Molecular structure of crosslinked polyethylene as revealed by ^{13}C nuclear magnetic resonance and infra-red spectroscopy and gel permeation chromatography

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The molecular structure of low-density, high-pressure polyethylene crosslinked with peroxide or according to the silane process has been studied by gel permeation chromatography (g.p.c.), infra-red (i.r.) spectroscopy, ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy, solvent extraction and rubber elastic modulus measurements. It is shown that the degree of chain branching in the soluble part of the crosslinked samples (SOL) is the same as that in the polymer prior to crosslinking (BASIC). G.p.c. analysis provides evidence that the SOL samples are low-molecular-weight material compared with the corresponding BASIC samples and that they have bimodal molecular weight distributions. Model calculations assuming a 100% efficient crosslinking agent predict a dominance of chemically totally unmodified molecules in the SOL constituting the low-molecular-weight peak of the bimodal distribution. The model calculations furthermore predict that the next most important member of the SOL is the combination of two molecules linked together by one crosslink. There is an almost perfect fit between the calculated molecular weight distribution of these molecules and the experimentally found high-molecular-weight peak of the SOL. The discrepancies observed between measured and calculated contents and molecular weight distributions of SOL can be explained on the basis of an inefficient crosslinking agent due to possible side reactions and intramolecular crosslinking. The crosslink density determined by elastic modulus measurements using the theory of rubber elasticity compares fairly well with calculated values based on a 100% efficient crosslinking agent.

(Keywords: crosslinked polyethylene; molecular structure; gel permeation chromatography; infra-red spectroscopy; ^{13}C nuclear magnetic resonance spectroscopy; model calculations)

INTRODUCTION

This paper, which is one of a series[1,2] dealing with crosslinked polyethylene (XLPE), presents data on the molecular structure of XLPE. The XLPE samples (crosslinked by peroxide or according to the silane process) studied in these papers are all based on high-pressure, low-density polyethylene of the kind used in insulation of high- and medium-voltage power cables. The aim of the studies is to present information regarding the relationship between crosslinking process, molecular structure, crystallization behaviour, morphology and properties.

The chemistry of the crosslinking of PE with dicumyl peroxide is well known and can be described according to ref. 3 in the following schematic way: The peroxide is decomposed at elevated temperatures and oxy radicals are formed. The oxy radicals abstract hydrogen from the polymer molecules and the polymer radicals combine and form a molecular network. Some side reactions are possible: e.g. disproportionation, leading to molecular scission and the formation of molecular branches. There has been some interest in measuring the efficiency of the peroxide, i.e. the number of crosslinks formed for each molecule of peroxide used[4–6]. It can be concluded that the efficiency depends on the type of polyethylene used. Towards a linear polyethylene with a low vinyl group concentration (0.07 per 1000 carbons) the peroxide has an efficiency of 20–40%, whereas towards a linear polyethylene with a higher vinyl content (0.5 per 1000 carbons) the efficiency was 76%[4]. With a branched polyethylene the efficiency approaches 100%[5,6]. Campus and Matey[7] observed a decrease in the efficiency of crosslinking with increasing temperature and explained this observation in terms of a higher activation energy for the disproportionation reaction than for the crosslinking reaction.

A two-step process for the crosslinking of polyethylene using an organic silane compound was introduced by Dow Corning in 1967[8]. Vinyl silane is initially grafted onto the polyethylene chains. The actual crosslinking occurs at relatively low temperatures, lower than 100°C, and requires the presence of water and a tin catalyst. The silane groups are hydrolysed in the presence of water. Crosslinking occurs by a condensation reaction of the hydroxysilane groups.

The aim of the work described in the present paper has been to apply the theory of gelation, in a manner similar to that used earlier by Flory[9] and Stockmayer[10], to obtain information about the crosslinking process and the detailed molecular structure. Topics such as the relationship between molecular weight and degree of chain branching have been considered. Another aim of this study has been to obtain data concerning the molecular structure necessary to interpret the data of crystallization kinetics presented in a parallel paper[1].

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EXPERIMENTAL

Materials

Samples of crosslinked polyethylene (XLPE) insulation in four different power cables have been investigated in this study. Details of the crosslinking processes for the different samples are presented in *Table 1*.

Prior to crosslinking the materials—here referred to as BASIC—were all conventional low-density polyethylene grades with a density between 920 and 922 kg m^{-3}. The crosslinking catalyst, e.g. dicumyl peroxide in samples PG and PS, was removed from the BASIC samples before analysis to avoid crosslinking of the samples during subsequent analyses. The BASIC samples were dissolved in hot *p*-xylene, precipitated by the addition of methanol and cooling, separated from solution and dried *in vacuo* to constant weight.

The crosslinked samples (TOT) were treated with hot *p*-xylene in order to isolate the soluble fraction (SOL) of the TOT samples: pieces, about 0.2 mm thick, cut from the TOT samples were treated under agitation with *p*-xylene at 403 K for 24 h. The concentration of dissolved polyethylene was always less than 1 wt%.

To the solution that was separated from the swollen XLPE residues (GEL), an excess of methanol was added to precipitate the dissolved polymer. The system was kept at 273 K for about 15 h to ensure complete precipitation. After centrifugation, the PE crystals were separated from the solution by decanting and the precipitate was dried *in vacuo* to constant weight.

Gel permeation chromatography (g.p.c.)

The g.p.c. analysis, which was carried out by Dr S. Holding at the Rubber and Plastics Research Association of Great Britain, involved the dissolution of 20 mg samples in 1,2-dichlorobenzene stabilized with 2,6-di-t-butyl-*p*-cresol at 423 K. After filtration, the sample solutions were injected in a P.L. gel column which was thermostated at 403 K and equipped with an i.r. detector recording at 3.4 μm. The data were analysed using the 'universal' calibration procedure with the Mark–Houwink parameters for LDPE.

Infra-red (i.r.) spectroscopy

Films, about 20 μm thick, were analysed in the molten state at 433 K in a Perkin–Elmer 580 B i.r. spectrophotometer equipped with an i.r. data station. The absorbance spectra obtained (A_S) were compared with the absorbance spectrum of polymethylene (A_{PM}). The computer made it possible to normalize the spectra, i.e. eliminate thickness effects, to obtain difference spectra ($A_S - A_{PM}$) and to determine the absorbance at 1378 cm^{-1} (A_{1378}), which is assigned to methyl groups[11,12]. The absorption band at 1467 cm^{-1}, assigned to methylene groups[11,12], was determined and used as an internal standard. The i.r. spectra of a number of well characterized polyethylenes were recorded and a calibration curve could be established. For ethyl and butyl side groups the following relationship was established:

$$\mathrm{CH_3}(\%) = 25.6 A_{1378}/A_{1467} \qquad (1)$$

Table 1 Details of crosslinking process

Material code	Crosslinking temp., T_{XL} (K)	Heat medium	Crosslinking time, t_{XL} (min)	Crosslinking process
PG	570	dry N_2	5	dicumyl peroxide
PS	480	steam	5	dicumyl peroxide
SA	368	water	2000	Sioplas
SN	363	water	2000	Monosil

^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy

The ^{13}C n.m.r. spectra were recorded for 25 wt% solutions in 1,2,6-trichlorobenzene with deuterobenzene at 393 K using a Bruker WP-200 (200 MHz, pulse interval of 1 s).

The ^{13}C n.m.r. spectra were interpreted according to Bovey *et al.*[13].

Measurement of elastic modulus for the determination of crosslinking density

Dumb-bell shaped specimens with applied ink spots (original longitudinal distance $= L_0$) were subjected to a constant load (nominal stress $\sigma_n = 0.2$ MPa) at 473 K for 10 min, at which time the longitudinal distance (L) between the ink spots was measured to determine the elongation $\lambda = L/L_0$. By using classical theory for rubber elasticity and considering that the terminal chain segments do not contribute to the elastic force[9], the number average molecular weight for a chain between adjacent crosslinking points ($\bar{M}_c$) was obtained according to the following equations:

$$\bar{M}_c = [(\bar{M}_n + A)^2 + A\bar{M}_n]^{1/2} - (\bar{M}_n + A)/2 \qquad (2)$$

$$A = (RT\rho/\sigma_n)[\lambda - (1/\lambda)^2] \qquad (3)$$

where $\bar{M}_n$ is the number average molecular weight of the polymer prior to crosslinking, R is the gas constant, T is the absolute temperature, ρ is the density of the sample—at 473 K equal to 753.6 kg m^{-3} (ref. 14).

RESULTS AND DISCUSSION

The ^{13}C n.m.r. spectrum presented in *Figure 1* shows that PS and PG BASIC is a conventional low-density polyethylene with a major content of butyl branches and smaller amounts of ethyl, amyl and longer branches (*Table 2*).

A comparison of the ^{13}C n.m.r. spectra for PS BASIC and PS SOL reveals no significant differences in terms of chain branching between these samples. The total amount of methyl groups in PS SOL is 1.6%, which is 0.2% higher than that in PS BASIC. This difference can be explained, in accordance with the data presented in *Table 3*, on the basis of a difference in molecular weight between the two samples. The data for the concentration of methyl groups determined by i.r. spectroscopy (a typical spectrum is shown in *Figure 2*) are in fair agreement with the data obtained by ^{13}C n.m.r. (*Table 2*). There seem to be no measurable differences between the corresponding BASIC and SOL samples. However, data obtained by i.r. are about 0.3–0.4% higher than those obtained by ^{13}C n.m.r.

The similarity in degree of chain branching between BASIC and SOL samples disagrees with the suggestions earlier made by Kao *et al.*[15]. They explained their crystallization kinetic data on similar samples in terms of a lower degree of chain branching in SOL than in BASIC.

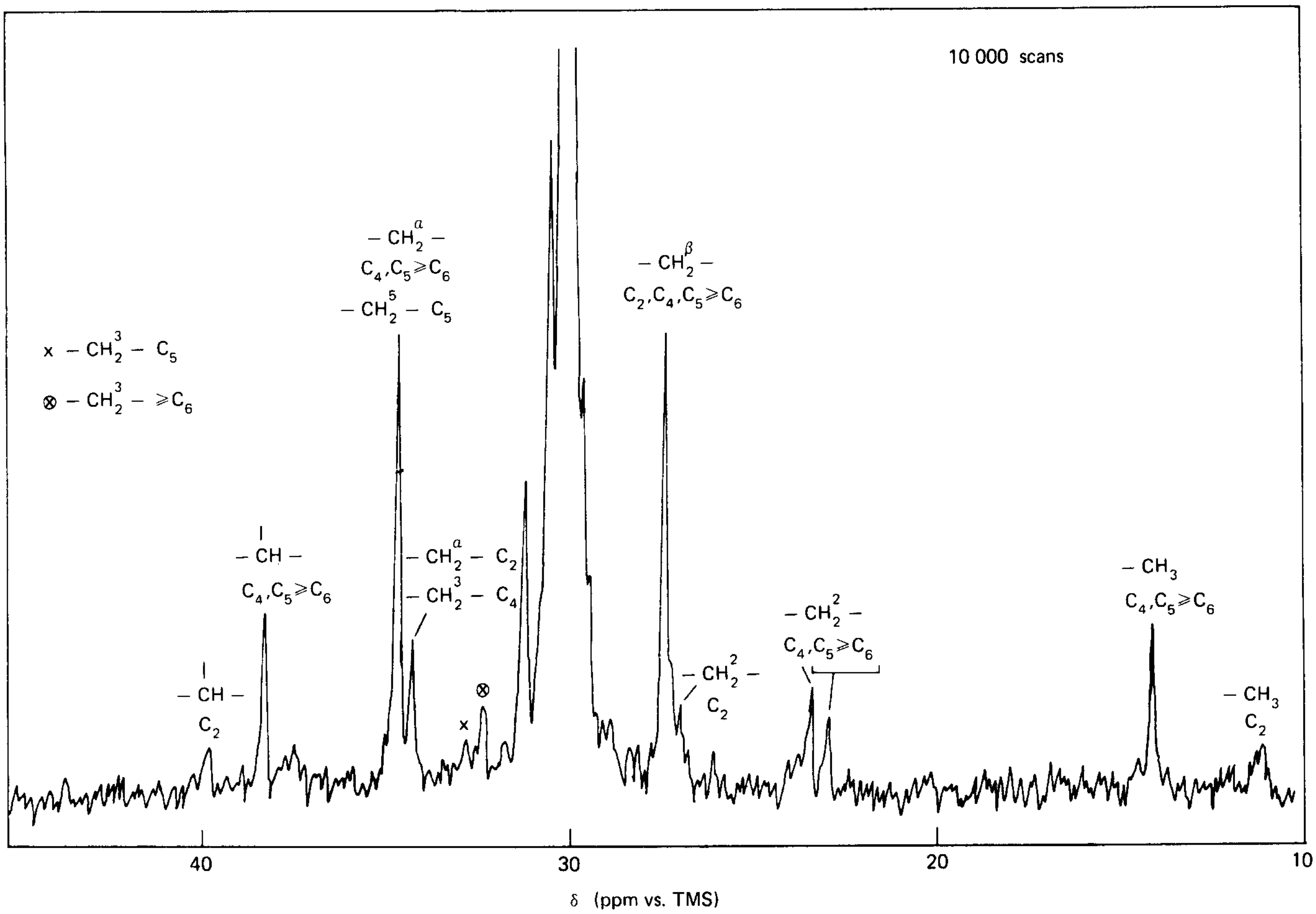

Figure 1 ^{13}C n.m.r. spectrum of PG and PS BASIC. The peaks are associated with a certain carbon and a certain branch type (C_i, i is the number of carbons in the branch) as indicated in the figure. The major peak at 30 ppm vs. TMS is assigned to methylene groups

Table 2 Molecular structure: chain branching

Sample	Concentration[a]					
	C_{CH_3}[b]	$C_{C_2H_5}$[b]	$C_{C_4H_9}$[b]	$C_{C_5H_{11}}$[b]	$C_{\geq C_6H_{13}}$[b]	C_{CH_3}[c]
PG BASIC	1.4	0.3	0.7	0.1	0.3	1.8
PS BASIC	1.4	0.3	0.7	0.1	0.3	1.8
PS SOL	1.6	0.3	0.7	0.1	0.4	1.9
SA BASIC	–	–	–	–	–	1.6
SA SOL	–	–	–	–	–	1.7

[a] Molar fraction as a percentage
[b] As determined by ^{13}C n.m.r.
[c] As determined by i.r.

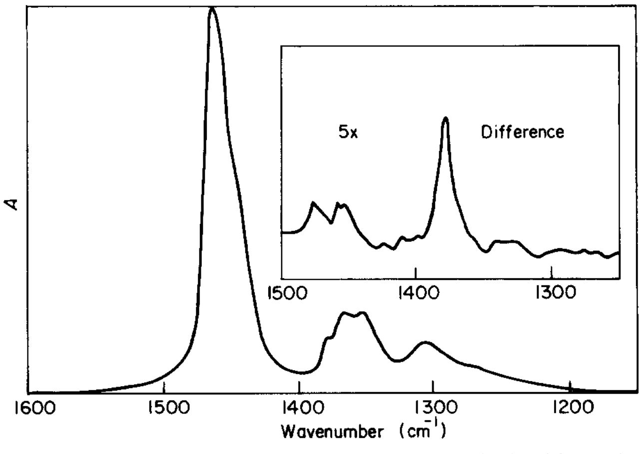

Figure 2 Infra-red absorbance spectrum of PG and PS BASIC. The inset graph is the difference absorbance spectrum between PG and PS BASIC and polymethylene (magnified 5 ×)

Table 3 Molecular weight data

Sample	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	log M_p[a]
PG BASIC	13.8	74.9	4.7
PG SOL	7.8	25.4	4.1 (4.35)
PS BASIC	13.8	74.9	4.7
PS SOL	7.0	27.1	4.1 (4.3)
SA BASIC	12.6	126.0	4.85
SA SOL	8.0	27.7	4.1 (4.35)
SN BASIC	11.6	106.0	4.85
SN SOL	6.2	23.9	4.1 (4.25)

[a] Peak value of *MWD* (dW/d log M vs. log M). Values within parentheses refer to high-molecular-weight peak in bimodal *MWDs*

The molecular weight distributions (*MWD*) of PG BASIC and SOL are shown in *Figure 3*. The *MWDs* of BASIC and SOL samples of PS, SA and SN are qualitatively similar to those shown in *Figure 3*. Number and weight average molecular weights and peak values of the *MWDs* of the studied samples are recorded in *Table 3*. In all cases, the SOL samples have lower molecular weights than the corresponding BASIC samples. The low-molecular-weight tail of the SOL samples coincides fairly well with the corresponding part of the BASIC

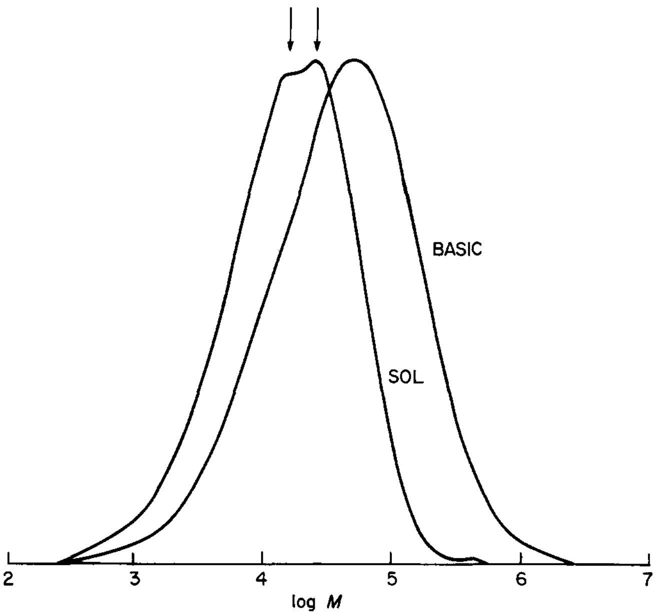

Figure 3 Molecular weight distributions (d*W*/d log *M* vs. log *M*) of PG BASIC and SOL

samples. An interesting point is that both SN SOL and SN BASIC are dominated more by low-molecular-weight material than are the other samples. Thus, all these facts indicate that the SOL samples essentially constitute the low-molecular-weight parts of the BASIC samples. The occurrence of bimodal *MWD*s of all SOL samples indicates the existence of another, complicating factor, which will be dealt with later in this paper.

Model calculation of molecular weight distribution of SOL

The probability $P(I,N)$ that a chain with N carbons is associated with other chains via I crosslinks is given by the expression:

$$P(I,N)=(1-P_t)^{N-I}P_t^I N!/[(N-I)!I!] \qquad (4)$$

where P_t is the probability that one carbon is crosslinked. Equation (4) assumes equal probabilities for all carbons to be crosslinked, i.e. the probability that an arbitrary carbon is crosslinked is independent of the length of the molecule it belongs to.

Another assumption made in the analysis is that the efficiency of the crosslinking agent, the peroxide for PG and PS, is 100% (equation (5)):

$$P_t=2X_{XL} \qquad (5)$$

where X_{XL} is the molar fraction of peroxide (calculated on the basis of the number of crosslinkable units, methylene groups). It is known that both PG and PS prior to crosslinking contained 1.6 wt% dicumyl peroxide (DCP). *Figure 4* shows the probability function P as a function of $\log M$ for different values of I assuming 1.6 wt% DCP.

The molecular weight distribution $F(I,M)$ of primary molecules prior to crosslinking with I potential crosslinking carbons can be calculated in accordance with equation (6) provided that the molecular weight distribution $F^0(M)$ of BASIC is known:

$$F(I,M)=F^0(M)P(I,M) \qquad (6)$$

Figure 5 shows the calculated results for PG and PS BASIC according to equation (6).

A number of quantities, useful in the subsequent analysis, can be calculated on the basis of these distributions:

$$X_n(I)=\frac{\sum_J F(M_J,I)/M_J}{\sum_J F^0(M_J)/M_J} \qquad (7)$$

$$X_w(I)=\frac{\sum_J F(M_J,I)}{\sum_J F^0(M_J)} \qquad (8)$$

$$X_{nr}(I)=\frac{IX_n(I)}{\sum_I IX_n(I)} \qquad (9)$$

$$\bar{M}_n(I)=\frac{\sum_J F(M_J,I)}{\sum_J F(M_J,I)/M_J} \qquad (10)$$

$X_n(I)$ is the number fraction of primary molecules with I crosslink points, $X_w(I)$ is the weight fraction of primary

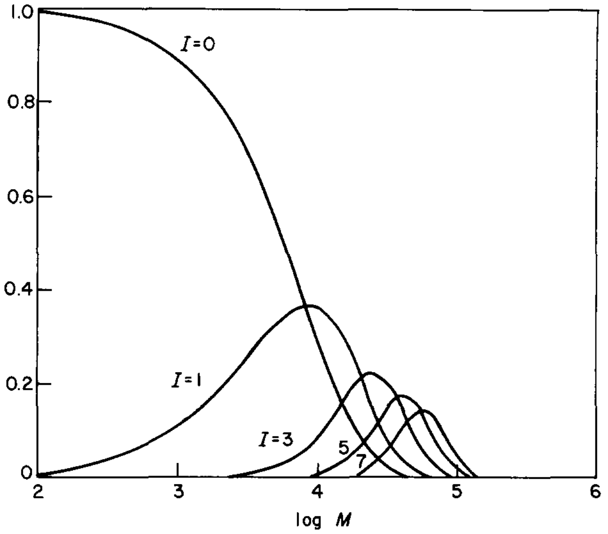

Figure 4 Calculated probability *P* for PS and PG that a chain of molecular weight *M* has *I* crosslinks

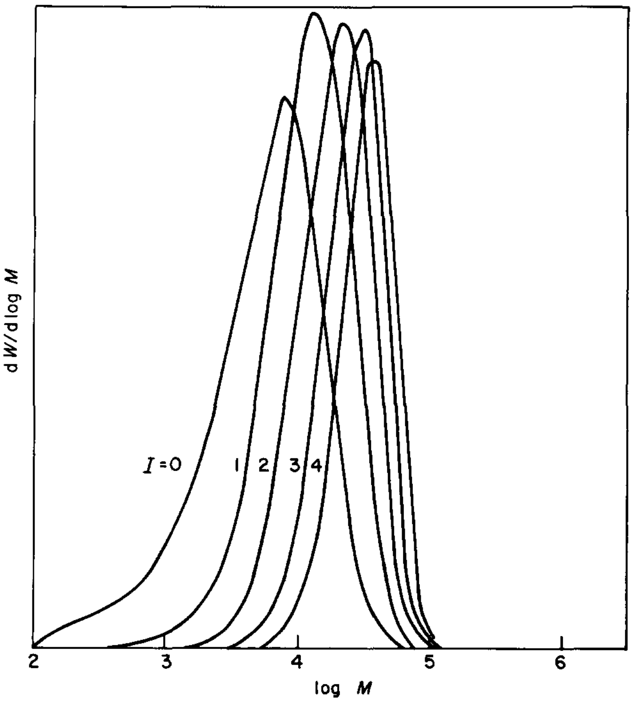

Figure 5 Calculated molecular weight distributions (PS and PG) for 'primary' molecules with different crosslinking numbers *I*

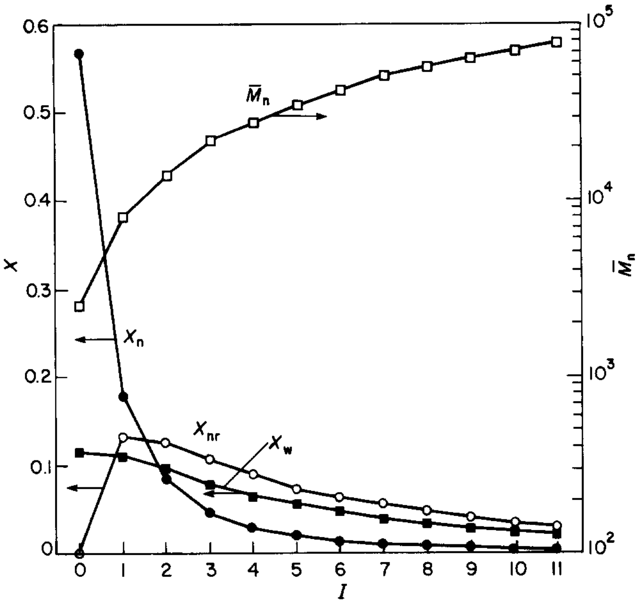

Figure 6 Calculated X_n, X_w, X_{nr} and $\bar{M}_n$ (defined in the text) plotted vs. the crosslinking number *I*. The data relate to PG and PS

molecules with I crosslink points, $X_{nr}(I)$ is the number fraction of crosslink points in the group of primary molecules with I crosslink points, and $\bar{M}_n(I)$ is the number average molecular weight for primary molecules with I crosslink points. *Figure 6* presents graphs of these quantities plotted against I for PG and PS BASIC.

The molecular weight distribution of SOL, $F_{SOL}(M)$, has been estimated on the basis of the calculated data presented in *Figures 5* and *6* according to the expression:

$$F_{SOL}(M) = F(0,M) + F^*_{11}(M) + F^*_{12}(M) + \ldots + F^*_{ijk}(M) \qquad i, j, k, \ldots \leqslant 3 \qquad (11)$$

where $F^*_{ijk}(M)$ is the molecular weight distribution of the combined molecules composed of primary molecules with $I = i, j$ and k.

The method used for calculating the molecular weight distributions of the combined molecules requires some comment:

(a) The weight fraction of the sample with a certain combination of molecules (characterized by I) was first calculated. For example, the weight fraction of the sample with a 11 combination amounts to $X_w(1)X_{nr}(1)$.

(b) An approximate molecular weight distribution of the combined molecules was calculated assuming that an arbitrary molecule with molecular weight M_i which is combined with a molecule of $I = j$ forms a molecule with a molecular weight M_s:

$$M_s = M_i + \bar{M}_{nj} + \ldots \qquad (12)$$

(c) The molecular weight distribution obtained according to (b) was finally normalized considering the earlier calculated weight fraction.

The weight fractions of SOL for PG and PS were estimated based on this analysis to be about 15%, which is significantly lower than the experimentally determined values (see *Table 4*). However, the real discrepancy is smaller. The content of non-polymer soluble material in these samples is about 2 wt% and the polymeric SOL thus constitutes about 19% for PS and 23% for PG. As discussed in the introduction, side reactions that do not contribute to the formation of crosslinks are possible. It has been shown[7] that the crosslinking efficiency decreases with increasing processing (vulcanization) temperature, which is consistent with data obtained for PG and PS (cf. data presented in *Tables 1* and *4*). Intramolecular crosslinking is another source of inefficiency. A third possible reason may be the existence in the SOL of combinations of molecules with $I > 3$.

The model calculations for PG and PS show that the totally unmodified molecules ($I = 0$) dominate and constitute about 80 wt% of the SOL. The next most important member of PG and PS SOL is the 11 combination, which constitutes about 10 wt% of the SOL.

A comparison of the calculated $F_{SOL}(M)$ presented in *Figure 7* and the corresponding measured distributions (*Figure 3*) shows that the high-molecular-weight part of the measured distributions is missing in the calculated one. It seems reasonable in accordance with the above discussion to assume that possible side reactions and intramolecular reactions might be important when considering the quoted discrepancy. The bimodal character of the measured distribution also appears in the calculated $F_{SOL}(M)$ distribution: the low-molecular-weight peak corresponds to 'unreacted' molecules ($I = 0$), whereas the high-molecular-weight peak is dominated by the 11 combination. This is supported by the almost perfect agreement in position between the high-molecular-weight peaks for PG SOL and PS SOL (*Figure*

Table 4 Crosslink density and gel content

Sample	$\bar{M}_c \times 10^{-3}$	Gel content (%)
PG	6.9	75.5
PS	7.0	78.3
SA	5.9	73.6
SN	6.1	68.1

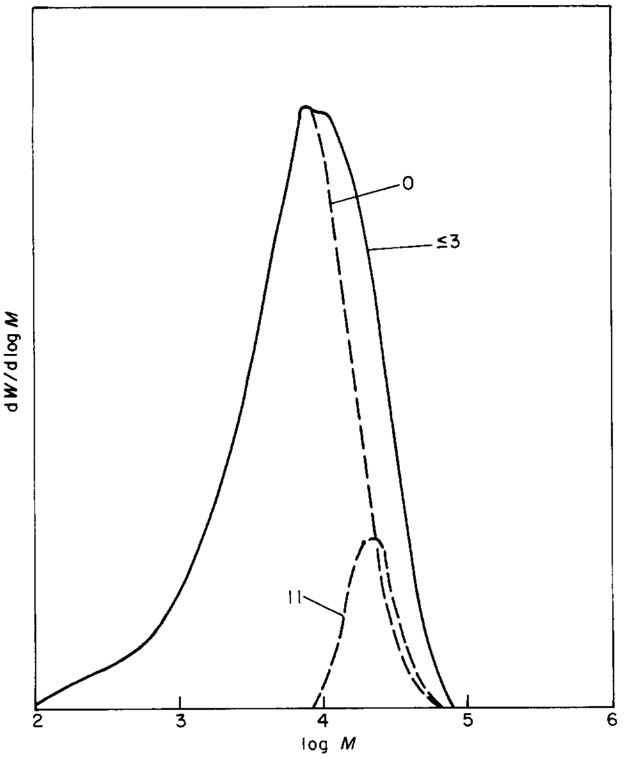

Figure 7 Calculated molecular weight distributions (combinations 0, 11 and ≤3, see text) for PG and PS SOL

3 and *Table 3*) and the calculated peak of the 11 combination (*Figure 7*).

The results presented in *Table 4* show that the silane crosslinked samples, SA and SN, despite their comparatively low gel content, have a lower $\bar{M}_c$ than the samples crosslinked by peroxide. Similar observations have been made earlier, for example by Voigt[8]. The calculation of $\bar{M}_c$ for PG and PS assuming 100% efficiency of the peroxide reveals a value for $\bar{M}_c$ of about 8000, which is of the same order of magnitude as the experimental data (cf. *Table 4*).

CONCLUSIONS

The molecular structure of low-density, high-presure polyethylene crosslinked with peroxide or according to the silane process is the subject of this paper. It is shown by i.r. and ^{13}C n.m.r. spectroscopy that for both types of crosslinked polyethylene the degree of chain branching is the same in the soluble part of the crosslinked samples (SOL) as in the polymer prior to crosslinking (BASIC). G.p.c. analysis shows that the SOL samples are in all cases lower-molecular-weight material than the corresponding BASIC samples. The molecular weight distributions of the SOL samples are all bimodal, in contrast to the unimodal distribution of the BASIC samples. Model calculations carried out for the peroxide-crosslinked samples assuming a 100% efficient crosslinking agent predict a dominance of chemically totally unmodified molecules in the SOL constituting the low-molecular-weight peak of the bimodal distribution. The model calculations also predict that the next most important member of the SOL is the combination of two molecules linked together by one crosslink. There is an almost perfect fit between the calculated molecular weight distribution of these molecules and the experimentally found high-molecular-weight peak of the bimodal molecular weight distribution of SOL. The discrepancies obtained between calculated and measured contents and molecular weight distributions of SOL can be explained on the basis of an inefficient crosslinking agent due to possible side reactions and intramolecular crosslinking. The crosslink density determined by elastic modulus measurements using the theory of rubber elasticity compares fairly well with calculated values based on a 100% efficient crosslinking agent. It is noted, in agreement with observations reported in the literature[8], that the silane crosslinked samples, despite their comparatively low gel content, have a lower $\bar{M}_c$ than the samples crosslinked by peroxide.

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