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Crosslinking of poly(ethylene-*co*-1,9-decadiene) by electron beam irradiation

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Abstract

The response to electron beam irradiation of poly(ethylene-*co*-1,9-decadiene) was examined and compared to a reference polyethylene. The polymers were produced in a low-pressure process using a chromium-based catalyst giving relatively high levels of inherent unsaturations through thermal termination of the polymerisation. The copolymerisation with 1,9-decadiene gave an additional 63% vinyl end groups. A dramatic improvement in the crosslinking response was observed for the decadiene polymers and consequently considerably smaller radiation doses were needed to obtain a certain degree of crosslinking. The reason for the improved response was the overall higher amount of vinyl groups as well as the placement of vinyl groups along the molecular weight distribution; the longer molecules contained more vinyls than the shorter ones. A certain amount of vinyls remains after irradiation. It is likely that the restricted mobility due to the crystalline structure makes these vinyls less accessible for reaction. Elongation at break data at room temperature exhibited significant differences between the reference and decadiene materials, although M_c determinations showed little difference in actual crosslinking density. This is likely to depend on the changes in the amorphous part of the material where the crosslinks are formed whereas the M_c calculation is based on the same concentration of crosslinks but they are instead spread in the whole material. Therefore, larger differences could be seen in the solid state. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Crosslinking; Electron beam; Polyethylene

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1. Introduction

There is a need to improve the properties of polyethylene (PE) in many applications, in particular with respect to heat deformation resistance, chemical resistance, stress cracking, shrinkage and resistance against crack propagation may be important as well. Crosslinking is then an obvious alternative and it is used today on a large commercial scale. The most common technique is radical crosslinking [1] initiated by peroxides or by irradiation. A third method is silane crosslinking where water is used as the crosslinking agent [2].

Today radical crosslinking using peroxide or irradiation is used for a range of product groups such as high-performance hot and cold water pipes, cable insulation materials, shrink sleeves and a wide range of special products needing certain superior properties. A common desire of manufacturers is, of course, to increase the production rate or the production efficiency. A reduced irradiation dose demand, for example, leads to a proportionally shorter exposure time and a correspondingly higher production rate, as the dose is directly proportional to the effect and time in the accelerator.

There are many ways in which the crosslinking rate and the crosslinking efficiency can be increased, including fundamental polymer properties, using different external additives, thermal treatments or physical environments. Among the latter, the temperature at which the crosslinking is performed counts as a significant factor [3]. The influence of thermal history on the results of irradiation and the subsequent crystalline structure after irradiation is well described by Keller and Ungar [4]. Finally, the effects of using an inert environment instead of air during irradiation is discussed [5,6]. Among additives, several so-called crosslinking boosters can be found in the market place, e.g. low molecular weight EPDM-compounds. Interesting trials have been made to enhance the crosslinking efficiency in LDPE by blending it with low molar mass polybutadiene as a crosslinking booster [7].

There are, however, three fundamental and inherent

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Fig. 1. Structural formulas of examined materials: (a) ethylene with butene as comonomer; and (b) ethylene copolytmerised with butene and 1,9-decadiene.

polymer properties that are of significant importance for the crosslinking of PE; molecular weight (MW), molecular weight distribution (MWD) and the amount and type of unsaturations [8]. The importance of available unsaturations in common PEs at crosslinking has been demonstrated elsewhere [9]. The actual peroxide concentration needed in order to obtain the initial gel was compared with the theoretically calculated concentration for a number of different linear PEs. The obtained ratios could differ by a factor of three between the two similar resins, similar in respect of MW, MWD and density. However, there was a significant difference between the more effective resins compared to the others; a seven times higher concentration of vinyl groups. Similar effects have also been shown in the field of electron beam irradiation of LDPE [10].

In the articles referred to above, normal PEs of Phillips or Ziegler–Natta type have been investigated, i.e. polymers where unsaturations are formed mostly during the termination step of the polymerisation resulting in a vinyl group at the end of the molecular chain. In this paper, however, a substantial part of the unsaturations has been introduced in the polymer via copolymerisation of 1,9-decadiene. In addition, unsaturation formed during termination is still present. This combination has hence resulted in a considerable increase in double bonds. A careful characterisation of these materials has been done together with the investigation of the response of the materials to electron beam irradiation. The electron beam treatment was performed in air at ambient temperature in order to make the investigation under conditions normally used in practice. The results from these investigations are presented in this paper. A parallel study instead reports on LDPE where ethylene is copolymerised with diene via radical polymerisation [11].

2. Experimental

2.1. Materials

Three different ethylene copolymers were used in this study; a reference material (a) containing butene as comonomer and two materials (b) containing 1,9-decadiene as well as butene as comonomers (Fig. 1). Butene was used in order to control the density and keep it on the same level for all three materials. All three materials have been produced by polymerisation in a low-pressure process using a chromium based catalyst [12], giving a relatively narrow molecular weight distribution. The target was to produce materials with density 944 kg/m^3 and a MFR21 (Melt Flow Rate using 21.6 kg weight) of 10 g/10 min, with the only difference being the content of vinyl groups introduced via copolymerisation of 1,9-decadiene. Some basic properties of the materials are given in Table 1. The sample names have been derived from the vinyl content, e.g. V105 is the sample containing 1.05 vinyl per 1000 CH_2.

2.1.1. Infrared spectroscopy

Infrared spectroscopy measurements were performed using a Perkin–Elmer 783 dispersive device. Films of even thickness (0.5–1 mm) were pressed and carefully analysed. The amount of unsaturations per 1000 CH_2 was then calculated according to the following equations [13]:

$$\text{Number of vinyl/1000 CH}_2 = \frac{\text{Abs}(910\ \text{cm}^{-1}) \times 44.2}{\text{Thickness} \times 39.37 \times \text{dens}} \tag{1}$$

where Abs is the absorbance units; thickness is the film thickness in mm; dens the density of sample in g/cm^3 and 44.2 and 39.37 are constants.

Vinylidene and *trans*-vinylene groups were calculated by using the same equation, only the constants were different. For *trans*-vinylene and vinylidene the constants used were 49.8 and 39.37, and 46.5 and 39.37, respectively.

2.1.2. ^{13}C NMR

The carbon-13 NMR measurements were performed on a JEOL GSX-400 21 kHz spectrometer using trichlorobenzene (TCB) and deuterated benzene as solvent. The temperature was kept at 150°C and hexamethyldisilane was used as reference instead of tetramethylsilane because

Table 1
Base characteristics for the examined resins

Sample	Density (kg/m^3)	MFR21[a] (g/10 min)	MFR5[b] (g/10 min)	MFR21/MFR5
V070	944	10.4	0.62	16.8
V105	944	8.9	0.54	16.5
V114	944	10.6	0.70	15.1

[a] Melt flow rate (MFR) with 21.6 kg weight (measured at 190° C).
[b] Melt flow rate (MFR) with 5.0 kg weight (measured at 190° C).

of the high temperature used. The number of scans was 3000, and the pulse delay was 11.0 s.

2.1.3. Gas chromatography

In order to find out if some remaining decadiene comonomer was solved in the polymer matrix, a gas chromatographic test was performed on a Varian 6000 gas chromatograph. One gram of material was put in 120 ml headspace bottles that had been purged with nitrogen gas. The bottles were then sealed and heated up to 175°C for 30 min. One ml of the resulting gas phase was then injected into the gas chromatography device. The oven temperature was 200°C. It should be noted that the boiling temperature of 1,9-decadiene is 165°C.

2.1.4. Gel permeation chromatography

Gel permeation chromatography (GPC) was used in order to determine the molecular weights for the three samples involved. A Waters 150 CV apparatus containing two Shodex AT-80 M/S (7 μm) columns and refractive index detector (RI-detector) were used, at 135°C, with 1,2,4-TCB as solvent. In addition, the device is equipped with an online viscosity detector as well as a Low-Angle Laser Light Scattering detector (LALLS-detector). Narrow PS-standards as well as linear PEs were utilised for the calibration using the following Mark–Houwink relationship:

$$\eta = KM^{\alpha} \qquad (2)$$

where $K = 3.92 \times 10^{-4}$, $a = 0.725$, η is the viscosity and M the molecular weight.

The concentration of dissolved polymer was ca 0.5 g/l. The solution was filtered prior to injection through a 0.5 mm Waters original metal net filter.

It is well known that chromium based materials are significantly more difficult to dissolve and to analyse by GPC, because of the tendency to plug the columns resulting in an increased column pressure, when compared to the other PE-types. Therefore one sample was also treated with HF (35% HF in water, 20 h) [14] resulting in an approximately 80% reduction of the amount of silica, facilitating the complete dissolution in TCB.

2.1.5. Differential scanning calorimetry

Thermal measurements were undertaken using a Mettler TC 10A differential scanning calorimetry (DSC) device (DFC 20 heating cell) recording the melting of samples originally crystallised at 5°C/min cooling rate from a melt of 180°C. The melting was performed at a heating rate of 5°C/min. For calculation purposes 290 J/g has been used as melting enthalpy for a 100% crystalline sample [15].

2.2. Fractionation

In order to figure out the comonomer distribution in the polymer, a solvent/non-solvent fractionation [16] was performed. This method fractionates the polymer according to molecular weight. Xylene was used as solvent and ethylene glycol monoethylether (Cellosolve) was used as non-solvent. About 2.5 g of polymer was added to 150 ml Cellosolve kept at 117°C. In order to obtain the first fraction a small proportion of xylene was added to dissolve the smallest molecules. After 15 min, the non-dissolved part of the material was filtered off and the dissolved part was precipitated with acetone, dried and pressed to films for IR analysis. The non-dissolved part was then treated in another mixture of Cellosolve/xylene with a larger proportion of xylene in order to obtain the second fraction and so on.

2.3. Decaline extraction for gel content determination

The gel content was determined by means of decaline extraction [17]. After milling and sieving (particles larger than 100 mesh), the sample was put in a metal net cushion which was kept in boiling decaline for 7 h. The solvent was replaced after 6 h. After drying, the extracted amount was determined gravimetrically.

2.4. Tensile testing

A tensile testing machine of type ALWETRON TCT 25 (Lorentzen & Wettre, Sweden) was used at ambient temperature (23°C) for determining the mechanical properties. A digital extensometer equipment was used and the speed of testing was 100 mm/min except for the determination of the E-modulus, where 1 mm/min was used instead.

2.5. Hot set

The hot set test should better reflect the network structure of a crosslinked PE polymer than a normal tensile test as the former is performed above the crystalline melting point. Test specimens in form of dumbbells, of a total of 50 mm length, were produced according to DIN 53504-S2. The specimens were then subjected to a nominal stress of 0.2 MPa at 200°C. The sample elongation, E, was measured after 15 min on a specimen mid-section according to Eq (3):

$$E = ((L_1 - L_0)/L_0) \times 100 \qquad (3)$$

where L_1 is the mid-section length after 15 min of loading and L_0 the original sample mid-section length (20 mm). By using the classical theory of rubber elasticity [18] the number-average molecular weight for a chain between adjacent crosslinking points (M_c) was obtained according to Eq. (4) given below [7]. It is assumed that the terminal chain segments do not contribute to the elastic force [7,18]:

$$M_c = \frac{1}{2/M_n + \sigma_n/\rho R T(\lambda - 1/\lambda^2)} \qquad (4)$$

where $\lambda = L_1/L_0$, M_n is the number average molecular weight of the material before crosslinking, R the gas constant, T the temperature in Kelvin, ρ the density of the sample (753.6 kg/m^3 at 200°C) [19] and σ_n the nominal stress applied (0.2 MPa).

Table 2
Molecular weight measured as number average (M_{n}), weight average (M_{w}) and determined by light scattering (M_{LS})

Sample	M_{n}[a] ($\times 10^{-3}$ g/mol)	M_{w}[a] ($\times 10^{-3}$ g/mol)	M_{LS}[b] ($\times 10^{-3}$ g/mol)
V070	19.5	1256	
V105	19.9	1634	
V114	15.3	934	
V-114-HF[c]		545	572

[a] As determined by GPC using linear calibration.

[b] As determined by light scattering after GPC.

[c] Sample treated with hydrofluoric acid.

2.6. Irradiation

Compression-moulded plaques of 2 mm thickness were used as samples for the irradiation test. The plaques were pressed directly from powder at 180°C for 10 min at two different pressure levels and then cooled at 15°C/min. Prior to compression-moulding the powder was dry blended with 0.1% phenolic antioxidant (Irganox 1076 from Ciba-Geigy).

As irradiation source a commercial 10 MeV electron beam accelerator [20] was used. In order to determine the exact dose obtained by the material, careful measurements were performed for each dose level by using irradiation sensitive films. The irradiation was performed in air at ambient temperature, ca 25°C.

3. Results and discussion

3.1. Characterisation of materials

Before doing any other tests it was seen if any comonomer had been dissolved in the polymer matrix and consequently not been incorporated into the polymer chain. In order to make this analysis a gas chromatographic test was performed according to what has been described in Section 2. Only 8 ppm by weight of 1,9-decadiene was detected, i.e. 0.0008 wt%. As 0.4 wt% decadiene was detected by NMR, according to what will be described later, it can thus be stated that almost all detected unsaturations are incorporated in the polymer and only a negligible part is due to decadiene being dissolved in the matrix. As a comparison, 0.4 ppm was registered for the reference sample, V070.

Table 3
Amount and type of unsaturations in the examined resins as determined by Infrared Spectroscopy. Standard deviation within brackets

Sample	Vinyl/1000C (at 910 cm^{-1})	Vinylidene/ 1000C (at 888 cm^{-1})	*trans*-vinylene/ 10 000C (at 965 cm −)
V070	0.70 (0.02)	0.046 (0.0011)	0.0063 (0.0014)
V105	1.05 (0.018)	0.069 (0.025)	0.018 (0.0011)
V114	1.14 (0.015)	0.072 (0.0017)	0.017 (0.0017)

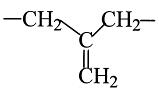
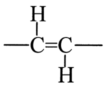
In order to determine molecular weights of the materials high-temperature GPC runs were conducted. The results from the measurements are given in Table 2. It is well known that chromium based materials are significantly more difficult to dissolve and to analyse by GPC than the other PE types. The reason behind this is their tendency to form aggregates with the catalyst carrier; therefore also leading to a tendency to plug the columns resulting in an increased column pressure that may even damage the columns. Therefore one sample was also treated with a hydrofluoric acid solution (35% HF in water, 20 h) resulting in an approximately 80% reduction of the amount of silica which facilitated the complete dissolution in TCB.

The molecular weights given in Table 2 are higher than expected. This could possibly be explained by aggregates caused by the catalyst carrier. It is described elsewhere [14] that very high molecular weights could be detected by the LALLS detector before HF-treatment, whereas afterwards this material disappeared completely, but no other changes in molecular structure could be observed. After the HF-treatment, therefore, the M_{w}-value is considerably lower as can be seen in Table 2. This is a more realistic value that is also supported by the LALLS-detector that measuring absolute molecular weights [21]. LALLS gives roughly the same value as obtained from the linear calibration using the response of the RI-detector, 572 000 and 545 000, respectively. In addition, online viscosity measurements obtained for non-HF-treated material also indicated the existence of large molecules at lower elution volumes than was observed by the RI-detector.

The obtained M_{n}-values from the GPC measurements (V070, V105) show that a number-average chain contains ca 700 ethylene units, i.e. there are two end groups per 700 ethylene units and hence 1.4 end groups per 1000C. If thermal termination of the polymerisation is assumed this would hence give us 0.7 vinyls per 1000C which is in very good agreement with IR and NMR results presented below.

All three samples were carefully analysed by IR spectroscopy. A homogeneity test was undertaken in order to get an idea of the homogeneity of the product; 8–9 films were pressed and each of them was measured for vinyl, vinylidene and *trans*-vinylene, all of them giving small standard deviations, i.e. the material can be considered as homogenous in this respect. The results are presented in Table 3 where the standard deviations are given within brackets. The studied structures are given in Table 4 and a typical spectrum is given in Fig. 2 (IR-spectrum 1200–700 cm^{-1}). The content of vinyl groups in the reference material, 0.7 per 1000C, indicates that it is a polymer produced via a chromium catalyst. In case of a normal Ziegler material we would instead have had around 0.1–0.2 vinyls per 1000C. The data further shows that an increase in unsaturations at 910 cm^{-1} by 63% has been possible by the copolymerisation of decadiene, cf. V114.

Table 4
Structural formulas of examined unsaturations

1	$-CH=CH_2$	Vinyl at 910 cm^{-1}
2	 $-CH_2-C(=CH_2)-CH_2-$	Vinylidene at 888 cm^{-1}
3	 $-CH=CH-$	*trans*-vinylene at 965 cm^{-1}

If all vinyl groups at 910 cm^{-1} in V070, the reference sample without diene, are assumed to be vinyl end groups formed by thermal termination of the growing chains, the amount exceeding 0.70 in V105 can be attributed to the incorporated diene. This assumption leads to 0.35 decadienes per 1000C for V105. For V114 the corresponding calculation gives a somewhat lower value, 0.24 decadienes per 1000C, taking the lower M_n value into account. If, however, V114 is considered to have the same M_n as V105 and V070, the values 0.35 and 0.44 (1.14–0.70) vinyls per 1000C are valid and would correspond to ca 0.07 and 0.088 mol% decadiene for V105 and V114, respectively, i.e. there is less than one decadiene unit per M_n molecule.

In Table 5 results according to ^{13}C NMR are given. A spectrum of V105 is shown in Fig. 3 with designations according to Ref. [22]. The results are in good agreement with the results obtained via IR spectroscopy given above. The NMR measurements give about 0.1 mol% of decadiene for V114, i.e. almost exactly the same result as obtained via IR. The content of butene is given in Table 5. It must be considered, however, that determination of such small amounts of comonomer may suffer from large deviations from the real value. As an approximation the error could be estimated to ca 0.15–0.2 unsaturations per 1000C. Even if the deviations of these values could be large, the results give a constant total amount of comonomers of around 0.6% by weight. This is a relatively low value considering the sample density. The expected values in case of butene as the only comonomer should instead be more close to 1% by weight. In this case, however, a mix between butene and decadiene has been used, resulting in a lower demand for comonomer in order to obtain a certain density.

Finally, the materials were thermally characterised by DSC. The results are given in Table 6. The results principally show the similarities between the reference and the decadiene-containing samples. However, the reference sample has a somewhat higher degree of crystallinity than the other two. This can probably be explained by the relatively high content of short ethyl branches compared to the two other samples also containing C_8-branches (Table 5). According to common knowledge, longer side groups give rise to a reduced crystallinity. On the other hand, side chains longer than six carbons may be subjected to side-chain crystallisation [23] which, in this case, obviously does not give any significant contribute to the overall crystallinity.

3.2. Irradiation response

In Fig. 4 the gel content obtained is given for the reference materials, V105 and V114, for different levels of electron beam doses. For the materials containing decadiene the crosslinking obviously starts immediately, i.e. relatively small irradiation doses give rise to a considerable gel content. The material with the best response, V114, reaches the level of 45% gel when exposed to 26 kGy whereas the reference sample does not exhibit any gel at all. The reference, V070, needs approximately 75 kGy in order to reach the same gel level, i.e. three times as much. Especially worth noting is that V114, already at such a small dose of 10 kGy, exhibits more than 20% gel.

The overall explanation for the differences in irradiation response among the samples can be attributed to a larger total amount of vinyl groups in V114 and V105 compared to V070. However, as mentioned earlier, the estimated decadiene content in V114 corresponds to ca one decadiene unit per 1000 ethylene units (0.1 mol%), i.e. less than one

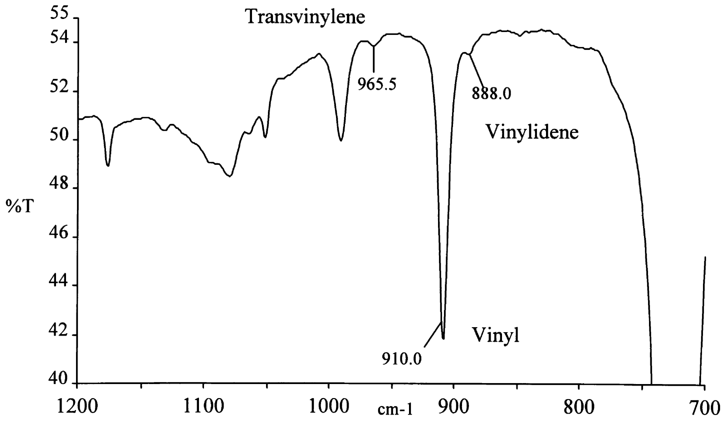


Fig. 2. Typical IR spectrum (700–1200 cm^{-1}) of untreated poly(ethylene-*co*-butene-*co*-1,9-decadiene), V114.

Table 5
Comonomer content as determined by NMR

Sample	1-butene (wt%)	1-butene (mol%)	decadiene (wt%)	decadiene (mol%)	decadiene No/1000C	1-butene No/1000C
V070	0.6	0.3				1.5
V105	0.3	0.15	0.2	0.04	0.2	0.75
V114	0.2	0.1	0.4	0.08	0.4	0.5

decadiene per M_n-molecule. The difference in the total amount of vinyl groups among the three different samples is hence not so dramatic and may, therefore, not account directly for the whole difference in response to irradiation. Other reasons are also likely to contribute as well.

To find out the distribution of double bonds across the molecular weight distribution the samples were fractionated and the fractions were analysed for double bonds by FTIR. In Fig. 5 the content of vinyl groups is given for the different fractions, where increasing fraction number represents increasing molecular weight. As vinyl chain end groups account for the majority of double bonds, in both V070 and V114, the concentration of double bonds is highest in the low molecular weight fractions. It is however obvious that there are differences in vinyl content between the reference sample and V114, and the difference is significant for the higher molecular weight fractions. It is reasonable to assume that the difference between the two samples is caused by the presence of diene in V114. Although the absolute concentration is rather low, from 0.5 to 0.2 vinyls per 1000C going from fraction three to five, it should be remembered that the molecular weight of these fractions are considerably higher than the M_n value for the whole distribution. Considering an average sized chain from fraction 3, containing four times the amount of monomer units of an M_n chain or 2800 ethylene units, calculations show that the V114 fraction contains three vinyls per chain compared to the expected one vinyl per chain in the V070 fraction. The higher molecular weight fractions crosslink more easily per se [24]; in addition, the presence of several groups per molecule with increased reactivity towards the radicals leads to a significant enhancement of the probability to

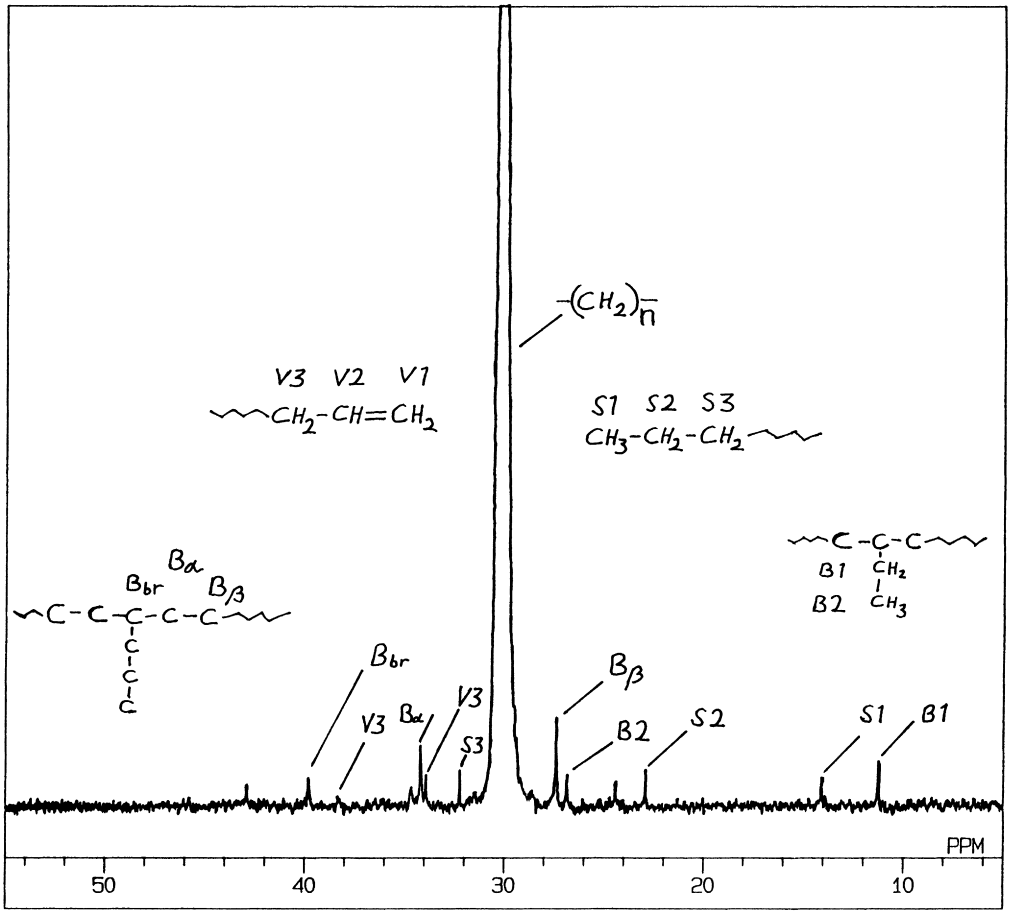


Fig. 3. ^{13}C NMR spectrum of poly(ethylene-*co*-butene-*co*-1,9-decadiene), in the range of 6–54 ppm, 3000 scans. V1 and V2 at 115 and 140 ppm, respectively.

Table 6
Melt peak temperature (T_m), heat of fusion and crystallinity data obtained from DSC measurements

Sample	T_m (peak) (°C)	Heat of fusion (J/g)	Crystallinity (%)
V070	130.7	188.3	64.9
V105	129.4	180.8	62.3
V114	131.3	180.7	62.3

react with other large molecules forming a network. It should also be stressed that fractions three and five represents the majority of the whole distribution, ca 70% (see Fig. 6). Together these factors explain the much faster gel formation in the diene copolymers at low radiation doses.

The type of comonomer distribution discussed above, i.e. that a larger number of diene per chain and per 1000C can be found on the longer chains compared to the shorter chains is an important conclusion. This is in contrast to what is normally found for the more frequently used monomers, e.g. butene, in chromium or Ziegler–Natta catalyst type of polymerisation. This is illustrated in Fig. 7 for the three materials described in this paper. It can clearly be seen that the number of butene per 1000C is higher for smaller molecules than for the larger ones, whereas the opposite situation seems to be true for decadiene.

The electron beam irradiation crosslinking takes place in the solid state, i.e. the actual crosslinking reactions occur primarily in the amorphous parts of the polymer [4,25], where the concentration of double bonds will be considerably larger than the average determined value as side branches tend to be forced out in the amorphous regions on crystallisation. With a crystallinity of ca 65% and hence 35% amorphous material this would lead to around three times the average concentration, i.e. ca 0.3 mol% double bonds in the amorphous regions in V114 originating from decadiene. This is also a fact worth considering when looking at the improved response to irradiation for the decadiene-containing materials.

Generally a number of different mechanisms are involved when a PE-material is subjected to high-energy irradiation, e.g. electron beam irradiation (β-radiation). The main mechanisms are given in Fig. 8 [26]. In PE the crosslinking reaction, as shown by (a) in Fig. 8, is considerably more frequent than the chain scission reaction shown in (c). According to Ref. [26] $G(x) = 3.0$ whereas $G(s) = 0.88$, i.e. crosslinking is more than three times as frequent as chain scission which makes PE relatively easy to crosslink compared to polypropylene. Formation of *trans*-vinylene unsaturations according to (b) in Fig. 8 is also relatively common in PE with a *G*-value equal to 1.3. As a consequence of some of the reactions mentioned above hydrogen is formed, in addition, a number of oxidation products are formed during irradiation. The degree of oxidation obtained by IR at 1720 cm^{-1} was measured to be between 0.04 and 0.14 carbonyl per 1000C. According to our earlier experience on oxidation of PE under different conditions this level of oxidation is low. It is not associated with any observable changes in molecular weight. Disappearance of vinyl and vinylidene groups are reported in literature [26].

In Fig. 9 the decline of vinyl groups at 910 cm^{-1} is shown. It corresponds well with earlier findings from normal HDPE, cf. V070 for example. However, a certain amount of vinyls remains after the highest applied irradiation dose. It is likely that the restricted mobility due to the crystalline structure makes some vinyls inaccessible for reaction by irradiation.

Calculations on the given dose in relation to the number of consumed vinyls are given in Table 7. Some interesting observations can be made from this table. The number of

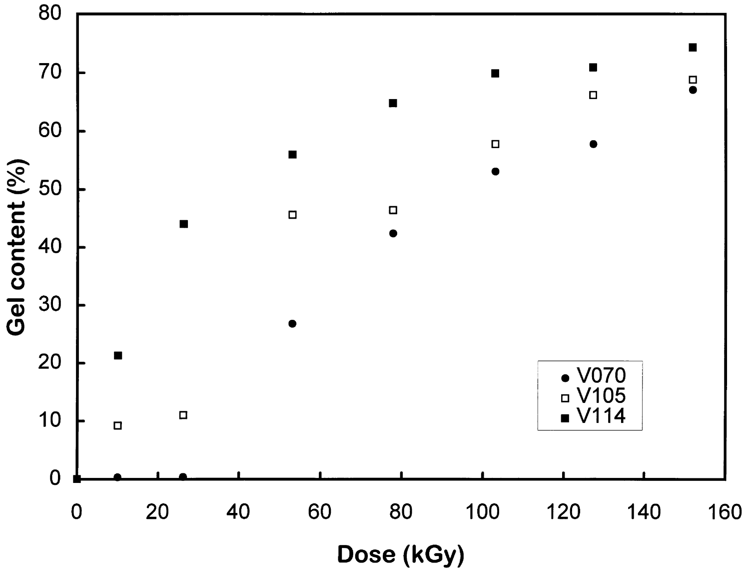


Fig. 4. Formed gel as a function of the given dose for the three examined materials: (●) V070; (□) V105; and (■) V114.

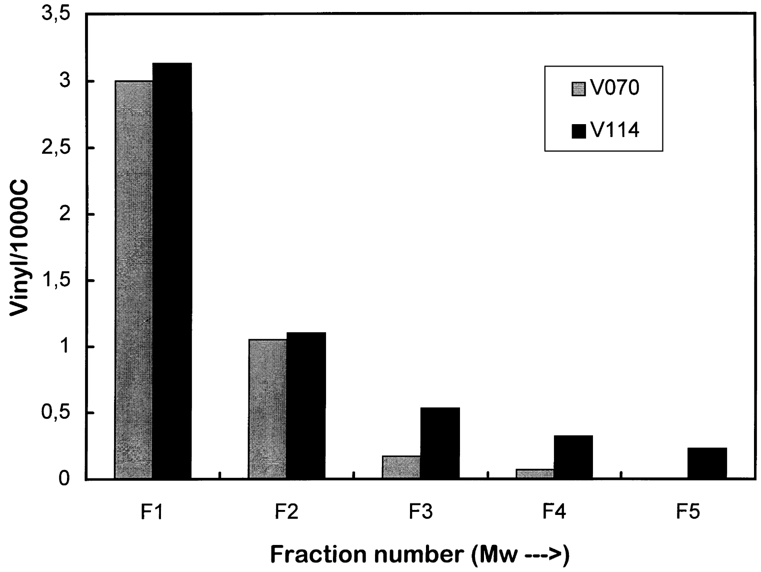


Fig. 5. Vinyl content per 1000C analysed by IR for different fractions obtained from solvent/non-solvent fractionation. Increased M_w to the right: (black) V114; and (grey) V070.

consumed vinyls per given dose, i.e. the dose that the sample in question has been subjected to, is considerably higher at lower doses compared to higher doses. The second observation to be considered is that the samples containing decadiene generally show (with one exception) a higher consumption of vinyls per given dose unit than the reference. If a comparison is made between V114 and V105 the same trend is obvious, i.e. the more unsaturations from decadiene, the higher is the consumption of vinyls per given dose. To summarise these findings one can say that a lower dose provides a more effective use of the emitted electron energy regarding the transformation of vinyls with subsequent crosslinking of the material. A reasonable explanation to these findings is that at high doses a large number of radicals are formed, and due to a relatiavely small concentration of available double bonds, a termination reaction between two secondary radicals is more likely than a reaction involving a double bond. At lower doses, however, secondary radicals are likely to be transformed to the energetically favoured allylic radicals that could then react further.

Assuming radical formation occurs mainly due to hydrogen abstraction, the values in kJ/mol obtained in Table 7 can be compared to the dissociation energy of the C–H bond in methylene units and in allylic positions, 398 and 362 kJ/mol, respectively [27]. It is worth noting in this

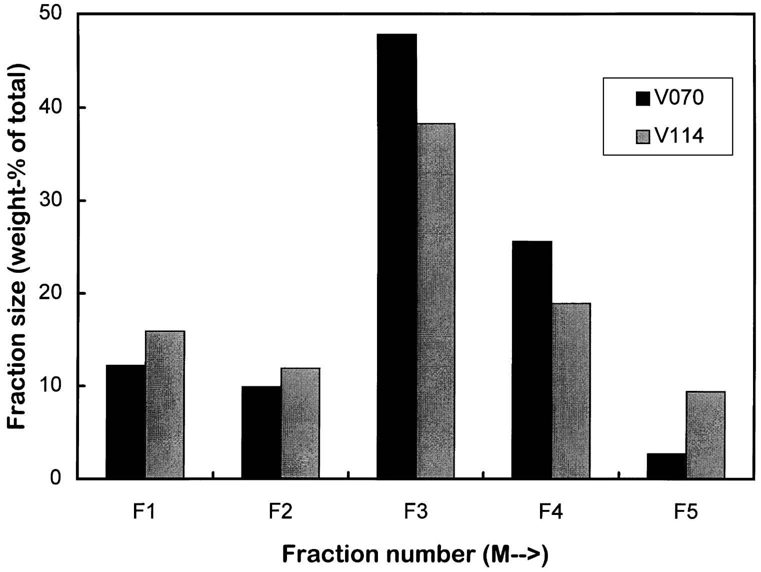


Fig. 6. Distribution of material as a function of molecular weight: (black) V070; and (grey) V114.

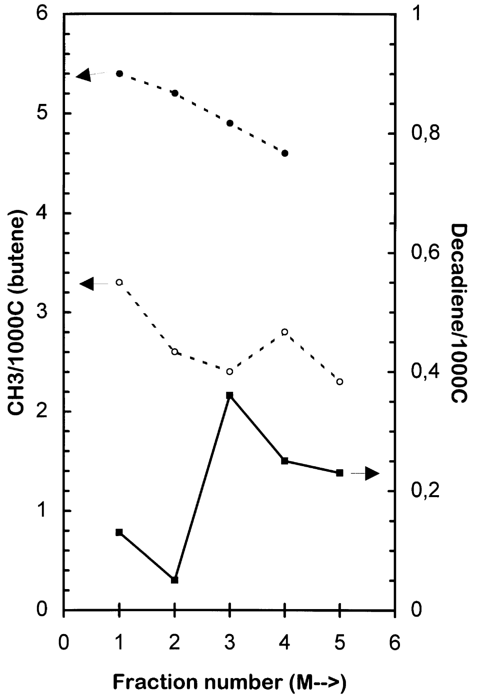


Fig. 7. Content of comonomers (butene and 1,9-decadiene) determined by IR as a function of molecular weight: (●) butene in V070; (○) butene in V114; and (■) decadiene in V114.

context the clear difference between these values and the values obtained in Table 7, which are 2–10 times higher. Only the value for V114 at 10 kGy (778 kJ/mol) is relatively close to the dissociation bond energies referred to in the literature. Considering abstraction of secondary allylic hydrogens we get 778/362 = 2.1, i.e. double the amount of energy per mole of consumed vinyl would be needed than if we had a fully selective process. The natural explanation to this is of course that the electron energy dissipates for many other side reactions such as chain scission and heat evolution.

According to the literature data an increase in the amount of *trans*-vinylene groups could obviously be expected. In Fig. 10 this is also shown to be the case. The formed amount of *trans*-vinylene seems to be the same for all three samples. They follow almost the same curvature, leading to the assumption that no net effect in the *trans*-vinylene formation is given by the presence of decadiene groups. A linear formation of *trans*-vinylenes in LDPE vs. added amount of peroxide has been shown elsewhere [11]. In addition, the formation of *trans*-vinylenes was found to be totally independent of the content of diene. It can therefore be assumed that the main reaction in the formation of *trans*-vinylene groups would be according to (b) of Fig. 8. However, it could have been expected that *trans*-vinylene

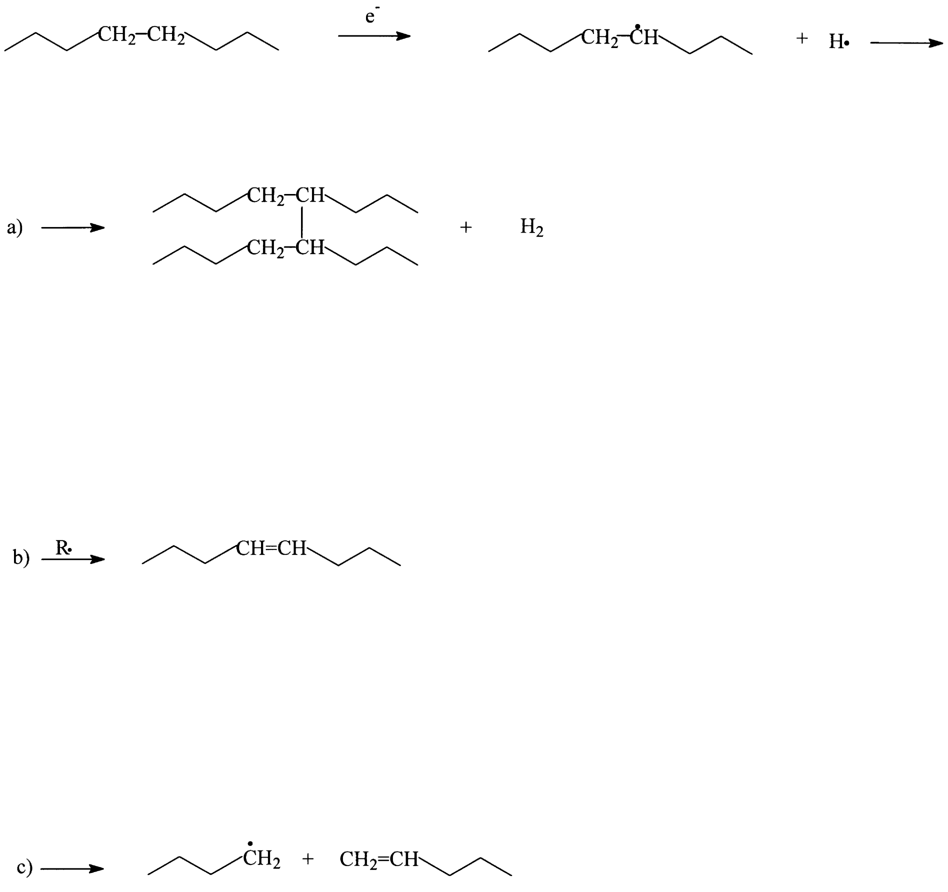


Fig. 8. Main mechanisms involved as polyethylene is subjected to electron beam irradiation.

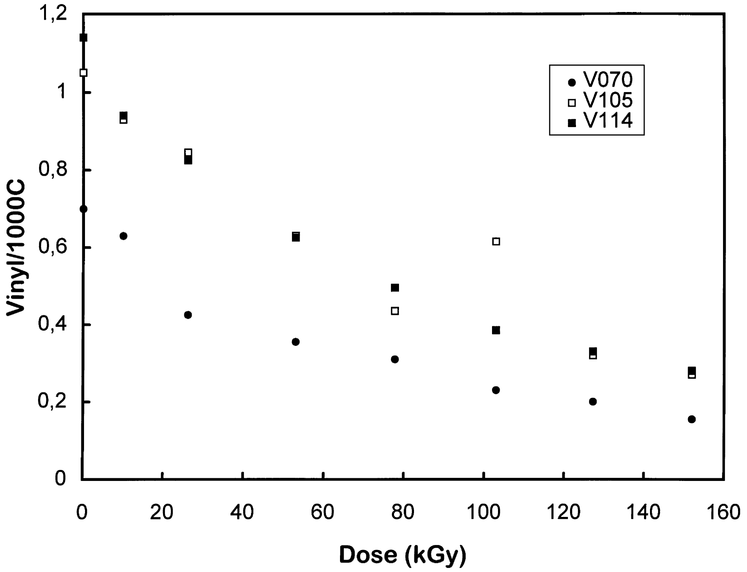


Fig. 9. Number of remaining vinyl groups per 1000C after irradiation with different doses: (●) V070; (□); and (■) V114.

could also be formed through the mechanism proposed in Fig. 11, where a vinyl group would be transformed to a *trans*-vinylene and simultaneously create an easily available crosslinking site. This mechanism would certainly also be valid for the vinyl end groups originating from thermal termination. The latter should, however, be of the same order of magnitude for all three samples and hence the presence of decadiene groups would lead to a larger formation of *trans*-vinylenes. Some indications for the support of this theory might be given through the evidence of allylic radicals that are reported elsewhere [26,28,29]. It is possible that the reaction can occur and should therefore not be excluded from the discussion. According to the literature [30] it is assumed that vinyl groups are consumed as described in Fig. 11. Our data, however, shows that the starting content of vinyl groups does not influence the formation of *trans*-vinylene. In addition, it can be noted that the consumption of vinyl groups is approximately three times larger than the amount of formed *trans*-vinylenes. Therefore, there must be another mechanism that explains the decrease in vinyl groups. A direct consumption according to Fig. 12 is a plausible explanation. The crosslinking finally could take place through a coupling reaction between two radicals.

Table 7
Consumption of vinyl unsaturation at exposure of electron beam radiation

Sample	Given dose (kGy)	Consumed vinyls/ 1000C	Dose/consumed vinyl (kJ/mol)
V070	10	0.07	2000
V070	26.2	0.275	1334
V070	152	0.545	3907
V105	10	0.11	1273
V105	26.2	0.195	1882
V105	152	0.77	2765
V114	10	0.18	778
V114	26.2	0.295	1244
V114	152	0.84	2534

Finally, the amount of vinylidene type of unsaturations have not been found to undergo any changes, only a negligible decrease in the order of 0.03–0.04 per 1000 CH_2 has been observed.

Fig. 13 shows the gel content vs. the number of consumed vinyls. For samples containing diene an immediate formation of gel follows on vinyl consumption whereas the reference sample consumes up to ca 0.25 vinyl per 1000C without any gel being formed. While consumption of vinyls in V105 and V114 leads to gel formation, the corresponding consumption probably only gives molecular weight enlargement in the reference sample and hence no real network is formed. The explanation for this difference in irradiation response between the materials is most likely due to the reasons discussed earlier in this paper, i.e. a higher amount of diene comonomers on the longer molecules.

In order to further examine the changes resulting in the materials from irradiation, mechanical testing was chosen as a tool. In Fig. 14 the relative elongation at break vs. dose is given. The elongation for V114 and V105 is constantly on a lower level when compared to the reference. In addition, an immediate drop in elongation is obtained for V114 and V105 whereas the reference seems to be relatively unaffected in elongations up to approximately 50 kGy. This can be compared to Fig. 4 where the gel starts to be formed somewhere between 25 and 50 kGy for V070, i.e. the elongation is hardly influenced before a measurable gel is formed. If this data is compared to Fig. 13, it follows that 0.2–0.3 vinyls per 1000C is consumed in V070 before the elongation at break starts to decrease, whereas an immediate drop in elongation occurs upon vinyl consumption for the

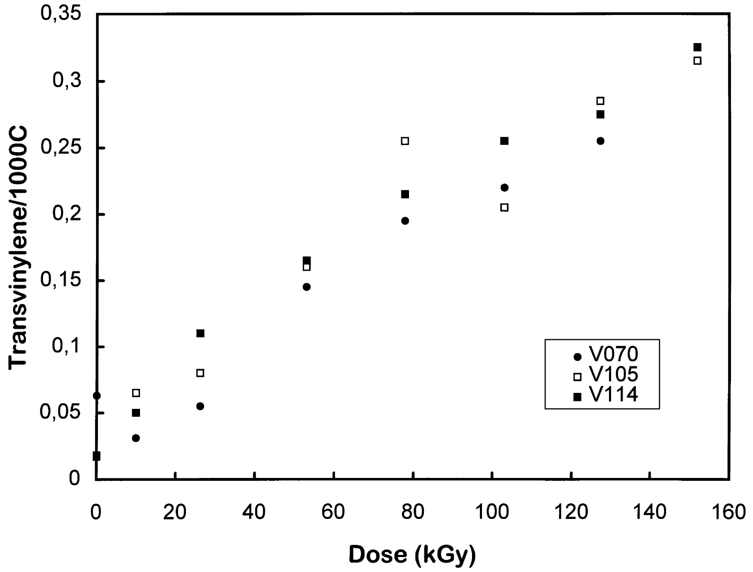


Fig. 10. Number of *trans*-vinylenes per 1000C after irradiation with different doses: (●) V070; (□) V105; and (■) V114.

materials containing dienes. Furthermore, Figs. 4 and 14 show that the different materials exhibit relatively large differences in elongation at break for a certain gel content.

In order to calculate the density of crosslinks, the classical theory of rubber elasticity was used in accordance to the description of the hot set test given in Section 2. This theory should be applicable as we are considering an isotropic material with a relatively low density of crosslinking points. In Fig. 15 the values of M_c vs. dose are given. The crosslinking density generally increases with dose and is constantly higher for the diene copolymers (cf. Fig. 14). Below 52 kGy, it was not possible to measure any value

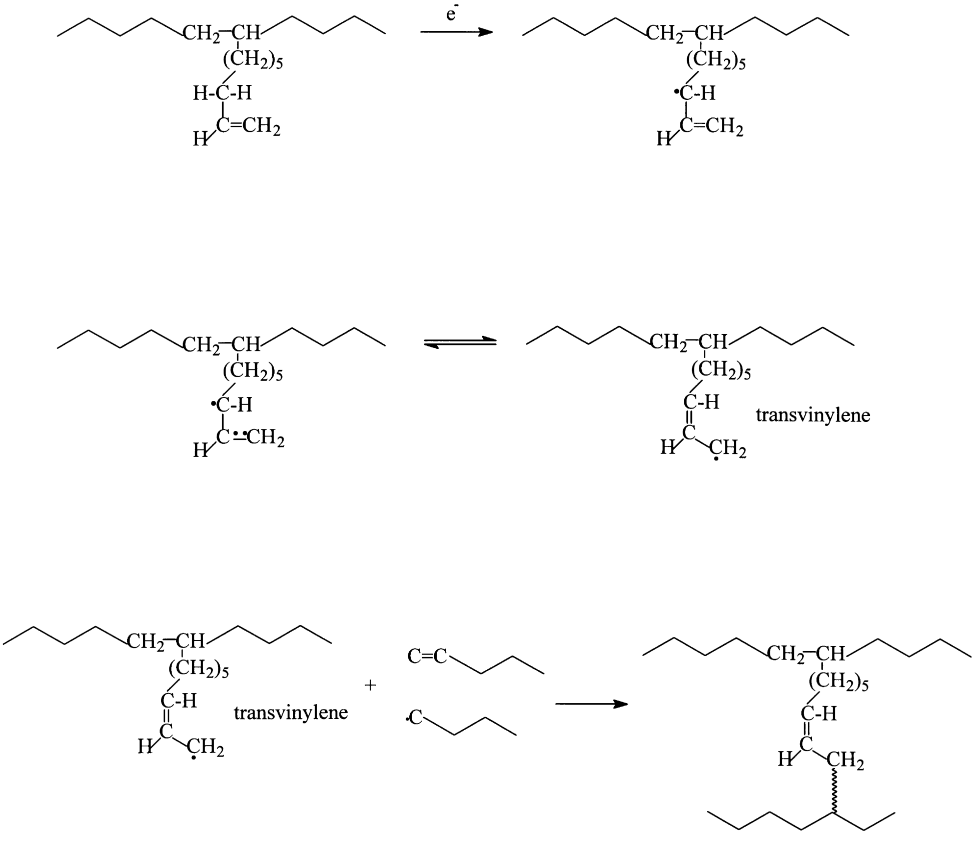


Fig. 11. Formation of *trans*-vinylene from end group and subsequent crosslinking.

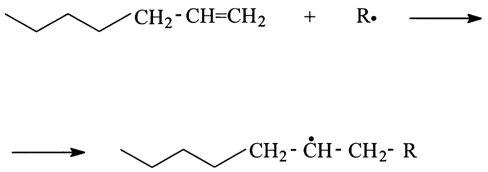


Fig. 12. Direct consumption of vinyl and subsequent crosslinking via a reaction with alkyl radical.

as neither V070 nor V105 could sustain 200°C for more than a couple of minutes. Only V114 was able to sustain at least 15 min under these conditions enabling the calculation of the M_c-value.

A comparison of Figs. 4 and 15 suggests that the difference in crosslinking density for a certain gel content, seems to be rather limited between the sample types (above 50% gel), in the order of 2–3000 g/mol. The large differences in relative elongation at break at room temperature, at a certain gel level, can hence not be explained by differences in crosslinking. It is however important to bear in mind that the values of elongation at break are obtained during tensile testing at room temperature, whereas the M_c values have been calculated from elongation values obtained during test conditions much above the crystalline melting point (200°C). The elongation at break obtained by tensile testing at room temperature is likely to depend on the changes in the amorphous part of the material as the crosslinks are formed here. The hot set test measures the same concentration of crosslinks but they are instead spread in the whole material. Therefore, larger differences should be obtained in the solid state. The creation of new and fixation of old entanglements could also contribute to the decrease in elongation at break experienced in the solid state measurements. Additional information is given by the short-time *E*-modulus in Fig. 16, which increases with dose and shows a certain difference among the samples at all dose levels. The increase of the *E*-modulus can be explained by the crosslinking but also by the slightly increased crystallinity described below.

In the following section, data obtained from DSC-runs will be presented and discussed. In Fig. 17 the crystallinity vs. given dose is shown. Looking at the results from the first melting cycle, a slight increase in crystallinity is obtained. This might be explained by chain loops in the amorphous regions that are cut at irradiation; after which they are able to crystallise. The most obvious effect is the decrease in crystallinity observed for the second melting cycle when higher doses are used. The crosslinks formed during irradiation will hinder crystallisation upon melting and recrystallisation. An additional effect may be obtained by the new crosslinks that are formed due to trapped radicals set free to react when the material is melted in the first heating cycle. The number of radicals decline relatively rapidly after irradiation [5] and is therefore assumed to have a less pronounced influence in this case. No actual difference in crystallinity between the samples is observed. All three samples loose 7–10% units in crystallinity. This drop is accompanied with a decrease in T_m by 0.6–3.8°C. It has been shown elsewhere [4] that crystallinity is significantly impaired by irradiation and eventually totally destroyed at high doses around 20 000 kGy, i.e. considerably higher than used here.

In summary, the DSC-data do not exhibit any significant differences among the three compared materials in this study. The minor differences among the samples are not likely to lead to any major influence on mechanical properties. Although the irradiation does have an

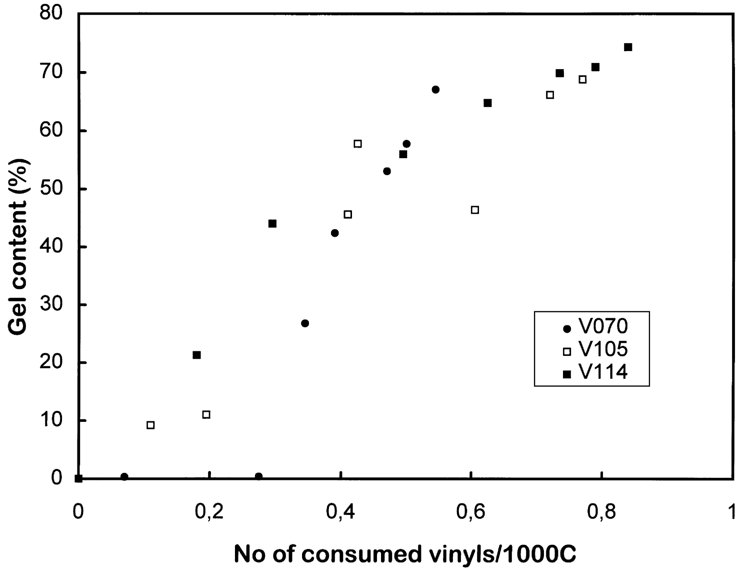


Fig. 13. Formation of gel as a function of consumed vinyls per 1000C: (●) V070; (□) V105; and (■) V114.

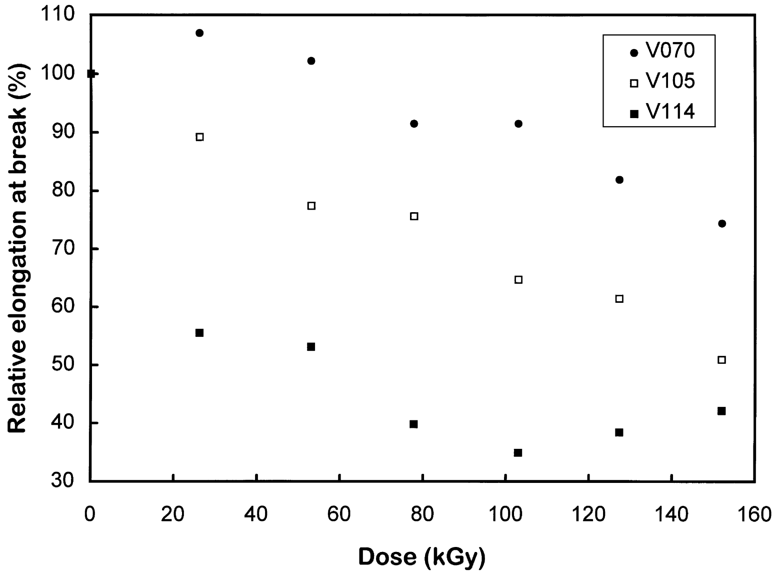


Fig. 14. Relative elongation at break resulting from different doses: (●) V070; (□) V105; and (■) V114.

influence on the materials, it influences all three materials to the same extent.

4. Conclusions

By copolymerising ethylene with 1,9-decadiene using a chromium based catalyst it is possible to increase the number of vinyl end groups by more than 60%. At the same time, the crosslinking response to electron beam irradiation is dramatically improved. Considerably smaller doses are needed in order to obtain a certain gel content.

The reasons for the improved response to electron beam irradiation is in general related to the overall higher content of double bonds, but more specifically to the distribution of double bonds along the molecular weight distribution. The M_n molecule contains one vinyl per 1000C whereas the larger molecules have been found to contain several vinyls per 1000C.

The number of vinyl groups decline upon irradiation with the electron beam. However, a certain amount of vinyls remains even after the highest applied irradiation dose. It

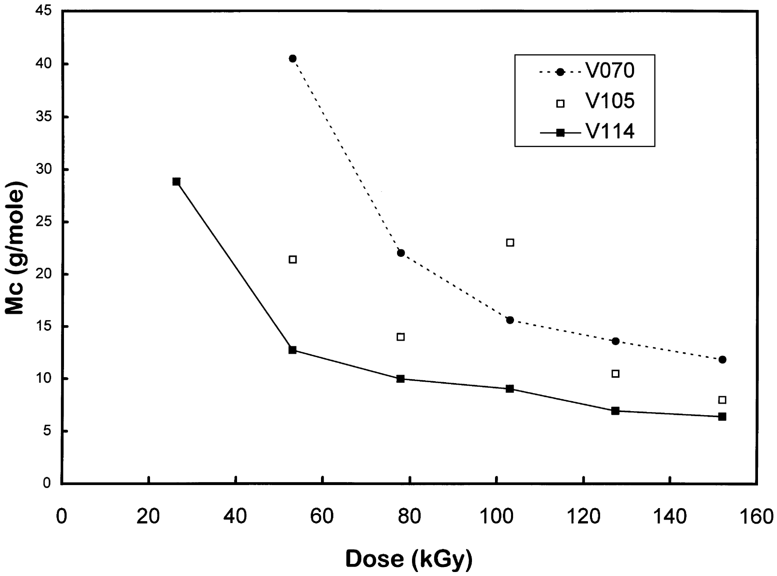


Fig. 15. Number average molecular weight for a chain between adjacent crosslinking points (M_c) as obtained from hot set measurements vs. dose: (●) V070; (□) V105; and (■) V114.

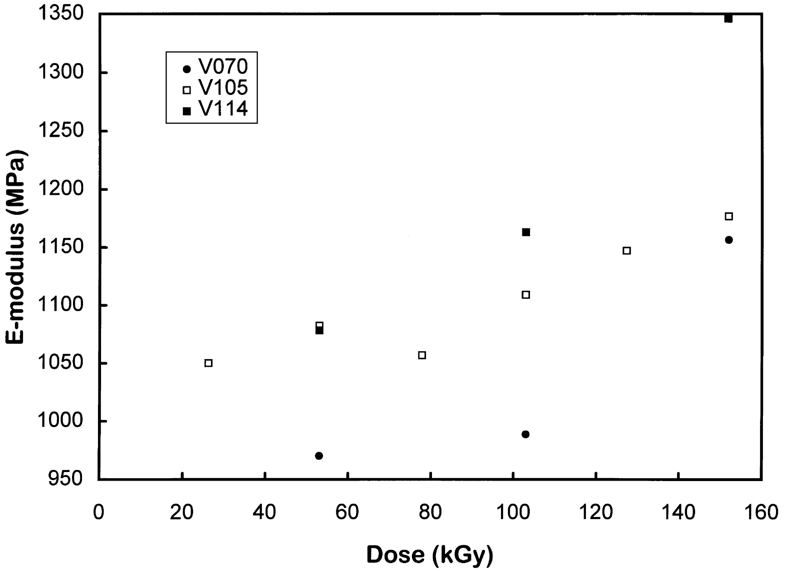


Fig. 16. *E*-modulus measured at a tensile speed of 1 mm/min vs. dose: (●) V070; (□) V105; and (■) V114.

is likely that the restricted mobility due to the crystalline structure makes some vinyls inaccessible for reaction at irradiation. The content of *trans*-vinylene type of unsaturations increases linearly with dose and independently of the original number of vinyls.

Upon electron beam irradiation the decadiene-containing materials exhibit a greater decrease in elongation at break properties at room temperature than the reference PE. M_c determinations based on measurements above the crystalline melting point, however, show very small differences in elongation properties between decadiene materials and the reference for a certain gel content. The elongation at break at room temperature is likely to depend on the changes in the amorphous part of the material where the crosslinks are formed, whereas, the M_c calculation is based on the same concentration of crosslinks but is instead spread in the whole material. Therefore, larger differences could be seen in the solid state.

DSC analyses exhibit great differences between the first and second melting cycle. For the first melting cycle a slightly increased crystallinity is obtained with increased irradiation dose whereas a marked decrease is observed

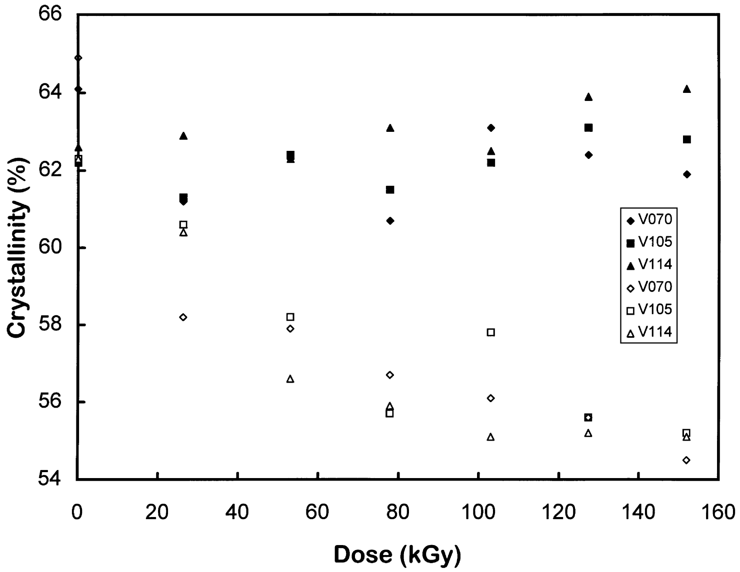


Fig. 17. Crystallinity measured from the first and second melting cycle as a function of dose: (◆, ◇) V070; (■, □) V105; and (▲, △) V114. First cycle (closed symbols), second cycle (open symbols).

for the second melting cycle. Crosslinks are responsible for the latter case.

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