Pure & Appl. Chem., Vol.53, pp.1519-1529.
Printed in Great Britain.

0033-4545/81/081519-11$02.00/0
Pergamon Press Ltd.

CHARACTERIZATION OF SPECIAL INHOMOGENEITIES IN POLYMER NETWORKS BY THEIR PROPERTIES IN THE PRE-GEL STATE

W. BURCHARD, S. BANTLE, M. MÜLLER and A. REINER

Institute of Macromolecular Chemistry, University of Freiburg
Stefan-Meier-Str. 31, 7800 Freiburg, FRG

ABSTRACT: A general theory for heterogeneously branched polymers on the basis of cascade theory is presented and applied to the examples of fibrin, glycogen and cured epoxide resins. Full agreement with experiment was achieved for fibrin. The model of densely branched nuclei which are connected through linear chains gives in the case of glycogen a correct description of the angular dependence of scattered neutrons only up to values of $q = 0.05\ A^{-1}$, where $q = (4\pi/\lambda)\sin\theta/2$ with θ the scattering angle. For the cured epoxide resin the increase of M_w as function of $\varepsilon = 1 - \alpha/\alpha_c$ or $1 - q/q_c$ has been studied. In all cases an asymptotic behaviour $\sim 1/\varepsilon^c$ is found, but characteristic deviations at larger ε are observed.

INTRODUCTION

In 1953 Professor Stockmayer (Ref.1) made an interesting remark at a conference on branching. He said, whenever problems appeared in the interpretation of properties of linear chains, branching is made responsible for it and is made thus a whipping boy. Today 30 years later we have a much deeper understanding of branching and gelation phenomena, but still the situation has only changed in that now the whipping boy himself is the point of controversy. This controversy has been introduced mainly by theoretical physicists who claim that the so-called Flory-Stockmayer theory is in principle wrong as it gives the wrong critical exponents (ref. 2-5). This claim is based on the results of the critical exponents of thermodynamically reversible systems and on the confidential belief in universality of these critical exponents.

It has been often overlooked in this dispute that the classical Flory-Stockmayer theory (Ref. 6,7) gives very satisfactory results for the increase of M_w, $\langle S^2 \rangle_z$ and the scattering behaviour of the products in the pre-gel state, and moreover in simple systems also the gel point is correctly predicted (Ref. 6,8,9). It should be stressed that up to now no other theory could give a description of equivalent accuracy.

The actual polymer systems are mostly not simple in their branching mechanisms, and here in fact, one has sometimes great difficulties to interpret the experiments in terms of an idealized theory like the Flory-Stockmayer or the percolation theory (Ref. 10,11). The chemists had already very early conjectures on the reasons for the observed deviations, and they have in fact many experimental indications for the presence of local heterogeneities. Much effort has been invested in the past to determine such heterogeneities uniquely and to a satisfactory accuracy, with little success so far (Ref. 12-16).

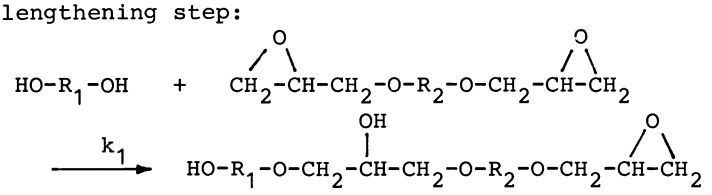
EXAMPLES OF HETEROGENEOUSLY BRANCHED POLYMERS

In this situation we thought it useful to prepare and study polymeric networks with well defined special heterogeneities which also can be treated theoretically. I shall confine here to three examples.

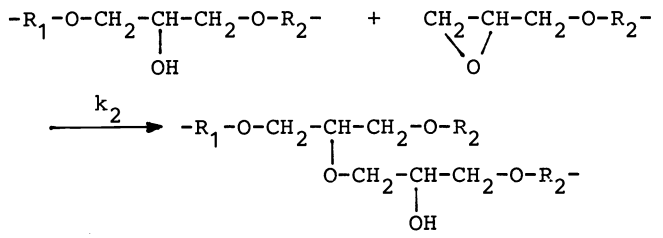
One type of heterogeneity, we have in mind, is the curing reaction of polymer resins. These resins are undercritically branched polymers. On curing these densely branched nuclei become cross-linked through bifunctional linear chains.Fig. 1. A typical example is the epoxide resin formed by the co-condensation of a di-epoxide with bis-phenol A. See Scheme 1. At first sight only linear chains are expected; however, when an epoxide-group reacts with a phenolic OH-group a new functional OH-group is created, and this again can react with an epoxide-group though with a much lower rate than the phenolic OH-group. This additional OH-group causes extensive branching and can be

described satisfactorily by Gordon's branching or cascade theory (Ref. 32,34)

Chain lengthening step:

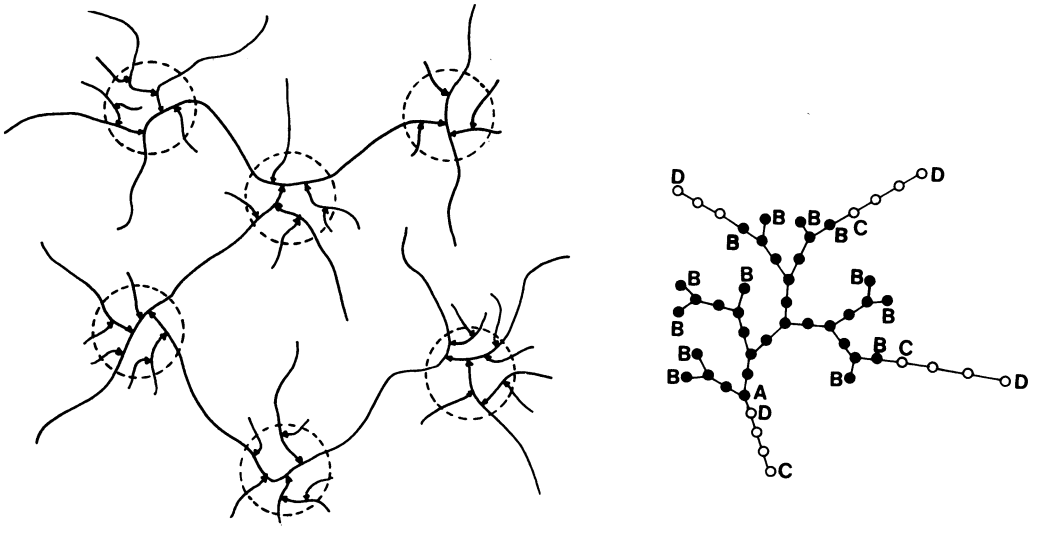


Branching:



Scheme 1 : Formation of epoxide resin. k_1 is the rate constant for a chain lengthening step and k_2 that for branching.

The mentioned curing reaction differs from the process treated by Dušek and his coworkers (Ref.16, 18-20) who considered the curing of the bis-phenol diglycidic ether, which is a monomeric resin only.



a b

Fig. 1 : (a) Model of a heterogeneous network; (b) detailed structure of a highly branched nucleus.

The second example of a heterogeneously branched polymer which we studied in detail is glycogen from a shell fish, called edible mussels. Glycogen is a densely branched polysaccharide which is used in organisms as an energy store. The chemical structure is given by Fig. 2. Please note, if we designate the functional groups in C1, C4 and C6 position of the sugar ring by A, B, B, then A could react with B exclusively, and all other reactions would not be allowed. Thus condensation of this monomer with unlike functional groups deviates substantially from the simple Flory-Stockmayer branching models, for reasons which I shall explain a little later. Also this homogeneous branching model could be treated exhaustively by the cascade theory(ref. 21). We have measured M_w, $\langle S^2 \rangle_z$ and the particle scattering factor by light scattering and coherent neutron scattering (Ref. 23), and

fairly good agreement was found with our model calculations. See Fig. 6. Then, however, we came across a paper by Schramm (Ref. 24,25), who deduced

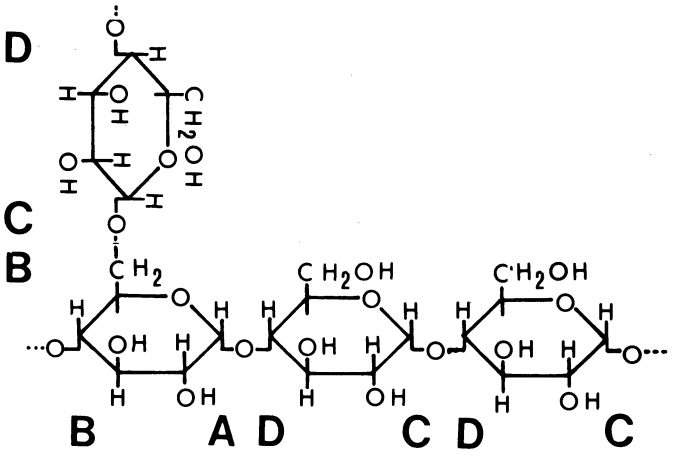


Fig. 2 : Chemical structure of a section of glycogen. The letters A,B,C,D denote the functional groups.

from degradation experiments with the enzyme α-amylase that glycogen from shell fish is strongly heterogeneously branched (Ref. 26). Here is not the place to show how this could be prooved experimentally, I only wish to mention that we repeated these experiments and found indeed about 22-30% of the material resists a complete degradation. The resistant product has M_w = 48 kg/mol, M_n = 6.48 kg/mol, and a diffusion coefficient of $D_z = 7.21\ 10^{-7}$ cm^2/s. It has a branching density where every third unit is a branching unit. For comparison, the molecular data of the undegraded glycogen are M_w = 1630 kg/mol , M_n = 260 kg/mol, $\langle S^2 \rangle_z^{1/2}$ = 14.7 nm and $D_z = 1.27\ 10^{-7}$ cm^2/s. Thus, again we have a heterogeneity of the type given by Fig. 1. Here we are faced with the problem to derive a theory which takes account of these heterogeneities and also gives the right angular dependence of the neutron scattering experiments.

The third example is again a biological material and is concerned with the network that is formed during blood clotting. Experiment shows (Ref. 27-29) that this fibrin network consists of long and fairly thick fibrillic elements which are linked through trifunctional branching points. The fibrils have typical lengths of 550 nm and are thus in the order of the wavelength of the light. Here the scattering behavior can no longer be described by a homogeneous branching theory. As will be shown in the following, also this type of inhomogeneity can be treated by the same theory as for the two other examples.

TYPES OF HETEROGENEITIES

First, however, I have to make a few remarks on what we understand by heterogeneity. Generally speaking, heterogeneity is defined by the sudden change of a property when passing from one point in space to another one. This definition embraces heterogeneities (i) in the optical density or refractive index, heteronegeities in (ii) density and (iii) branching density. In polymer science we have in addition to deal with (iv) heterogeneity in the chain length which connect the branching points and (v) a heterogeneity in flexibility. A rod for instance shows significantly different behavior than a flexible Gaussian chain, and this last type of heterogeneity turns out to be the most difficult to treat theoretically.

The simplest heterogeneous polymers are poly-co-condensates and they offer no difficulties to the theory already in the old Flory-Stockmayer notation. Heterogeneity in branching even in homopolymers occurs when substitution effects become effective, i.e. when the reaction of the f similar functional groups are changed after the reaction of one or more functional groups of the same monomer. This sort of reaction has all features of a first order Markovian process or a linear Ising model, and of course, a so called mean field

theory will not be capable of describing the local heterogeneities. However, the so called Galton-Watson process (Ref. 30), developed more than a hundred years ago (Ref. 31), or what we call now the cascade theory (Ref. 32), is a first order Markovian process par excellence (Ref. 33). In fact this first shell substitution effect could be solved in 1964 by Gordon and Scantlebury (Ref.34 &35) with the aid of cascade theory.

This sort of local heterogeneity persists only over a short range, although it has substantial influence on the gelpoint, and it has not yet been detected directly by scattering experiments (Ref. 16). This will be possible only if the wave-length used of the radiation source is in the order of the correlation length of the heterogeneity. This situation is on the other hand, different for the three examples mentioned before because here the domains of different properties have dimensions in the order of the radiation source wavelength.

THEORETICAL

Turning now to the mathematical treatment of the more extended heterogeneities we need a graphical representation by which we can make clear to ourselves what is going on. Physicists prefer to use lattices in the three dimensional space as a framework on which the various polymers and monomers are thrown at random. Fig. 3.

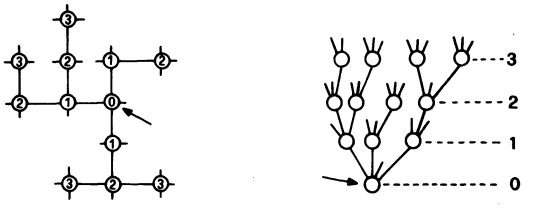


Fig. 3 : Branched macromolecules placed on a lattice (left). Note: The units in the shells of 1st, 2nd etc. next neighbours appear on generations in the rooted-tree representation of the macromolecule. The arrows indicate which unit was selected to become the root of the tree.

However, this point is crucial, because we are dealing here with long range correlations, we do not wish to introduce unconsciously a sort of correlation in the very beginning of our theory. Actually the statistics of how monomeric units are linked together has nothing to do with the Euclidian space, but only with connectivity and this problem is only one-dimensional. Therefore I prefer to use here the tree representation where already in the graph it is made clear that we are dealing here with a probabilistic problem rather than with a problem in space. A rooted tree is obtained by selecting at random one monomeric unit and considering it as the root of the tree. Instead of speaking in terms of 1st, 2nd etc. shells of nearest neighbours we have now generations 1, 2 etc.

The next question is how to introduce long range correlations which would describe the extent of a domain of the same property, expressed in terms of generations. The answer is very simple and known to everybody from daily life. Consider for instance the road network of a big town. In former days we were allowed to use these roads in both directions with our cars, and to get from one point to another we could choose the shortest path. However, the town concils have been forced in most towns to introduce a system of one way roads and no-left-turn restrictions. By this simple labeling a long range correlation is introduced, because one may be forced to take a long distance path although in an unlabeled network the path may be very short.

In terms of molecules this correlation may be illustrated by the polycondensation of monomers with the two unlike functional groups C and D, where C can only react with D and vice versa, but not with itself. By this restriction we have introduced some order such that the one chain-end bears always a C group and the other a D group. The labeling is thus equivalent to a correlation length which describes the extent of a domain with special defined properties. The chains can now become coupled with domains of another structure, for instance with a branched nucleus that was formed by the poly-

condensation of monomers with a functional group A and two alike functional groups B, where A had reacted exclusively with B groups only.Let us introduce probabilities of reaction : γ for the reaction of a C-group with a D-group. $(1-\gamma)w_B$ for the coupling reaction of the chain end-group C with an A-group of the branched domain, and $(1-\gamma)w_A$ for the coupling reaction of a D chain-end with an A-group of the branched domain. Labeling is achieved by multiplying γ with s_D and $(1-\gamma)w_B$ with s_B, if the reaction of a C functional group is considered, and similar can be done for the other functional groups. We can now go one step further and sum all these labeled events which can occur with one functional group, and if we make the convention that the different s-parameters can be differentiated within the range of $s = 0$ and $s = 1$ we obtain a continuous function which is called a probability generating function. This proceedure leads for the four functional groups A, B, C and D to the generating functions

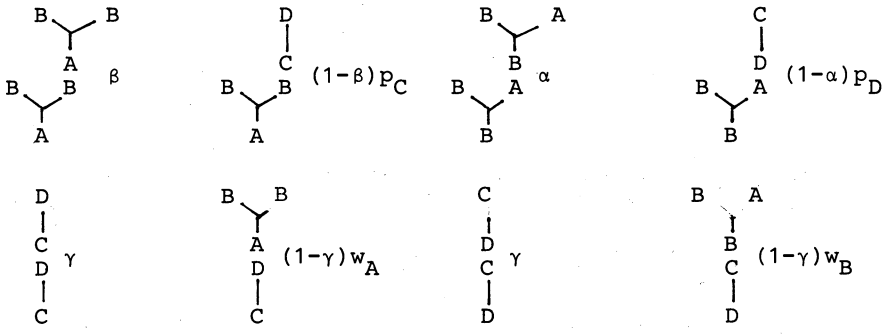
$$F_A = (1-\alpha)(1-p_D) + (1-\alpha)p_D s_D + \alpha s_B \qquad (1a)$$

$$F_B = (1-\beta)(1-p_C) + (1-\beta)p_C s_C + \beta s_A \qquad (1b)$$

$$F_C = (1-\gamma)(1-w_B) + (1-\gamma)w_B s_B + \gamma s_C \qquad (1c)$$

$$F_D = (1-\gamma)(1-w_A) + (1-\gamma)w_A s_A + \gamma s_D \qquad (1d)$$

For normalization reasons we have added also that no reaction took place at the end groups which have been multiplied with $s_D^0 = 1$ etc. The following scheme gives a survey over the various kinds of reaction and their probabilities.



Scheme 2 : Possible types of reaction between the various functional groups of a tri-functional and a bi-functional unit,and the corresponding probabilities of reaction.

The labeling technique has led us to the very powerful probability generating functions by which even very complex probabilistic problems can be solved with ease.

MOLECULAR WEIGHT, MEAN SQUARE RADIUS OF GYRATION AND PARTICLE SCATTERING FACTOR

Applying the rules of generating functions (Ref. 33) we find that the weight average molecular weight is given by the equation

$$M_w = (\underline{n} \cdot [\underline{1} + \underline{\underline{C}} \sum_{n=1}^{\infty} \underline{\underline{P}}^{n-1}] \underline{M}_o) = (\underline{n} \cdot [\underline{M}_o + \underline{\underline{C}}(\underline{1}-\underline{\underline{P}})^{-1} \cdot \underline{M}_o]) \qquad (2)$$

where we have used a vector-matrix notation: $\underline{n} = (n_1, n_2, \ldots n_N)$ is the composition vector and contains the mole fraction n_1 of monomeric units of the kind 1 in the polymer etc., $\underline{M}_o = (M_{o1}, M_{o2}, \ldots M_{oN})^t$ is the corresponding column vector of the N various monomer molecular weights, and the doubly underlined symbols denote matrices. The matrix $\underline{\underline{C}}$ contains the various probabilities of the two types of monomers with the different functional groups of another monomer, and $\underline{\underline{P}}$ is a transition matrix whose elements are the probabilities of reaction of a special functional group of a monomer in the n-th generation to another special functional group of a monomer in the n+1 th generation,if one of the functional groups of the monomer in the n-th generation was linked to the n-1 th generation. These transition probabilities can be easily read off from the Scheme 2.

$$\underline{C} = \begin{array}{c} \begin{array}{cccc} A & B & C & D \end{array} \\ \left\| \begin{array}{cccc} 2\beta & \alpha & 2(1-\beta)p_C & (1-\alpha)p_D \\ (1-\gamma)w_A & (1-\gamma)w_B & \gamma & \gamma \end{array} \right\| \end{array} \quad \begin{array}{l} \text{Monomer 1} \\ \text{Monomer 2} \end{array} \tag{3}$$

$$\underline{\underline{P}} = \begin{array}{c} \text{linked to a functional group in generation } n+1 \\ \begin{array}{cccc} A & B & C & D \end{array} \\ \left\| \begin{array}{cccc} 2\beta & 0 & 2(1-\beta)p_C & 0 \\ \beta & \alpha & (1-\beta)p_C & (1-\alpha)p_D \\ 0 & (1-\gamma)w_A & \gamma & 0 \\ (1-\gamma)w_B & 0 & 0 & \gamma \end{array} \right\| \end{array} \quad \begin{array}{l} A \\ B \\ C \\ D \end{array} \quad \begin{array}{l} \text{functional group linked to a unit in } n-1 \text{ th generation} \end{array} \tag{4}$$

Eq.(2) expresses clearly the Markovian character of the branching process and the relationship is very convenient in computational work. It also includes the random Flory-Stockmayer case of homopolycondensation of f-functional monomeric units. Here we have only one component and the matrices $\underline{C}$ and $\underline{\underline{P}}$ reduce to scalars with the only elements αf and $\alpha(f-1)$. Thus

$$M_w = M_o(1 + \alpha f/\ 1-\alpha(f-1)\ ) = M_o(1+\alpha)/\ 1-\alpha(f-1) \tag{5}$$

which in fact is Stockmayer's famous formula (Ref. 7). Note the formal equivalence between eq. (5) and eq. (2). The Flory-Stockmayer theory turns out to be the degenerate Ising case where no correlation at all exists, all groups of the f-functional monomer can react at random with any other functional group of another monomer.

The particle scattering factor which describes the angular distribution of scattered light or neutrons can likewise be expressed in the vector-matrix notation, if ideal flexibility of the subchains in the polymer can be assumed, i.e. Gaussian statistics. Then cascade theory shows (Ref. 22,36)

$$M_w P_z(q) = \left(\underline{n}\cdot\left[\underline{\Phi} + \underline{\underline{C\Phi}}\ (\underline{1} - \underline{\underline{P\Phi}})^{-1}\right] \underline{M}_o^t\right) \tag{6}$$

with $\underline{\Phi} = \underline{1}\cdot\phi$, $\underline{\phi} = (\phi_1, \phi_2, \phi_3, \ldots \phi_N)$

and $$\phi_j = \exp(-b_j^2 q^2/6) \tag{7}$$

where b_j is the effective bond length of the j-th type of monomer and $q = (4\pi/\lambda)\ \sin\Theta/2$ with Θ being the scattering angle.

The mean square radius of gyration follows from the particle scattering factor from the condition $\langle s^2\rangle_z = -3\left[dP_z(q)/dq^2\right]_{q^2=0}$ which yields

$$\langle s^2\rangle_z = M_w^{-1}\left(\underline{n}\cdot\left[\underline{C}\ (\underline{1}-\underline{\underline{P}})^{-2}\ \underline{\underline{B}}\underline{M}_o\right]\right) \tag{8}$$

with $\underline{\underline{B}} = \underline{1}\cdot\underline{b}$ and $\underline{b} = (b_1^2, b_2^2, \ldots b_N^2)^t$.

Eqs.(2),(6) and (8) are very convenient for numerical calculations but are restricted to Gaussian statistics for the subchains within the branched molecule and can therefore not be applied to molecules like fibrin where one component consists of rigid fibrils. No general solution for $P_z(q)$ and $\langle s^2\rangle_z$ has been possible for rigid branched structures. However, if the different domains of a heterogeneously branched molecule are linked through freely moving hinges, a solution is obtained which has the same formal structure but where the matrix $\underline{\underline{P}}^*$ has a different meaning.

$$M_w P_z(q) = \left(\underline{n}\cdot\left[\underline{\Phi} + \underline{\underline{C\Phi}}^*(1-\underline{\underline{P\Phi}}^*)^{-1}\right] \underline{M}_o\right) \tag{9}$$

The diagonal matrix of our special example has the two different elements (in general there are N elements)

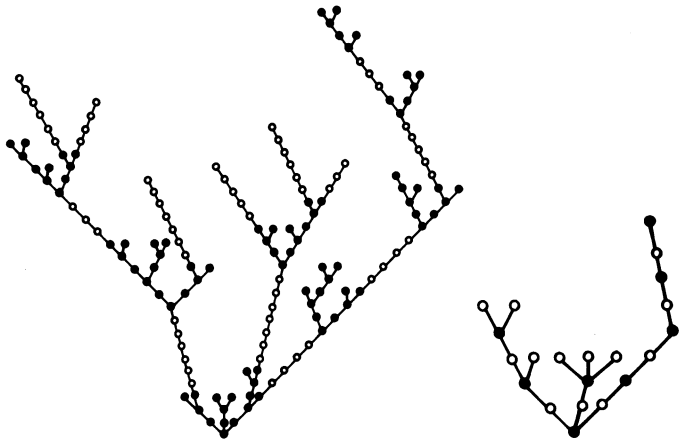
$$\phi_b^* = \sum \alpha^{n-1}\ \phi_{nb} \quad ; \quad \phi_1^* = \sum \gamma^{n-1}\ \phi_{nl} \tag{10}$$

with $$\phi_{nb} = \langle(\sin qr_{nb})/qr_{nb}\rangle \quad \text{and} \quad \phi_{nl} = \langle(\sin qr_{nl})/qr_{nl}\rangle \tag{11}$$

The matrix $\underline{\underline{P}}^*$ is similar to $\underline{\underline{P}}$ but now contains the coupling

$$\underline{\underline{P}}^* = \begin{pmatrix} 0 & 0 & 2(1-\beta)p_C & 0 \\ 0 & 0 & (1-\beta)p_C & (1-\alpha)p_D \\ (1-\gamma)w_A & 0 & 0 & 0 \\ 0 & (1-\gamma)w_B & 0 & 0 \end{pmatrix} \tag{12}$$

elements only.



(a) (b)

Fig. 4 : (a) Representation of a branched block-copolymer as a full rooted tree, (b) corresponding reduced rooted tree of the same polymer.

Fig. 4 shows the graph representations which correspond to the non-reduced and the reduced matrices $\underline{\underline{P}}$ and $\underline{\underline{P}}^*$. Note the matrix $\underline{\underline{C}}$ remains unchanged, thus the graph of Fig. 4b does not fully represent the zero's generation correctly. The factorization of eq.(9) has great advantages. (i) If we know the mechanism of polymerization of the various homo-blocks and if we know how these blocks are coupled, then the solution is eq.(9), and we have no longer to go through the details of the theory. (ii) The evaluation is greatly simplified because of the zeros in the diagonal area of $\underline{\underline{P}}^*$, and the inversion of $(\underline{\underline{1}} - \underline{\underline{P}}^*)$ can in some cases be carried out by hand. (iii) The sums in eq.(10) are easily solved for Gaussian statistics where $\phi_{nb} = (\phi_{1b})^n$ and $\phi_{n1} = (\phi_{11})^n$, and for subchains which do not obey Gaussian statistics, the sums can be approximated by Laplace integrals or directly calculated by summation on a computer. The sums converge rapidly if the extent of the homoblocks is not too large, i.e. if α and γ are not too close to unity.

APPLICATION TO FIBRIN AND GLYCOGEN

The transition matrix $\underline{\underline{P}}$ in eq.(4) contains 7 different link probabilities which, however, are not fully independent of each other. The restriction imposed on the branched domain that functional group A can react with a group B only within the domain implies the necessary condition $\alpha = 2\beta$. Furthermore we have to take into account that the number of B→ C linkages must equal the number of C→B linkages, and similar holds for the A ↔D bonds which yields

$$2(1-\beta)p_C w_A = (1-\alpha)p_D w_B \qquad (13)$$

For the remaining 5 link probabilities , five different properties have to be measured. Suitable quantities are the composition of the copolymer, the molecular weights M_w and M_n , the mean square radius of gyration $\langle S^2 \rangle_z$ and the diffusion coefficient D_z of the individual blocks and the total polymer. Finally, the angular dependence of scattered light or neutrons can be used for a determination of the link probabilities. Often some of the link probabilities can be determined from kinetic measurements. In many cases only some of the mentioned quantities are accessible to measurement, and reasonable assumptions have to be made. Such a case is met with fibrin and the intermediate fibrin structures because within a rather short time (about 5 hours) before clot formation occurs the aggregation process could be followed by light scattering only (Ref. 27). We thus had to use observations from other experiments to complete the picture of a model. Electron microscopy (EM), for instance, showed that the branching domains consist actually of one branching unit, thus $\alpha = \beta = 0$. The fibrin monomer is a symmetric molecule where two alike parts are held together by disulfide bonds, and this implies equal reactivity of both ends of the rod-like molecule, i.e. $w_A = w_B$. We made now the additional assumption that also the A-group of the branching unit has the same reactivity, i.e. $p_C = w_A = w_B$. This leaves us with the branching probability p_C and the chain growth probability γ as the only unknown parameters, and these had to be found from the light scattering meas-

urements. These LS measurements gave information on the increase of $\langle S^2 \rangle_z$ as function of M_w ; they further revealed a rod-like or fibrillic structure for the chains between the branching points and they showed that the branching probability p_C increases from a very low value at short length up to $p_C = 1$ when a certain rod-length is reached. Finally from the asymptotic behaviour of the angular dependence of the scattered light a side-by-side aggregation was found, and the extent of lateral aggregation could be determined without assumptions.

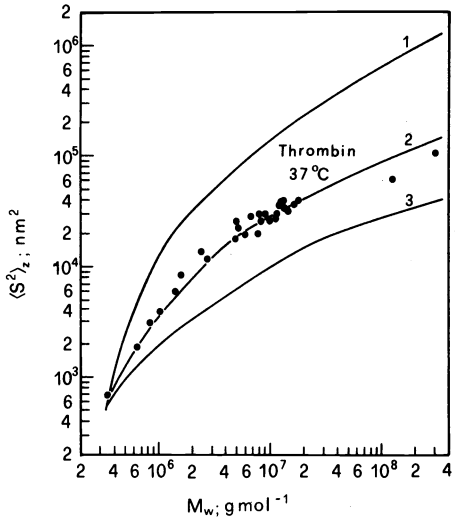


Fig. 5 : Dependence of $\langle S^2 \rangle_z$ on M_w for fibrins initiated by thrombin at 37 °C (- ● -) ; curve 1 gives the theoretical dependence if no lateral aggregation exists. Curve 2 represents the best fit, and curve 3 a structure with pronounced lateral aggregation.

Fig. 5 shows a series of experimental data of $\langle S^2 \rangle_z$ as function of M_w. A very satisfactory fit with our theory became possible with a fibril length of 550 nm and a lateral aggregation, Lat, which proceeds with a power a = 1.1 of the molecular weight, i.e. $Lat = M_w^a$ (curve 2). Curve 1 shows the increase of $\langle S^2 \rangle_z$ when no lateral aggregation is assumed and curve 3 results for a = 2.5 . The initial steep part of the curve is determined by the fiber growth and the flat part at large M_w is caused by the branched structure. A much flatter initial part results if flexible interconnecting chains are assumed. Also the angular dependence is correctly described by our theory with the same parameters. The curves have been published elsewhere and are not reproduced here.

The angular dependence is a fairly sensitive check for the validity of a model. This will be shown now with the example of glycogen. We have invested much effort into the determination of the various relevant parameters. The data of M_w , M_n and D_z of highly branched macrodextrines allowed the determination of $\alpha = 2\beta$ and the effective bond length of the repeating unit, $b_M = 1.27$ nm. Furthermore, since no free chains are present in the glycogen we have $w_B = 1$, which means that all chains are coupled with their C-end to a B-group of a macrodextrin. Then we have the experimentally determined mass fraction of the macrodextrins and this allowed the elimination of p_C. The remaining two unknown link probabilities w_A and γ had to be found from the molecular weight and the mean square radius of gyration. At a first sight this should cause no difficulties. However, the problem is a little more complex since we do not know the correct value of the effective bond length of the linear chain and we have to some extent to take a certain excluded volume into consideration. Finally we do not know the correct value of the effective bond length of the linear chain and we have to some extent to take a certain excluded volume into consideration. Finally we do not know whether the interconnecting chains are monodisperse in length, i.e. $\gamma = 0$, or polydisperse. A description of the structure by theory appears therefore to be highly ambiguous. This is, however, not

the case, because the conditions that none of the various probabilities must not exceed unity implies strong restriction such that most of the assumptions do not give a solution.This is to say, within the allowed region of probabilities the radius of gyration is found to be either too large or too short. We have not yet checked through all the various possibilities and the result shown in Fig. 6 has only preliminary character.

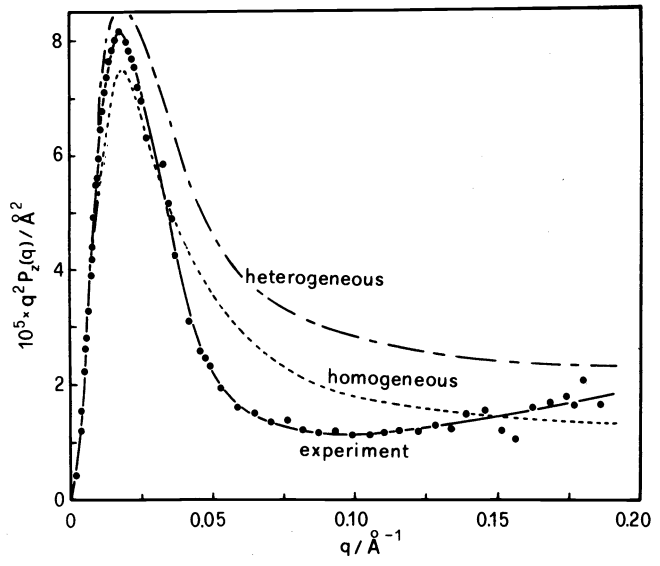


Fig. 6 : Angular dependence of coherent neutron scattering by glycogen dissolved in D_2O (Kratky plot). -•- points of measurement, dotted line : calculated with the model of homo-condensation of a trifunctional monomer with three unlike functional groups A,B,C ; chain line : best fit for a hetero-geneously branched molecule.

The curve labeled"heterogeneous" was found with monodisperse chains with an effective bond length of 1.2 nm for the monomer unit and with a maximum excluded volume effect i.e. $\langle S^2 \rangle_{z,chain} = P_w^{1.2}$. According to this fit the glycogen molecule consists of 31 macrodextrines which bear on the average 2.25 chains of 18 monomer units in length. The agreement is not fully satisfactory, and this may result from an oversimplification of the present model. Possibly the macrodextrins are connected through slightly branched chains rather than through strictly linear chains. Further calculations are in progress.

CURING OF EPOXIDE RESINS

The last example to be discussed differs from the two others because the branched nucleus of the epoxide resin is itself already a co-polymer. We have not yet enough experimental data at hand for a close comparison of theory with experiment, but some theoretical aspects may be of interest. The molecular weight can be calculated from eq. (2) with the matrices

$$\underline{C} = \begin{pmatrix} 0 & 2\alpha & 0 & 0 \\ 2(1-p)\beta & 2p\beta & 2p\beta & 2(1-\beta)q \\ 0 & 2\gamma & 0 & 0 \end{pmatrix} \qquad (14)$$

and

$$\underline{P} = \begin{pmatrix} 0 & \alpha & 0 & 0 \\ (1-p)\beta & p(1+\beta) & p\beta & (1-\beta)q \\ (1-p)(1+\beta) & p(1+\beta) & p & 0 \\ 0 & \gamma & 0 & 0 \end{pmatrix} \qquad (15)$$

Here are α the extent of reaction for a phenolic OH group, β the extent of reaction of an epoxide group, γ the extent of reaction of an acid group of adipinic acid, which is taken as curing agent. p is the probability of reaction for a secondary OH group of the reacted epoxide group and $(1-\beta)q$ is the probability for the reaction of an epoxide group with an adipinic acid group. The first row in $\underline{\underline{C}}$ refers to bis-phenol, the second to the di-epoxide and the third to adipinic acid. The four columns correspond to reactions with a phenolic OH-group, with an epoxide group, with a secondary OH-group of a reacted epoxide and to the reaction with the acid group of adipinic acid respectively. In the non-cured resin, we have $\gamma = q = 0$, i.e. the last row and the last column in the matrices $\underline{\underline{C}}$ and $\underline{\underline{P}}$ are missing.

First we notice that gelation takes place when M_w tends to infinity. This leads to the condition of the gel point

$$|\underline{\underline{1}} - \underline{\underline{P}}| = 0 \qquad (16)$$

by which a critical extent of reaction for the phenolic OH group, α_c, or of the epoxide group with an acid group of the curing agent q_c is defined, assuming full reaction of the adipinic acid, i.e. $\gamma = 1$.

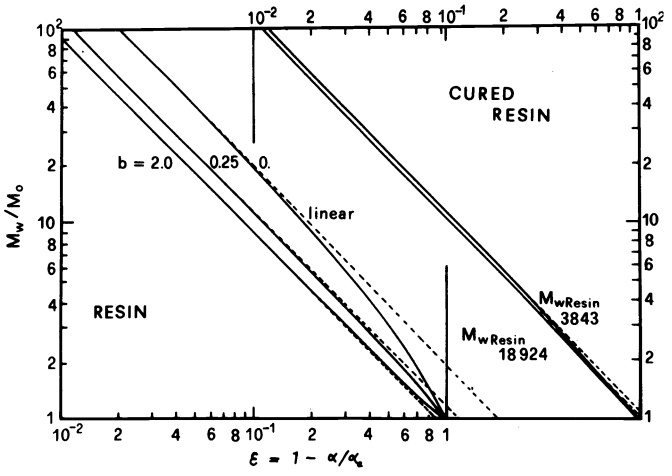


Fig. 7 Plot of the relative increase of the molecular weight M_w as function of $\varepsilon = 1-\alpha/\alpha_c$ for the epoxide resin and as function of $\varepsilon = 1-q/q_c$ (upper scale) for the cured resin. M_o is the average monomer molecular weight in the resin, and for the cured resin, M_o is the $M_{w,resin}$ of the resin before curing.

In Fig. 7 we have plotted the relative increase M_w/M_o of the molecular weight against $\varepsilon = 1 - \alpha/\alpha_c$ or $\varepsilon = 1 - q/q_c$, respectively. The parameter $b = k_2/k_1$ is a measure for the extent of branching and is closely related to the branching probability p of the resin. M_o is the average molecular weight of the epoxide and bis-phenol monomer units, and in the cured resin, we have $M_o = M_{w,resin}$ which is the weight average molecular weight of the resin before curing. In all cases the same asymtotic behaviour at large M_w is observed with critical exponents of $\nu = 1$ in the relationship $M_w/M_o \sim \varepsilon^{-\nu}$. It is now of interest that (i) this asymtotic behaviour is reached for linear, alternating copolymer resin not before $\varepsilon = 10^{-2}$; (ii) a deviation towards higher M_w/M_o is obtained for the linear product but a deviation towards lower molecular weight for the highly branched resin; (iii) on curing the asymtote is reached earlier with the higher resin molecular weight than with the lower one.

Measurements of M_w, $\langle S^2 \rangle_z$ and D_z are in progress and will be combined with kinetic measurements already performed. It will be interesting whether the predictions of the theory are observed in the experiment.

ACKNOWLEDGEMENT

This work was kindly supported by Deutsche Forschungsgemeinschaft

REFERENCES

1. W. H. Stockmayer and M. Fixman, Ann. N. Y. Acad. Sci. 57, 334 (1953)
2. M. E. Fisher, Rept. Prog. Phys. 30,615 (1967)
3. H. E. Stanley, editor, Cooperative Phenomena Near Phase Separation, M.I.T. Press, Cambridge, Mass. 1973
4. J. W. Essam in Phase Transitions and Critical Phenomena, eds. C. Domb and M. S. Green, Academic Press, New York 1973
5. D. Stauffer, Physics Reports 54, 1 (1979)
6. P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca 1953
7. W. H. Stockmayer, J. Chem. Phys. 11, 45 (1943); 12, 125 (1944)
8. W. Burchard, Macromolecules 10, 919 (1977)
9. W. H. Stockmayer in Advancing Fronts in Chemistry, editor S. B. Twiss, Reinhold Publ. Corp., New York 1945, Chap. 6; see also Ref. 6.
10. R. S. Whitney and W. Burchard, Makromol. Chem. 181, 869 (1980)
11. M. Schmidt and W. Burchard, Macromolecules, submitted
12. K. Dusek and W. Prins, Adv. Polymer Sci. 6, 1 (1969)
13. M. Moritani, T. Inoue, M. Motegi and H. Kawai, Macromolecules 4, 433 (1970)
14. K. L. Wun and W. Prins, J. Polymer Sci. 12, 533 (1974)
15. K. L. Wun, G. T. Feke and W. Prins, Farad. Discus. Chem. Soc. 57, 146 (1974)
16. K. Dusek, J. Plestil, F. Lednicky and S. Lunak, Polymer 19, 393 (1978)
17. W. Burchard, S. Bantly and S. A. Zahir, Makromolekulare Chem. accepted
18. K. Dusek, M. Ilavsky and S. Lunak, J. Polymer Sci. Symposium 53, 29 (1975)
19. S. Lunak and K. Dusek, J. Polymer Sci. Symposium 53, 45 (1975)
20. S. Lunak, J. Vladska and K. Dusek, Polymer 19, 931 (1978)
21. W. Burchard, Macromolecules 5, 604 (1972)
22. M. Müller and W. Burchard, Makromolekulare Chem. 179, 1821 (1978)
23. M. Rinaudo and W. Burchard, to be published
24. M. Schramm in Control of Glycogen Metabolism, editor W. J. Whelan, Academic Press 1968, p. 179
25. J. Heller and M. Schramm, Biochim. Biophys. Acta 81, 96 (1964)
26. G. L. Brammer, M. A. Rougvie and D. French, Carbohyd. Research 24, 343 (1972)
27. M. Müller and W. Burchard, Biochim. Biophys. Acta 537, 208 (1978)
28. M. Müller and W. Burchard, Int. J. Biol. Macromolecules (1980) in press
29 W. Burchard and M. Müller, Int. J. Biol. Macromolecules (1980) in press
30. T. E. Harris, The Theory of Branching Processes, Springer Verlag, Berlin 1963
31. H. W. Watson and F. Galton, Educ. Times 19, 103 (1873)
32. M. Gordon, Proc. Roy. Soc.,London, A 268, 240 (1962)
33. W. Feller, An Introduction to Probability Theory, Wiley, London 1968 Vol. 1, Chapt. 11
34. M. Gordon and G. R. Scantlebury, J. Chem. Soc. 1967, 1 (1967)
35. M. Gordon and G. R. Scantlebury, Trans. Farad. Soc. 60, 604 (1964)
36. W. Burchard, B. Ullisch and Ch. Wolf, Farad. Discuss. Chem. Soc. 57, 56, (1974)