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My Fifty Years with Polymer Gels and Networks and Beyond*

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Introduction

I started my scientific career in 1953 as a PhD student in Pardubice (Eastern Bohemia) at the Research Institute for Synthetic Resins and Lacquers (RISRL) and my PhD Thesis was dealing with something related to crosslinked polymers but not yet quite crosslinked – kinetics of the initial stages of manifold reactions of thiourea with formaldehyde [1], [2]. By the end of my study, I got interested in research done by another group – synthesis of crosslinked styrene-divinylbenzene copolymers as matrices for ion exchange resins. During the PhD study, I was lucky to get photocopies of some chapters of Flory's book "Principles of Polymer Chemistry" [3]. Only two pieces existed at that time in the country due to currency problems and central regulation of import. I was very impressed by the way Flory was treating formation of polymers and their properties and could offer the fellow researchers the equilibrium swelling as a method for characterization of crosslink density. Later, I joined that group.

Swelling, phase separation and phase transition in crosslinking systems

At that time, the porous or macroporous matrices and ion exchange resins were emerging. They were obtained by copolymerization of styrene and divinylbenzene in the presence of non-polymerizable additives (diluents). The effect of additives was peculiar; some of them, like poor solvents (precipitants) for polystyrene, could be understood, but it seemed strange that good solvents and even linear polystyrene above certain molecular weight and concentration limits were also effective. In the (patent) literature, there appeared some wild speculations of replicas of polystyrene coils. However, the voids were by one or two orders of magnitude larger then was the coil diameter. Being nurtured on Flory's ideas, I felt that the reason must be in

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thermodynamics – the thermodynamic instability: the crosslinking process must induce phase separation, and both phases should be in equilibrium. The key should be found in the swelling equation. I took first a simple system of crosslinking of a polymer dissolved in a diluent. My reasoning was that the thermodynamic equilibrium was existing not only between swollen gel and diluent but also between swollen gel and diluent vapor expressed correctly by solvent fugacities but with a good approximation solvent vapor pressures. The key was to be found, I reasoned, in the swelling equation for binary solvent/ crosslinked polymer system [4]:

$$\frac{\Delta\mu_1}{RT} = \ln a_1 = \ln\varphi_1 + \varphi_2 + \chi\varphi_2^2 + \nu_e V_1[A\varphi_2^{1/3}\varphi_0^{2/3} - B\varphi_2]$$
$$\ln a_1 \approx \ln(p_1 / p_1^0) \qquad \textbf{(1)}$$

where $\Delta\mu_1$ is the change of chemical potential of the diluent with respect to pure diluent, φ_1, and φ_2 are volume fractions of solvent and polymer, respectively, χ is the Flory-Huggins interaction parameter, ν_e is the concentration of elastically active network chains, V_1 is molar volume of the diluent, A and B are factors depending on chain interactions, a_1 is the activity of diluent, and p_1 and p_1^0 are vapor pressures of diluent over the gel and pure solvent, respectively. The key parameter in phase separation was the memory term φ_0. It was originally not considered [3] but was introduced later [5], [6]. The memory factor expresses, disregarding the interaction effects, the state of network chains in the dry state when the diluent present during polymerization has been removed. Thus $\varphi_0 = V_{\text{dry}}/V_{\text{network formation}}$. A simple condition should hold that the volume of the diluent in the forming gel cannot exceed the swelling capacity of the forming gel and the excess must phase-separate. In terms of eq. (1) it means that at incipient phase separation [7]

$$\varphi_2 = \varphi_0 \qquad \textbf{(2)}$$

or

$$0 = \ln(1-\varphi_0) + \varphi_0 + \chi\varphi_0^2 + \nu_e V_1[A\varphi_0 - B\varphi_0] \qquad \textbf{(3)}$$

What happens, when a network is formed beyond the gel point, when the sol fraction is negligible, is shown schematically in Fig. 1.

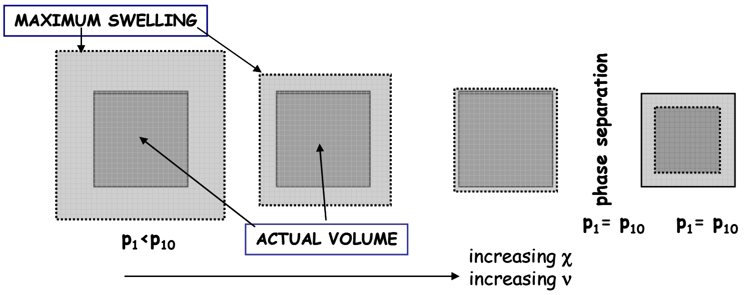

Figure 1. Macrophase separation during formation of network in the presence of diluent.

Initially, the activity of the solvent is lower than 1 and the system is in equilibrium with solvent of activity $a_1 < 1$, i.e., $p_1 < p_1^0$. If such a piece of gel is immersed into pure diluent, it will swell (much) more. If crosslinking continues, as the diluent vapor pressure increases, the gel volume after immersion in pure solvent increases less, until at $p_1 = p_1^0$ there is no volume change upon immersion into the solvent, but $p_1 = p_1^0$ continues to hold. Further crosslinking causes separation (sweating out) of excess diluent and the gel volume shrinks (macrosyneresis). The condition for binary system was later extended to ternary systems – network + two additives [4], [8] because the real system, we were dealing with, was at least ternary: polymer-monomer(s)-diluent. Thus, the limits of appearance of porosity and pore volumes well correlated with the amount of diluent (φ_0), its interaction with the network polymer (χ), concentration of elastically active network chains (effective crosslink density) (ν_e) and increasing molar volume of the diluent (V_1) – remember the effect of polystyrene. This was summarized in our review compiled with the Mainz group where GPC as an analytical tool was being developed [9].

However, we were aware of the fact that this model is too simple for formation of porous structures by crosslinking chain copolymerization in the presence of diluents. As stated above, the system is multicomponent. Not two bulk phases, but interdispersion of phases is formed. Interfacial energy plays a role in determining the morphologies of the separated phases, and phase separation occurs in the vicinity of the gel point, so that the sol fraction plays a role. Also, what we did not know at that time, the crosslinking chain copolymerization is one of the most non-ideal network formation processes.

However, this initial involvement in the world of crosslinking and networks at the end of fifties and early sixties determined my further scientific pathways. The stifling political atmosphere of the Communist regime and its mistrust in intellectuals initiated by Communist experience of Hungarian revolution in 1956 launched in 1958 political purges. They affected also RISRL and made the atmosphere hardly bearable. I decided to accept the invitation by Otto Wichterle, my former university teacher, to join his new Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences in Prague. At that time, the Academy was somewhat less prosecuted and became a refuge for some scientists from universities and from elsewhere. But it took six years more before I was allowed to leave Pardubice and to continue my further career in Prague. The experience with crosslinked polymers, swelling, and phase separation affected my look at Wichterle's hydrogels and I was soon able to understand many things characteristic of the macroporous network formation. Phase separation occurred in hydrogels initially in the form of microsyneresis when χ was changed and the crosslink density was low. This was, however, not a stable state and this state was slowly transformed into the equilibrium macrosyneresis (Fig. 2) [10].
However, when the thermodynamic instability arises during crosslinking, the microsyneretic state is fixed and turbidity and porosity are permanent (Fig. 2) [11].
The morphology of the microseparated phase is determined by the interfacial tension between gel and liquid, on the progress of the network formation process and on the ratio of volumes of concentrated and dilute (solvent) phases, $\phi = V_{\text{conc}}/V_{\text{dil}}$. The droplets in gel morphology are formed at low crosslink densities, at high ϕ and higher interfacial tension. A structure with communicating pores corresponds to the vicinity of the gel point, to low ϕ and to a range of lower interfacial tensions. This is approximately the case of crosslinking copolymerization. In reality, the situation can be much more complex because the kinetics is too fast and equilibrium is not reached, because the monomer is also a component, the system is at least pseudoternary or in

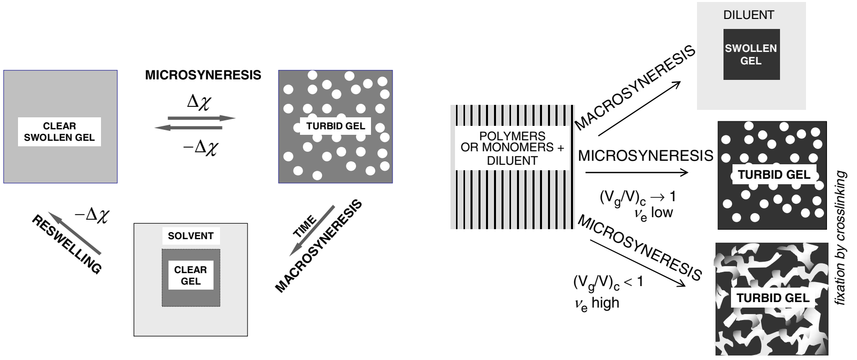

Figure 2. Phase separation (left) in crosslinked gel upon change of polymer solvent interactions; (right) during crosslinking.

most cases pseudoquaternary (monomer, diluent, polydisperse sol, crosslinked polymer). Transfer of liquid components between phases and fractionation may also occur. For high reaction rates, spinodal decomposition instead of nucleation and growth may be operative. Despite of these complications, it has been confirmed that thermodynamics is the driving force in phase separation and that predictions based on equilibrium thermodynamics are valuable for system selections as is well demonstrated in a recent monograph [12].

The macrosyneresis case shown in the upper part of Fig. 2 (right) was the only form of phase separation observed in our later studies [13] of phase separation in high-solid polyurethane coating formulations. Phase separation took place well beyond the gel point at a relatively high and slowly rising crosslink density. The model used there was a pseudoternary one – solvent - polydisperse sol – network polymer. It took into account the change of molecular weight of the sol as well as differences in sol and gel composition and, as a result, the change of the three interaction parameters. Our knowledge of modeling of the network formation developed by that time was very helpful. In the film formation process, crosslinking, increasing the solvent activity, a_1, is accompanied by solvent evaporation by which a_1 is lowered. Thus, the theoretical analysis can help in selection of the solvent to avoid phase separation but to keep the solvent activity high in order to assist the evaporation in the later stages of film formation.

There was another line of ideas developed from the studies of styrene-divinylbenzene copolymers and phase separation studies. When examining the effect of the memory term φ_0, characterizing the dilution at network formation, on solvent chemical potential dependences, I found that some dependences have two maxima (at that time only logarithmic tables and hand-driven calculators were available!) (Fig. 3 (left)). Such a behavior reminded a van der Waals gas and it suggested that phase equilibria between gel phases of different degrees of swelling should exist (Fig 3 (right)).

At the Prague IUPAC Macromolecular Symposium 1965, I met Donald Patterson, who was well known for his important contribution to understanding polymer solution by developing the corresponding states theory, and we were discussing the strange phenomenon predicted for simple systems and based on simple mean-field thermodynamics. The physical essence of the phenomenon is that the repulsive forces of the supercoiled network chains are opposed by attractive interactions of polymer

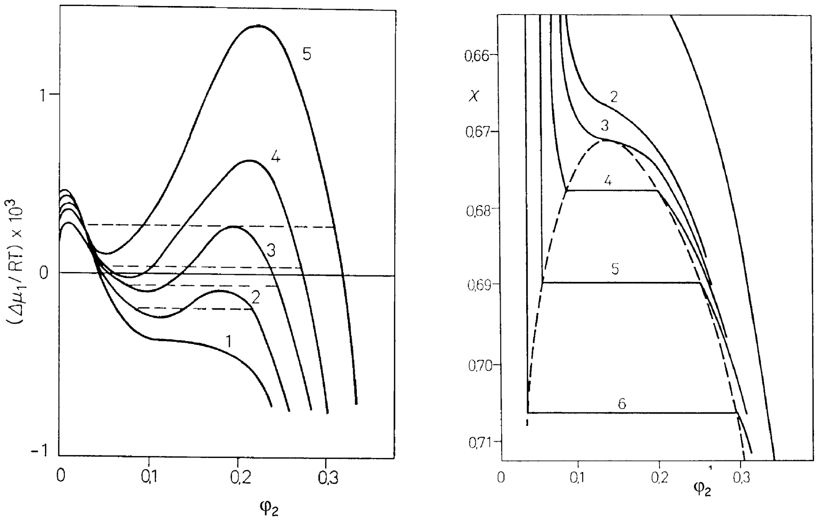

Figure 3. (left) dependence of the chemical potential of solvent on polymer concentration for gel exhibiting phase transition; (right) phase equilibria as a function of the interaction parameter χ (e.g., temperature) for different concentration of elastically active network chains [14].

segments in a moderately poor solvent. Don drew my attention to the lecture of Oleg Ptitsyn on coil-globule transition of single chain where chemical potential curves of similar shape as those in Fig. 3 (left) were obtained but for an ionized chain. We decided to write a paper [14]. However, for me it was puzzling how such transition could look like experimentally and I was somewhat worried by the fact that nobody so far had reported on such a finding. Eventually, the thermodynamic analysis showed that it would be difficult to prepare such gels because high dilution and higher crosslink density were mutually exclusive and might end up in the gel-liquid phase separation discussed before. The optimistic outlook was that tensile deformation or concentration dependence of the χ-parameter will facilitate the transition. One of the referees of the paper suggested a drastic reduction of the manuscript because a phenomenon which has not been observed experimentally and is hardly observable does not deserve much space [15]. So, among other things, the considerations about concentration dependences of χ were taken out. As it came out later, the dependence was important. Ten years later, Toyoichi Tanaka discovered this transition experimentally examining ionized gels [16] and interpreted it independently as first-order transition. Since then, thousands of papers and many monographs have been published on this subject, because the volume phase transition is interesting not only theoretically but it is a basis for many applications especially in medicine but not only there. I personally did not take part in the boom of gel transition research activities after Tanaka's discovery because I was absorbed by other problems, but I have to mention two instances where I got involved.

The first one was the almost forgotten effect of concentration dependence of the χ parameter on volume phase transition. Also, the early days finding that the concentration dependences of χ such that found for poly(2-hydroxyethyl methacrylate) in some alcohols do not have the critical temperature for infinite molecular weight located at zero polymer concentration [17] as is the classical definition of

Θ-temperature. Moreover, Flory and Erman [18] reasoned later that the swelling transition can be induced by complex interaction. Inspired by results accumulated on poly(*N*-isopropylacrylamide) (PNIPA) gels, one class of few uncharged gels exhibiting phase volume transition, we - Ron Koningsveld, Hugo Berghmans, and myself - focused on the concentration dependences of χ problem and Karel Solc, master of phase equilibria, was in lead in formulating the categories of systems with "off-zero" critical concentration according to the functional form of concentration dependences of χ [19]. The rigorous experimental and thermodynamic analysis of PNIPA and poly(vinyl methyl ether) systems [20] revealed, among other things, the fact that for transition in this type of gels crosslinks are not necessary. The crosslinks just secure the gel integrity at temperatures where the gel would go over to solution.

More recently we, my wife Mirka and I, were motivated by interaction with my former colleague and world known specialist in medical gels in the University of Utah, Jindrich (Henry) Kopecek. His group was developing hybrid gels [21] in which (ordered) polypeptidic motifs were chemically bonded to or strongly complexed with disordered hydrophillic chains as crosslinks or side chains. A detail of such gel is shown in Fig 4.

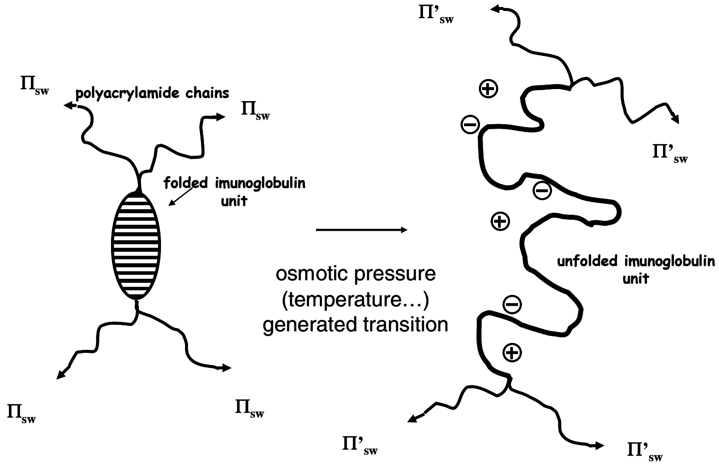

Figure 4. Hybrid biopolymer gel containing built-in imunoglobulin units. They unfold under the action of tensile force and expose new interacting surface [22].

The gel shown in Fig. 4 contains immunoglobulin units of the cardiovascular protein titin. When a tensile force is applied to the end of a titin molecule the immunoglobulin (IG) units reversibly unfold. The primary role of polyacrylamide (PA) gel is to collect and sum responses of individual IG units, so that the collective response is sensed on macroscopic scale.

Here, the role of the PA gel is much more active: it is a generator of osmotic forces that act at the ends of IG units and force them to unfold when the force exceeds the critical value. Since the interacting surface exposed by unfolding is more hydrophilic, all IG units are unfolded at once and an abrupt swelling transition developes [22]. Because the new interacting surface is exposed after transition, a hysteresis in reswelling-deswelling curves is expected. Interesting is the predicted case when the order-disorder transition is coupled with classical transition (supercoiled – normally

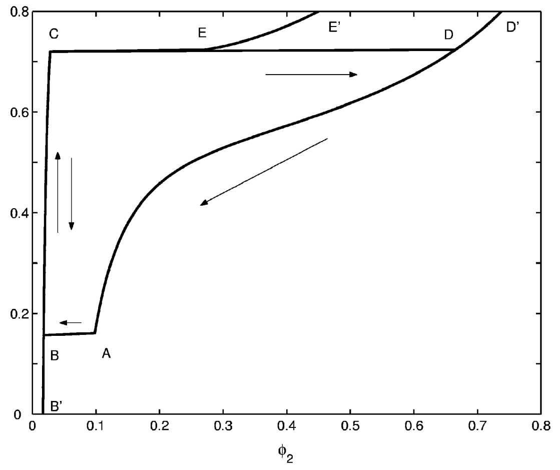

Figure 5. Order-disorder swelling transition (A to B) (see Fig. 4) combined with disorder to order transition and conventional collapse transition (C to D). The transition goes along the arrows. For details, see [17].

coiled) discussed above. A model example is seen in Fig. 5. Starting at point D', swelling increases continuously until point A is reached, then swelling increases jumpwise as a result of the order-to-disorder (folded-unfolded) transition. From B to C, swelling degree is high but does not change much and at C, the gel starts collapsing in a jump until point D is reached. In the field of gels and hydrogels in particular, many challenges for both experimentalists and theories are ahead.

Network formation/free-radical copolymerization

Let us move along another path originating in my early days spent with styrene-divinylbenzene networks. Free-radical copolymerization of mono- and polyunsaturated monomers has been a common way of preparing crosslinked polymers. At the time of my involvement in the styrene-divinylbenzene research, it was commonly accepted that this "three-dimensional" polymerization is nothing but extension of linear polymerization of monounsaturated monomers differing in the formation of pendant double bonds and their further involvement in copolymerization. Many copolymerization parameters studies were performed and published and discussions were going on about the same or different reactivity of pendant double bonds. Today these studies are worthless. There were indications in the literature pointing to non-idealities – formation of inhomogeneities [23] or enhanced cyclization [24]. Also, we were finding strong deviations from the concept of normal branching in the development of fraction of pendant double bonds, in swelling of postcritical weak gels, high gel-point conversion, etc. Very meaningful was the study of pregel polymers isolated from the reaction mixture at conversions around 1 % or less [25]. It was found that already at this level, compact, internally crosslinked polymer structures are formed primarily due to strong cyclization. In these compact structures the pendant double bonds lose their reactivity and only the double bonds in the peripheral shell are active in branching.

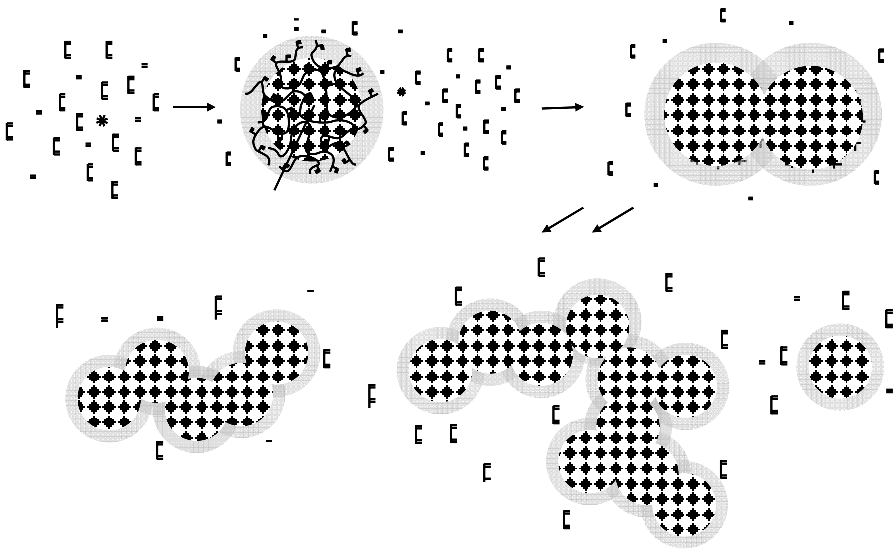

Figure 6. Mechanism of network formation by crosslinking chain copolymerization at higher concentrations of the divinyl monomer. The periphery of compact structures where pendant double bonds are accessible is in light gray.

Using these data and other taken from the literature, the picture of network formation was presented in a review [26]. It reminds somewhat colloid coagulation. The non-ideality manifests itself by a shift of the gel point conversion by a factor of 10 – 10^2 compared to the ring-free case. Such a picture is valid for higher concentration of the bis- or polyunsaturated monomer. For low concentrations and long bridges between the double bonds in the bisunsaturated monomer, cyclization is weak and the mechanism approaches that of ring-free random branching [27]. Everybody who wants to update the knowledge of the specificities of chain crosslinking copolymerization should consult reviews by Matsumoto [28] and Okay [29].

Milestones

To explain what is happening structurally during network formation was always our concern. The first milestone in my scientific career was the move from Pardubice to Prague to join the Institute of Macromolecular Chemistry. In this context, I have to mention two events important for me. The first one was the invitation by Prof. Willem Prins to come to Technical University in Delft for five months. Willem was a student of Debye and son of famous physicist Jan Prins. We knew each other only from our correspondence and Otto Wichterle kindly arranged permission for me to be allowed to go. It was late 1967 on the verge of Prague Spring. Willem said: “You and I will write a review on networks. It must be finished during these five months”. (Unfortunately, Willem perished in a storm sailing on Ontario Lake in 1974.) We decided to include description of structure evolution during network formation. I was relatively well acquainted with the combinatorial approach used by Flory and Stockmayer. I knew of the new cascade theory by Manfred Gordon, but initially I understood nothing. After weeks of study, working through the mathematical language of his co-author, Good followed by a short hop off to Colchester to discuss with Manfred, I started to enjoy the generating functions and recurrence of cascades of bonds. Meeting Manfred and being in touch with him was the second major event. Manfred, born in Leipzig, emigrated to Switzerland and then to England. He was a great personality, knowledgeable in philosophy and linguistically gifted (he was able to read Dante Alighieri in original). Later on, realizing what the limits of statistical theories were, I always preferred the clear definition of fractions of building units in different reaction states and bond types connecting them using probability generating functions as a tool to describe various chemically complex pathways. Equipped with this powerful tool, we in our Polymer Networks Laboratory at Institute of Macromolecular Chemistry could address many problems interesting for industrial research. Long-lasting collaborations with DuPont and DSM companies as well as with my parent Pardubice Institute (now SYNPO) have been very important for me and have taught me to look for the solutions to problems that are needed.

Network formation/step reactions

At that level of our knowledge, the very non-ideal chain crosslinking copolymerization was too difficult to be treated by theory with sufficient rigor. In the early seventies we started looking into curing of epoxy resins and crosslinking of liquid rubbers.

Although the chemistry of epoxide group was relatively well known, the cured epoxy resins were considered at that time to be intractable materials. They were said to be inhomogeneous (electron microscopy, calorimetry) and they disintegrated during swelling. We were able to show that some cured epoxies are very ideal networks without any inhomogeneities [30], even ideal in the sense that there was practically no cyclization. The combined experimental and theoretical work on amine-epoxide systems showed how the gel point conversion depended on composition, functionality and reactivities of involved amine groups [31]. Also, the "critical molar ratio" at which gelation does not occur at all, was defined and usefulness and experimental easiness of work with non-reactive off-stoichiometric networks was demonstrated. The combined experimental-theoretical work was extended to other epoxy systems and the results were summarized in a review [32] which was a part of a multivolume monograph "Epoxy Resins and Composites" [33] published by Springer in the series *Advances in Polymer Science.* About the same time, we organized the 9th Prague Discussion Conference "Crosslinked Epoxies". The epoxy networks work continued with an intensive study of curing of *N*,*N*,*N'*,*N'*-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM, Ciba-Geigy epoxy resin MY720) which was selected for C-fiber-epoxy high-performance composites used mainly in aircraft applications in the U.S. and Europe. The diglycidylamine group has several special features in curing with polyamines due to the closeness of glycidyl groups: formation of small six- to eight-membered cycles, intramolecular catalysis, when the formed amino alcohol catalyses ring opening of the neighboring glycidyl group, etc. (see sample papers [34]). The reaction scheme in Fig. 7 shows the small rings formed on the right.

In polyepoxide curing, there are such reactions that cannot be well described by statistical theory. Then the kinetic theory should be used instead, or the so-called "combined method" where the kinetic theory was applied to finite chemical fragments (superspecies) and these were recombined to form a network. The instances of such

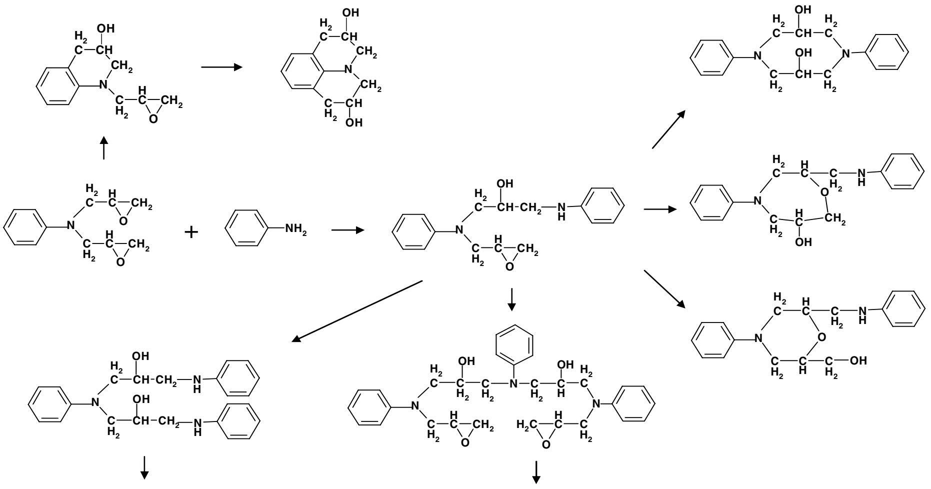

Figure 7. Various reaction paths in reaction of *N*,*N*-diglycidylaniline with primary amine as model for curing of epoxy resins with *N*,*N*,*N'*,*N'*- tetraglycidyl-4,4'-diamino-diphenylmethane [34].

processes are ionic curing and polyetherification released by the OH group formed in the epoxy-amine reaction [35]. On the example of acid curing (polycarboxylic acids and cyclic anhydrides), it was shown how important the reaction mechanism can be for network structure development [36]. Another issue addressing us during the curing studies was the transition of the system from the rubbery into glassy state. It affected not only the kinetics (transition from the kinetics into the overall diffusion control, but there was also a question whether gelation and network build-up were affected by diffusion control [37]. The answer was such that the gel point conversion and other network parameters did not depend on whether the reaction took place well above T_g or in the glass transition region (much slower).

The investigation of *polyurethane networks* by our group started in conjunction with crosslinking of telechelic OH functional polymers (polyethers, polybutadiene) in which also other laboratories in Czechoslovakia took part. Development of cast tire was one of the possible goals. Again, combined theoretical and experimental approaches were used. For stoichiometric and off-stoichiometric polyurethane networks, it was clearly shown that side reactions meaning additional crosslinking took place when isocyanate groups were in excess [38]. The effect of side reactions on network formation (allophanate, biuret formation) could be quantified [39] (cf. also the review in Ref [38]). Compared to epoxy systems, the probability of various side reactions was higher and cyclization played a more important role.

For us an evergreen, the polyurethane chemistry has been continuing in our research program since about 1975, recently more in the direction of coatings. A new issue came into the focus of our attention: polymer networks precursors of designed architecture, i.e. various structures having functional groups of the same type, and especially, their effect on network structure development and properties [40],[41]. The purpose of varying the precursor architecture – the skeleton carrying functional groups - has several reasons, such as

- bringing a special chemical environment into the network that determines thermomechanical and other end-use properties

- adjusting pot life which is given by precursor functionality and group reactivity
- adjusting initial viscosity necessary for the selected processing technology
- adjusting crosslink density of the final network
- adjusting shrinkage
- introducing controlled nano- or microheterogeneities into the network that affect network properties

The variation of architecture and various ways of preparation has introduced other at that time not well understood problems of *distributions* in degrees of polymerization, molecular weights, number of functional groups per precursor molecule, group reactivity in one precursor molecule, and among precursor molecules of different size and shape (microgels, hyperbranched polymers). The other problem requiring more

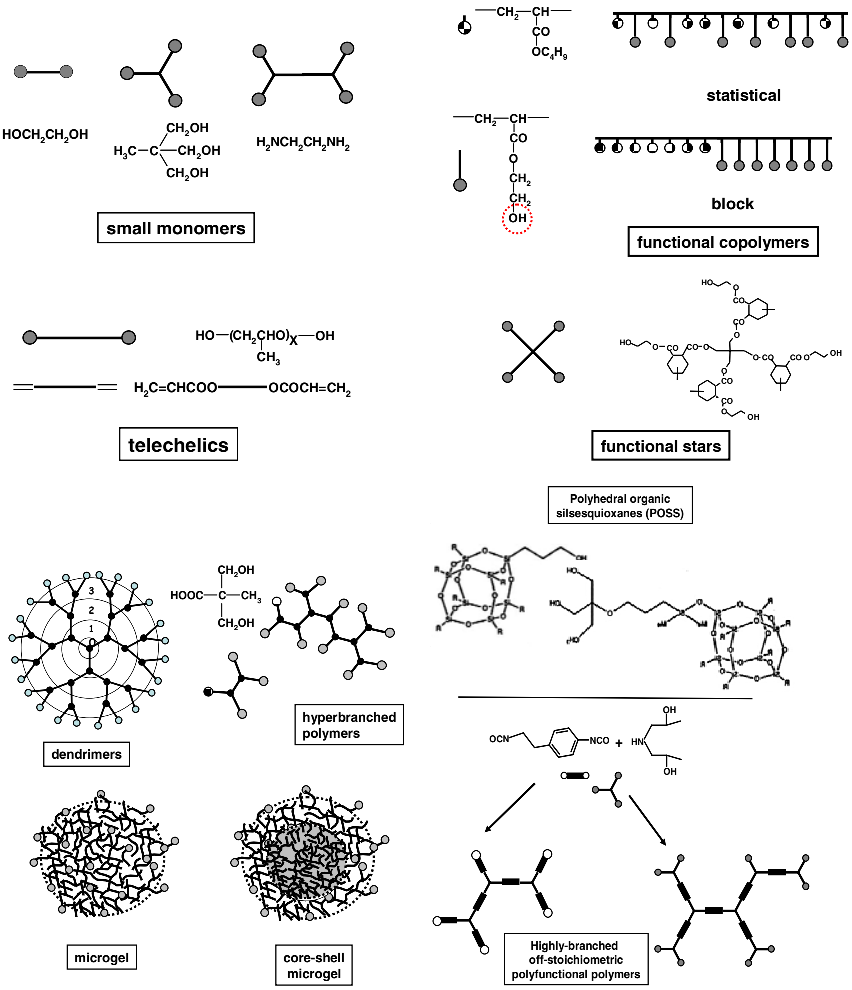

Figure 8. Functional precursors of polymer networks of various architecture. Schematic representation of the shape and functional groups of the precursor is sometimes accompanied by examples of chemical structures.

understanding was the contribution of the precursor to crosslink density by its internal branch points. These contributions range from a simple increase in concentration of elastically active network chains to filler effects. Here, it is still a long way to go both on experimental and theoretical paths.

With respect to coating applications, new relations have been elucidated, such as coating film formation by simultaneous crosslinking and solvent evaporation, especially in systems in which, during crosslinking and solvent evaporation, the systems passes from liquid to glassy state. The appearance of glass transition is crucial. On its road to final state, the coating film meets various physical phenomena playing role in network formation and development of gradients [42].

Modeling of network formation and structure

Modeling of polymer formation in general and of branched and crosslinked structures in particular interested me from the beginning and the combinatorial approach by Flory and Stockmayer brought me into contact with the basic elements of the probability theory. The considerations in conjunction with phase separation during network formation were based on this approach.

However, it was the acquaintance with the theory of branching processes (TBP) in 1967-8 which influenced me most. This theory was developed by Manfred Gordon and his group in Colchester [43]. It was based on statistical assemblage of branched and crosslinked structures from building units in different reaction states. This method used *generating functions* as a transformation tool for dealing with distributions and *cascade substitution* for generating distributions of molecules and various substructures. Although these terms have sounded intimidating for majority of polymer chemists, what is needed for their application is very simple. All that is necessary to know about generating functions can be learned in one or two hours with the basic knowledge of differentiations and possibly integration. Cascade substitution means in fact formulation of a recursive equation for repeating addition of building units. Assigning temporarily generating function variables to building units and bonds binding them to neighbors, leads the user safely through the forest of implicit distributions to the end result, where the variables disappear having performed their job. This is important especially for complex reaction paths and multicomponent systems. The "recursive" approach of Doug Miller and Chris Macosko [44] gives, for the same initial assumptions, identical results. This approach has been sometimes preferred by users because for simple systems the theory does not use the probability generating functions and works with averaged expectations. The same "cascade" reasoning then leads to the same recursive equation. However, more complex systems with distributions were a hard nut to crack and Dough and Chris preferred to use generating functions [45]. The advantages and disadvantages of the approaches were often a subject of friendly disputations among us starting by Chris's and Doug's visit to Prague in the late seventies.

The first successful application of TBP was that to curing of epoxy resin by polyamines described above. It was so perhaps not because of the theoretical approach used, but because of showing that epoxide-amine systems are almost ideal polymer networks and not intractable material as was assumed before. However, the introduction of *critical molar ratio* and work with non-reactive *off-stoichiometric* *systems* gained general significance. The contact with many other real systems and use of newly developed precursors required developing TBP further or looking for another kind of theory. One of the first problems was *formation of cyclic structures*. While at that time, the importance of the Jacobson-Stockmayer analysis was recognized and several experiments and interpretations of pregelation and gelation studies were available, the situation beyond the gel has been less transparent. This is due to the fact that beyond the gel point the cyclic structures (closed circuits) exist in the gel anyway. However, among them there are such that do not contribute to the equilibrium elasticity (loops). The spanning-tree approach was used in which the bonds in the network were classified as "branching" or "ring-forming" and the "branching" ones could have finite or infinite continuation. Moreover, in addition to ring forming there exists during network formation a ring activation process in which a loop can be transformed into a circuit with chains effective in equilibrium elasticity [46]. Cyclization was a subject of a few other studies made by us. Now, after so many years the problem of cyclization is still not fully understood. More on that can the reader find in Bob Stepto's contribution to this special volume and references therein. Bob devoted the major part of his scientific life to cyclization and holds the major share of knowledge. The intramolecular reaction should always be taken as relative to the intermolecular reaction and the latter one is also affected by existing cycles too as we say in our contribution to this special volume.

In many of our experimental studies, it was recognized that the viscoelastic properties depend on the gel structure - elastically active crosslinks, elastically active network chains, dangling chains – and on their size and composition. Therefore, methods based on TBP were developed to characterize them [47], [48] and it was shown how to design networks with few long or many short dangling chains and how their behavior differs [48].

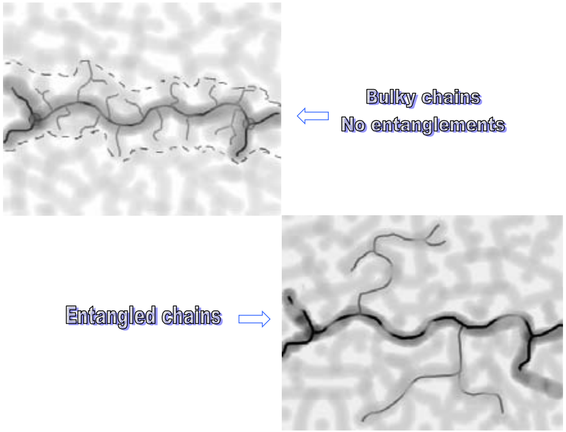

Figure 9. Schematic view of an elastically active network chain (EANC) with many short dangling chains (upper left) and with few long dangling chains (lower left); corresponds to Ref [48].

Moreover, dangling chains can be designed such that they have different composition compared with EANCs.

The statistical branching theories are rigorous for equilibrium systems, but in overwhelming majority of cases they were used for kinetically controlled irreversible reaction or for reversible systems where the equilibrium has not been reached. What kind of approximation we were using for these branching systems was my, at that time somewhat vague, concern. But it must be similar to linear systems, I reasoned. Were Flory's and Case's methods not good for such systems? Then Sergei Kuchanov came with his book [49] showing that reactivity differences such as substitution effect gave rise to deviations from Flory's most probable distribution in linear systems and Stockmayer distribution for branched polymers. This immediately stressed the importance of the kinetic approach at least in some cases. Two questions were raised: (a) is then the statistical theory a poor or good approximation and (b) OK, let us use the kinetic treatment, but it does not work beyond the gel point or at least for the gel part; so, what then? This was a stimulus also for us to show that the kinetic treatment can be extended beyond the gel point and offers a parameter identical with the extinction probability appearing in TBP [50]. Then, we developed an off-space Monte Carlo simulation method [51] for kinetically controlled branching processes in which the largest molecule in the vicinity of the gel point was much larger (by several orders of magnitude) than the second largest molecule. Thus the largest molecule represents the gel. The simulation proved that the reactivity differences treated by TBP and by the simulation are negligible in most cases, so that application of the statistical methods is fully legitimate. However, there are groups of network formation processes, where application of statistical methods is not appropriate, such as initiated reactions, cyclization reactions, group reactivity dependent on size and symmetry of that molecules that cannot be treated well by the statistical method. The generalized Monte-Carlo simulation was based on Smoluchowski coagulation equations describing the reactions of any possible pair of molecules [52]. It could simulate the spatial effects such as limited access to functional groups, control limited by diffusion, etc. Such constraints lead to non-mean-field critical exponents and affect the position of the gel point. The kinetic method and the solution of infinite sets of differential equations by the moment method remained a valuable tool up to the gel point or for polydisperse precursors. Henryk Galina's group made an important progress in this direction [53].

The fact that in network formation some steps are non-Markovian and some other occur at random initiated the birth of so-called *combined method* [54]. Typical examples are ring-free copolymerization of monovinyl and divinyl or multivinyl monomers, initiated copolyaddition of monofunctional and polyfunctional monomers, like polyetherification of diepoxides. In addition to the ring-free condition, there must exist independence of reactivity of all or some functional groups in the polyfunctional monomer. In the first step, the bonds connecting independent groups are cut and the points of cut labeled. Superspecies (chemically connected clusters) are formed. In the second steps the labeled fragments are recombined into original bonds. Several systems were treated by this method (cf., e.g., [27], [35]). In connection with the reaction irreversibility vs. reversibility problem, one remark is appropriate. In many cases, when generating structures, we should make decision which of several possible paths to take. In statistical theories, it corresponds to assemblage of Markov chains governed by transition probabilities. In the irreversible case, these probabilities should conform the irreversible course (cf. [55]). More crude approximations can be used and were used in the past without analyzing the magnitude of possible deviations.

Perhaps, a few other applications of branching theories we tried to develop should be mentioned. One of them is the technologically very important *multistage process*. The final network is formed in several irreversible steps. The trick consists in labeling variables associated with each step and marking also the functional groups existing in the unreacted state. The products of the preceding stage are initial components in the following stage. Two-step formation of polyesters and their crosslinking with a polyepoxide in the third step can be shown as an example [56] which helped developing a powder coating at DSM Resins. The other application concerned the use of polymer networks precursors containing *internal branch points*. When the precursor unit is attached only with one or two bonds, the internal branch points do not contribute to the number of elastically active network chains (EANC). When the number of connections of this precursor unit with the gel component increases, more and more internal branch points get activated and contribute to the concentration of EANCs. The key logic is to ask, considering a selected branch point, about the probability that a selected path of bonds continues to infinity [57]. The third example of characterizing internal gel structure made possible by statistical theories is the existence of *topological clusters*. They are formed in multicomponent networks when some of the units differ in a specified property. A classical example comes from polyurethane systems where the units are classified as hard or soft. In linear systems, some sequences are hard and some soft; in a branching system the hard clusters are branched, too. They grow during network formation and eventually can become infinite. This hard-cluster gelation occurs beyond the macroscopic gel point and is associated with a change of mechanical properties [58]. In rubber elasticity consideration, cluster crosslinks of varying functionality rather than pointlike crosslinks should be considered. Figure 9 illustrates the case of "hard" triol units, "hard" diisocyanate units, and "soft" macrodiol units. While the pointlike crosslinks have always functionality 3, the cluster crosslink functionality grows from 3 up.

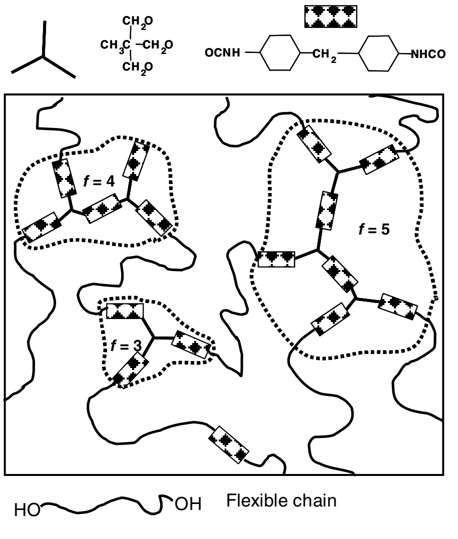

Figure 10. Hard cluster crosslinks in a polyurethane network; *f* is functionality of a cluster crosslink.

An overview of what we have been doing should be perhaps followed by listing of developments equally or more important for network science we should have been involved in but were not. But, *c'est la vie*.

Polymer Networks Community

Let me conclude my reminiscence by a few words about the community of people fostering the world science of polymer networks. The idea of having some frame of international organization emerged at the end of sixties in the discussions with Henri Benoit, director of Centre de Recherche sur les Macromolécules in Strasbourg, one of the great personalities of French polymer science. These ideas have gained some more shape at the Faraday Discussion Conference in Colchester in 1974 when discussed within a group of scientists (Allen, Burchard, Dusek, Gordon, Herz, Hild, Rempp, Ross-Murphy, Stepto, and Ziabicki). Later an informal Polymer Networks Group (PNG) was formed and managed by Gerard Hild as secretary, and eventually in 1986 a more formal Polymer Networks Group was constituted under the first chairmanship of Bob Stepto (see http://www.polymernetworks.group.shef.ac.uk/history.php). For over 15 years I was serving as officer of the Group committee. PNG was fostering not only the science but also friendship among scientists who were meeting every two years at PNG conferences. I am pleased seeing many of them here.

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