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Crosslinking reactions in an unsaturated low density polyethylene

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The peroxide crosslinking properties of a new group of low density polyethylenes (LDPE), unsaturated LDPE, were investigated. These are copolymers between ethylene and 1,9-decadiene and contain a higher number of vinyl groups than 'ordinary' LDPE, situated on pendant carbon chains. Copolymers with different amounts of vinyl groups were crosslinked with dicumylperoxide at 180°C and the crosslinking reaction was followed by *FT*i.r. and gel content measurements. Compared with the reference material, the unsaturated LDPE crosslinked faster and produced higher final gel contents. Two crosslinking reactions take part simultaneously in the copolymers: polymerization of vinyl groups and combination crosslinking, i.e. coupling of macroradicals. © 1997 Elsevier Science Ltd.

(Keywords: LDPE; vinyl groups; crosslinking)

INTRODUCTION

Polyethylene is the most widely used thermoplastic material today. In some applications, it is essential to modify polyethylene in order to enhance certain properties. For instance, by introducing crosslinks between the polymer chains, a network is formed which improves heat and chemical resistance, stress cracking and shrinking. There are presently several methods for providing network formation via a crosslinking reaction[1]: with peroxides, by use of radiation and also, in some applications, by the use of silanes. Peroxide crosslinking, however, remains the most important method in commercial use today. When free radicals are used to initiate the crosslinking reaction, it is generally accepted that crosslinks are formed by the combination of macroradicals. In this paper, this type of crosslinking is termed combination crosslinking.

Industrially, peroxide crosslinking is performed in two steps. First, the polymer, containing a peroxide, is extruded at relatively low temperatures, in the order of 130°C, and is subsequently passed through a pressurized tube in which the temperature is rapidly increased to about 180°C. The temperature increase induces decomposition of the peroxide, which in turn gives rise to crosslinks. Thus, the peroxide must fulfil the requirements of having sufficient stability to be processed, but also rapidly decompose when the temperature is raised. As a result of these considerations, dicumylperoxide is the peroxide most commonly used for low density polyethylene, LDPE[2].

At the onset of the 1980's Hulse *et al.*[3] showed that the crosslinking efficiency of dicumylperoxide towards linear polyethylene depends to a great extent on the amount of terminal vinyl groups present. Later, Peacock[4,5] proposed that a reaction involving terminal vinyl groups could possibly compete with combination crosslinking. A rapid initial drop in terminal vinyl groups was ascribed to the preference of dicumylperoxide to react with these groups. Bremner and Rudin[6–8] proposed a mechanism by which the allylic hydrogens in terminal vinyl groups are preferentially abstracted. A combination of allylic radicals, which gives a crosslink, takes place after rearrangement of the terminal vinyl group into a *trans*-vinylene group. Hendra *et al.*[9] suggested that the methyl radical, one of the decomposition products of dicumylperoxide, could, since it is sufficiently small, add to the double bond, thereby explaining the rapid initial drop in terminal vinyl groups. Recently, in radiation crosslinking of LDPE, vinyl end groups were found to be highly active, and the observed improved melt extensional properties and network homogeneity were ascribed to vinyl end group involvement[10].

Commercially, both linear and branched polyethylene are used in applications requiring crosslinked materials. However, the effects of vinyl groups on the crosslinking reactions so far investigated have mainly concerned linear polyethylene. This is probably because low density polyethylene, produced by a radical mechanism under high pressures, normally has a very low content of vinyl groups, ~0.1/1000 C. However, the introduction of terminal vinyl groups in LDPE has been commercial practice for many years by the use of propylene as a chain transfer agent[11] (CTA). This method has an inherent limitation, since a maximum of only one terminal vinyl group per transferred chain can be incorporated.

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Table 1 Molar mass and branch content/1000 C

Sample	M_n(RI)^a (g mol^{-1})	M_w(RI)^a (g mol^{-1})	M_w(LS) (g mol^{-1})	LCB^b	C_1^{c}	C_2^{c}	C_4^{c}	C_{5+}^{c}
ref-0.13	17.000	67.200	187.000	1.5	—	1.2	6.2	5.5
P-0.40	17.700	60.100	142.000	1.5	4.4	0.5	5.8	4.6
P-0.45	16.000	80.900	265.000	1.7	3.7	0.8	6.5	4.4
D-0.42	14.900	73.300	224.000	1.8	—	1.3	6.5	6.6
D-0.65	18.000	64.200	147.000	1.3	—	0.9	5.8	5.5
D-0.68	16.100	69.100	221.000	1.8	—	1.4	6.1	5.7
DP-0.79	15.700	71.700	229.000	1.5	3.0	1.1	5.8	4.8
DP-0.82	14.900	73.100	236.000	1.6	2.8	0.9	6.1	4.9

^{a} Apparent molar mass, not corrected for long chain branches (LCB)
^{b} LCB calculated from LS and viscosity data
^{c} Determined by ^{13}C n.m.r., C_{5+} includes C_5 and longer branches

Table 2 The amount of unsaturation/1000 C in the investigated samples

Sample	Vinyl	Vinylidene	*trans*-Vinylene
ref-0.13	0.13	0.36	0.07
P-0.40	0.40	0.24	0.06
P-0.45	0.45	0.38	0.08
D-0.42	0.42	0.40	0.11
D-0.65	0.65	0.27	0.11
D-0.68	0.68	0.34	0.12
DP-0.79	0.79 (0.75)^a	0.33 (0.35)^a	0.11 (0.11)^a
DP-0.82	0.82	0.37	0.12

^{a} After extraction in heptane, 4 h, 45°C

The present work investigated the crosslinking properties of a new group of low density polyethylenes, unsaturated LDPE. This polyethylene is a copolymer between ethylene and 1,9-decadiene[12]. It has been found that this type of diene is incorporated homogeneously into the polymer chain without any side reactions[13], resulting in a 'new' type of vinyl group situated on pendant carbon chains. This type will be referred to as 'pendant vinyl groups'. Vinyl groups situated at the end of the backbone polymer chain, as in the case of propylene as the chain transfer agent, are referred to as 'terminal vinyl groups'.

The aim of this study was to follow the crosslinking reaction in LDPE materials containing both types of vinyl groups, individually as well as in combination. The effect of molar mass distribution, MMD, and the amount of vinyl groups present were investigated with respect to vinyl group consumption and formation of gel for different crosslinking times. The influence of temperature on the reactivity of the two types of unsaturation was also investigated.

EXPERIMENTAL

Sample preparation

The samples investigated are all LDPE materials produced in a commercial plant[13]. The investigation included three ethylene–decadiene copolymers with different amounts of diene and MMD, D-0.42, D-0.65 and D-0.68, two samples with propylene as CTA with different MMD, P-0.40 and P-0.45, and two ethylene–decadiene copolymers with propylene as CTA, DP-0.79 and DP-0.82, and, finally, a reference material, 'ordinary' LDPE, ref-0.13. The numbers show the initial value of vinyl groups per 1000 carbon atoms. All samples were received in granular form containing no additives and were used without further purification. Additional information with regard to the samples is given in *Tables 1* and *2*.

The granules were cooled in liquid nitrogen and ground in a Retsch rotary cutter. Dicumylperoxide, Dicup R from Hercules, was used as received and dissolved in methanol. The samples, in powder form, were impregnated with the solution and then dried under vacuum. This method was found to be an easy way of incorporating the peroxide homogeneously. Three peroxide concentrations were investigated, 0.5, 1 and 2 wt%.

Thin films, 0.1–0.15 mm, were crosslinked in a hot press. Initially, the samples were melted between two Teflon sheets in a low temperature press, 125°C, 30 s without pressure followed by 2 min with a pressure of 30 bar. They were then transferred directly to another press and allowed to crosslink for different periods of time, i.e. 1, 4, 6, 10 and 15 min, at 180°C with a pressure of 30 bar. To study the influence of crosslinking temperature on the changes in unsaturation, the crosslinking time was set at 1 min and temperatures between 150 and 240°C were employed. This investigation was limited to the samples D-0.68, P-0.45 and DP-0.82 containing 2 wt% of peroxide. Crosslinked films were washed in methanol at 45°C for 2–3 h to remove the non-decomposed peroxide and the decomposition products of the peroxide, and then subsequently dried under vacuum. The need for this extraction arises from the fact that these products have i.r. absorptions in the same regions as the double bonds under study.

Sample analysis

Size exclusion chromatography (s.e.c.) was used to determine molar masses and the content of long chain branches (LCB). The analyses were performed at 135°C, using 1,2,4-trichlorobenzene (TCB) as solvent, on a Waters 150 CV, equipped with an on-line viscometer, a Refractive Index (RI) detector and a Wyatt Dawn F Multi Angle Light Scattering Detector (MALLS). Samples (~ 2 g l^{-1}) were dissolved overnight in TCB at 135°C, filtered and then injected onto a column system packed with a polystyrene–divinylbenzene gel. A more detailed description of the procedure and data handling is presented elsewhere[13].

The number of branches were calculated from proton-decoupled ^{13}C-n.m.r. spectra obtained with a Varian VXR-300 spectrometer at 120°C. The sample, 200–300 mg, was dissolved at 120°C in 3–4 ml pure TCB. On complete dissolution, the temperature was decreased so that it was possible to add benzene-d_6 as locking solvent. The acquisition time was 1.8 s, the tip angle 90° and 10 000 scans were accumulated with a pulse interval of 2 s.

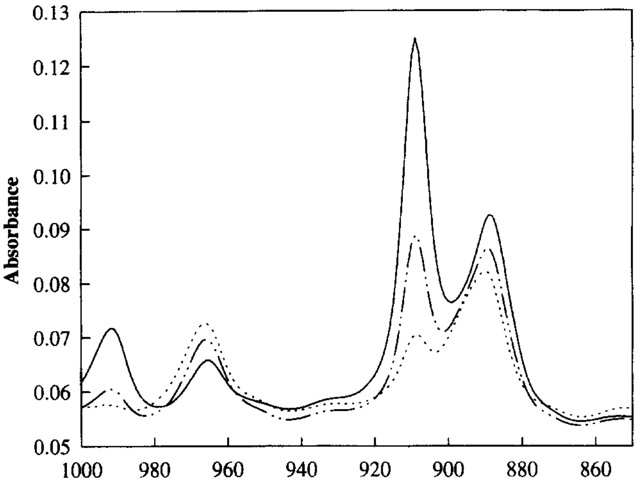


Figure 1 Changes in unsaturation in D-0.68, 1 wt% peroxide, after different crosslinking times: (———) before crosslinking; (– - - –); 1 min; (- - - - -) 6 min

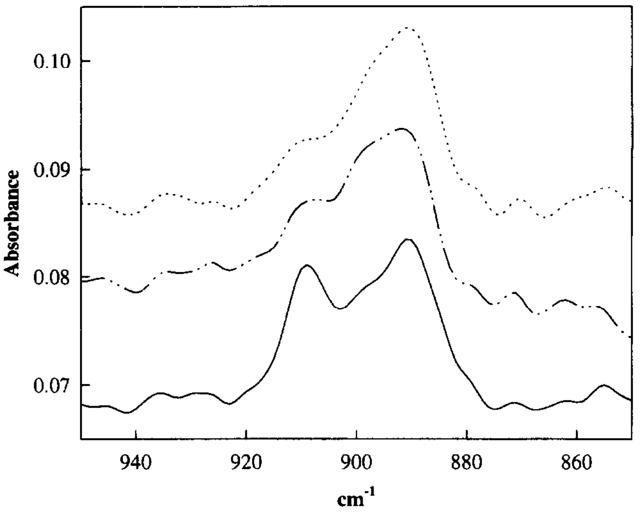


Figure 2 Absorptions of branches at 887 and 893 cm^{-1} in the gel in D-0.68, 2 wt% peroxide, after different crosslinking times: (———) 1 min; (– - - –) 4 min; (- - - - -) 6 min

*FT*i.r. measurements were performed on the films using a Perkin-Elmer *FT*i.r. 2000 (25 scans, resolution 4 cm^{-1}). The unsaturated structures of interest are[14]:

- vinyl (909 and 990 cm^{-1})
- vinylidene (890 cm^{-1})
- *trans*-vinylene (965 cm^{-1})
- *cis*-vinylene (735 cm^{-1})
- trisubstituted double bonds (~ 840 cm^{-1})

Of these, the following peaks were evaluated quantitatively: vinyl (909 cm^{-1}), vinylidene (890 cm^{-1}) and *trans*-vinylene (965 cm^{-1}). *Cis* unsaturation, unfortunately, is not possible to measure because of an overlap from the large CH_2 absorption at 720 cm^{-1}. The number of double bonds were calculated by utilizing extinction coefficients reported by Haslam *et al*[15].

Gel content was determined by a solvent extraction technique. A known amount of a crosslinked PE sample was placed in a preweighed 100 mesh stainless steel basket. Twelve baskets were extracted in 1.1 l decaline, decahydronaphthalene, together with a stabilizer (10 g Irganox 1076) for 6 h. The solvent was renewed (0.9 l) and the extraction continued for a further hour. The samples were finally dried under vacuum at 80°C for 5 h. The non-soluble fraction was weighed and the gel content calculated. A double test was performed for every sample and the reported gel contents are average values. For the majority of the samples, the reproducibility was ±1%.

RESULTS

In our work, the changes in unsaturation, i.e. vinyl, vinylidene and *trans*-vinylene, were followed with crosslinking time using *FT*i.r. Typical changes in the i.r. spectra are presented in *Figure 1*. Vinyl groups have absorptions at both 990 and 909 cm^{-1}, but only the absorption at 909 cm^{-1} was used in this study due to its higher extinction coefficient. A peak at 935 cm^{-1} is noticeable in samples in which propylene was used as chain transfer agent. This absorption is assigned to the methyl group formed when propylene is copolymerized into the chain. A proper measurement of vinyl and vinylidene during crosslinking is difficult since butyl and hexyl branches[16], both present in LDPE, also absorb in that region, 887 and 893 cm^{-1}, respectively. That these branch absorptions are present is easily seen with *FT*i.r. when measuring an extracted sample without sol fraction using a beam condenser, *Figure 2*. This makes

Table 3 Content of vinyl groups/1000 C after different crosslinking times

Crosslinking time (min)	0.5 wt%			1 wt%			2 wt%				
Sample	1	4	6	1	4	6	1	4	6	10	15
ref-0.13	0.11	0.08	0.08	0.08	0.07	0.06	0.07	0.06	0.06	0.06	0.06
P-0.40	0.28	0.16	0.15	0.15	0.09	0.09	0.14	0.09	0.09	0.09	0.09
P-0.45	0.28	0.19	0.18	0.21	0.13	0.12	0.16	0.10	0.10	0.10	0.10
D-0.42	0.28	0.19	0.18	0.21	0.12	0.11	0.14	0.08	0.08	0.08	0.08
D-0.65	0.40	0.24	0.23	0.29	0.12	0.12	0.13	0.06	0.05	0.05	0.05
D-0.68	0.41	0.26	0.24	0.31	0.15	0.14	0.15	0.08	0.07	0.07	0.07
DP-0.79	0.53	0.33	0.27	0.43	0.22	0.20	0.25	0.12	0.12	0.12	0.12

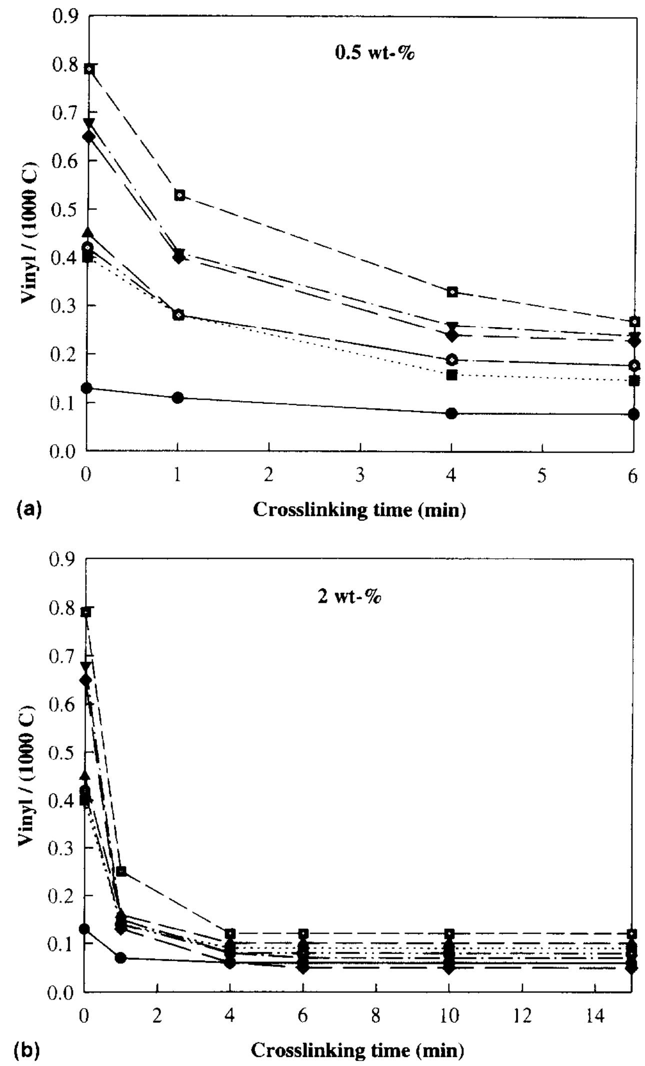
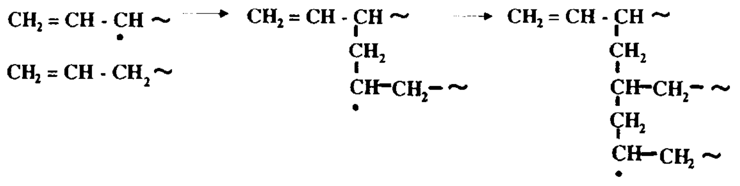


Figure 3 Consumption of vinyl groups after different crosslinking times with (a) 0.5 wt% and (b) 2 wt% dicumylperoxide. (——●——) Ref-0.13; (- - - - ■ - - - -) P-0.40; (——▲——) P-0.45; (- - - -●- - - -) D-0.42; (——◆——) D-0.65; (– - –▼– - –) D-0.68; (– –▣– –) DP-0.79

it difficult to draw a correct baseline, especially after long crosslinking times when many of the vinyl- and few of the vinylidene groups have reacted. However, as these branch absorptions contribute in a constant fashion to the measured values, no attempts have been made to correct for this error.

The amounts of vinyl groups in samples crosslinked for different times with 0.5, 1 and 2 wt% peroxide are given in *Table 3*. The *FT*i.r. data clearly show that vinyl groups are consumed and that, after longer crosslinking times, the number of vinyl groups approaches the same level as in the reference sample. This is illustrated in *Figure 3* for the results obtained with 0.5 and 2 wt% peroxide.

The consumption of vinyl groups is insensitive to whether the vinyl group is of a terminal or pendant character, as well as to the molar mass distribution. More decisive is the initial value, compare, e.g., samples P-0.40 and D-0.42 with D-0.68 in *Table 3*. The higher the peroxide concentration, the faster a low and constant level of about 0.1 vinyl/1000 C is reached. The observation that all samples contain a similar amount of vinyl groups after complete crosslinking, most significantly at 2 wt% of peroxide, may indicate that the reaction is an equilibrium reaction, a balance between a chain scission reaction and a vinyl consuming reaction. However, considering the crosslinking conditions used, chain scission reactions are not likely to occur (A. Holmström, personal communication). An explanation may also be that vinyl groups are transferred during the crosslinking reaction, to a minor extent, into vinyl groups with reduced reactivity. The slight shift in the position of the 909 cm^{-1} peak to shorter wave numbers, about 907 cm^{-1}, observed after long crosslinking times might support this. The final structure of a vinyl group undergoing abstraction followed by addition to a double bond would be



According to model compounds[17] the absorption of this vinyl group is still expected to be 909–910 cm^{-1}.

The concentration of *trans*-vinylene is found to increase during the crosslinking reaction (see results for 0.5, 1 and 2 wt% peroxide in *Figure 4*). Obviously, the formation of *trans*-vinylene is independent of the sample, i.e. independent of the amount of vinyls. On the other hand, it is clearly dependent on the peroxide concentration, about 0.055 *trans*-vinylenes/1000 C with 0.5 wt% peroxide and about 0.17–0.18/1000 C with 2 wt%. This is not in agreement with the literature[3,6–8]. Since the amount of *trans*-vinylenes formed is not related to the amount of vinyl consumed, our results disagree with the proposed transformation reaction of vinyls reported by Bremner and Rudin[6–8]. They suggest that, for one vinyl group used, the formation of one *trans*-vinylene would result. This was concluded from experiments with samples containing ~ 0.2 vinyl/1000 C. If our data are extrapolated to samples containing this level of vinyl groups, we would also observe such a relation. It must be pointed out, however, that this observation is purely accidental. Our result clearly indicates that a transformation reaction cannot be involved.

The concentration of vinylidene also decreases to a minor extent during the crosslinking reaction (*Figure 5*). No clear relations between the consumption of vinylidene and the number of vinyl groups or the concentration of peroxide could be observed. Since this double bond is situated directly on the polymer chain, it is probably too sterically hindered to be directly consumed in a polymerization reaction. A vinylidene group is surrounded by four allylic hydrogens that can be abstracted. An allylic radical formed from a vinylidene can be rearranged into a trisubstituted double bond if it combines

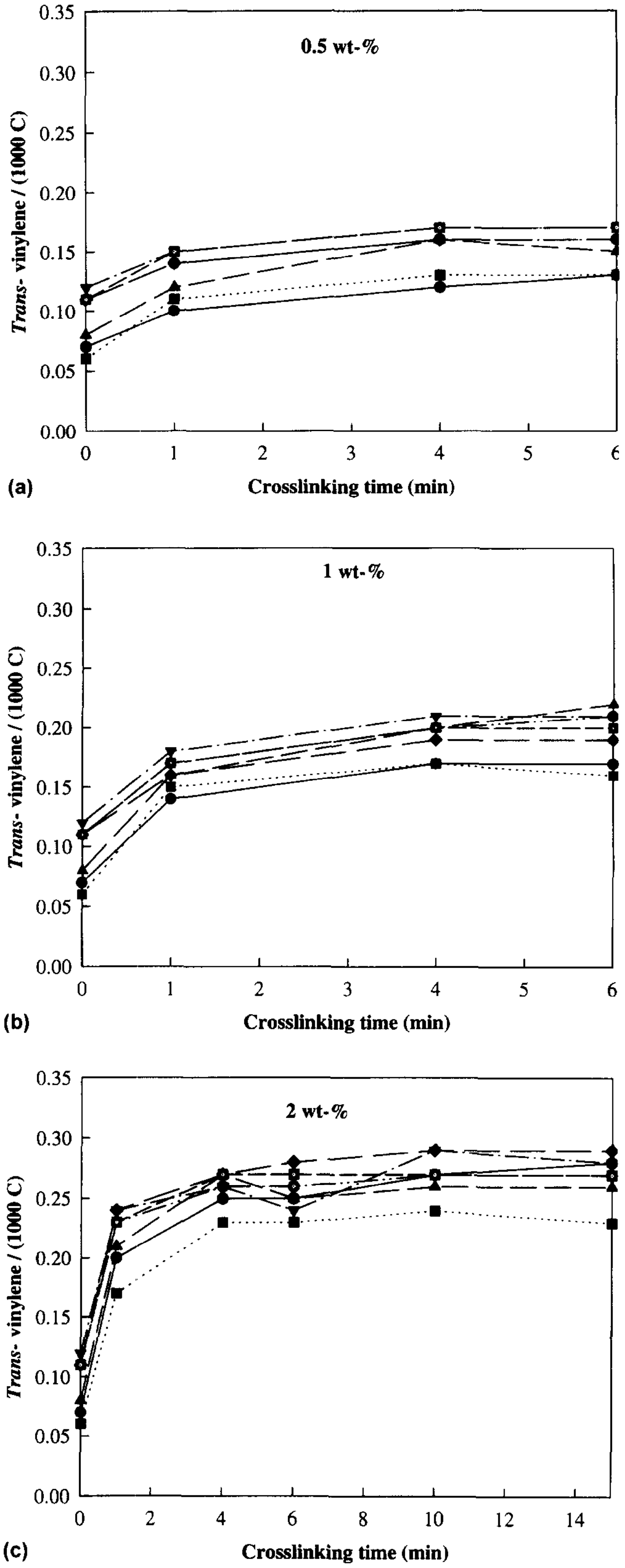


Figure 4 Formation of *trans*-vinylene groups after different crosslinking times with (a) 0.5 wt%, (b) 1 wt% and (c) 2 wt% dicumylperoxide (symbols and lines as in *Figure 3*)

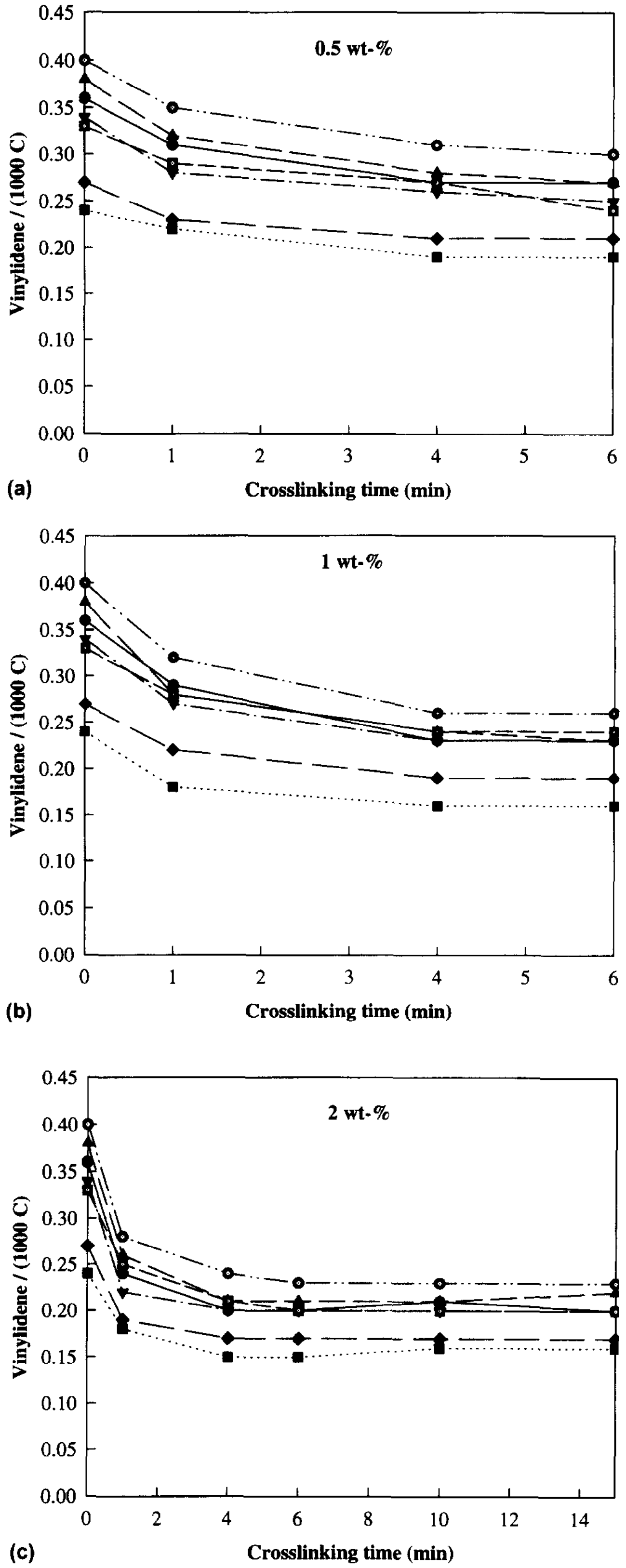


Figure 5 Consumption of vinylidene groups after different crosslinking times with (a) 0.5 wt%, (b) 1 wt% and (c) 2 wt% dicumylperoxide (symbols and lines as in *Figure 3*)

with another radical or adds a vinyl group. Indications of these trisubstituted double bonds were observed in the i.r. spectra in the 840–860 cm^{-1} region after crosslinking. No quantitative relation between consumed vinylidene and formed trisubstituted double bonds was, however, found.

If it was assumed that vinyl groups were consumed by the abstraction of allylic hydrogens and subsequent rearrangement, a maximum of one vinyl per radical formed would disappear. For the samples investigated, *Table 4* shows that almost two C=C bonds are consumed per peroxide radical in materials containing high numbers of vinyl groups. The calculation is based on

Table 4 Number of vinyl groups consumed per peroxide radical theoretically formed with 0.5 wt% peroxide after 1 min crosslinking

Sample	Vinyl/radical
Ref-0.13	0.13
P-0.40	0.79
P-0.45	1.12
D-0.42	0.92
D-0.65	1.65
D-0.68	1.78
DP-0.79	1.72

the number of vinyl groups consumed per dicumylperoxide radical theoretically formed after 1 min. The half-life time for dicumylperoxide in paraffin oil at 180°C is 119 s[18], i.e. about 30% of the peroxide molecules are decomposed after 1 min. Furthermore, initiator radicals are also consumed in other reactions, e.g. combination crosslinking and a cage reaction forming *trans*-vinylene, see below. The amount of vinyl groups consumed per radical should thus be even higher than those reported in *Table 4*. The only way to explain why so many vinyl groups are consumed after short crosslinking times, such as 1 min, is that the vinyl groups are consumed in a polymerization reaction.

The content of gel obtained is presented in *Figure 6*. It is obvious that, compared with the reference material, the vinyl containing materials crosslink faster, and higher amounts of gel are formed. These differences are more pronounced at low levels of peroxide concentration. In the reference sample, no gel is formed at all when using 0.5 wt% of peroxide after 1 min of crosslinking, *Figure 6* for 0.5 wt%. The same is observed for P-0.40, even if vinyl groups are, according to *FT*i.r., consumed in amounts equivalent to those consumed in D-0.42. This can be explained if one considers that the terminal vinyl groups are confined to the low molar mass region[13] of the MMD when propylene is used as chain transfer agent. When some of these short chains combine, no gel is formed directly, but a chain enlargement instead results. The ethylene–decadiene copolymer with propylene as chain transfer agent, DP-0.79, has the highest content of vinyl groups, but the amount of gel formed is not in accordance with the amount of consumed vinyl groups, possibly because some of the vinyl groups must take part in chain enlargement reactions. Because of low gel contents in DP-0.79, a ~ 0.1 mm thick film was extracted in heptane for 4 h at 45°C. This resulted in a loss of vinyl groups equivalent to 5%, probably originating from extraction of free decadiene in the sample.

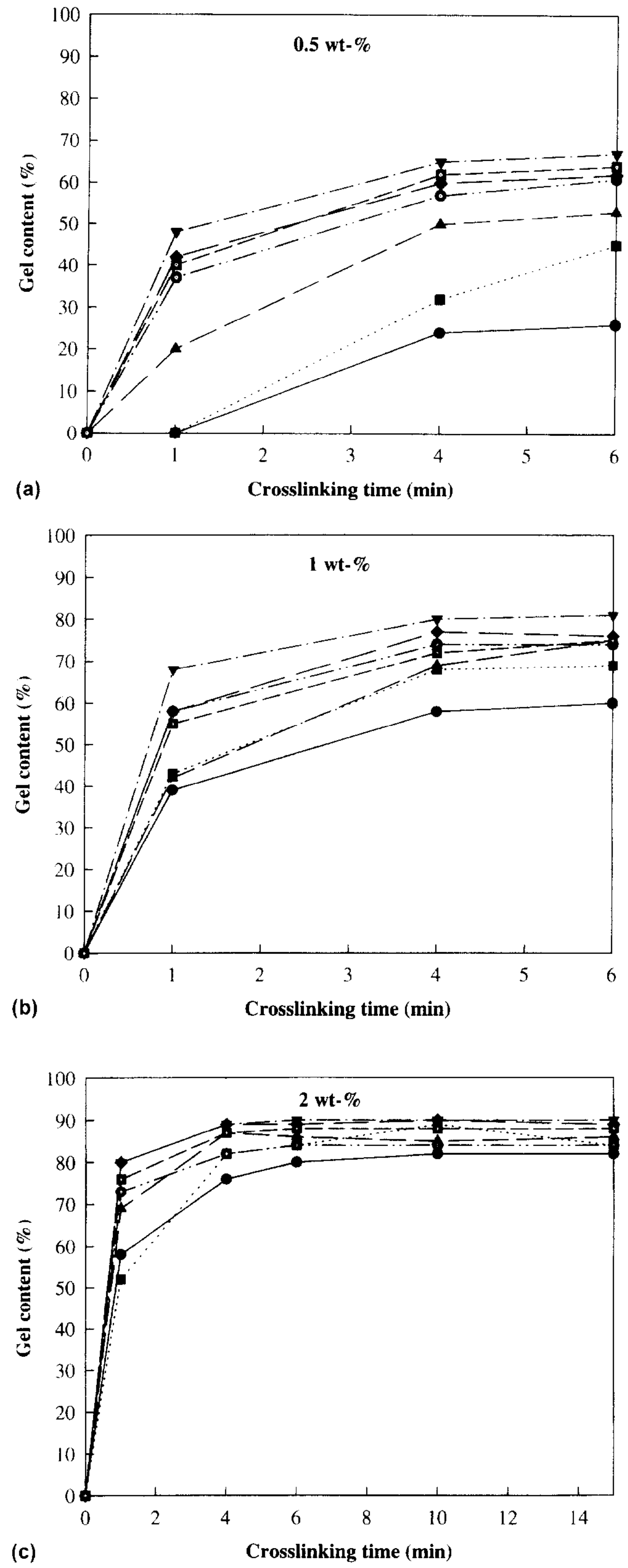


Figure 6 Gel content after different crosslinking times with (a) 0.5 wt%, (b) 1 wt% and (c) 2 wt% dicumylperoxide (symbols and lines as in *Figure 3*)

Samples containing pendant-type vinyl groups produce higher amounts of gel faster than do samples with the vinyl groups in a terminal position after the same number of vinyl groups have been consumed (*Figure 6*). It is especially pronounced with a low peroxide content at short crosslinking times. The vinyl groups of the ethylene–decadiene copolymer are homogeneously incorporated over the entire MMD[13] and, consequently, the high molar mass material contains many double bonds per molecule and thus has a high probability to crosslink. This is probably the reason for the fast initial formation of gel in these samples. There is also some difference in gel formation between the samples when the MMD is narrow or broad, samples P-0.40 and P-0.45, respectively, and D-0.65 and 0.68, respectively. This may be caused by the high molar mass chains in the broad MMD that initially assist in the gel forming reaction, thus giving a higher value; however, the final value, after long crosslinking times, is about the same for both types of MMD.

Since crosslinking involving vinyl groups appears to be a polymerization reaction, we found it interesting to investigate the temperature dependence of this reaction. The sample chosen, P-0.45, D-0.68 and DP-0.82, were crosslinked with 2 wt% dicumylperoxide for 1 min at different temperatures. It is understood that a different amount of radicals is formed at each crosslinking temperature (*Table 5*). At low crosslinking temperatures, very little peroxide has decomposed and, consequently, the amount of vinyls is little affected, see *Figure 7*. Also, minor changes in the content of vinylidene and *trans*-vinylene groups are observed in the interval 150–200°C. Although the relation between vinyls consumed and *trans*-vinylenes formed varies with temperature, the vinyl consumption is always much larger. This clearly indicates, as discussed above, that the crosslinking chemistry cannot include a rearrangement of vinyls into *trans*-vinylenes to any major extent. At even higher temperatures, the reaction becomes increasingly non-selective and chain scission occurs, as the amount of vinyl again increases together with increases in vinylidene and *trans*-vinylene. Gel content was determined for samples crosslinked in the temperature interval between 150 and 180°C, and the results are presented in *Table 6*.

DISCUSSION

Dicumylperoxide decomposes when it is exposed to heat, and two cumyloxy radicals of equal reactivity are formed. Alkoxy radicals are known to be strong hydrogen abstracting species. The cumyloxy radical can also decompose via a β-scission reaction into acetophenone and a methyl radical. The different C–H bonds present in polyethylene are not of equal stability, although the differences are not large. The radicals from the decomposed peroxide abstract hydrogen atoms from the polyethylene chains, forming macroradicals. Because of the high reactivity of the alkoxy radicals, it can be assumed that two macroradicals are formed close to each other and, when they combine, a crosslink is formed[19]. Depending on the structure of the macroradical, the crosslink formed could be either tetrafunctional (X-point) or trifunctional (Y-point). An X-point is formed when two secondary radicals combine and a Y-point when a secondary and a primary combine[20]. According to this mechanism, a maximum of one crosslink can be formed per dicumylperoxide molecule. The reactions discussed above, only exemplified with X-point, are summarized in *Scheme 1*. In addition to combination, some side reactions are known to occur with the macroradicals to a minor extent; these include disproportionation and chain scission.

That unsaturations, preferentially vinyl groups, present in polyethylene affect the crosslinking reaction is quite clear, and different mechanisms to explain this effect have been suggested. Bremner *et al.*[6–8] suggest that the activated allyl hydrogens are abstracted, and after

Table 5 Calculated amount of dicumylperoxide decomposed after 1 min at different temperatures

Temp (°C)	% dicumylperoxide decomposed
150	3
160	7
170	15
180	29
190	51
200	76
220	99
240	100

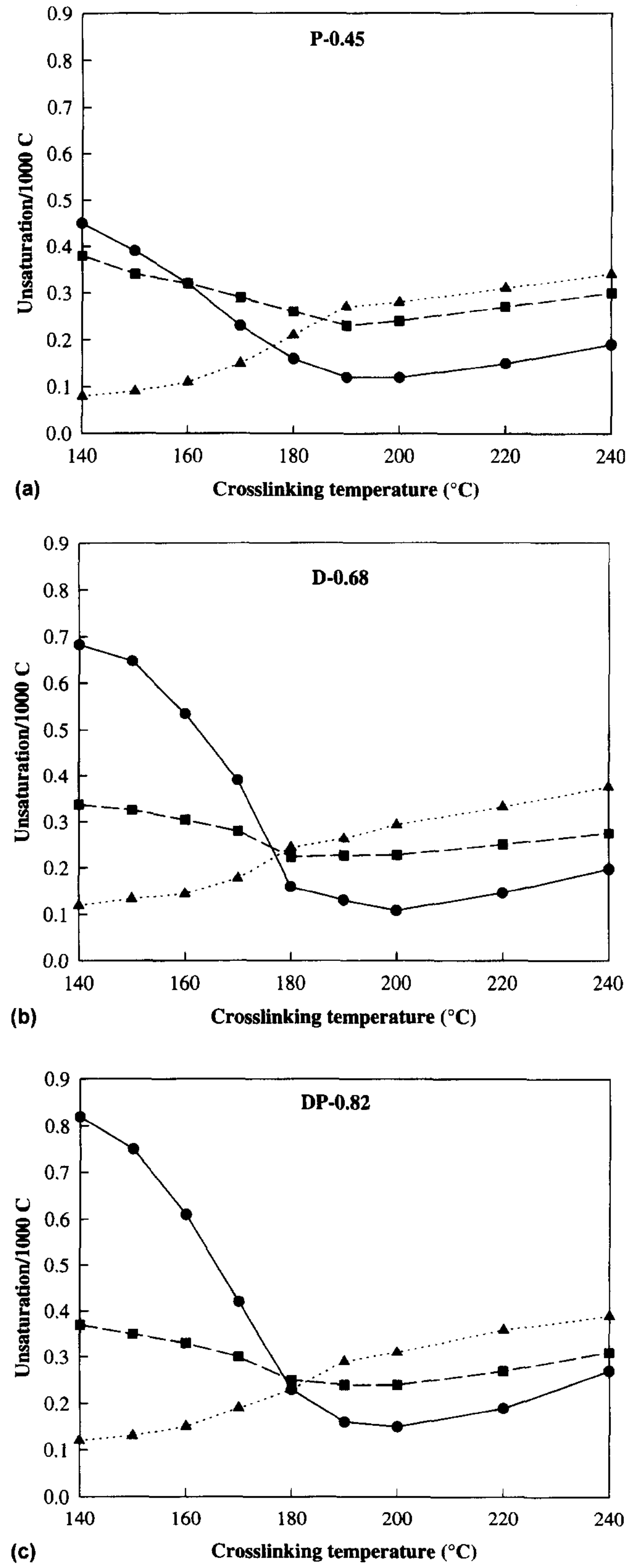


Figure 7 Changes in unsaturation at different crosslinking temperatures for (a) P-0.45, (b) D-0.68, and (c) DP-0.82, crosslinked with 2 wt% peroxide for 1 min. The number of double bonds given at 140°C show the initial values. (——●——) vinyl; (– —■— –) vinylidene; (- - -▲- - -) *trans*-vinylene

Table 6 Gel content after crosslinking at different temperatures, 1 min 2 wt% peroxide

	Temp (°C)			
Sample	150	160	170	180
P-0.45	0	3	43	69
D-0.68	0	35	56	80
DP-0.82	0	33	62	78

rearrangement create a crosslink by combination with another radical, regardless of whether it is allylic (*Scheme 2*). The terminal vinyl group is thus converted into a *trans*-vinylene bond; the *cis* configuration is not energetically favoured. This, of course, could explain why polyethylene containing higher levels of vinyl groups crosslinks with increased reaction rates. However, it fails to explain why final gel contents increase, since one peroxide molecule is still required to form one crosslink.

Parks and Lorentz[21] studied the crosslinking efficiency of dicumylperoxide towards two low molar mass substances, 2,6-dimethyloctadiene and 1-decene. 2,6-Dimethyloctadiene seems to exclusively form the dimer in contrast to 1-decene, which seems to form both the dimer and some high molar mass material. This high molar mass material indicates that a polymerization reaction involving vinyl groups is taking place. The fact that 2,6-dimethyloctadiene does not form high molar mass material probably has to do with steric hindrance of the double bond. In addition, the ratio between formed cumylalcohol to acetophenone was different for the two substances, which is probably a result of the amount of easily abstracted hydrogens present, 16 allylic in 2,6-dimethyloctadiene as compared with two in 1-decene.

Proposed reaction kinetics and mechanisms

As discussed above, there are many indications that the vinyl groups are partly consumed by a polymerization reaction. However, more information can be gained from the kinetics. If the initial consumption of vinyl groups (after one min of crosslinking) is plotted against peroxide concentration in a log–log plot, all samples show a linear relation with a slope of about 0.5 (*Figure 8* and *Table 7*). Thus, the consumption of vinyl groups is proportional to the square root of the peroxide concentration. This is a standard relation between monomer consumption and initiator concentration in radical polymerization initiated by peroxides

If the number of vinyls consumed after 1 min is plotted against the initial number of vinyls present in the material, a linear relation is found for each peroxide concentration (*Figure 9*). These two observations indicate that the kinetics for the consumption of vinyl groups can be written as follows:

$$-\frac{\mathrm{d[vinyl]}}{\mathrm{d}t} \propto [\mathrm{peroxide}]^{1/2}[\mathrm{initial\ vinyl}]$$

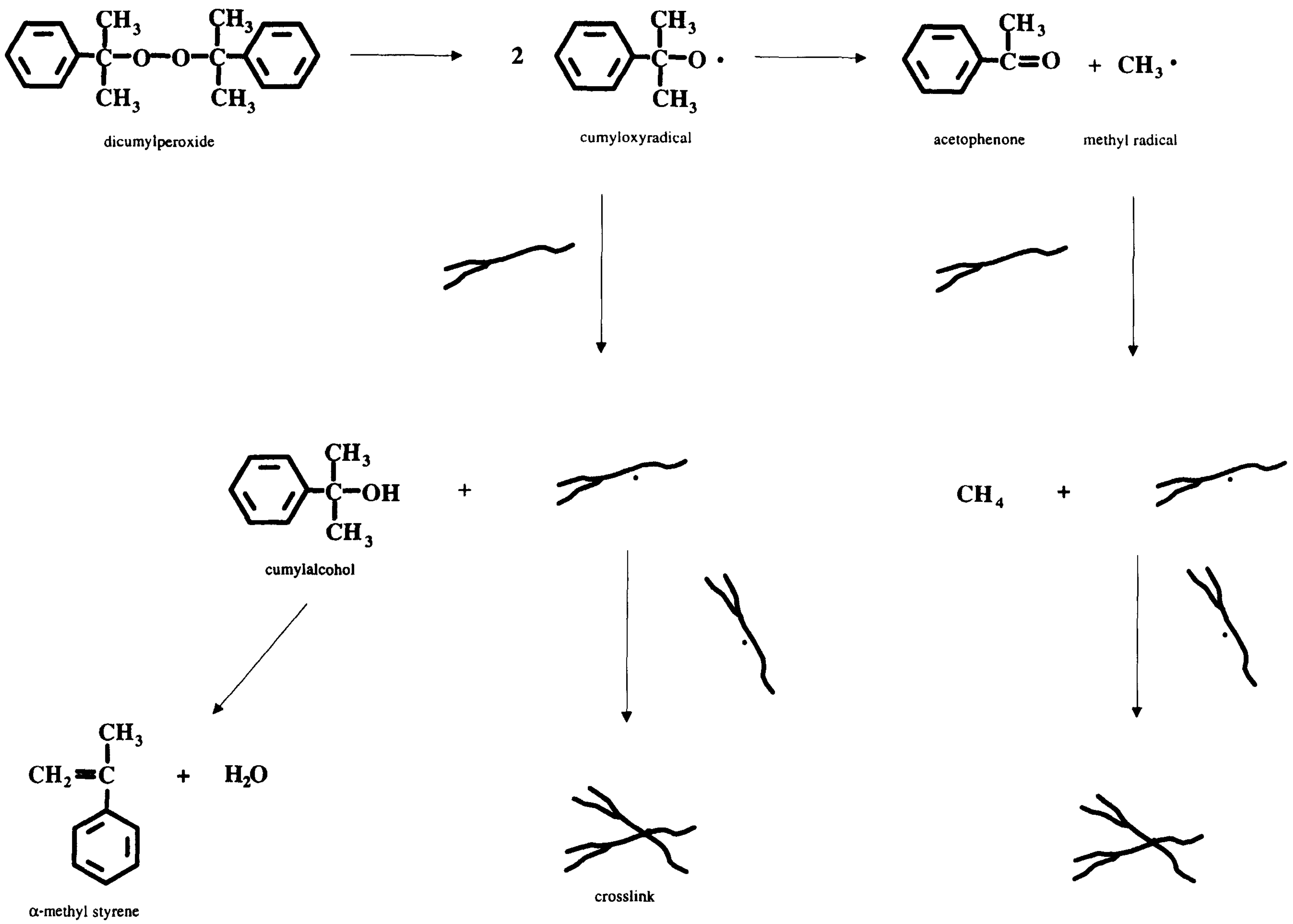
These are very important observations for the commercial crosslinking of polyethylene. As the amount of gel is related to the number of vinyl groups consumed, both initiator concentration and initial content of vinyls can be used to control the gel formation.

A nice linear relation is found when the concentration of *trans*-vinylenes formed after 1 min of crosslinking is plotted against peroxide concentration in a linear plot, see the examples in *Figure 10*. The slope is almost the same in all the samples investigated, including the reference. For most materials, the regression coefficient is between 0.99 and 1, P-0.40 being an exception, $r^2=0.92$. Again, it can be stressed that the reaction leading to *trans*-vinylenes seems to be totally independent of the reaction involving vinyl groups.

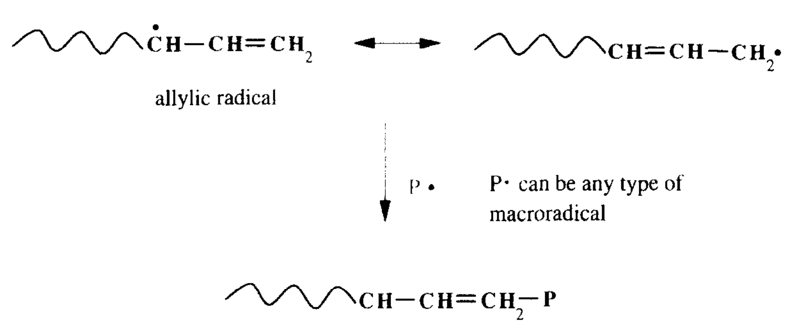
When the peroxide has decomposed into radicals, a hydrogen is abstracted from the polymer chain. There are different types of hydrogens present in LDPE, primary, secondary, tertiary and allylic, and which will be abstracted depends on both reactivity and concentration. Most likely, a secondary hydrogen is abstracted in the first place. Relative reactivities for abstraction of hydrogens in *t*-butylhypochlorite chlorination at 40°C[22,23] are presented in *Table 8*, and the inherent order is probably the same even at 180°C as was used in our study. Normally, polyethylene contains 10–35 methyl groups/1000 C and a small amount of unsaturation, which gives the following amount of the different types of hydrogens: 10–35 of tertiary H, 30–105 of primary H, 2 of allylic H and about 1900 of secondary H! The differences in reactivities for different types of hydrogens are therefore lost in this huge difference in concentration. As the initially formed secondary macroradical, if it does not immediately combine with another radical, is quite reactive, it probably abstracts a hydrogen. The result of this is that one radical is still present, but in a new position. The radical probably 'moves around' like this in the material until it finds a site of lower energy, i.e. a tertiary or an allylic position. This theory is accepted in degradation and stabilization studies[24] (A. Holmström, personal communication). From there, it can add to a vinyl group and start a chain reaction, or combine with another radical. Converting a double bond into a single covalent bond is energetically favoured. If a vinyl group is added, the resulting secondary radical is probably transferred via a 1,4-hydrogen transfer reaction into a tertiary allylic, since the lowest possible energy level is preferred. Of course, a tertiary radical may also lead to chain scission but, as long as there is a considerable amount of unsaturation present in the material and since the temperature used is too low to favour scission reactions, addition to a second vinyl group should occur. The proposed reaction mechanisms are seen in *Scheme 3*. However, other mechanisms than those described cannot be excluded.

Trans-vinylenes are probably formed owing to the cage effect of the peroxide (A. Holmström, personal communication), presented in *Scheme 4*. This is a state in which the peroxide has just decomposed but the radicals formed are still situated close to one another. If one of these radicals abstracts a secondary hydrogen from the polymer chain, a macroradical is formed. Hydrogens in the β-position to this radical are activated, i.e. more easily abstracted. Since the remaining peroxide radical is still in the near vicinity, it is likely to believe that the radical abstracts the hydrogen in the β-position to this first formed macroradical, resulting in a *trans*-vinylene double bond. Some *cis*-vinylene is probably formed too, but *trans* is energetically more favoured.

Thus, in the vinyl containing materials, there are two crosslinking reactions taking part simultaneously: polymerization of vinyl groups and combination crosslinking. Since the vinyl groups are rapidly consumed



Scheme 1 The different decomposition reactions of dicumylperoxide and peroxide crosslinking of 'ordinary' LDPE



Scheme 2 The crosslinking reaction involving vinyl groups proposed by Bremner and Rudin

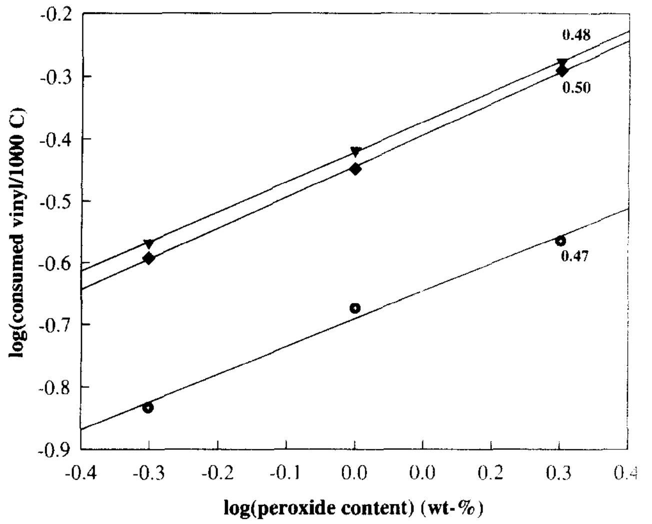


Figure 8 Log initially (1 min) consumed vinyl groups vs log (peroxide content) for (●) D-0.42, (◆) D-0.65 and (▼) D-0.68

Table 7 The value of the slope in a log–log plot for consumption of vinyl groups

Sample	Slope	r^2
P-0.40	0.46	0.835
P-0.45	0.38	0.964
D-0.42	0.45	0.989
D-0.65	0.50	0.999
D-0.68	0.48	1
DP-0.79	0.52	0.994

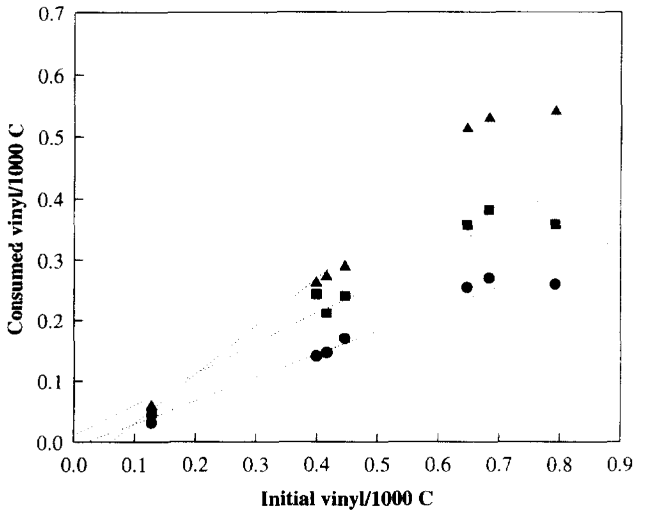


Figure 9 The number of vinyl groups initially (1 min) consumed vs the initial number of vinyl groups. (●) 0.5 wt%, (■) 1 wt%, (▲) 2 wt% peroxide

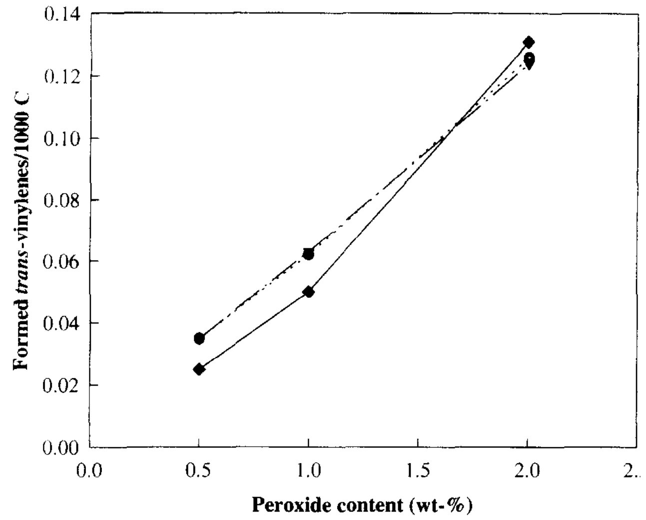


Figure 10 Formed *trans*-vinylene groups vs peroxide content for (●) D-0.42, (◆) D-0.65 and (▼) D-0.68

Table 8 Relative reactivities for abstraction of different types of hydrogens

Type of hydrogen	Paraffin	Allylic
Primary	1.0	20
Secondary	12.2	61[a] 93[b]
Tertiary	44	176[c]

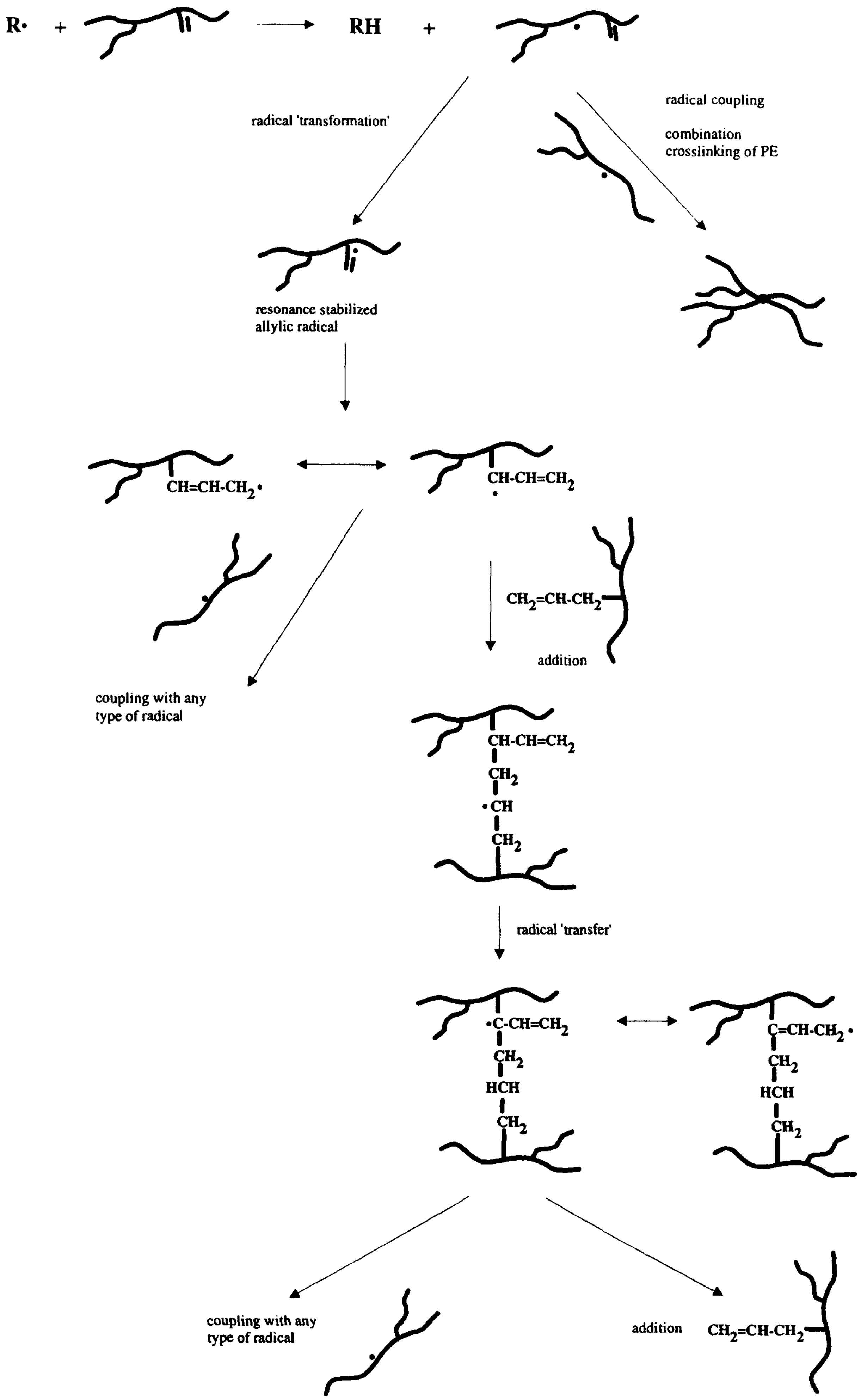
[a] The allylic radical formed has its odd electron delocalized between a primary and a secondary carbon

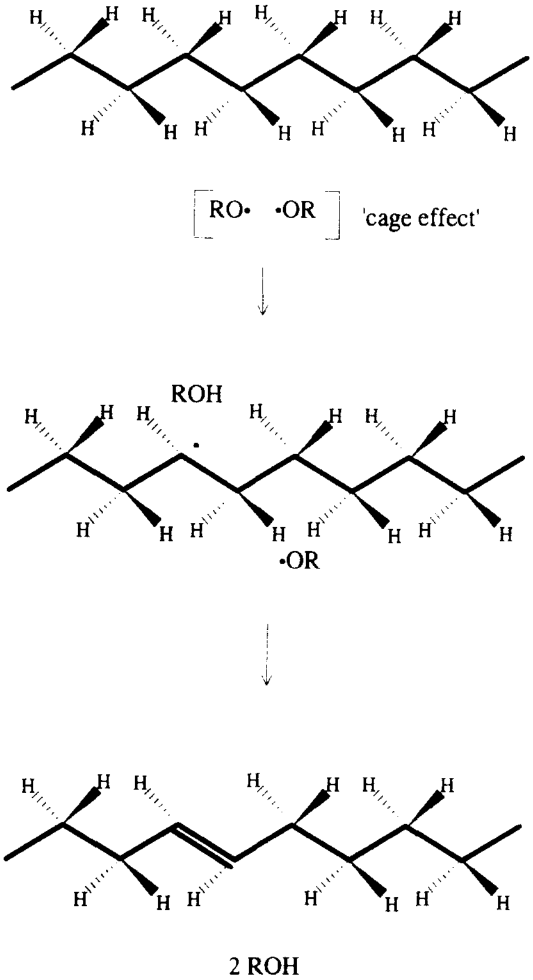
[b] The allylic radical formed has its odd electron delocalized between two secondary carbons

[c] The allylic radical formed has its odd electron delocalized between a tertiary and a primary carbon

after short crosslinking times and the gel contents are high, especially in the diene copolymers, it is tempting to believe that a loose network consisting of the polymerized vinyl groups is initially formed. After 1 min of crosslinking, about 30% of the peroxide has decomposed and most of the vinyl groups have been consumed, most clearly seen with 2 wt% of peroxide. Still, 70% of the peroxide remains, which probably will be used exclusively for combination crosslinking. Thus, the vinyl groups create a loose network which gives rise to a high gel content. This network is later densified by combination crosslinks; meanwhile the gel content increases to a minor extent. The effect of combination crosslinks is more pronounced when examining the

Scheme 3 The proposed reaction mechanisms in the vinyl-containing copolymer


R•
+
RH
+
radical 'transformation'
radical coupling
combination
crosslinking of PE
resonance stabilized
allylic radical
CH=CH-CH$_2$•
CH-CH=CH$_2$
coupling with any
type of radical
CH$_2$=CH-CH$_2$
addition
CH-CH=CH$_2$
CH$_2$
•CH
CH$_2$
radical 'transfer'
•C-CH=CH$_2$
CH$_2$
HCH
CH$_2$
C=CH-CH$_2$•
CH$_2$
HCH
CH$_2$
coupling with any
type of radical
addition
CH$_2$=CH-CH$_2$



Scheme 4 The proposed reaction for the formation of *trans*-vinylene groups

crosslink density. The crosslink density of the samples investigated in this study was measured but will be presented elsewhere.

CONCLUSIONS

The crosslinking properties of unsaturated LDPE copolymers with different numbers of vinyl groups were investigated by *FT*i.r. and gel content measurements. The vinyl groups are incorporated either by copolymerizing ethylene with 1,9-decadiene, leading to a vinyl group situated on a pendant six carbon-long chain or by using propylene as chain transfer agent, giving a vinyl group situated at the end of a polymer backbone. The location of the vinyl group does not affect the reactivity, but is, however, of great importance for the gel formation, especially after short crosslinking times and at low peroxide concentrations. All the vinyl-containing samples crosslink faster and produce higher final gel contents than the reference material, 'ordinary' LDPE. This higher final gel content can also be obtained in the 'ordinary LDPE' when higher peroxide concentrations are used.

The consumption of vinyl groups has been found to be proportional to the square root of the peroxide concentration and linearly proportional to the initial concentration of vinyl groups. The formation of *trans*-vinylene groups is linearly proportional to the peroxide concentration and is independent of the presence of vinyls. Since more than one vinyl group is consumed per initially formed radical, we believe that two crosslinking reactions take place simultaneously: polymerization of vinyl groups and combining crosslinking as a result of the coupling of macroradicals.

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