(2) M. M. Kops-Werkhofen and H. M. Fijnaut, *J. Chem. Phys.*, **77**, 2242 (1982).
(3) G. D. J. Phillies, *J. Chem. Phys.*, **60**, 983 (1974).
(4) B. J. Berne, in "Photon Correlation Spectroscopy and Velocimetry", H. Z. Cummins and E. R. Pike, Ed., Plenum Press, New York, 1977, p 344.
(5) B. U. Felderhof, *J. Phys. A*, **11**, 929 (1978).
(6) P. Mazur and W. van Saarlos, *Physica*, **115A**, 21 (1982).
(7) C. W. J. Beenacker and P. Mazur, *Phys. Lett. A*, **91**, 290 (1982).
(8) G. D. J. Phillies, *J. Chem. Phys.*, **77**, 2623 (1982).
(9) G. D. J. Phillies, *J. Chem. Phys.*, **74**, 260 (1981).
(10) G. D. J. Phillies, *J. Chem. Phys.*, **79**, 2325 (1983).
(11) J. M. Schurr, *Chem. Phys.*, **65**, 217 (1982).
(12) C. R. Jones, C. S. Johnson, Jr., and J. T. Penniston, *Biopolymers*, **17**, 1581 (1978).
(13) R. S. Hall, Y. S. Oh, and C. S. Johnson, Jr., *J. Phys. Chem.*, **84**, 756 (1980).
(14) K. J. LaGatutta, V. S. Sharma, D. F. Nicoli, and B. K. Kothari, *Biophys. J.*, **33**, 63 (1981).
(15) A. P. Minton and P. D. Ross, *J. Phys. Chem.*, **82**, 1934 (1978).
(16) G. Gros, *Biophys. J.*, **22**, 453 (1978).
(17) K. H. Keller, E. R. Canales, and S. I. Yum, *J. Phys. Chem.*, **75**, 379 (1971).
(18) G. D. J. Phillies, G. B. Benedek, and N. A. Mazer, *J. Chem. Phys.*, **65**, 1883 (1976).
(19) G. Scatchard, *J. Am. Chem. Soc.*, **68**, 2315 (1946); G. Scatchard, A. C. Batchelder, A. Brown, and M. Zoza, *J. Am. Chem. Soc.*, **68**, 2610 (1946); G. Scatchard, A. C. Batchelder, and A. Brown, *J. Am. Chem. Soc.*, **68**, 2320 (1946).
(20) R. F. Probstein, W. F. Leung, and Y. Alliance, *J. Phys. Chem.*, **83**, 1228 (1979).
(21) M. M. Kops-Werkhofen, H. J. Mos, P. N. Pusey, and H. M. Fijnaut, *Chem. Phys. Lett.*, **81**, 365 (1981).
(22) M. M. Kops-Werkhofen, C. Pathmamanoharan, A. Vrij, and H. M. Fijnaut, *J. Chem. Phys.*, **77**, 5913 (1982).
(23) M. B. Weissman, *J. Chem. Phys.*, **72**, 231 (1980).
(24) P. N. Pusey, *J. Phys. A*, **11**, 119 (1978).
(25) B. J. Ackerson, *J. Chem. Phys.*, **64**, 242 (1976).
(26) W. Dieterich and I. Peschel, *Physica*, **95A**, 208 (1979).
(27) S. Hanna, W. Hess, and R. Klein, *Physica*, **111A**, 181 (1982).
(28) M. van Saarloos and P. Mazur, *Physica*, **120A**, 77 (1983).
(29) J. M. Burgers, Second Report on Viscosity and Plasticity, Amsterdam Academy of Sciences, Amsterdam, The Netherlands, 1938.
(30) E. L. Chang and R. M. Mazo, *J. Chem. Phys.*, **64**, 1389 (1976).
(31) B. M. Ladanyi and J. T. Hynes, *J. Chem. Phys.*, **77**, 4739 (1982).
(32) J. A. McCammon and P. G. Wolynes, *J. Chem. Phys.*, **66**, 1452 (1977).

Radiation Cross-Linked Paraffins and Percolation Model

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ABSTRACT: A percolation process on a lattice was used to model the cross-linking of paraffins induced by ^{60}Co γ-radiation. The molecular weight distribution of cross-linked paraffins was characterized by gel permeation chromatography (GPC). The GPC traces were compared with the chromatograms calculated from the size distribution of site clusters obtained by a random introduction of bonds into square, triangular, and Bethe lattices. The comparison revealed that the cross-linking produces significantly more of high molecular weight material and less of dimer than calculated from the models. This shows that the cross-linking is not random; the clustering of cross-links in paraffins is in excess of that predicted by percolation models based on random statistics. It was found that this excessive clustering is only little influenced by the state and crystallographic phase of the paraffins; hence more fundamental factors (recombination of radicals in spurs, chemical changes introduced by the cross-links) have to be responsible for this effect. However, it was confirmed that the crystal lattice has a profound influence on the position of the cross-links along the paraffin chains; in paraffin crystals the cross-links are more concentrated toward the chain ends than when irradiated in the melt. It was also confirmed that the crystallinity affects the cross-linking efficiency of the radiation; the yield of cross-linked material is higher if irradiated in the melt.

1. Introduction

Cross-linking and chain scission are the two major effects that determine the change of molecular weight in polymers subjected to ionizing radiation. In polyethylene and paraffin the cross-linking is dominant, resulting in a continuous increase of the molecular weight average with the dose and, finally, in the formation of an infinite network.[1,2] Because of its application the radiation-induced cross-linking of polyethylene was widely studied in the past[3] and it was found that most of the cross-links were located in the disordered, fold region of polyethylene crystals.[4–6] In contrast to polyethylene the crystallinity of paraffins is high and comparable with that of low molecular weight compounds. In paraffin crystals the chains are extended and the disordered regions associated with the chain folds in polyethylene are absent.[7] The molecular weight of paraffins is uniform and lower than in polyethylene, which simplifies the molecular weight analysis of the cross-linked products.

Two different techniques were used in the past for molecular weight analysis of cross-linked paraffins: gas chromatography (GLC)[8] and gel permeation chromatography (GPC).[9,10] The former technique is limited to low molecular weights only as the volatility of paraffins decreases rapidly with the molecular weight. This restriction does not apply to the GPC, which can be used in principle for all soluble polymers. However, in the molecular weight region common to both techniques, the resolution of GPC is inferior to GLC, which is capable of separating fully not only homologues of different molecular weights but also different isomers of the same molecular weight.[8]

In paraffin crystals the chains are fully extended and packed parallel in layers in a three-dimensional crystal lattice. If the linking of chain ends belonging to different layers is neglected, the intralayer cross-linking can be modeled by a percolation process on a two-dimensional lattice. The latter is constructed by the projection of chain axes onto a plane perpendicular to the chain direction.

In the percolation process[11] certain pairs of points (or sites) are connected and properties of such systems (size of clusters, their shape and density, appearance of an infinite size cluster, etc.) are studied.

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In this work paraffins were cross-linked by ^{60}Co γ-radiation under different conditions and products were analyzed by GPC. The chromatograms were compared with those calculated from the size distributions of site clusters generated by introduction of bonds into different two-dimensional lattices. The aim was to scrutinize the randomness of the distribution of the cross-links in irradiated paraffins in different crystallographic phases and states.

2. Experimental Section

2.1. Materials. Linear paraffins tricosane ($C_{23}H_{48}$) and tetracontane ($C_{40}H_{82}$) were irradiated by γ-rays at different temperatures under vacuum using a ^{60}Co γ source as described elsewhere.[12] After the irradiation the samples were analyzed for gel content by extraction in refluxing toluene. It was found that samples irradiated by a dose of less than about 800 Mrd remained fully soluble and were therefore suitable for GPC analysis.

2.2. Gel Permeation Chromatography. A Waters GPC 200 instrument with *o*-dichlorobenzene at 135 °C as the solvent was used. The system contained fcur Styragel columns of upper porosities 1000, 500, 350, and 350 Å connected in series. The column system was deliberately chosen to give a curved calibration line with a sharp cutoff at high molecular weights. This facilitates the detection of the high molecular weight tail in the cross-linked produce while maintaining good resolution in the low molecular weight region. An internal standard, *n*-decane, was used for improving the accuracy of the elution volume measurements.[13]

3. Results and Discussion

3.1. Gel Permeation Chromatography. Figure 1 shows an example of GPC traces of radiation cross-linked paraffins. The traces indicate the dependence of the refractive index difference between the solution and the solvent on the elution volume. At a constant concentration the refractive index difference depends on the chemical composition of the solute. For linear oligomers it varies with concentration of end groups and hence the molecular weight. However, in paraffins the influence of the end groups on the refractive index difference becomes negligible for chains longer than about 20 carbons.[9,14] By the same argument the effect of cross-links on the refractive index difference should also be small for long-chain paraffins as the fraction of tertiary carbons participating in cross-links in an *n*-mer decreases with the increasing chain length of the starting material.

In the GPC analysis the molecules of the solute are separated according to their size in solution so that their elution volume is inversely related to their hydrodynamic volume.[15] For a linear polymer the hydrodynamic volume depends on the chain length and hence its molecular weight. However, if the polymer chains are branched or cross-linked the relation between the elution volume and the molecular weight does not hold because the size of such molecules in solution depends also on their structure. The size of a nonlinear molecule in solution is always smaller than that of its linear counterpart; hence the linear chain is eluted earlier than the corresponding cross-linked or branched molecule of the same molecular weight.

A typical GPC trace of irradiated paraffins obtained under conditions used in this work exhibits two peaks, which correspond to the original un-cross-linked paraffin and its cross-linked dimer (Figure 1). The rest of the trace toward the lower elution volumes belongs to the unresolved higher *n*-mers ($n > 2$). The wide spread of this trace coupled with the fact that the monomer peak remains the most prominent in the whole dose range up to and above the gel point shows that the molecular weight distribution of the cross-linked product is very broad. The position and width of the monomer peak (Table I) do not change with the dose, confirming that scission is relatively unimportant.[3,16]

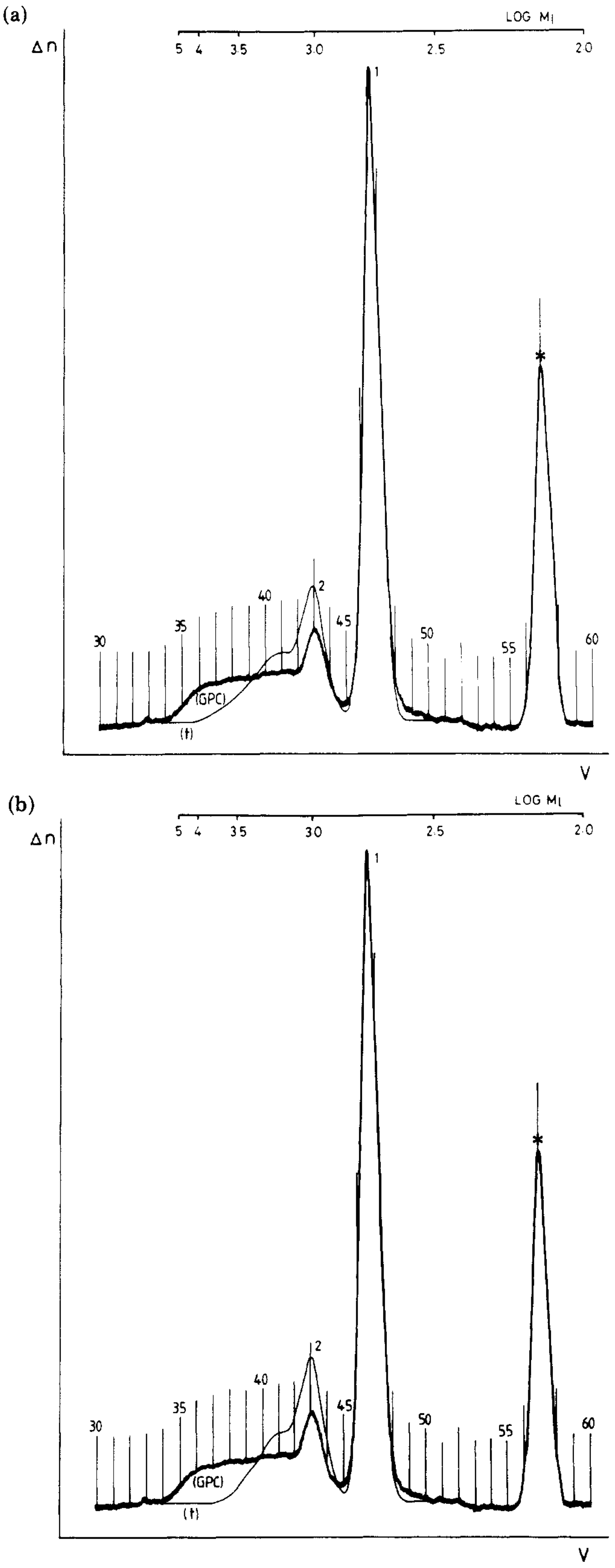

Figure 1. Comparison of the GPC trace of tetracontane irradiated to 500 Mrd with chromatograms (t) calculated from percolation models: (a) Flory–Stockmayer model (Bethe lattice), $f = 82$; (b) triangular lattice. Δn = refractive index difference; M_l = molecular weight of linear paraffins eluted at the elution volume V. The residual weight fraction $w_{res} = 1 - \sum_{s=1}^{s_{max}} sn(s)$ omitted from the chromatograms by neglecting the clusters larger than s_{max} is (a) 8.1×10^{-5}, $s_{max} = 20$; (b) 6.0×10^{-3}, $s_{max} = 6$. The peaks labeled 1, 2, and (*) correspond to the monomer, the dimer, and the internal standard (decane).

Table I
Results of GPC Analysis of Irradiated Paraffins

	irradiation			elution vol (corr), counts		peak width param		branch-ing param g	wt fraction	
				monomer	dimer[a]	monomer	dimer		monomer	dimer
sample	state and phase	temp, °C	dose, Mrd	v_1	v_2	h_1	h_2		w_1	w_2
$C_{40}H_{82}$	crystalline orthorhombic	40–45	219	46.64	43.04	1.35	0.84	0.945	0.772	0.106
		40–45	500	46.64	43.09	1.32	0.93	0.934	0.652	0.121
		1	800	46.66	43.12	1.36	0.90	0.930	0.641	0.132
$C_{23}H_{48}$	crystalline orthorhombic	33	200	50.53	46.22	1.47	1.04	0.938	0.936	0.045
		33	500	50.50	46.25	1.48	1.24	0.933	0.862	0.079
		33	800	50.53	46.31	1.47	1.15	0.924	0.751	0.104
	crystalline hexagonal	43	300	50.50	46.39	1.48	1.23	0.912	0.872	0.082
	melt	53	300	50.51	46.43	1.48	1.30	0.907	0.822	0.078

[a] Linear dimer elution volume $v_2(C_{80}H_{162})$ = 42.73; $v_2(C_{46}H_{94})$ = 45.77.

The elution volume and the peak width of the dimers are both larger than those expected for the linear paraffins (Table I). In addition, it is seen from the table that, for a given paraffin, the elution volume of the dimer is not a constant but it is affected by the state in which it has been irradiated. Thus, e.g., in case of tricosane, the elution volume is lowest and closest to that of the linear dimer when irradiated in the crystalline orthorhombic phase as compared with the molten liquid phase. An intermediate value of the elution volume is obtained if irradiated in the hexagonal phase. Further, it was noticed that the dimer elution volume increased slightly with dose in paraffins irradiated in the orthorhombic phase (Table I).

The above findings have the following significant information to convey. First, cross-linking is not confined to the terminal methyl groups of the paraffin molecule but must be distributed along its chain. This is in agreement with a number of earlier works[8-10] but contrary to deductions by Bovey et al.[16] Nevertheless, the facts that the physical state affects the dimer elution volume and, further, that in crystalline paraffins the volume increases with the dose mean that the distribution of cross-link positions along the chains cannot be the same in all cases. In the crystalline state, particularly in the orthorhombic phase, the cross-links are concentrated in the chain ends region with their mean positions moving toward the chain interior as the dose is increased. The two conclusions, first that there is a distribution of cross-link positions along the chain (as opposed to them being confined exclusively to the chain ends) and second that in the orthorhombic phase this distribution of cross-links is nevertheless concentrated toward the chain ends (as opposed to a random distribution), are both significant in the context of the present work. The first will justify the treatment of cross-linking in the crystalline state as a two-dimensional problem confined to layers of stacked chains while the second provides support to the previous assertions based on different evidence that on irradiation in the crystalline state the cross-links do not form randomly along the polymer chains in the crystal lattice. Apart from the position of the cross-links, the physical state of the paraffins affects also the cross-linking efficiency of the radiation. As shown previously and as now supported by present evidence (Table I) paraffins irradiated in the molten state[9] or in the hexagonal phase[17] are more susceptible to cross-linking than in the orthorhombic phase.

3.2. Models for Cross-Linking. The cross-linking of paraffins can be treated as a polymerization of polyfunctional monomers resulting in the formation of a three-dimensional network. The theory of this process was first discussed for some special cases by Flory[18] and extended and generalized by Stockmayer.[19] He derived a formula relating the weight fraction of an n-mer to the extent of reaction and the functionality, which was defined as the number of reactive groups in the monomer capable of forming the link. The conditions assumed in the theory and essential for exact solution were as follows: (1) The intramolecular links were postulated not to occur; hence cyclic structures did not exist. (2) All groups that could form a link were equally reactive; hence the linking process was random. The polymerization or the cross-linking can be regarded as a special case of a more general percolation problem.[11,20] In percolation certain pairs of points in an infinite set are connected and the properties of such a system (size of clusters, their shape and density, and the appearance of an infinite cluster) are studied. In the simplest percolation the points are arranged in a lattice, the nearest neighbors only are paired, and the process is random. The pairing of points can be achieved by occupation of lattice points in an empty lattice (site problem), by occupation of links between the points (bond problem), or by both (site–bond problem[21]). The cross-linking or polyfunctional polymerization corresponds to a bond problem. However, in a pure bond percolation the properties of clusters of bonds are considered, whereas in polymerization or cross-linking the main interest is in the molecular weight of resulting n-mers, which corresponds to the size of clusters of sites in what otherwise is a bond problem.

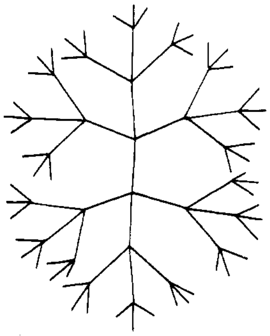

Figure 2. Bethe lattice of coordination number 4. Random linking on this lattice corresponds to a Flory–Stockmayer model with functionality f = 4.

The linking on common lattices inevitably leads to the appearance of ring structures which arise from an intracluster linking. However, in the Flory–Stockmayer model this is postulated not to occur and their model can be represented by a percolation process on a special pseudolattice which is in a form of an infinite homogeneous Cayley tree (Figure 2). The cluster size and percolation on such a pseudolattice (Bethe lattice) was solved exactly by Fisher and Essam[22] and their formula for cluster size distribution is identical with the formula for molecular weight distribution derived earlier by Stockmayer[19] for

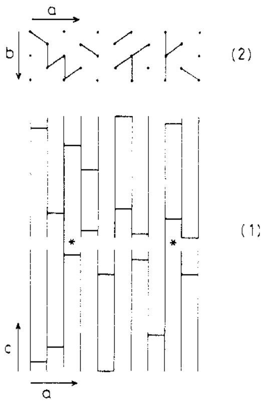

Figure 3. Schematic representation of cross-linking in the layered structure of orthorhombic paraffin crystals (1). If the interlayer linking (marked (*)) is neglected, the linking in a single layer can be represented by linking in a two-dimensional lattice (2). The arrows a, b, and c show the direction of the unit cell axes.

polyfunctional polymerization.

The linking on a Bethe lattice (which is equivalent to the Flory–Stockmayer model) is the most efficient bond process for growth of the site clusters. As the formation of cyclic structures is forbidden the number of sites in a cluster increases with each additional bond. The number of sites s in a cluster is therefore related to the number of bonds b by $s = b + 1$. However, if the linking takes place on a common lattice which allows formation of rings, then there is no single relation between the number of sites and the number of bonds in a cluster. In such lattices the number of bonds in a cluster with s sites can vary from a minimum given by the formula for the Bethe lattice up to the maximum, which apart from the cluster size depends also on its shape and the type of the lattice.

In solid paraffins the chains are aligned parallel in a crystal lattice and the chain ends form stacked layers in the crystal. As shown previously[8-10] and confirmed in this work, the linking is not confined exclusively to the chain ends; hence the ratio of interlayer to intralayer linking will decrease with increasing chain length of the starting material. If the interlayer linking is neglected, the cross-linking in a single layer can be represented by a bond percolation process on a two-dimensional lattice. The sites of this lattice are the projections of the chains on a plane perpendicular to the chain direction and the bonds are the links between the nearest-neighbor sites (the multiple cross-links possible between nearest-neighbor chains count as a single bond in this model). The cross-linking in the layered structure of paraffin crystals and the corresponding two-dimensional lattice model is shown in Figure 3.

Solid paraffins were irradiated in two different crystal phases: orthorhombic, which is stable at low temperatures, and hexagonal, stable in a temperature interval of a few degrees just below the melting point.[7] The corresponding two-dimensional lattice for bond percolation is triangular for cross-linking in the hexagonal phase because all six nearest neighbors of a given chain are equivalent. In the orthorhombic lattice the cross-linking can occur in two different crystallographic planes[23] indexed (110) and (200); hence, in principle, the linking of a chain with its two nearest neighbors in the (200) plane is different from the linking with the neighbors in the (110) plane. According to Guiu and Shadrake[23] the linking in the (110) plane is more favorable because it produces smaller lattice distortion. Therefore, the cross-linking in the orthorhombic lattice can be represented by a bond percolation on a triangular lattice where the bond occupancy in one direction ($p_{(200)}$) is less likely than in the other two ($p_{(110)}$).

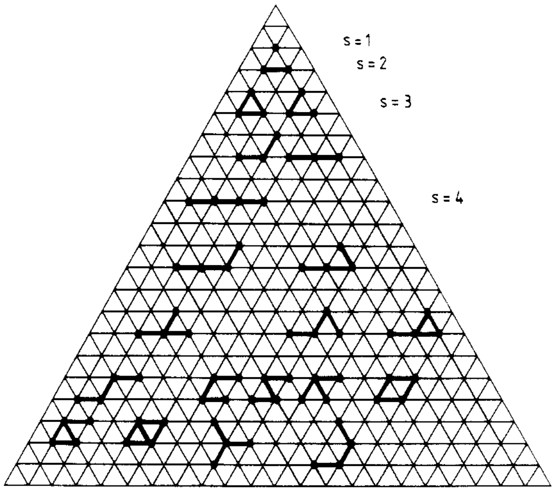

Figure 4. Geometrically different clusters (up to site number $s = 4$) generated by introduction of bonds into a triangular lattice. The perimeter polynomials $n(s)$ are q^6 for $s = 1$, $3pq^{10}$ for $s = 2$, $2p^3q^{12} + 6p^2q^{13} + 9p^2q^{14}$ for $s = 3$, $24p^3q^{16} + 36p^3q^{17} + 29p^3q^{18} + 15p^4q^{15} + 12p^4q^{16} + 3p^5q^{14}$ for $s = 4$.

If the linking takes place only in the (110) planes, the lattice is transformed into a square lattice; if the probability of linking in the (200) is the same as in the (110) planes, the case is identical with the linking in the hexagonal phase.

3.3. Cluster Size Distribution. There are two possible ways to determine the cluster size distribution in percolation on a lattice: (1) to model the percolation process on a lattice by a Monte Carlo method; (2) to calculate exactly the probability of each cluster size (perimeter polynomial method).

In the first method the accuracy of the model is determined by the size of the lattice and the number of runs that can be accommodated in a computer. The results reported so far[11,20] are not directly applicable to the cross-linking because they do not give the distribution of site clusters in a bond percolation.

In the second method the probability of a particular cluster is calculated exactly by using the number and the probability of cluster elements (occupied bonds or sites in the bond or site problem, respectively) and the number and probability of empty bonds or sites on the cluster perimeter. The expressions for cluster probabilities are then summed up for clusters with a given number of bonds or sites, resulting in a perimeter polynomial. As the number of different clusters increases rapidly with the cluster size, the perimeter polynomial is practical for small clusters only. The perimeter polynomials for clusters of bonds in a bond problem (and for site clusters in a site problem) were obtained by Sykes et al.[24,25] However, they are also not applicable directly for cross-linking and have to be regrouped to yield the probabilities of site clusters in a bond problem.[38] This rearrangement has been first carried out for small clusters by the author[26] and further extended for larger clusters by Braunholtz.[27] An example of clusters of sites in a bond problem on a triangular lattice and corresponding perimeter polynomials are shown in Figure 4.

The perimeter polynomial $n(s)$ for a cluster of size s gives the number of clusters of size s per lattice site. The product $sn(s)$ gives the number of sites that are in the clusters of size s divided by the total number of sites in the lattice. In the model adopted for the cross-linking of paraffins the sites are all occupied; hence, $sn(s)$ is the fraction of sites found in clusters of size s and corresponds to the weight fraction of the paraffin molecules with the degree of polymerization s. This gives the molecular weight distribution in cross-linked paraffins.

The perimeter polynomial $n(s)$ can be expressed in the form[27]

$$n(s) = \sum_b \sum_g Z(s,b,g) p^b (1 - p)^g \quad (1)$$

where $Z(s,b,g)$ is the number of geometrically different clusters per lattice site containing s number of sites, b number of occupied bonds, and g number of empty bonds. The cluster is defined as a set of sites joined by occupied bonds. As expected, the Stockmayer formula[19] for weight fraction of linked polymer and the $sn(s)$ expression for linking on a lattice gives identical polynomials for very small clusters where the ring structures are impossible (up to $s = 3$ for the square lattice or functionality $f = 4$ in the Flory–Stockmayer model and up to $s = 2$ for the triangular lattice or functionality $f = 6$.

3.4. Comparison of the Experimental Data with the Theory. The experimental GPC trace of linear polymer can be regarded as a composite of individual peaks belonging to monodisperse components. It has been found[28] that the chromatogram $F(v)$ of a monodisperse compound can be described by a Gaussian function

$$F(v) = A \frac{h}{\pi^{1/2}} e^{-h^2(v-v_0)^2} \quad (2)$$

and the chromatogram of a polydisperse compound

$$F(v) = \sum_s A_s \frac{h_s}{\pi^{1/2}} e^{-h_s^2(v-v_{0s})^2} \quad (3)$$

where A_s is a constant related to the concentration of the component with the degree of polymerization s, h_s is a parameter inversely proportional to the width of the Gaussian peak of the sth component, v is the elution volume, and v_{0s} is the elution volume of sth component at the peak maximum.

There are several methods of obtaining the set of A_s values from the chromatogram;[29] however, the inaccuracies and noise in the chromatogram can become amplified in the deconvolution process and give rise to oscillations. In order to avoid this difficulty a theoretical chromatogram was computed from the weight distribution of clusters in an appropriate percolation model and compared directly with the corresponding experimental GPC trace.

The weight distribution of clusters $sn(s)$ was obtained by finding the weight fraction of the monomer from the experimental chromatogram and determining p (the fraction of occupied bonds) from the expression for the fraction of isolated sites, which is $n(1)$. Equation 1 was then used to generate a set of $sn(s)$ for a particular percolation model. The set is limited by the number of $Z(s,b,g)$, which was obtained by Braunholtz[27] up to the size $s = 6$ for the triangular lattice and $s = 9$ for the square lattice. This restriction does not apply for the Flory–Stockmayer model and the polynomials can be obtained from a generating formula for any size cluster. The chromatograms, however, were calculated only for cluster sizes up to $s = 20$ because the weight fraction contained in all higher size clusters $(1 - \sum_{s=1}^{20} sn(s))$ was negligibly small (Figure 1).

As follows from eq 3, a set of h_s and v_{0s} in addition to the set of weight fractions A_s is needed for each chromatogram. In a linear polymer the elution volume v_{0s} is related to the molecular size s by a calibration curve; h_s varies slowly with the size and is usually considered constant. In branched or cross-linked polymers each peak for a given size s is a composite of Gaussian peaks belonging to different isomers. Hence the weight fraction of each isomer, its peak elution volume, and the peak width parameter are needed for constructing the chromatogram exactly. As the number of different isomers of cross-linked paraffins increases rapidly with size, this information is practically impossible to obtain and an approximate and simplified approach has to be used.

In general, cross-linking produces branched molecules that can elute in a range of elution volumes depending on the position of cross-links. The lowest volume corresponds to a linear polymer where linking was at the chain ends, and the highest volume belongs to the branched molecules linked in the center of the chains (providing that the multiple linking between the same pair of chains is neglected). The elution volume of a polymer molecule is a function of its hydrodynamic volume under given conditions which can be expressed by the radius of equivalent hydrodynamic sphere R. Hence the parameter $g = R_b^2/R_l^2$, the ratio of such radii corresponding to branched and linear molecules of the same molecular weight, can be obtained from the elution volume of branched molecule v_b, its molecular weight M, and the calibration curve $M = \psi(v)$ relating the molecular weight and elution volume of linear molecule by using the expression

$$g = \psi(v_b)/M \quad (4)$$

The parameter g for 1,1,2,2-tetra(tridecyl)ethane (which can serve as a model for a paraffin dimer cross-linked exactly at the chain center) was found to be 0.843.[30] This was considerably less than g obtained for the radiation cross-linked dimers (Table I). The peak width of radiation cross-linked dimer is higher than that of the above cross-linked model paraffin or the linear paraffin, which, together with the parameter g, shows that the cross-links in irradiated paraffins are distributed along the paraffin chains and not confined exclusively to any particular carbon.

If the parameter g, the peak shape, and peak width of an s-mer are assumed to be the same as those for the dimer, the expected GPC chromatogram for random cross-linking can be computed from eq 3. The expected weight fractions of s-mers for random linking on different lattices were obtained by a perimeter polynomial. The fraction of occupied bonds p needed for this was determined by matching the area fraction of the monomer peak in the experimental chromatogram to the expression for the fraction of isolated sites in a particular percolation model. The peak shape of the s-mer was assumed to be Gaussian, with the peak width h_s to be the same as the dimer peak. The elution volume corresponding to the peak maximum of an s-mer was obtained from eq 4 and the chromatogram computed according to eq 3. It is obvious that the computed chromatogram is a rather crude approximation mainly because of the uncertainty in the parameters g and h. However, the comparison between the computed and the experimental chromatograms shows an important difference which cannot be accounted for by the errors introduced by these assumptions.

The chromatograms calculated for various percolation models are superimposed on the experimental GPC trace in Figure 1. The comparison shows that they differ basically in two main features. For the same weight fraction of monomer the experimental trace shows that (1) there is considerably less dimer than the random percolation models predict and (2) the cross-linking produces more of high molecular weight material than expected from the random linking in the percolation models.

The predicted and experimentally observed weight fractions of the dimer for different samples irradiated at various conditions are shown in Table II. The expression

Table II
Comparison of the Dimer Weight Fraction w(2) Found by GPC and Calculated from Percolation Models

	irradiation				$w(2)$ (percolation)			
sample	state and phase	temp, °C	dose Mrd	$w(2)^a$ (GPC)	$f = 3$ (honeycomb lattice)	$f = 4$ (square lattice)	$f = 6$ (triangular lattice)	$f \to \infty$
$C_{40}H_{82}$	crystalline orthorhombic	40–45	219	0.106	0.176	0.170	0.165	0.154
		40–45	500	0.121	0.225	0.214	0.202	0.182
		1	800	0.132	0.228	0.216	0.204	0.183
$C_{23}H_{48}$	crystalline orthorhombic	33	200	0.045	0.060	0.059	0.059	0.058
		33	500	0.079	0.119	0.117	0.114	0.110
		33	800	0.104	0.186	0.180	0.173	0.161
	crystalline hexagonal	43	300	0.082	0.111	0.110	0.108	0.104
	melt	53	300	0.078	0.146	0.143	0.139	0.132

[a] The experimental values of $w(2)$ are reproducible within ±10%.

for the dimer weight fraction is a function of p and the coordination number (or the functionality f in the Flory–Stockmayer model) and, as expected, it is the same for percolation on different lattices, including the Flory–Stockmayer model.[39] The calculated weight fraction of the dimer w_2 for a given w_1 decreases with the parameter f, reducing in this way the discrepancy between the experiment and the theory. However, even in the limit for $f \to \infty$ the calculated w_2 (which in the limit is equal to $-w_1^2 \ln w_1$) is still significantly higher than the experimental values (Table II). This result shows that no percolation model based on random statistics can explain the low population of dimers found by the experiment.

As shown in Figure 1 the experimental chromatograms extend farther into the low elution volume region than the theory predicts. This cannot be explained by the fact that the larger size clusters were omitted in the calculation because their cumulative weight fraction was much smaller than the observed difference (Table II). Another possible cause of this discrepancy is the uncertainty in the elution volume of cross-linked isomers introduced by a possible error in the parameter g. However, the nonlinear cross-linked isomers of the same degree of polymerization s are always eluted at higher elution volumes than their linear counterparts. Therefore, the chromatograms calculated for linear isomers (which are not subject to the uncertainty in their elution volumes) can be regarded as the limiting case having the maximum extended "tail" possible in the low elution volume region.

Figure 5 shows a comparison between an experimental chromatogram and the calculated one for the linear isomers only and using the Flory–Stockmayer model. The Flory–Stockmayer model was chosen because it gives rise to the largest low elution volume tail than any other percolation model. The Flory–Stockmayer model precludes the formation of ring structures and therefore it yields larger size clusters for a given p than linking on any other lattice. This is because the introduction of each link in the Flory–Stockmayer model increases the size of a cluster and the link is not "wasted" by closing the ring. However, even this extreme and unrealistic model does not reach the experimentally found abundance of cross-linked material in the low elution volume region and the basic assumption of randomness in the percolation model has to be questioned in order to explain the disagreement.

3.5. Correlated Percolation Process as a Model for Cross-Linking. It can be inferred from the observed difference in the experimental and calculated chromatograms that the already cross-linked molecules tend to increase their size more readily than the random statistics predicts. This conclusion can explain both the shortage of dimers and the abundance of the high molecular weight material in the low elution volume region. Such a behavior can be modeled by a correlated percolation process with different probabilities p for introduction of links depending on the state of molecules to be linked. A minimum of two probabilities p_1 and p_2 is necessary to express the different reactivity of un-cross-linked and cross-linked molecules. If p_1 is the probability that the link is introduced between two un-cross-linked chains (hence forming a dimer) and p_2 is the probability of a link involving at least one already cross-linked molecule, then the higher reactivity of already cross-linked chains can be expressed by the condition $p_2 > p_1$. The dimer and trimer clusters will contain only one link introduced with the probability p_1, and the larger size clusters can contain variable numbers of such links depending on how many smaller clusters were linked together to form the final one. If the proportion of links of different probability in the larger size clusters is not known, the size distribution of clusters cannot be obtained by the perimeter polynomial method. However, in the extreme case when the total fraction of bonds occupied is low and p_2

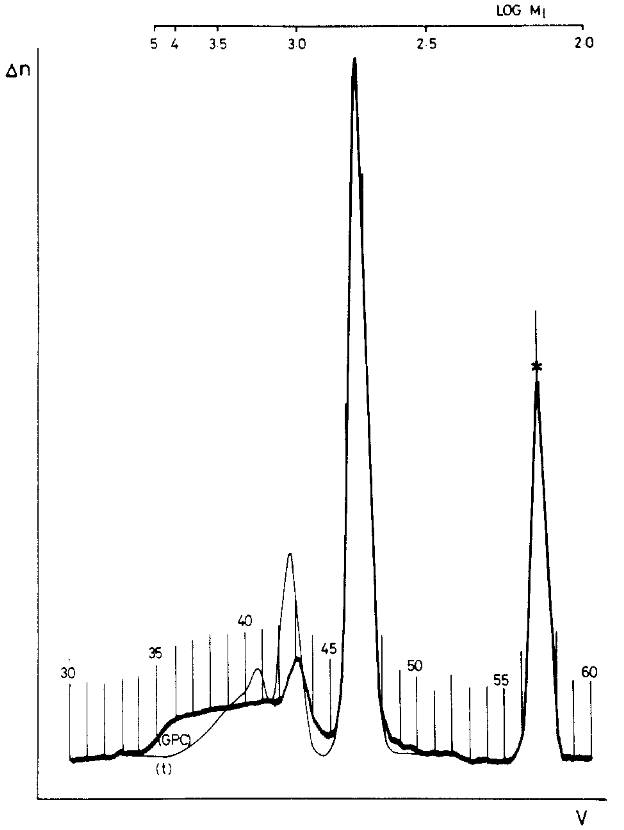

Figure 5. Comparison of the GPC trace of tetracontane irradiated to 500 Mrd and the chromatogram (t) calculated from the Flory–Stockmayer model (f = 82) assuming linear isomers only. $w_{res} = 8.1 \times 10^{-5}$, $s_{max} = 20$.

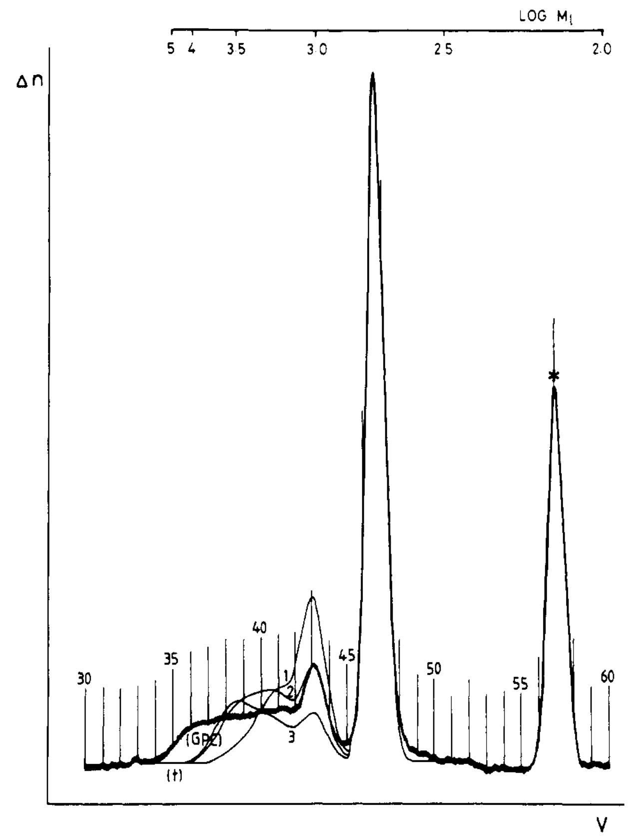

Figure 6. Comparison of the GPC trace of tetracontane irradiated to 500 Mrd and the chromatograms (t) calculated from correlated percolation model with different ratios of p_2/p_1 (square lattice, $s_{max} = 9$): (1) $p_2/p_1 = 1$, $w_{res} = 3.5 \times 10^{-4}$; (2) $p_2/p_1 = 2$, $w_{res} = 2.0 \times 10^{-2}$; (3) $p_2/p_1 = 3$, $w_{res} = 1.1 \times 10^{-1}$.

$> p_1$, then most of the smaller clusters will contain only one link introduced with the probability p_1. This is analogous to a two-step process of a slow nucleation followed by a rapid growth of the clusters. The nucleation step corresponds to the formation of dimers which then rapidly link with the surrounding monomer, resulting in a fast growth of the clusters. If the fraction of occupied links is small the chance of intercluster linking (especially for small clusters) is also small and the approximation that clusters contain only one link occupied with the probability p_1 is justified. Figure 6 shows the comparison of experimental and theoretical GPC spectra calculated from perimeter polynomials for different p_2/p_1 ratio assuming only one link with probability p_1 per cluster. The best fit is obtained for p_2/p_1 of about 2. It can be further improved by introducing probability p_3 for linking of the trimer; however, the difference in the p_1 and p_2 probabilities is sufficient to demonstrate the nonrandomness of the linking process.

As follows from Figure 1 and similar other chromatograms and also from the results expressed in terms of the weight fractions of the dimer as listed in Table II, the cross-linking is nonrandom. It can be seen from Table II that this departure is hardly influenced by the nature of the crystalline phase and more surprisingly hardly depends on whether the paraffins are in a crystalline or liquid state. This shows that the crystal lattice is not the controlling factor responsible for the nonrandomness of the linking process.

At this stage it needs to be recalled that the above nonrandomness refers to the linking of monomers (paraffin molecules) regarded as points and the degree of nonrandomness is arrived at by consideration of the weight fractions of the different polymerization products (dimers etc.). These arise by cross-linking, and their weight fractions are determined from the observed GPC traces and compared with those calculated from the percolation models. It is this nonrandomness that is largely unaffected by the physical state of the paraffins. This is not to say that the same holds for the cross-link positions along a given chain. Previous conclusions[6,8-10,16] about nonrandomness of cross-linking and its dependence on the crystalline state referred to this latter aspect, namely to the link position along the chain. The direct experimental manifestation of this effect should be displacement of the position of the dimer peaks in dependence on the nature of the crystalline phase and the physical state. Indeed such a dependence, even if small, has been revealed by the previous[6,9] and the present experiments (Table I), indicating a preference for linking to take place around the chain end region. This nonrandom distribution of cross-link positions along the chain should be distinguished from the nonrandomness of the linking between chains which appears to be an intrinsic feature of the cross-linking process itself.

The limited role, if any, of the crystallinity may perhaps appear surprising as the chains in the lattice are widely separated for ready linking. However, once such a link is introduced it will produce lattice distortions in its vicinity,[23,31] which then should facilitate further cross-linking around it. This would lead to nonrandomness in chain linking; however, if such a source of nonrandomness exists, it is not of primary importance because the observed nonrandomness does not rely on the physical state for its existence.

Regarding the primary source of nonrandom cross-linking of monomers, one may consider that a change of a secondary into a tertiary carbon atom associated with an introduction of a cross-link into a pair of paraffin chains could influence their further linking. It may be suggested that the different reactivity of the tertiary carbons together, perhaps, with their nearest-neighbor secondary carbons could make the cross-linked paraffins more susceptible for further linking with surrounding chains. It is known[32] that the reactivity of secondary and tertiary carbon radicals is different and because reactions of radicals are responsible for the formation of cross-links, this could be the reason for an enhanced susceptibility of already cross-linked paraffins to further linking. The probability p in percolation models on a two-dimensional lattice (or p_1 and p_2 if the structure of molecules to be linked is taken into account) is the probability of forming a bond between two adjacent chains irrespective of its position along their length. Its value is therefore the sum of probabilities of forming individual cross-links at different positions along the chain length. If the introduction of a cross-link increases the reactivity of its tertiary carbons, leaving the reactivity of the secondary carbons in the rest of the molecule unchanged, the probability of a further cross-link at the tertiary carbon arising through the previously formed cross-link can be determined from the overall probabilities p_1 and p_2 for the linking of un-cross-linked and cross-linked chains. A simple calculation shows that for C_{40} paraffin the probability of further linking at the tertiary atom would have to be 41 times higher than at the other carbons in order to obtain the ratio of $p_2/p_1 = 2$. If together with the tertiary carbon, the reactivity of the nearest-neighbor secondary carbons in the chain is increased, their average probability to further linking would still have to be about 14 times higher than the rest. Such a high reactivity to cross-linking associated with the presence of tertiary carbons, however, has not been observed; the G (cross-linking) of branched polyethylene is about the same or perhaps lower than the G(cross-linking) of linear polyethylene.[33]

A feasible explanation for the excessive clustering of cross-links in solid and liquid paraffins can follow from the fact that the initial distribution of intermediates formed by high-energy radiation in the condensed phase is exceedingly inhomogeneous.[34] In ^{60}Co γ-irradiation the main process of energy deposition is Compton scattering.[1] The typical recoil electron produces a multiple number of ionizations and excitations in separated groups; these localized regions of a few nanometers in size containing high concentrations of intermediates are referred to as spurs. The commonly postulated random distribution of cross-links in a ^{60}Co γ-irradiated homogeneous polymer matrix[1,35] rests on the assumption that the radicals and their precursors can diffuse away from the spurs before the cross-linking occurs. However, there is extensive experimental evidence that in low molecular weight liquid paraffins some cross-linking is completed in the spurs before the radicals have dispersed.[36] Such a mechanism can also explain the clustering of cross-links in solid and liquid paraffins observed in this work which is in excess of those predicted by random percolation models.

An inhomogeneity in the effect of radiation on paraffin crystals was observed recently on a much larger scale.[12,37] Using calorimetry and electron microscopy techniques, it was deduced that two different phases, one rich and the other poor in cross-links, form on irradiation, which, by X-ray and electron diffraction, were identified as amorphous and crystalline respectively.[12,37] The heterogeneity of this two-phase structure was on a scale readily identifiable under the electron microscope, where it could be seen as the nucleation and growth of liquid droplets which coexist with apparently undamaged crystalline phase. It is believed that the cross-linking is responsible for destruction of crystallinity on irradiation, which, accordingly, is highly nonrandom even to the extent of leading to visible heterogeneities. The present work has shown the existence of this nonrandomness down to the level of individual cross-links themselves and, further, that it is fundamental to the cross-linking process itself and not a consequence of the crystalline state even if the position of the cross-links along the chain is influenced by the crystal lattice.

4. Conclusion

The main conclusion of this work is that the distribution of cross-links in paraffins is not random. This follows from the fact that the cross-linked paraffins contain more of high molecular weight material and less of dimer than calculated from percolation models. This means that the clustering of cross-links is in excess of that predicted by random statistics. This nonrandomness is fundamental to the cross-linking process itself and not confined to a particular state or crystallographic phase of the paraffins. However, it was confirmed that the crystal lattice has an influence on the position of the cross-links along the paraffin chains; in the orthorhombic phase the cross-links are more concentrated toward the chain end regions than in the paraffins irradiated in the hexagonal phase or in the liquid state.

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Registry No. $C_{23}H_{48}$, 638-67-5; $C_{40}H_{82}$, 4181-95-7; $C_{40}H_{82}$ dimer, 91606-40-5; $C_{23}H_{48}$ dimer, 91606-41-6.

References and Notes

(1) A. Charlesby, "Atomic Radiation and Polymers", Pergamon Press, Oxford, 1960.

(2) A. Chapiro, "Radiation Chemistry of Polymeric Systems", Wiley-Interscience, New York, 1962.

(3) L. Mandelkern, in "The Radiation Chemistry of Macromolecules", Vol. 1, M. Dole, Ed., Academic Press, New York, 1972.

(4) R. Salovey and A. Keller, *Bell Syst. Tech. J.*, **15**, 1397, 1409 (1961).

(5) G. N. Patel and A. Keller, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 323 (1975).

(6) A. Keller in "Development in Crystalline Polymers", Vol. 1, D. C. Bassett, Ed., Applied Science Publishers, London, 1982.

(7) M. G. Broadhurst, *J. Res. Natl. Bur. Stand., Sect. A*, **66A**, 241 (1962).

(8) R. Salovey and W. E. Falconer, *J. Phys. Chem.*, **69**, 2345 (1965); **70**, 3203 (1966).

(9) R. Salovey and M. Y. Hellman, *Macromolecules*, **1**, 456 (1968).

(10) G. N. Patel and A. Keller, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 333 (1975).

(11) J. W. Essam, *Rep. Prog. Phys.*, **43**, 833 (1980).

(12) G. Ungar, *Polymer*, **21**, 1278 (1980).

(13) G. N. Patel and J. Stejny, *J. Appl. Polym. Sci.*, **18**, 2069 (1974).

(14) E. I. du Pont Instrument Product Division, Technical Information on the HPLC Infrared Detector.

(15) Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci., Part B*, **5**, 753 (1967).

(16) F. A. Bovey, F. C. Schilling, and H. N. Cheng, *Adv. Chem. Ser.*, **No. 169**, 133 (1978).

(17) G. Ungar and A. Keller, *Polymer*, **21**, 1273 (1980).

(18) P. J. Flory, *J. Chem. Phys.*, **63**, 3083, 3091, 3096 (1941).

(19) W. H. Stockmayer, *J. Chem. Phys.*, 11, 45 (1943); 12, 125 (1944).

(20) D. Stauffer, *Phys. Rep.*, **54**, 1 (1979).

(21) P. Agrawal, S. Redner, P. J. Reynolds, and H. E. Stanley, *J. Phys. A: Math. Gen.*, 12, 2073 (1979).

(22) M. E. Fischer and J. W. Essam, *J. Math. Phys.*, **2**, 609 (1961).

(23) F. Guiu and L. G. Shadrake, *Proc. R. Soc. London, Ser. A*, **346**, 305 (1975).

(24) M. F. Sykes and M. Glen, *J. Phys. A: Math. Gen.*, **9**, 87 (1976).

(25) M. F. Sykes, D. S. Gaunt, and M. Glen, *J. Phys. A: Math. Gen.*, **14**, 287 (1981).

(26) J. Stejny, referred to by A. Keller in "Developments in Crystalline Polymers", Vol. 1, D. C. Bassett, Ed.; Applied Science Publishers, London, 1982.

(27) D. A. Braunholtz, Project No. T4, University of Bristol, 1981; to be submitted to *J. Phys. A, Math. Gen.*

(28) L. H. Tung, *J. Appl. Polym. Sci.*, **10**, 375 (1966).

(29) J. H. Duerksen and A. E. Hamielec, *J. Polym. Sci., Part C*, **21**, 83 (1968).

(30) R. L. Bennett, A. Keller, and J. Stejny, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 3021 (1976).

(31) F. Guiu and L. G. Shadrake, *Philos. Mag. A*, **42**, 687 (1980).

(32) R. L. Huang, S. H. Goh, and S. H. Ong, "The Chemistry of Free Radicals", E. Arnold, London, 1974.

(33) W. F. Busse and G. H. Bowers, *J. Polym. Sci.*, **31**, 252 (1958).

(34) F. Williams, in "Fundamental Processes in Radiation Chemistry", P. Ausloos, Ed., Wiley-Interscience, New York, 1968.

(35) R. Salovey, in "The Radiation Chemistry of Macromolecules", Vol. 2, M. Dole, Ed., Academic Press, New York, London, 1973.

(36) R. A. Holroyd, in "Fundamental Processes in Radiation Chemistry", P. Ausloos, Ed., Wiley-Interscience, New York, 1968.

(37) G. Ungar, D. T. Grubb, and A. Keller, *Polymer*, **21**, 1284 (1980).

(38) The linking of sites by introducing bonds into a lattice in order to obtain the distribution of clusters of sites is equivalent to a special case of a more general site–bond problem[21] where all sites are occupied ($p_s = 1$).

(39) The topology of the lattice becomes important only for trimers and higher s-mers that are capable of forming ring structures.