

MOLECULAR HETEROGENEITIES AND ASSOCIATION OF MACROMOLECULES

B. VOLLMERT

*Polymer-Institut der Universität Karlsruhe, Kaiserstrasse 12,
Karlsruhe 75, GFR*

ABSTRACT

The degree of interpenetration of random coils in concentrated polymer solutions, gels and films has been investigated by means of a chemical method. *cis*-1,4-Polybutadiene containing OH-groups has been converted with *cis*-1,4-polybutadiene containing NCO-groups. The experiments have shown that the maximum attainable conversion of this reaction depends on the polymer concentration. It increases up to 45 per cent with solvent-free films. Since incompatibility could be excluded this conversion is a measure of the degree of interpenetration of macromolecules.

Unlike polymer solutions and films prepared from solutions by evaporation, polymer samples directly formed by polymerization have prevalingly interpenetrated structure. This can be concluded from the higher conversion of pendant double bonds, if a monomer is polymerized in the presence of the corresponding polymer with pendant double bonds, and from the different swelling and deformation behaviour of networks prepared by crosslinking copolymerization and by reaction of polymers with functional groups.

INTRODUCTION

The word 'heterogeneous' is an artificial word, which did not exist in the Old Greek language, contrary to the alternative term 'homogeneous' (ὁμογενής) which means 'related'. The present general meaning of the word 'heterogeneous' is illustrated in the *Random House Dictionary* by the following sentence: 'The party was attended by a heterogeneous group of artists, business men and social climbers.' In the field of chemistry the dissimilarity or heterogeneity not only refers to the kinds of components of a group or system but also to their distribution within a certain volume. If we consider it precisely, no material system at all is homogeneous in the wide sense of equability and uniformity, because even a single atom has no continuous mass distribution. Therefore we can distinguish only different degrees of homogeneity and have to explain from case to case what heterogeneity means.

In our case the heterogeneity relates to the kind of association of the macromolecules, more precisely, to the degree of interpenetration of chains. As *Figure 1* shows, we can distinguish as extremes two different kinds of macromolecular associations and resulting aggregation states: the state with completely interpenetrated and entangled polymer chains (a) and the state with completely separated individual random coils (b).

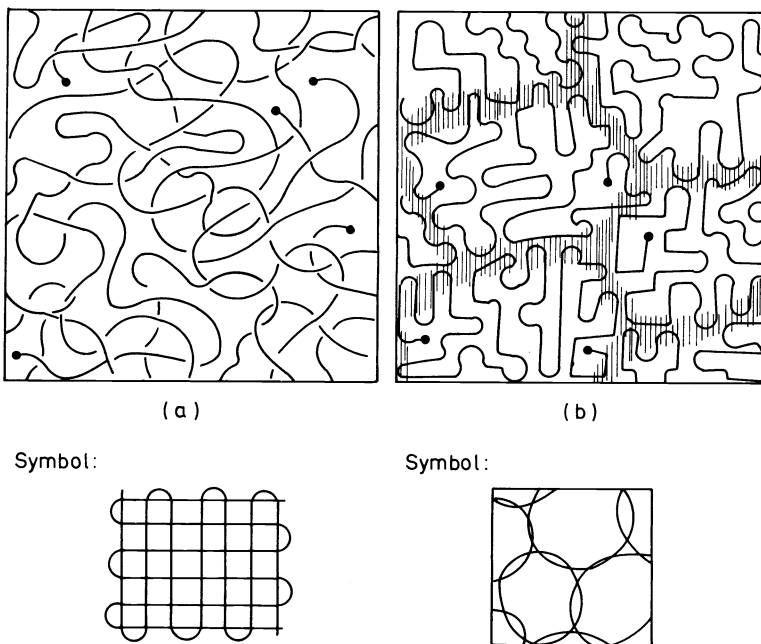


Figure 1. Schematic representation of the molecular association of macromolecules: (a) Homogeneous interpenetration, (b) Individual coil structure.

Thermodynamic reflections of P. J. Flory¹ have led to the statement that the radius of gyration of macromolecules in concentrated solutions and in the solvent free state is the same as in theta solvents. This statement includes a molecular association in the sense of a complete interpenetration according to Figure 1(a).

On the other hand S. H. Maron² and S. Onogi *et al.*³ have concluded from rheological measurements of concentrated polymer solutions that the polymer molecules do not interpenetrate but reduce their volume with increasing polymer concentration as demonstrated by Figure 1(b).

Because no one can assume that a polymer coil or a part of a polymer coil is able to migrate through a neighbouring coil or a part of a neighbouring coil, the Maron-model seems to be clear for flowing solutions. The flowing coils glide closely along one another under deformation. But the rheological arguments did not suffice to convince the polymer scientists and so Maron's structural concept was overlooked or fell into oblivion. The homogeneously interpenetrated structure according to Figure 1(a) was in general also furthermore considered as the only tenable possibility.

Thermodynamical reflections alone are no proof for the existence of particular material structures especially if sterical factors cannot be excluded. Thus, we have tried to investigate the problem of the interpenetration of random coils in concentrated polymer solutions by chemical experiments.

THE $P_X + P_Y$ -REACTION AND THE DEGREE OF INTERPENETRATION

For this purpose we have used a method, a characteristic of which is the marking by analytically controllable functional groups as follows: The chains of a polymer are provided with different reactive functional groups, having distances of 10 to 100 structural units along the polymer chains, the one part with OH-groups and the other one with NCO-groups. Solutions of both parts were mixed so that the molar ratio of NCO-groups to OH-groups was 1/1, and the maximum attainable conversion was determined.

In that part of the volume of this mixture in which the chain segments of the two functional polymers are interpenetrated, the functional groups can react by formation of urethane groups, evidenced by the nearly quantitative conversion of the reaction of OH-group-containing polymers with the equivalent amount of hexamethylene diisocyanate. Consequently, that part of the macromolecules where the functional groups remain unreacted corresponds to the non-interpenetrated part of the coil volume.

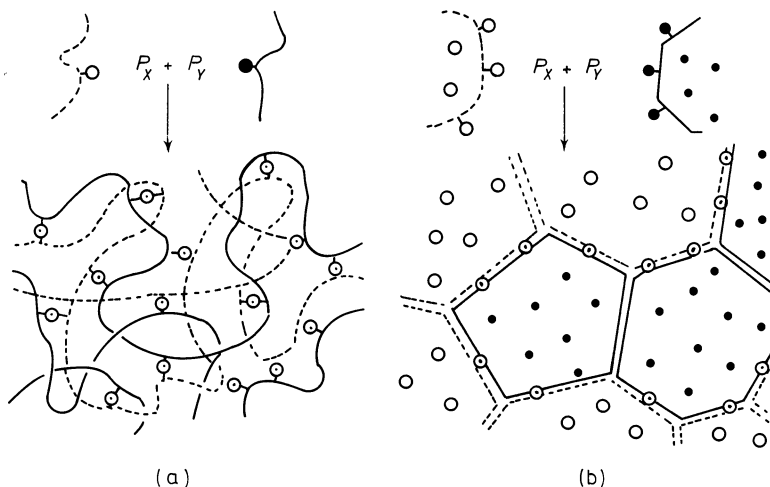


Figure 2. Schematic representation of the reaction of a polymer P_X containing OH-groups with a polymer P_Y containing NCO-groups ($P_X + P_Y$ -reaction): (a) Complete coil interpenetration, (b) Individual packing. O, OH-groups, ●, NCO-groups, ○, urethane groups.

Figure 2 shows schematically the results we have to expect in the two cases: (a) nearly quantitative conversion with complete interpenetration and (b) low conversion with non-interpenetration. It is evident that the conversion will increase with increasing degree of interpenetration. Therefore it is convenient to use the conversion of the $P_X + P_Y$ -reaction as a measure of the degree of interpenetration.

This interpretation is only correct if we take into consideration the following points: (1) We have to pay attention to the possibility that the two modified polymers can become incompatible because of the different kinds of their functional groups. (2) We have to attempt to carry out the reaction so that

the diffusion of chain segments is not blocked by the crosslinking reaction before the steady state is attained.

Both phenomena can be controlled by variation of the concentration of the functional groups along the polymer chains: (1) The lower the concentration of the groups the smaller the difference of the polymers and the smaller, therefore, the incompatibility. (2) The lower the concentration of the functional groups in the two reacting polymers the smaller the possibility of diffusion blocking by crosslinking. Therefore the conversion of the $P_X + P_Y$ -reaction should increase with decreasing concentration of functional groups in the case of incompatibility or diffusion blocking and the extrapolation to the concentration zero allows us to eliminate the influence of both effects. Independence of the conversion from the concentration of functional groups shows that incompatibility or diffusion blocking has no influence on the conversion of the $P_X + P_Y$ -reaction.

RESULTS WITH POLYBUTYLACRYLATE

We have investigated the question of coil-interpenetration at first with polybutylacrylate. The P_X -polymer (*Figure 2*) was in this case a copolymer of butylacrylate and 1 to 10 mol% of the monoacrylate of butanediol. The P_Y -polymer was a copolymer of butylacrylate and 1 to 10 mol% isocyanatoethylacrylate, i.e. the little spheres in *Figure 2* are OH-groups and the points are NCO-groups or vice versa.

The conversion was determined by measurement of the degree of swelling with the aid of a standard curve⁴. To be sure to determine the maximum attainable conversion of the reaction, the reaction time was varied over a wide range, e.g. it was found that the conversion reached a steady state after 24 hours and that this conversion remained unchanged over a period of six days more.

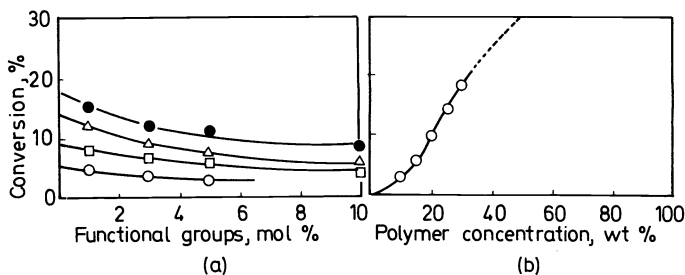


Figure 3. Conversion of the $P_X + P_Y$ -reaction with polybutylacrylate: (a) conversion as a function of the content of functional groups in the polymers P_X and P_Y ; (b) conversion as a function of the polymer concentration during the $P_X + P_Y$ -reaction.

The results are plotted in *Figure 3*. It is to be seen that the maximum conversion values increase slightly with decreasing concentration of functional groups (3a). Therefore the 3a-curves were extrapolated to the concentration zero to eliminate a possible influence of incompatibility or diffusion blocking. The extrapolated conversion values are plotted against

MOLECULAR HETEROGENEITIES OF MACROMOLECULES

the polymer concentration during the crosslinking reaction in *Figure 3(b)*. This result, the strong increase of the conversion with increasing polymer concentration, is not consistent with a completely interpenetrated molecular association according to *Figure 1(a)* but only with an individual coil structure with increasing degree of interpenetration dependent on the polymer concentration. The question is: can we generalize this result obtained with polybutylacrylate? To answer this question we have translated our experimental technique by reference to *cis*-1,4-polybutadiene.

EXPERIMENTS WITH *cis*-1,4-POLYBUTADIENE

If one compares the primary structures of polybutylacrylate and *cis*-1,4-polybutadiene (see *Figure 4*) one understands at once why just this polymer was investigated instead of any other one. The polybutylacrylate

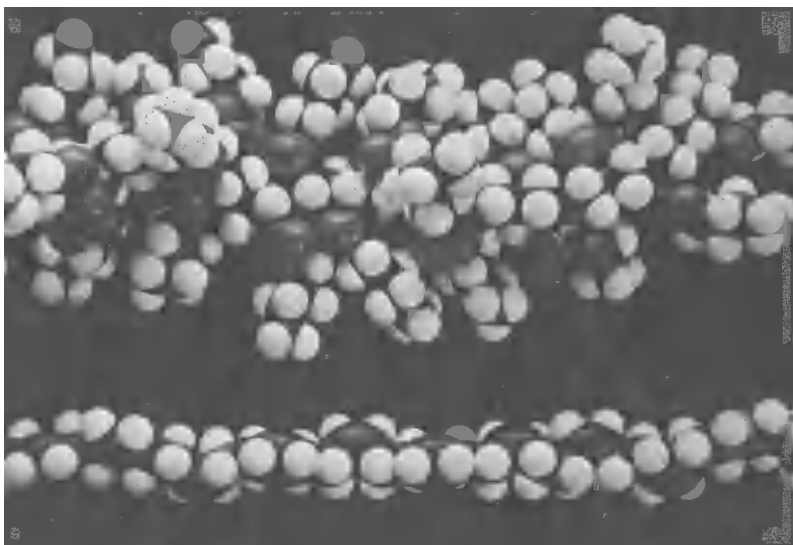


Figure 4. Stuart-Briegleb models of polybutylacrylate and *cis*-1,4-polybutadiene.

chain is closely surrounded by the pendant butylester side groups. Therefore one could suppose that the reaction of the OH-group-containing chains with the NCO-group-containing chains is sterically hindered by a normal shielding effect, well-known also with many non-macromolecular organic compounds. However, 1,4-polybutadiene molecules are bare chains, completely free of side chains so that a trivial sterical hindrance of the functional groups by neighbouring groups is impossible.

Since the providing of the chains with functional groups by copolymerization with suitable monomers is not possible with polybutadiene, the way shown in *Figure 5* was followed⁵. As original material we used a *cis*-1,4-

B. VOLLMERT

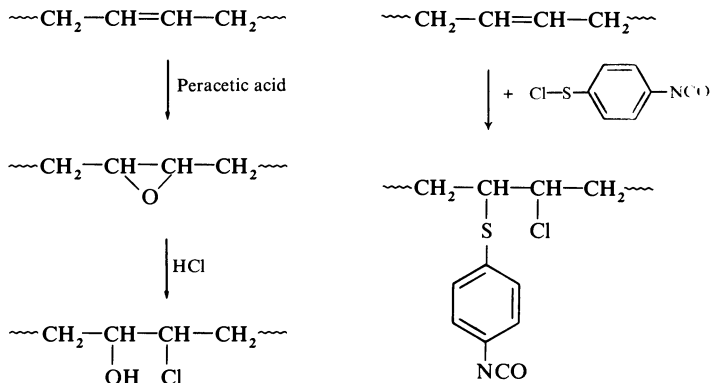


Figure 5. Reaction schemes for the introduction of OH- and NCO- side-groups into *cis*-1,4-polybutadiene.

polybutadiene with high *cis*-1,4-content (>99 per cent), kindly presented by the Chemische Werke Hüls AG. Oxidation with peracetic acid leads to a modified *cis*-1,4-polybutadiene with epoxy-groups in the chain, which were hydrolysed by hydrochloric acid giving hydroxy groups with a neighbouring chlorine. In order to prepare the reaction partner the same *cis*-1,4-polybutadiene was modified with NCO-groups by reaction with *p*-isocyanatosulphenylchloride.

With both reactions the molecular weight was controlled by light scattering, osmometric and viscometric measurements after each step. The polymerization degree, according to a molecular weight of 300000, remained unchanged during and after the reactions. Oxidative chain degradation and undesired crosslinking were prevented by a dry nitrogen atmosphere throughout the preparatory work.

The polybutadiene containing OH-groups and the polybutadiene containing NCO-groups were brought to reaction with different concentrations of functional groups and with different polymer concentrations.

The conditions (temperature and catalyst concentration) were so chosen that the first symptoms of crosslinking and gel formation were noticeable after not less than 24 hours. Therefore we can be sure that the diffusion of chain segments, which is necessary for the interpenetration, had time enough to effect a stationary state, whether the diffusion processes are limited by a thermodynamic equilibrium state or by sterical factors.

To be sure of measuring the maximum attainable conversion the reaction time was in most experiments three weeks at 25°C and then subsequently one further week at 50°C. This is a multiple of the time which was necessary for a 90 per cent conversion of the reaction of the polybutadiene containing OH-groups with hexamethylene diisocyanate and is a multiple excess of the time required to attain constant conversion values. Subsequently raising the reaction temperature from 25 to 50°C did not increase the conversion.

The reaction was carried out in two different ways: (1) by mixing the polymer solutions in benzene of the intended concentrations in the molecular

ratio $\text{OH}/\text{NCO} = 1/1$, and (2) by mixing diluted polymer solutions (0.5 per cent) and by slow evaporation in evacuated vessels until the intended polymer concentration was reached. The evaporated solutions of films remained under a nitrogen atmosphere for a further two weeks until the determination of the conversion. In this way it was possible to determine the conversion of the $\text{P}_x + \text{P}_y$ -reaction also with high polymer concentrations up to solvent-free films.

The determination of the conversion was carried out in these experiments by direct titrimetric analysis of the non-reacted NCO-groups in the gels, which method was developed by J. Stemper⁵. It could be controlled with the gels prepared by the reaction of polybutadienes containing OH-groups with hexamethylene diisocyanate.

RESULTS OF THE $\text{P}_x + \text{P}_y$ -REACTION WITH POLYBUTADIENE

The results are presented in *Figure 6*. The single points and short lines represent average values of fifteen analytical determinations. *Figure 6(a)* shows the conversion as a function of the content of functional groups. The

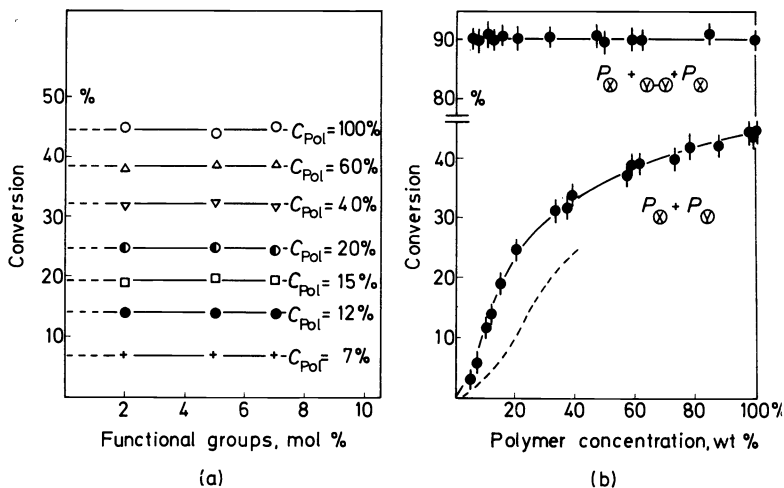


Figure 6. Conversion of the $\text{P}_x + \text{P}_y$ -reaction with *cis*-1,4-polybutadiene: (a) conversion as a function of the content of functional groups in the polymers P_x and P_y , (b) conversion as a function of the polymer concentration during the $\text{P}_x + \text{P}_y$ -reaction.

conversion values are constant within the limit of error, which means that there is no influence of incompatibility or diffusion blocking to be noticed. *Figure 6(b)* shows the conversion as a function of the polymer concentration in the whole range from zero to 100 per cent. The conversion curve increases with increasing polymer concentration up to 45 per cent conversion. It shows principally the same run as with polybutylacrylate, but the conversion values lie about ten per cent higher in the case of polybutadiene. This difference is possibly caused by the side groups of the polybutylacrylate.

But it cannot be excluded that the more complicated and less perfect analytical technique with polybutylacrylate explains the difference.

DISCUSSION

The experiments with 1,4-polybutadiene have shown that the relatively small conversion of the $P_X + P_Y$ -reaction and the strong dependence of the conversion on the polymer concentration is not a special property of a certain polymer. In the discussion of this phenomenon again and again the incompatibility of different polymers has been cited as a possible explanation of the experimental results. Incompatibility, however, cannot be the cause of the small conversions and can certainly not explain the increase of the conversion with increasing polymer concentration. In the case of incompatibility, just the opposite dependence should be expected, since the incompatibility of polymer solutions increases with increasing polymer concentration.

These arguments are additional arguments. The main argument for the exclusion of incompatibility and diffusion blocking by crosslinking is the independence of the conversion from the content of functional groups as illustrated by *Figure 6(a)*.

In sharp contrast to the conversion values of the $P_X + P_Y$ -reaction, the conversion of the normal crosslinking reaction of the polybutadiene containing OH-groups with hexamethylene diisocyanate is constant over the whole range of polymer concentration from 0 to 100 per cent and lies at 90 per cent [*Figure 6(b)*]. This reaction occurs in two inseparable steps. The first is the addition of a hexamethylene diisocyanate molecule to an OH-group which gives rise to a pendant NCO-group by means of a urethane-bridge. The second step is the reaction of this pendant NCO-group with an OH-group giving cross-linking. This second step would correspond completely to the reaction of an OH-group containing polymer with an NCO-group on the chain of the same or another macromolecule containing polymer, if the polymer coils would homogeneously interpenetrate; for the OH-groups, however, fixed somewhere along a chain and pushing against NCO-groups, we cannot distinguish if the NCO-groups are fixed at another chain segment of the same macromolecule or at a chain segment of another macromolecule.

In spite of this, we cannot, even with complete interpenetration, expect that the conversion of the $P_X + P_Y$ -reaction reaches 90 per cent because of the combinatorial statistics. But even in regard to the statistics with a polymer concentration of about ten per cent the conversion should be at least 50 per cent, if complete interpenetration were to take place. By contrast, the experimental value is 12 per cent conversion. A structure model which calls for a conversion of 50 per cent does not correspond to the real structure.

The form of *Figure 6(b)*—the stepless increase of the conversion with increasing polymer concentration—requires a structure model in which the contact of the random coils becomes more intimate with increasing polymer concentration. This claim is fulfilled by a structure model which is represented in *Figure 7*. We published it six years ago⁶ without any knowledge of the rheological experiments of S. H. Maron² and S. Onogi³, who have arrived

at the same structure from their own results. This model (*Figure 7*) is suitable for explaining and understanding the experimental results of *Figure 6* if we interpret the increasing conversion as an increasing interpenetration, or better still interlocking, of the superficial parts of neighbouring random coils.

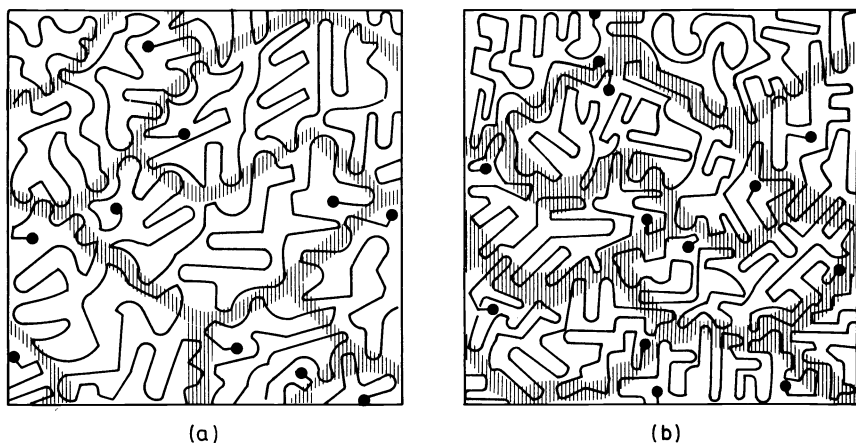


Figure 7. Schematic representation of individual coil structure with different polymer concentrations: (a) approximately 25%, (b) approximately 80%; shaded areas denote interpenetration zones.

We have called this kind of interpenetration a paranemic interpenetration following the nomenclature of double helices ('paranemic' means not entangled, contrary to 'plectonemic') and the model 'cell structure', or 'individual coil structure model'.

With regard to the interpretation of the conversion as degree of interpenetration, we have to consider that a degree of interpenetration in the sense of a volume which is occupied commonly by parts of neighbouring coils could only be defined exactly if random coils had a defined surface and a defined geometrical shape. They do not have these features and, therefore, we can only say that the conversion of the $P_X + P_X$ -reaction is an approximate measure for the degree of interpenetration.

It is to be considered moreover that in a dense packing not all coils, which adjoin an X-coil, are Y-coils. But on average only eight neighbours of the total of twelve neighbours of an X-coil are Y-coils (in a hexagonal system). X-polymers cannot react with X-polymers. Therefore the experimentally determined conversion refers only to the contact zones of 66.7 per cent of the neighbours, i.e. the whole overlapping volume is always larger than the volume corresponding to the conversion.

On the other hand we have to notice also that with the overlap-free contact of a system of densely packed coils (overlapping volume becomes zero) a certain conversion takes place, which can be estimated to be about ten per cent. These two effects compensate one another at least partially.

One could suppose that the low conversion relates to the excluded volume⁷

which becomes zero only in theta solvents. We have, therefore, investigated the conversion of the $P_x + P_y$ -reaction with polymethylmethacrylate in a mixture of solvents with almost theta state up to a polymer concentration of 30 per cent. The experimental conversion values did not exceed 20 per cent.

Concerning the reason for the incomplete interpenetration of random coils in concentrated polymer solutions, gels and films, it is convenient to assume that the homogeneously interpenetrated molecular association is the thermodynamically stable equilibrium state, because only in this state can the coils assume their most probable dimensions. If this is true, the incomplete interpenetration should be caused by a sterical hindrance of chain segments.

We have to regard polymer coils as irregular spatial lattices, which can indeed, because of the flexibility of the chains, interpenetrate but only to a limited degree. We should relinquish the apparently rather favoured conception that polymer chains could move and intertwine like snakes or worms.

POLYMER STATE WITH DOMINANTLY INTERPENETRATED STRUCTURE

An occurrence, which is connected with such a wormlike movement, takes place only once during the existence of a macromolecule transiently for one or two seconds, and this occurs during the chain propagation phase of a radical or ionic polymerization.

A growing tip of chain should be able to penetrate into the convolutions of polymer coils in concentrated solutions, especially as we have to assume that the decomposition of the initiator molecules and therefore the initiation of chains takes place preferably in the interior of coils with a conversion of more than five per cent. Such reflections lead to the supposition that polymer samples which are prepared by polymerization up to high conversions should have an interpenetrated structure opposite to samples prepared by evaporation of polymer solutions, which have been treated until now.

In order to investigate this question we have taken over our experimental technique on radical polymerization while we have studied the polymerization of butylacrylate in the presence of a polybutylacrylate with acrylic double bonds fixed as side groups on the polybutylacrylate chain, as schematically represented in *Figure 8*. We have found that about 70 per cent of the pendant acrylic double bonds copolymerize during the secondary polymerization and around 30 per cent remain unreacted in spite of complete polymerization of the secondary monomer. This result harmonizes with the investigations of crosslinking copolymerization by Kopeček, Jokl and Lim⁸, by Dušek, Klaban and Malinský⁹ and by Loshaek and Fox¹⁰, but does not agree with the results of Wesslau¹¹.

As an explanation for the remaining of the rest-double-bonds in general a diffusion hindrance is assumed which especially with higher conversions leads to a handicap of the pendant double bonds as against the relatively quickly diffusing free monomer molecules. If this explanation is true the structure of networks formed by crosslinking copolymerization and generally the structure of bulk polymers should be homogeneously interpenetrated. In every case the structure of these networks should be more interpenetrated

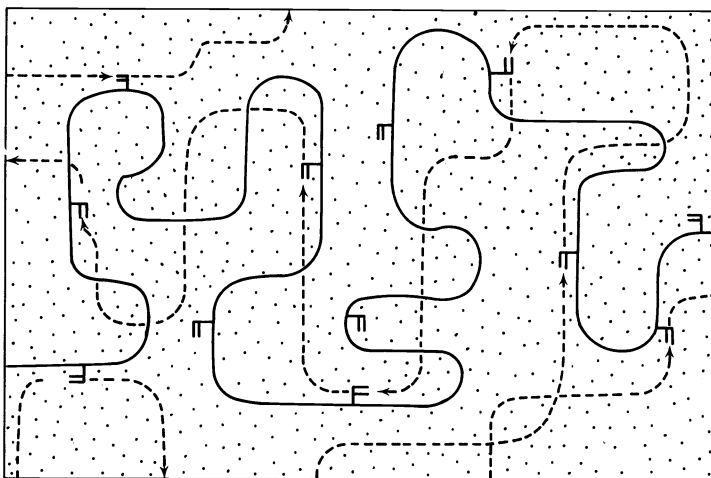


Figure 8. Schematic representation of crosslinking copolymerization in two steps: — primary polymer with pendant double bonds, - - - - - secondary polymer, ···· secondary monomer.

than the structure of crosslinked polymer samples prepared using the $P_X + P_Y$ -reaction.

AGGREGATION-STRUCTURE AND PROPERTIES OF DIFFERENT POLYMER NETWORKS

Figure 9 shows four different types of ordinary polymer networks with different molecular associations, ordinary in so far as they are prepared by the usual two methods of crosslinking: the connection of ready polymer chains with the aid of functional groups and crosslinking copolymerization. The difference of the aggregation structure is a necessary consequence if our interpretation of the conversion-results of the $P_X + P_Y$ -reaction according to Figure 7 is true.

The Figure 9(a) type is formed by the reaction of functional groups containing polymers with a di- or polyfunctional low-molecular compound. The crosslinks are, indeed, homogeneously distributed, but because of the incomplete coil interpenetration the intermolecular crosslinks are located in the border zones of the coils and the intramolecular crosslinks are located in the interior of the coils.

Type 9(b), which is formed by the reaction of two polymers with different functional groups according to the $P_X + P_Y$ -scheme, only contains intermolecular crosslinks, located in the contact zones, which are more or less broad, depending on the polymer concentration. The crosslinks in this case show a cell-pattern.

Type 9(c) is formed by polymerizing a monomer in the presence of a divinyl compound. It contains, like (a), inter- and intramolecular crosslinks but here, in contrast to (a), they are homogeneously distributed.

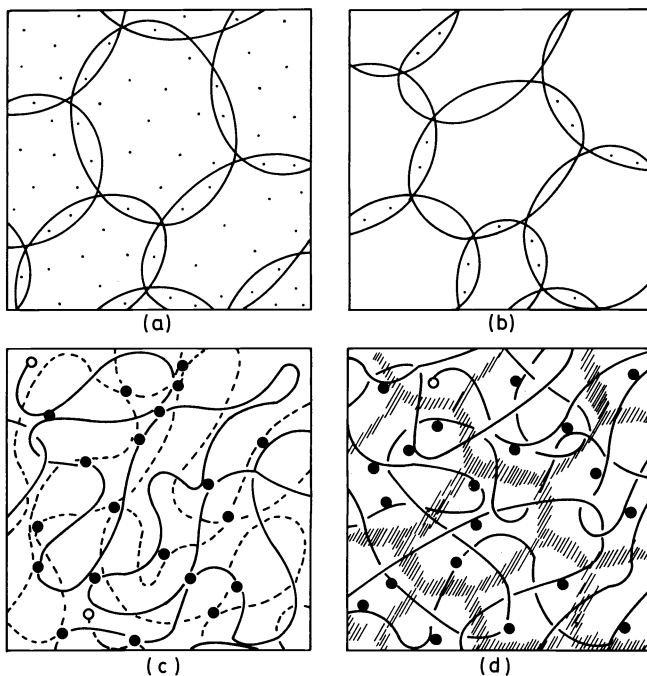


Figure 9. Schematic representation of gel structures: (a) Individual coil structure with homogeneously distributed inter- and intramolecular crosslinks (synthesis: $P_{X+Y-Y} + P_X$). (b) Individual coil structure with only intermolecular crosslinks, forming a cell pattern (synthesis: $P_X + P_Y$). (c) Interpenetrated structure with homogeneously distributed inter- and intramolecular crosslinks (synthesis: crosslinking copolymerization). (d) Interpenetrated structure and individual coil structure with homogeneously distributed intermolecular crosslinks (synthesis: two-step crosslinking copolymerization).

Type 9(d) is formed by polymerizing—according to *Figure 8*—a monomer in the presence of a polymer of the same type with pendant double bonds and it contains mainly intermolecular crosslinks but, in contrast to (b), they too are homogeneously distributed over the network.

If the structures of the four polymer networks really differ according to the schemes in *Figure 9*, it is to be expected also that the properties of the corresponding gels or rubbers will be different. The demonstration of the different character of the gels cannot serve, indeed, as evidence for a certain structure but it confirms the correctness of our interpretation of the conversion curve of the $P_X + P_Y$ -reaction (*Figure 6*), because the individual coil structure of concentrated polymer solutions (*Figure 7*) is the basis of the different gel structures of *Figure 9*.

Figure 10 shows, at first, the result of a comparison of the networks (a) and (b), which proceeded necessarily from our conversion experiments. The elastic force S —measured according to the method of Cluff, Gladding and Pariser¹² by compression of cylindrical gel samples of *cis*-1,4-polybutadiene

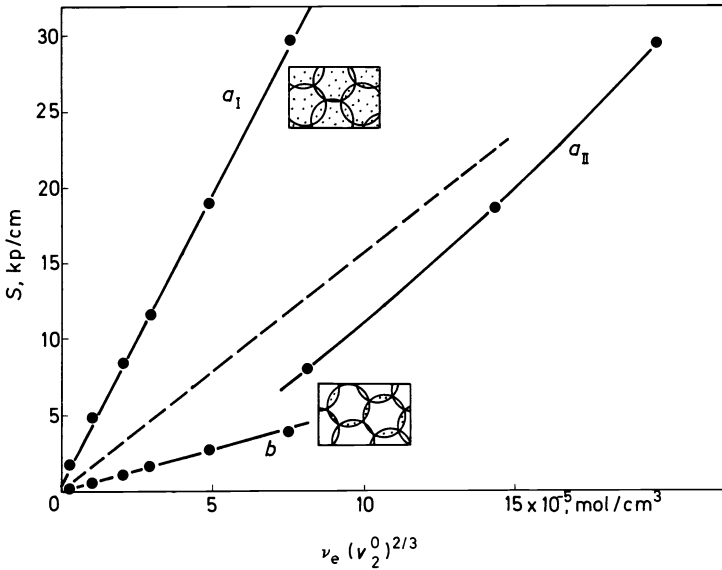


Figure 10. Elastic force S of gels (type a and b) as a function of the product of the degree of crosslinking v_e and the polymer concentration $(v_2^0)^3$, compared with the Flory equation for the elastic deformation of gels. The Flory equation, as modified by Gladding, Cluff and Pariser¹³, is $S = 3RTA_0/h_0 \times v_e(v_2^0)^3$ where S is the elastic force, v_e is the number of effective chain segments [mol/cm^3], $v_e/2$ is the number of crosslinks [mol/cm^3], A_0 is the floor space of the cylindrical sample before swelling, and h_0 is the height of the cylindrical sample before swelling. a_1 denotes inter- and intramolecularly crosslinked gels with the same proportion and the same distribution of intermolecular crosslinks as with the corresponding b -samples prepared at the same polymer concentration. a_1 relates to the same gels as a , but plotted with the supposition of an interpenetrated structure. b refers to intermolecular crosslinked gels only, prepared by $P_x + P_y$ -reaction. The dashed line denotes S -values calculated with the Cluff-Gladding-Pariser equation¹².

with 5 mol% of functional groups—is plotted against the product of the analytically measured intermolecular crosslinking degree and the polymer concentration (to the two-thirds power) during the crosslinking reaction. The experimental curves are compared with the corresponding Flory-curve¹³ (broken line).

If we look first at the curve b , concerning gels prepared by the $P_x + P_y$ -reaction, we notice that the moduli are considerably smaller than the corresponding values to be expected theoretically. Until now deviations of the theoretical curve have been explained by entanglements—if the experimental values were higher than expected—and by intramolecular crosslinks (loops), if the experimental values were lower than expected. Here, in the case of the b -samples, intramolecular crosslinks cannot be the reason for the low modulus values because no intramolecular crosslinks are present as a consequence of the preparation of the gels: OH-groups do not react with OH-groups, and NCO-groups do not react with NCO-groups under the conditions used. Because there is no reason to doubt the correctness of Flory's deduction

from his equation, we can only assume that the structure of our *b*-gels does not agree with the structure model of interpenetrating chains used as the basis for deducing the Flory equation. On the other hand it is evident that a system of coils crosslinked only in the contact zones and free of crosslinks in the interior is more easily deformed than a network of homogeneously crosslinked coils.

Plotting of the measured elastic forces *S* of the *a*-gels in the diagram is more problematical because of the presence of intramolecular crosslinks. The *a*-gels are prepared by reaction of polybutadiene containing 5 mol% OH-groups with the equivalent amount of hexamethylene diisocyanate with different polymer concentrations. The total degree of crosslinking, therefore, is the same with all samples of the *a*-series (90 per cent conversion, see Figure 6). Consequently, the increase of the elastic force *S* is caused by the increase of the ratio of inter- and intramolecular crosslinks. The experimental values can only be plotted in the diagram if the proportion of intermolecular crosslinks is known (or if we assume that no intramolecular crosslinks in the sense of ineffective loops have been formed).

The proportion of intermolecular crosslinks depends on the structure model assumed: according to our model with densely packed coils (Figure 7),

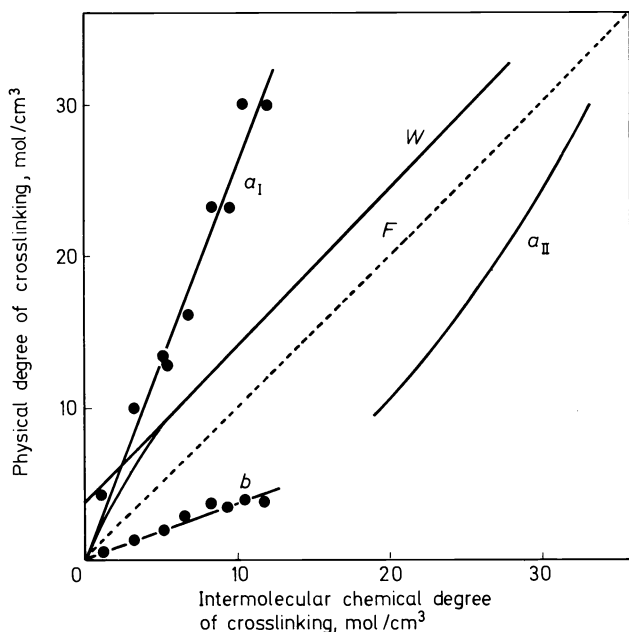


Figure 11. The physical degree of crosslinking calculated by means of the Flory equation¹² and the experimental *S*-values, plotted against the chemical (stoichiometrical) intermolecular degree of crosslinking. a_{II} denotes inter- and intramolecularly crosslinked gels, prepared by reaction of 1,4-polybutadiene containing OH-groups with hexamethylene diisocyanate [structure according to Figure 9(a)]. The values are plotted as if an interpenetrated structure were present. *W* relates to the inter- and intramolecular crosslinked gels of Wesslau¹⁴, prepared by crosslinking copolymerization [structure according to Figure 9(c)]. *F* is the Flory line with $v_{e(\text{phys.})} = v_{e(\text{chem.})}$. For a_I and *b*, see Figure 10.

the intermolecular part of crosslinks—and their distribution—are from case to case identical with the degree of crosslinking of the corresponding *b*-samples, prepared with the same polymer concentration. So the a_1 -curve is the result. One sees that the intramolecular crosslinks additionally present effect a considerable reinforcement of the gels.

Assuming an interpenetrating structure for the *a*-gels (which is understandable only by ignoring the experimental results of the conversion study of the $P_x + P_y$ -reaction) we have to use higher proportions of intermolecular crosslinks. The values, depending on the polymer concentration, result theoretically from the frequency of combination of the functional groups. According to a simple statistical calculation they increase from 50 per cent (with a polymer concentration of ten per cent) to approximately 75 per cent (with a polymer concentration of 20 per cent). If one plots the experimental *S*-values against these statistical values of the intermolecular crosslinks (as the product of $v_e(v_2^0)^3$), one obtains the curve a_{II} . The position of this curve contradicts the previous experimental facts of networks with interpenetrated structure¹⁴.

In order to illustrate this with an example, in *Figure 11* the mechanical behaviour of our gels is compared with that one of Wesslau's¹⁴ gels, which were prepared by crosslinking copolymerization. For this purpose we have to use the ordinary kind of representation, namely the plotting of the physical degree of crosslinking (calculated from the experimental *S*-values by means of the Flory-equation) against the intermolecular chemical degree of crosslinking (analytically determined or stoichiometrically calculated). It is to be seen that it is impossible to accommodate the a_{II} -curve beside the Wesslau-curve (*W*). Thereby we have to consider that the a_{II} -curve is a limit-curve with the lowest imaginable proportion of intermolecular crosslinks for an interpenetrated system prepared by crosslinking reaction through functional groups. With increasing proportions of intermolecular crosslinks the position of the a_{II} -curve would be more to the right.

The experimental results of *Figures 10* and *11* relate to compression measurements on *cis*-1,4-polybutadiene gels prepared by crosslinking of five per cent polymer solutions. Analogous results have been obtained with two per cent solutions of polybutadiene⁵ and by measurement of the degree of swelling⁵. They are contained in *Figures 12* and *13*. The swelling measurements are interpreted by means of the Flory-Rehner-equation¹⁵. The χ -parameters were determined by osmotic measurements.

It is striking that in all cases—in accordance with previous measurements with polybutylacrylate gels¹⁶—the only intermolecularly crosslinked gels [structure model as in *Figure 9(b)*] show no intercept. This intercept has always been interpreted as a proof of the presence of mechanical entanglements. The absence of an intercept, therefore, can be understood as an indication of the absence of entanglements. The intercept with the *a*-gels is so small that it may be within the limit of experimental error.

As against this, in *Figure 14* the swelling behaviour of gels prepared by crosslinking copolymerization is shown. The gels of the curves (d_1) and (d_2) are prepared by polymerization of butylacrylate in the presence of polybutylacrylate with pendant acrylic double bonds, (d_1) in the presence of a solvent and (d_2) without a solvent [supposed structure as in *Figure 9(d)*]. The gels of the curve (*c*) are prepared by ordinary crosslinking copolymeriza-

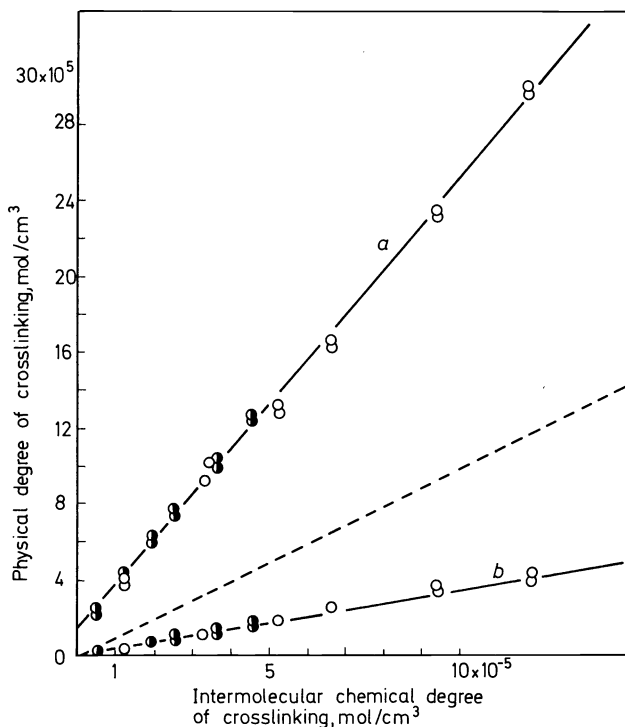


Figure 12. The physical degree of crosslinking from compression measurements of gels plotted against the intermolecular chemical degree of crosslinking. ● 2 mol% functional groups, ○ 5 mol% functional groups, *a* gels with inter- and intramolecular crosslinks, *b* gels with only intermolecular crosslinks.

tion of butylacrylate in the presence of butanediol diacrylate [supposed structure as in Figure 9(c)]. The comparison with curve (*b*) is not quite correct because it has not been proved that the χ -parameters in both cases are equal, but I think that with regard to the intercept there should be no doubt.

In accordance with the high degree of swelling, crosslinked rubbery polymers with *b*-structure [Figure 9(b)] show unusually high reversible stress. Figure 15 shows the comparison of four samples of butylacrylate picked out of a series of crosslinking experiments¹⁷ with masked isocyanato-groups fixed on the polymer chains. The *b*-samples are prepared by reaction of a polybutylacrylate with OH-groups at the chain with an equivalent amount of polybutylacrylate with masked NCO-groups at the chain. The two polymers were mixed in solution, the solutions were dried at room temperature and the films were heated under pressure in DIN-forms at 140°C. The *a*-samples were prepared in an analogous way but with an OH-group containing polybutylacrylate and masked toluylene diisocyanate.

Figure 15 shows the stress/force diagrams of four of these rubber samples, obtained with an Instron machine. It is to be seen that the *b*-rubbers have considerably higher stresses than the *a*-rubbers (nearly reversible stresses

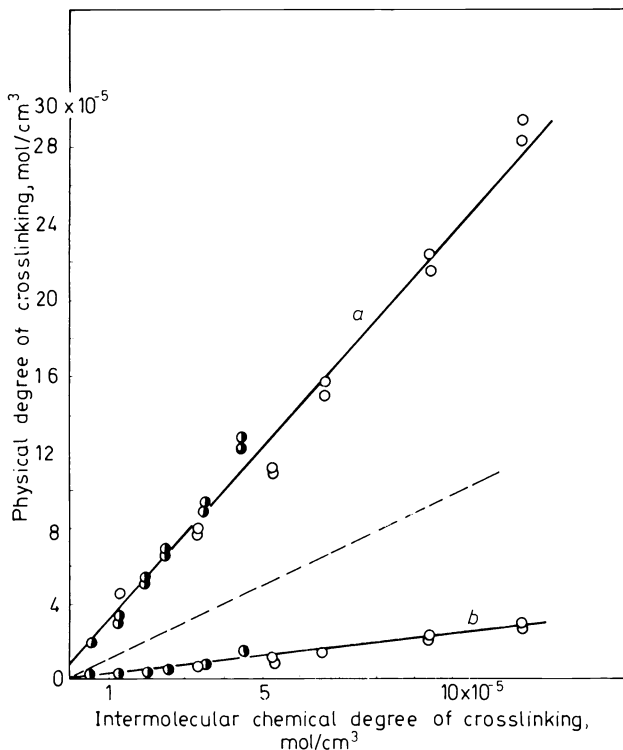


Figure 13. The physical degree of crosslinking (from swelling measurements) plotted against the intermolecular chemical degree of crosslinking. ● 2 mol% functional groups, ○ 5 mol% functional groups, *a* gels with inter- and intramolecular crosslinks, *b* gels with only intermolecular crosslinks.

up to 5300 per cent were measured). The *b*-curves show a characteristic run: after a normally increasing part a second part with constant force follows without a peak between the two parts.

The rubber samples are so selected that *a*(1) and *b*(1) have the same concentration of functional groups and *a*(2) and *b*(2) have the same degree of swelling. The much higher breaking-stress of *b*(1)—with lower tensile strength—is a consequence of the absence of intramolecular crosslinks, another example for the reinforcing effect of intramolecular crosslinks.

Especially interesting is the comparison of *a*(2) and *b*(2). Both samples have the same degree of swelling and, therefore, the same or at least a comparable degree of crosslinking*. In spite of this the breaking stress of *b*(2) is more than twice as high as that of *a*(2). The only structural difference, which might conceivably cause this considerable discrepancy of the mechanical properties, is the different distribution of the crosslinks: homogeneous in

* Really, the crosslink density of the *a*(2)-samples is even smaller than that of the *b*(2)-samples. This leads to a confirmation of the above conclusions.

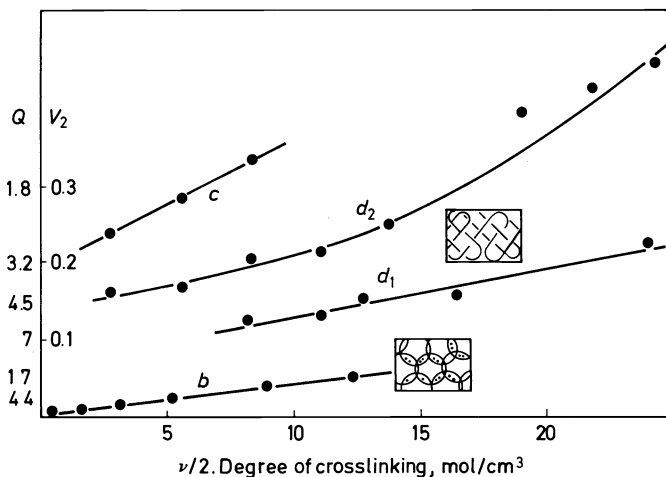


Figure 14. The degree of swelling as a function of the degree of crosslinking. Q denotes g solvent/g polymer, v_2 is cm^3 polymer/ cm^3 gel, d_1 relates to polybutylacrylate gels with predominantly intermolecular crosslinks prepared by copolymerization of polybutylacrylate with pendant double bonds with butylacrylate in the presence of 30 per cent acetone [assumed structure as in Figure 9(d)]. d_2 is the same, but copolymerized without the presence of an indifferent solvent, and c is for polybutylacrylate gels with inter- and intramolecular crosslinks prepared by ordinary crosslinking copolymerization of butylacrylate with 1, 2 and 3 mol% butanediol diacrylate.

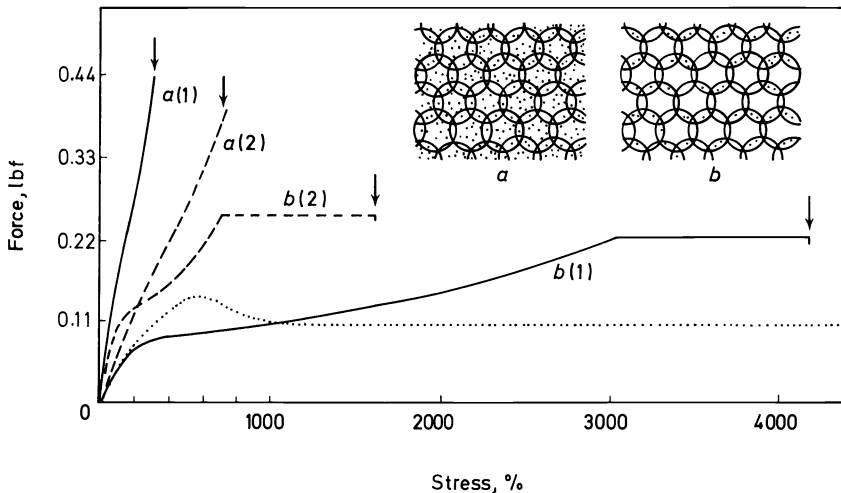


Figure 15. Stress/force diagram of solvent-free crosslinked polybutylacrylate samples, prepared by reaction of pendant OH-groups with masked NCO-groups at 140°C . a is for samples prepared by reaction of polybutylacrylate containing OH-groups with masked toluylene diisocyanate, while b denotes samples prepared by reaction of a polybutylacrylate containing OH-groups (P_x) with a polybutylacrylate containing masked NCO-groups (P_y). $a(1)$ and $b(1)$ samples have the same content of functional groups (1 mol%), and $a(2)$ and $b(2)$ samples have the same degree of swelling (7.5 g solvent/g polymer).

the case of $a(2)$ and heterogeneous in the sense of a cell pattern in the case of $b(2)$. The dotted line shows—for comparison—the behaviour of an uncross-linked polybutylacrylate sample.

If we comprehensively consider the results presented, obtained by deformation and swelling of gels and rubbers, we can say that there is indeed no direct proof for this or that certain aggregation structure, but we have made some experimental observations which cannot be understood with the supposition of the same interpenetrated molecular association for all gels and rubbers. This becomes understandable, however, if we assume the existence of different aggregation structures in the sense of *Figure 9*, depending on the method of preparation of the gels or rubbers. These different network structures were already postulated because of our conversion experiments on the $P_X + P_Y$ -reaction and two-step crosslinking copolymerization. We can, therefore, consider the results obtained by investigation of the mechanical behaviour of gels as a confirmation of the postulated structures.

SUMMARY DISCUSSION OF OUR EXPERIMENTS

We have studied different crosslinking reactions and the properties of the crosslinked polymers, in order to get information about the aggregation structure of polymers. Crosslinked systems are especially suitable for such investigations because we can fix from case to case any existing molecular association by crosslinks in a certain intended manner without destroying or changing the structure. If we interpret our experimental results rightly, we have to distinguish two different molecular associations.

In polymer solutions and films there exists a dense packing of individual polymer coils, which in the contact zones are more or less deeply interpenetrated in the sense of a paranemic interpenetration. The degree of interpenetration depends on the polymer concentration. In solvent-free films the overlap volume is about 40 to 50 per cent of the total volume and decreases continuously with decreasing polymer concentration to zero.

In polymer samples formed directly by polymerization there is probably a structure with plectonemically entangled or interpenetrated polymer chains. It is formed by the growth of polymer chains during chain propagation into already existing random coils.

This structure is probably stable only in a polymer material which has not been changed by deformation processes like injection moulding or extrusion. During the flowing phase the coils are disengaged and disentangled under the influence of the flow gradient. Otherwise a flow of molten polymer is not conceivable. How the macromolecules are arranged after the flow process depends not only on other external conditions like the rate of cooling but also on the primary chain structure of the polymers. I think that for example a melt of polycarbonate will behave in this situation quite differently from a melt of polystyrene or polymethylmethacrylate. It is well-known that the polymer molecules retain more or less completely their partially oriented state with strongly deformed coils. The difference between the different polymers may be given by the variable and strong tendency to reestablish the random coil state and by the proportion of chain segments, which is parallel-oriented by intramolecular chain folding and by intermolecular chain bundling.

COMMENTS ON EXPERIMENTS BY OTHER AUTHORS

In course of recent years some interesting papers have been published which have confirmed our concept of the aggregation structure of concentrated polymer solutions.

E. Turska¹⁸ and E. Turska, A. Dems and B. Bortnowska-Barela¹⁹ have shown in careful kinetic investigations that the rate of polycondensation is considerably greater in good solvents, i.e. in the state of lower coil density, than in poor solvents, in which the macromolecules are coiled more densely. According to Flory's theory, based on an interpenetrated coil structure, it should be inverted, because in theta solvents the excluded volume becomes zero. In accordance with the experiments of Turska, A. Horvath²⁰ has found that by reaction of pyromellitic dianhydride with benzidine in a short time polyimides with a weight average molecular weight of 500000 are formed, whereas polyimides with more flexible chains have much lower molecular weights (<30000) under optimum reaction conditions.

If we consider that all polycondensation reactions in the last phase (with conversions above 95 per cent) are reactions of different polymer coils in the sense of our $P_x + P_y$ -reaction, the effect of the coil density on the polycondensation rate is evident. Possibly the inability of random coils to interpenetrate is the main reason for the relatively low molecular weight of polymers formed by reaction of difunctional monomers compared with polymers formed by chain-reactions (e.g. radical or ionic polymerizations).

E. Papirer, J. B. Donnet, G. Riess and T. Nguyen²¹ have investigated the chain termination of anionically growing polystyrene at the surface of colloidal particles. The maximum amount of polystyrene molecules which can be fixed on the particle surface is explained with the limited interpenetration of the polystyrene coils.

S. H. Aharoni²² has shown that a homogeneous dense distribution of the chain segments, which permits only intermolecular interaction at the surface of the macromolecules (i.e. which allows an interpenetration of the coils only in the contact zones), is more suitable for describing the experimental behaviour (density measurements, calorimetric measurements and electron microscopy investigations) than a Gaussian density distribution, which requires a complete interpenetration in order to describe the behaviour of macromolecules in concentrated solutions.

J. B. Grebenscikoy, V. I. Irzhak, L. I. Kuzub, P. P. Kusch and N. S. Enikolopyan²³ have published a report of an investigation of the determination of the chain conformation of concentrated polyvinyl butyral solutions in ethanol through paramagnetic marking. Stable radicals forming groups were fixed on the chains and the average distance between the paramagnetic centres was determined by e.s.r. measurements of mixtures of marked and normal PVB with increasing total polymer concentrations. The results have shown that the PVB-coils are shrunk in concentrated solutions below the theta dimensions.

G. S. Y. Yeh²⁴ concludes from the distinct boundary and size limitation of nodules, which has been found by electron microscopy in PEPT, that the parallel chain segments in the nodules are caused by intramolecular chain folding.

Recently Maron²⁸ and co-workers could demonstrate by calorimetric measurements that the Maron-model is suitable for describing the polymer-polymer interactions.

On the other hand R. G. Kirste and W. A. Kruse²⁵ have shown by neutron scattering that in bulk polymers of polymethylmethacrylate the radius of gyration is the same as in theta solvents. Measurement in the glassy state has been made possible by polymerization of deuterium-methylmethacrylate in the presence of normal polymethylmethacrylate. The result is in accordance with the concept of the crosslinking copolymerization shown in *Figure 8*.

H. Benoit²⁶ has carried out the same experimental technique on polystyrene with the same result.

I am not sure that the light scattering method is the most suitable method for measurement of degree of coil interpenetration as a function of polymer concentration, because it relates to a linear dimension of the coil, namely the radius of gyration. It can be considered certain that the coils have an average shape of ellipsoids, but we cannot be sure that the coils—with increasing polymer concentration—will shrink isotropically without changing the ratio of the short to the long diameter of the ellipsoid. In other words: it is not obvious that a constant radius of gyration is always a proof of complete coil interpenetration.

With the method of chemical marking by functional groups the complicated relations between shape and diameter have no influence on the measurements (analytical determinations). The results relate directly to coil volume. The part of the volume is determined, which is commonly occupied by chain segments of neighbouring coils.

CHAIN ASSOCIATION INSIDE THE POLYMER COILS

The structure model of concentrated polymer solutions and non-crystalline films as deduced by means of our method (compare *Figure 7*) does not exclude a certain degree of order, which increases with increasing polymer concentration. But in contrast to the Pechhold-model²⁷, order in our model is based on an intramolecular folding of chain segments as schematically demonstrated in *Figure 16*.

Intramolecular folding of the polymer chains inside the coils results from the inability of parts of a coil to mix unrestrictedly by interpenetration. This, again, follows inevitably from the experimental results concerning incomplete interpenetration of coils in concentrated solutions. If different coils (of the same type) cannot interpenetrate, this must hold true also for different parts of the same coil. This becomes clear at once if we imagine that the chain ends of two polymer coils are connected with one another in the formation of a new coil with a correspondingly longer chain. There is no reason why the parts of the new bigger coil should behave basically differently from the two macromolecules (in a concentrated solution) before the combination. Random coils are, therefore, irregularly folded polymer chains. The micro-Brownian movement would be better characterized as an oscillation of chain segments than as a translational movement. Thus the structure (b) of *Figure 16* is—with regard to intramolecular chain folding—already preformed in the random coils of diluted solutions.

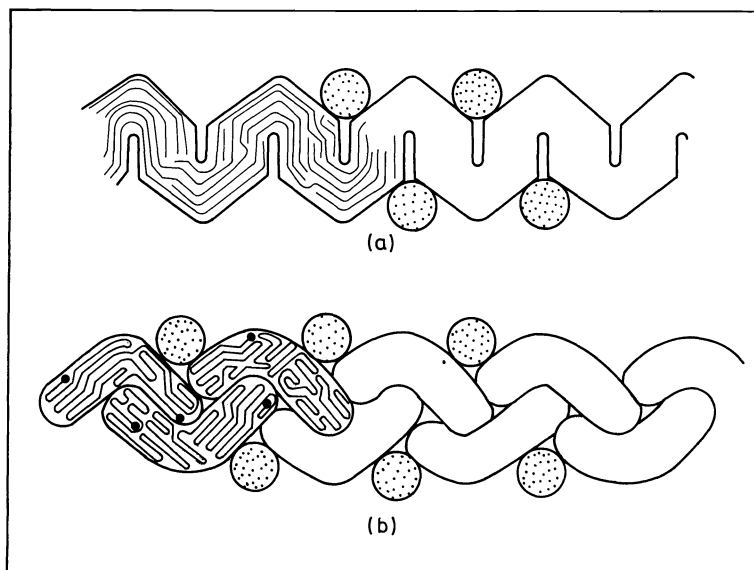


Figure 16. Chain association in highly concentrated polymer solutions and in polymer films. (a) Meander-model of Pechhold and Blasenbrey¹⁶ with intermolecular folded chains; (b) Individual coil structure-model according to Figure 7.

If we survey the results concerning association of macromolecules in non-crystalline aggregation states, we have the impression that this question soon will be less: do the random coils interpenetrate or not, but rather: when, i.e. under what conditions, do they interpenetrate and when do they form a densely packed association, and what is then the degree of interpenetration?

REFERENCES

- ¹ P. J. Flory, *Principles of Polymer Chemistry*, pp 458 and 505. Cornell University Press: Ithaca (1953); *International Symposium on Macromolecules, Helsinki (July 1972) (IUPAC)*, pp 1-17. Butterworths: London (1972).
- ² S. H. Maron, N. Nakajima and I. M. Krieger, *J. Polym. Sci.* **37**, 1 (1959).
- ³ S. Onogi, T. Masuda, N. Miyana and Y. Kimura, *J. Polym. Sci. A-2*, **5**, 899 (1967).
- ⁴ B. Vollmert and H. Stutz, *Angew. Makromol. Chem.* **20**, 71-101 (1971).
- ⁵ J. Stemper, *Dissertation*, Polymer-Institut der Universität Karlsruhe (1974).
- ⁶ B. Vollmert and H. Stutz, *Angew. Makromol. Chem.* **3**, 182-189 (1968).
- ⁷ See ref. 1, pp. 519-20 and 523-30.
- ⁸ J. Kopecec, J. Jokl and D. Lim, *J. Polym. Sci. C*, **16**, 3877 (1968).
- ⁹ J. Malinský, J. Klaban and K. Dušek, *J. Macromol. Sci. A-5*, 1072 (1972).
- ¹⁰ S. Loshaek and T. G. Fox, *J. Amer. Chem. Soc.* **75**, 3544 (1953).
- ¹¹ H. Wesslau, *Angew. Makromol. Chem.* **1**, 56-77 (1967).
- ¹² E. F. Cluff, E. K. Gladding and R. Pariser, *J. Polym. Sci.* **45**, 341 (1960).
- ¹³ J. P. Flory, *J. Amer. Chem. Soc.* **78**, 5222 (1956).
- ¹⁴ H. Wesslau, *Makromol. Chem.* **93**, 55-68 (1966).
- ¹⁵ P. J. Flory and J. Rehner, *J. Chem. Phys.* **11**, 521 (1943).
- ¹⁶ B. Vollmert and H. Stutz, *Colloidal and Morphological Behavior of Block and Graft Copolymers* (Ed.: G. Molau). Plenum: New York (1971).

MOLECULAR HETEROGENEITIES OF MACROMOLECULES

- ¹⁷ J. Stemper, *Diplomarbeit*, Polymer-Institut der Universität Karlsruhe (1972);
B. Vollmert, H. Stutz and J. Stemper, *Angew. Makromol. Chem.* **25**, 187–191 (1972).
- ¹⁸ E. Turska, *J. Prakt. Chem.* **313**, 387–396 (1971).
- ¹⁹ E. Turska, A. Dems and B. Bortnowska-Barela, *J. Polym. Sci. (Polym. Symp.)* **42**, 419–428 (1973).
- ²⁰ B. Vollmert and A. Horvath, *Angew. Makromol. Chem.* **23**, 117–139 (1972).
- ²¹ E. Papirer, J. B. Donnet, G. Riess and T. Nguyen, *Angew. Makromol. Chem.* **19**, 65 (1971).
- ²² S. H. Aharoni, *J. Macromol. Sci.-Phys. B*, **7**, 73–103 (1973).
- ²³ J. B. Grebenscikov, V. I. Irzhak, L. I. Kuzub, P. P. Kusch and N. S. Enikolopyan, *Dokl. Akad. Nauk SSSR, Ser. Khim.* **210**, 1124–26 (1973).
- ²⁴ G. S. Y. Yeh, *J. Macromol. Sci. B*, **6**, 465 (1972).
- ²⁵ R. G. Kirste, W. A. Kruse and J. Schelten, *Makromol. Chem.* **162**, 299–303 (1972).
- ²⁶ H. Benoit, Paper presented at Makromolekulares Kolloquium, Freiburg i.Br. (1974).
- ²⁷ W. Pechhold and S. Blasenbrey, *Kolloid-Z. Z. Polymere*, **241**, 955 (1970).
- ²⁸ S. H. Maron and R. B. Renznik, *J. Polym. Sci. A*, **2**, 309 (1969);
S. H. Maron and F. E. Filisko, *J. Macromol. Sci. B*, **6**(2), 413 (1972);
S. H. Maron and M. S. Lee, *J. Macromol. Sci. B*, **7**(1), 31 (1973).