B exhibit a too long elongation, while the other samples meet the requirements. Sample PE F shows an extremely small elongation and at 1% of peroxide, the elongation is still somewhat below 100%. In comparison, a peroxide addition of approximately 2% is normal in industrial production of XLPE for high voltage cable insulation.

Dynamic mechanical measurements were performed on samples PE A-PE D. Samples PE E and PE F had to be

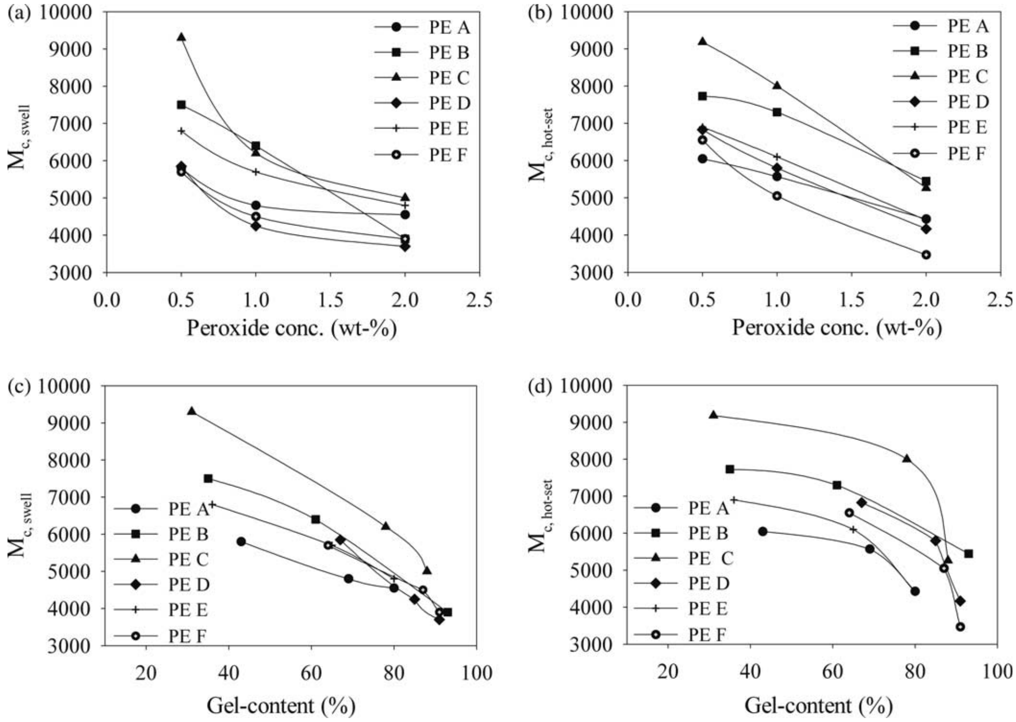

Fig. 2. Molecular weight between the crosslinks calculated as a function of (a,b) peroxide content and (c,d) gel-content.

excluded for technical reasons. Fig. 4 shows the torque as a function of curing time for the samples containing 2% peroxide. An almost constant torque is reached after approximately 5 min, which means that the curing reaction is completed. Therefore, the 10 min used for crosslinking of the films and hot set samples are more than enough to obtain completely cured samples. Also, the DMA results confirm the hot set tests concerning the order between the samples: PE D shows the highest torque and PE A and PE B the lowest. However, the quantitative difference observed in the DMA experiment is much smaller than the difference in modulus as measured by the hot set test.

4. Discussion

The major intention with this study is to further investigate the importance of long chain branches for the crosslinking of a polyethylene. The information obtained from the polyethylene suppliers is normally the density and the MFR-value. A low density value implies a high total content of branches as well as indicates that the content of LCB might be high (LCB only constitutes a minor part of the total branch content). In the case of high density polyethylene, HDPE, the MFR value can be used as a measure of molecular weight: a low MFR value indicates a high molecular weight. For LDPE, the situation is much more complex and the presence of long chain branches makes it difficult to find a straightforward connection between MFR and molecular weight.

The results above clearly demonstrate large differences in both crosslinking behaviour and network quality. The MFR values of the samples are in fact different but that difference alone is not sufficient to explain the rather large variations in crosslinking behaviour. The SEC-RI and SEC-MALLS measurements show that the molecular weights of the samples differ significantly, but not exactly in the order indicated by the MFR values, see Table 1. Previous studies [13–15] have suggested that an increasing amount of long chain branches would favour an intramolecular crosslinking mechanism over intermolecular crosslinking, creating a less efficient network.

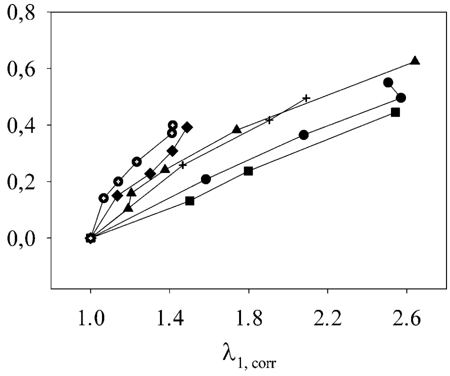

Fig. 3. Results from uniaxial strain tests, showing the elongation as a function of the applied stress at 200 °C.

Table 2
Values of the initial modulus calculated from Fig. 3

Sample	Initial modulus (MPa)
PE A	0.36
PE B	0.25
PE C	0.71
PE D	0.97
PE E	0.58
PE F	1.7

Table 3
Hot set elongation (%) for all samples at 1% resp. 2% of peroxide when subjected to a load of 0.2 MPa

DCP (%)	Sample					
	PE A	PE B	PE C	PE D	PE E	PE F
1	–	–	–	156	–	92
2	122	172	47	39	57	22

Here, we will show that it is not enough to consider only the amount of LCB, i.e. it is unsatisfactory to consider only one, and maybe even two parameters, when determining the crosslinking ability and the resulting network quality of a sample. This discussion will not give a complete answer either but some significant statements regarding the importance of different structural parameters for the crosslinking ability and network performance will be presented.

4.1. Influence of molecular weight

Fig. 1 shows the development of gel as a function of peroxide content. Clearly, the final gel-content, as well as the level of gel obtained at low amounts of peroxide, differ significantly between the samples. The final gel-content can be explained in terms of $\bar{M}_n$-values of the non-crosslinked samples. A low $\bar{M}_n$-value implies a sample containing many short polymer chains, and short chains are statistically more difficult to incorporate into a network than longer chains, at a given concentration of peroxide. The four samples reaching high final gel-contents all have high $\bar{M}_n$-values, while $\bar{M}_n$ for PE A and PE E is lower. The discrepancies between the samples in developing a gel at lower peroxide contents cannot only be explained in terms of $\bar{M}_n$. Out of the four samples that obtained a high final gel-content, PE D and PE F have a much higher $\bar{M}_{w,\mathrm{MALLS}}$-values. A high $\bar{M}_n$-value means that the polymer contains a larger portion of very large chains, and the probability that these chains are among the first to crosslink is larger than it is for shorter chains, something which has been clearly shown in a previous study [38]. Similarly, the crosslinking behaviour of PE A can be explained in terms of $\bar{M}_w$. The low $\bar{M}_n$-value for PE A causes a low final gel-content while the medium high $\bar{M}_w$-value explains the somewhat better crosslinking ability at lower gel-contents, compared to PE B, PE C and PE E. Hence, a high $\bar{M}_w$-value makes it possible to obtain a higher initial gel-content but the final gel-content level is governed by the amount of short chains, i.e. the $\bar{M}_n$-value.

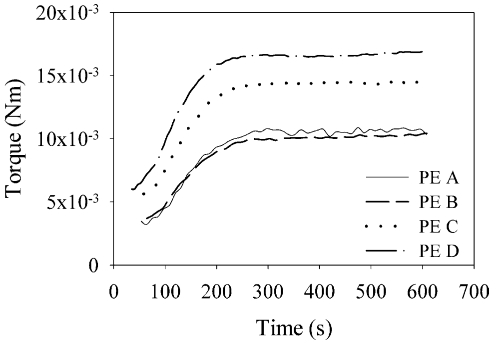

Fig. 4. DMA-measurements showing the torque as a function of curing time at 180 °C for samples PE A–PE D.

4.2. Influence of the network density

Fig. 2 shows the network densities of the samples, both as a function of gel-content and added DCP. The hot set method gives somewhat lower calculated network densities, i.e. the network appears to be looser. However, whereas the hot set measurements are performed on the entire sample, averaging over the crosslinked and the non-crosslinked parts, the results from the swelling experiments relate to the crosslinked fraction only. Contributions to the measurement from the non-crosslinked part naturally make the actual network appear less dense. However, both methods give approximately the same relative order between the samples. The order is also confirmed by the DMA-measurements (Fig. 4), even though they yield smaller differences in modulus between the samples. The torque tests only subject the samples to very small deformations, leading to less pronounced disentanglement effects.

The network densities are not actually measured parameters, but rather values calculated according to a mathematical model, developed for linear polymers. The accuracy of these calculations can be questioned as they apply to studies of polymers with long chain branches. The calculations involve a term which corrects for the presence of loose chain ends (see Swelling measurements in Experimental). This correction only takes two chain ends into account, assuming the polymer is linear, while this is clearly not valid for a branched polymer. It is not obvious how this affects the calculated M_c-values in detail, and we have chosen not to investigate this matter further. Instead, we have chosen to focus on Fig. 3. The stress–strain behaviour gives a clearer picture of the actual performance of the samples, as this figure shows measured and not calculated values.

Fig. 3 shows the strain response as a function of applied load for all samples crosslinked with 2% DCP. Two observables are of interest, the initial modulus and the elongation (λ_{corr}.) A high initial modulus implies a material which initially shows only a small deformation under load. This characteristic depends on the immediate ability of the network to withstand the applied stress. A tightly crosslinked material with a dense network structure corresponds well to such a behaviour. PE D and PE F exhibit such elongation behaviour as well as a modulus that is consistent with their high gel-content and dense network structure. The elongation behaviour also depends on the network structure and its ability to stretch out, features that are favoured by a loose network structure. PE B, having the loosest network structure, consequently demonstrates a low initial modulus and a high elongation, even at low stresses. The behaviour of PE A and PE C cannot be explained simply by looking at their network densities. According to the calculations, PE A has a notably denser network structure than PE C and is therefore expected to elongate less and having a higher initial modulus. Fig. 3 shows the opposite situation.

PE C has a clearly higher initial modulus and shows a much larger elongation at a given load. Considering the differences in LCB content between the two samples (see below), we therefore propose that long chain branches have a large impact on the network quality of crosslinked LDPE, both via the coil size [13] and via the length of the branches.

4.3. Influence of LCB on the coil size

Recent studies [13,14,38] have shown that a high amount of LCBs increases the probability of forming intramolecular crosslinks due to decreased coil size at a given molecular weight. The probability of intramolecular crosslinking in PE at 140 °C, with reference to all crosslinking, can be calculated according to [15]:

$$\chi_{\mathrm{intr}a} = \frac{1.400}{n^{1/2} g^{3/2}} \tag{7}$$

where n is the number of –CH_2– units and g the branching factor, here calculated according to Eqs. (3) and (4). Table 4 lists the calculated probabilities together with the branching factor, g, the weight average number of LCB/molecule, n_w, and the LCB frequency given as LCB/1000*C*. The values of χ_{intra} in Table 4 clearly show that the increased probability of intramolecular crosslinking in our systems is quite low, and there are only minor differences between the samples. It is difficult to see how a probability of 5–6% could have any significance for the quality of the network. However, the theory about intramolecular crosslinks is definitely valid, but it is obvious that a much larger amount of LCB is necessary for the probability of intramolecular crosslinking to be high enough. The three-dimensional plot shown in Fig. 5 indicates how the probability for creating intramolecular crosslinks varies with both $\bar{M}_w$ and the branching factor, g. The figure effectively visualises the importance of a low g-value, i.e. a highly branched polymer, in order to get any influence from intramolecular crosslinking. The LCB frequency for the LDPE samples in this study, calculated as LCB/1000*C*, ranges from 0.67 for PE C to 1.22 for PE A (Table 4). This is a considerable difference, but χ_{intra} only increases from 4 to 6%. Intramolecular crosslinking can thus be neglected in the present samples, but the actual coil size is still important.

Table 4
Calculations of the long chain branches and intramolecular crosslinking

Sample	η_{br} (dl/g)	*G*	LCB/ 1000*C*	n_{w}	χ_{intra} (%)
PE A	0.88	0.35	1.22	14.0	6.4
PE B	0.97	0.49	0.83	6.9	4.5
PE C	1.08	0.53	0.67	5.8	4.0
PE D	1.17	0.33	0.90	15.9	5.6
PE E	0.92	0.44	1.0	8.8	5.1
PE F	1.10	0.35	0.95	14.4	5.6

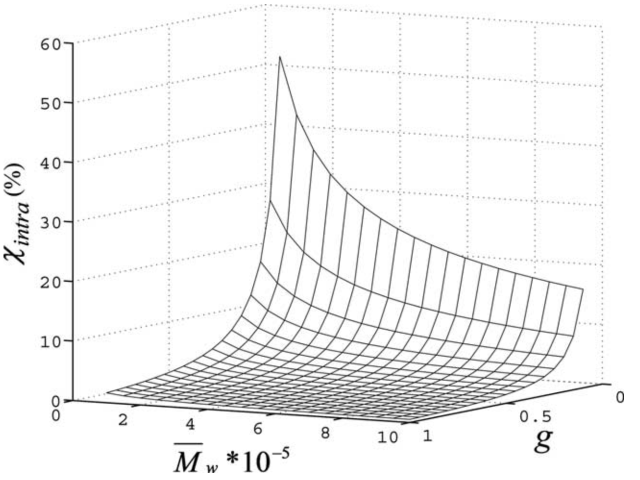

Fig. 5. The probability of intramolecular crosslinking, χ_{intra}, as a function of branching factor, g, and $\bar{M}_w$. The molecular weight ranges from 10^5 to 10^6 with every line representing 50,000, while g ranges from 0.1 to 1, with a spacing of 0.05.

Calculating the coil volume is not straightforward and we have therefore used three parameters to obtain a truthful measure of the volume, the z-average root mean square radius, $R_{\mathrm{g,z}}$, derived from the MALLS measurements, $[\eta] \times \bar{M}_{w,\mathrm{MALLS}}$, which is a measure of the hydrodynamic volume, and an empirical method based on $\bar{M}_{w,\mathrm{MALLS}}$ and the branching factor, g. The $R_{\mathrm{g,z}}$-values from the MALLS measurements are not obtained under theta conditions and they suffer from rather large variations due to the complexity of the method. The calculation of $[\eta] \times \bar{M}_{w,\mathrm{MALLS}}$ is relatively reliable but it also gives a measure for non-theta conditions. Due to these shortcomings, the third method was developed, based on the following expression for the RMS-radius at theta conditions (or in a melt) [39]:

$$\langle R_{g\theta}^2 \rangle = Cnl^2 \tag{8}$$

where n is the number of –CH_2– units in the polymer chain and l is the length of one such unit in the chain. C is a constant which depends on the polymer and the temperature. The number of repeating units is proportional to the molecular weight of the sample, and the length of 1 mer is constant, and Eq. (8) can thus be written:

$$\langle R_{g\theta}^2 \rangle_{\mathrm{lin}} = C_2 \bar{M}_{w,\mathrm{lin}} \tag{9}$$

where C_2 is a new constant. The subscript 'lin' signifies a linear polymer. By combining Eqs. (2) and (9), the following expression is obtained:

$$\langle R_{g\theta}^2 \rangle_{\mathrm{br}} = C_2 g \bar{M}_{w,\mathrm{lin}} \tag{10}$$

Since $V \propto C_3 R_{g\theta}^3$, where C_3 is a constant depending on the shape of the polymer molecule, we get the following expression as a measure of the volume:

$$V \propto (g\bar{M}_w)^{3/2} \tag{11}$$

The $\bar{M}_{w,\mathrm{MALLS}}$-values are used as the molecular weight in the calculations. This should give a volume under theta conditions provided that g is the same for theta and non-theta conditions, see 'Calculation of long chain branches'. It should be stressed that Eq. (11) does not give the actual volume, but only a number which is proportional to the volume. For further

Table 5
Volume calculations, normalised against sample PE E

Sample	V^*	$[\eta]\times M_{w,\mathrm{MALLS}}$	$R_{g,z}$ (nm)	$\mathrm{Vol}_{R_{g,z}}$
PE A	1.11	1.19	31	1.22
PE B	1.02	0.99	29	1
PE C	1.17	1.15	30	1.11
PE D	2.11	2.53	35	1.76
PE E	1	1	29	1
PE F	1.77	2.04	34	1.61

$R_{g,z}$ is obtained from the MALLS measurements.

discussion, it will be denoted as V^*. In Table 5, we find the different volume calculations normalised against sample PE E to simplify a direct comparison between the samples.

All three volume calculations indicate a large size difference between the samples, regardless of the method used. It is also clear that the coil volume is largely influenced by both the molecular weight and the degree of LCB. It is tempting to believe that the coil size affect the crosslinking behaviour in such a way that a large coil more easily interacts with other coils, thereby increasing the possibility for entanglement formation with other molecules and also reducing the effect of intramolecular crosslinks. The polymers that exhibit the strongest and most rapid crosslinking, and have the highest modulus, i.e. PE D and PE F, are also the polymers with the largest coil volumes. So far, we can thus conclude that the coil volume, as well as $\bar{M}_n$ and $\bar{M}_w$ are important parameters for the gel formation and the resulting network. This is, however, not enough to explain the behaviour of the two extremes in this study; PE C, which has the smallest amount of LCB, and PE A, the most highly branched sample.

4.4. Influence of LCB on entanglements

The M_c-values imply that PE C has a much looser network than PE A, see Fig. 2. The stress–strain behaviour (Fig. 3), however, shows the opposite, and the initial modulus of PE C is twice that of sample PE A. We suggest that this difference is related to the length of the long chain branches having a large impact on the entanglement performance of the branches. This is in line with the recent findings on the effect of branch molecular weight, $\bar{M}_{w,\mathrm{br}}$, on the zero shear-rate viscosity. Rheological studies have shown that certain metallocene catalysed polyethylenes, having a very low amount of long chain branches (less than ~0.1 LCB/1000C) display a higher zero shear-rate viscosity than linear polymers of the same molecular weight [40–43]. In contrast, high pressure polymerised LDPE exhibits lower shear rates than their linear counterparts. This has been explained by differences in the length of the long chain branches [43,44], which affects the ability to form effective entanglements. A long chain is more probable to create more effective entanglements, while shorter chains are more prone to disentangle. In a recent paper, Gabriel and Münstedt [43] showed that $\bar{M}_{w,\mathrm{br}}$ of some long chain branched metallocene HDPE and LLDPE ranged between 20, 000 and 70,000, whereas a highly branched LLDPE exhibited $\bar{M}_{w,\mathrm{br}}$-values in the range of 10–20,000[1] The long branches in metallocene catalysed PE could thus form many more entanglements leading to a higher viscosity. LCB have the same effect on the steady state compliance, J_e^o, as a small amount of long LCBs increases the value of J_e^o compared to linear products while a decrease in compliance is found for classical, highly branched, LDPE [43,45]. There is another explanation to this behaviour, complementary to the entanglement theory, suggesting that the relaxation of a polymer chain with long relaxation times is affected when surrounded with chains or chain segments having a shorter relaxation time [46,47]. In this theory, the more free long chain branches act as diluents making the material softer and less elastic.

Table 6
Average molecular branch weight and amount of LCB/volume unit

Sample	$\bar{M}_{w,\mathrm{br}}$	LCB/Vol
PE A	5300	12.6
PE B	7900	6.8
PE C	9700	5.0
PE D	7500	7.5
PE E	6600	8.8
PE F	7100	8.1

Table 6 shows the weight average molecular branch weights, $\bar{M}_{w,\mathrm{br}}$ for the polymers in this study, together with a calculation of long chain branches per volume unit, LCB/vol. In order to calculate $\bar{M}_{w,\mathrm{br}}$, the polymer chain is divided into segments assuming a statistical distribution of LCB, so that the amount of segments/polymer molecule equals $2n_w+1$. The number of long chain branches per volume is a relative value obtained by n_w/V^*, using the normalised value of V^*.

The branches in this study are short and their molecular weights are in the same range as reported by Gabriel and Münstedt upon recalculation. Hence, the entanglements are expected to be less effective and accordingly also relatively prone to disentangle. Four of our samples, PE B, PE D, PE E, and PE F, have values of $\bar{M}_{w,br}$ in a narrow range, 6600–7900, indicating that the ability to disentangle is similar for these samples. The two remaining samples, PE A and PE C, are different in this aspect. In spite of a somewhat higher $\bar{M}_w$, the higher LCB frequency of PE A (1.2 LCB/1000C) leads to shorter branches, $\bar{M}_{w,\mathrm{br}}=5300$. In contrast, the low LCB frequency of PE C gives longer branches, $\bar{M}_{w,\mathrm{br}}=9700$. This means that the entanglements of the long chain branches in sample PE A are more easily disentangled compared to those in PE C, resulting in a lower modulus for PE A. The amount of LCB/volume unit (Table 6) further stresses the effect of the difference in LCB between samples PE A and PE C. The higher amount of flexible chain ends in PE A contributes to the increased flexibility of this material.

The effect of the length of the branches on the entanglement becomes obvious when looking at a previously investigated

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[1] Gabriel and Münstedt did not include the segment between the LCB points in their calculation of M_{br} of the LDPE. We have recalculated their values according to our own way to calculate M_{br}, This still give lower values of M_{br}, in the range 5–10,000.

single-site polyethylene with $\bar{M}_n = 27,000$ and $\bar{M}_w = 99,000$ [13]. Upon crosslinking this polyethylene with only 0.35% DCP, a hot set test at 200 °C with an applied nominal stress of 0.2 MPa resulted in 100% elongation, while gel-content measurements showed that no gel was present. The peroxide causes a molecular enlargement through the creation of some long chained branched molecules. The average molecular weight of the branches should be high, $\bar{M}_{w,\mathrm{br}} = 49{,}500$, and it is expected that these branches are effectively entangled. In addition, these branched molecules have four-functional branch points, and such branches are expected to make somewhat more efficient entanglements [48]. The applied stress and time were not sufficient in disentangling such a network consisting of mainly physical, but very efficient crosslinks.

The discussion so far showed that at least five parameters are of importance for the crosslinking behaviour and the performance of the network:$\bar{M}_n$, $\bar{M}_w$, coil size, number of LCB/volume, and length of the LCB. The relative importance of these parameters may well differ between the samples making it difficult, but not impossible to relate the properties of the network to these parameters, at least in a qualitative way. However, samples PE B and PE E of this study do not fit completely into our model. Note, however, that sample PE B has shown large variations in most analyses, particularly so in the hot set measurements where it showed an uneven necking behaviour. This means that the measured elongation most certainly is too high. Without the necking behaviour, PE B would have appeared as a more stiff material in Fig. 3. Most likely, the results obtained on PE B depend largely on heterogeneities in the material.

Sample PE E can be compared with PE C and PE A based on their similar $\bar{M}_w$ and coil sizes. According to the discussion above on branch length and LCB/volume (Table 6), it is reasonable that PE E has a higher modulus than PE A. The lower $\bar{M}_n$ and somewhat higher LCB frequency of PE E compared to PE C, resulting in somewhat shorter branches and more LCB/volume for PE E, suggests that PE E should have a lower modulus than PE C. However, this is not the case. We believe that the use of average values give inconsistencies due to the actual distribution of LCB across the MWD. In a forthcoming paper we will address these issues both by experimental evidence, as well as theoretical modelling.

5. Conclusion

The main purpose with this work was to gain a deeper knowledge and understanding of how the structure of LDPE affects its crosslinking performance. LDPE is basically composed of simple –CH_2– units, but the relation between the structure of this polymer and its properties is astonishingly complex. To a large extent this complexity can be explained by the presence of long chain branches. This study gives further information on the effect of long chain branches, but it also clearly shows how difficult it is to give general explanations as so many other parameters come into play. To summarise our conclusions based on the work carried out in this study:

- The gel-content obtained at normal peroxide contents (2%) is primarily governed by the $\bar{M}_n$-value of the uncrosslinked polymer. The longer the chains, the higher the statistical probability of being incorporated into the network. Large numbers of shorter chains require higher amounts of peroxide in order to increase the probability of getting tied up in the network.
- The gel-content obtained at lower peroxide concentrations is more dependent on the $\bar{M}_w$-value. A high $\bar{M}_w$-value implies a presence of some very large chains having a high probability of getting crosslinked at an early stage of the network formation.
- Long chain branches affect the quality of the entanglements in such a way that a polymer with a relatively high amount of LCB is more prone to disentangle. The disentanglement effect depends on the length of the branch, which is a result of the amount of LCB and the molecular weight of the polymer. Short branches reduce the number of entanglements per branch, thus making the network less stiff.
- Care must be taken not to draw far-reaching conclusions based on calculations of the network densities from swelling or modulus determinations. The presence of long chain branches influences the validity of the calculations as a typical LDPE molecule has many loose chain ends, while the equations only take into account 2 loose ends per polymer chain.
- The presence of LCB increases the probability of creating intramolecular crosslinks. This effect only has a major impact on systems with a considerably higher amount of long chain branches than was the case in this study.
- The coil volume is important for the crosslinking behaviour of the polymer, as large coil volumes enhance interactions between adjacent polymer coils. The scope of this study was not enough to gain a more complete knowledge about the extent of the volume influence.

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