SPECIAL FEATURES OF NETWORK FORMATION BY CHAIN CROSSLINKING COPOLYMERIZATION

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Special features of free-radical crosslinking copolymerizations and the structure of the resulting products have been reviewed. Characteristic is the effect of spatial correlations on the apparent reactivity of pendant double bonds. These correlations make the apparent reactivity in the course of copolymerization to increase (cyclization) and decrease (steric hindrances). At intermediate and higher concentrations of the crosslinker, compact structures are formed which are internally crosslinked. Only pendant double bonds in the peripheral layer are able to take part in polymerization reactions whereas the internal ones cannot react. The state of theoretical simulations of this structure growth is discussed with a special emphasis on the development of the kinetic (coagulation) network formation theories so that the above mentioned features may be taken into account. Also, the important role of the presence of a diluent during polymerization is discussed. It can result in a change of network chain conformations necessary for networks exhibiting volume phase transitions. Alternatively, it can induce liquid-gel phase separations resulting in inhomogeneous networks having a variety of morphologies.

1. INTRODUCTION

A wide variety of lightly and highly crosslinked polymers are prepared by chain (free-radical) copolymerization of mono- and polyunsaturated monomers. The polymerization products range from soft and highly swollen gels to rigid, highly crosslinked high-performance composite matrices or porous sorption materials. Wichterle has shown that the same monomers, by changing the initial composition, can yield either a soft hydrogel[1], or a macroporous network[2,3]; alternatively, a colloidal solution of a microgel[4] can be obtained.

The free-radical crosslinking copolymerization of mono- and bisunsaturated monomers as a method for preparation of polymer networks (crosslinked polymers) has several special features compared with either the stepwise polycondensation or polyaddition or crosslinking (vulcanization) of primary chains[5]. The main difference consists in the activated (initiated) fast chain growth (propagation) which is responsible for the difference in the structure of the products. At the same time, the special features of the chain copolymerization make the modelling of network formation difficult and at present there does not exist any reliable method for predicting the formation–structure–properties relations.

This contribution attempts to review briefly special features of free-radical copolymerization of mono- and polyunsaturated monomers, the resulting network structure and its experimental evidence. Also, the results of the presence of a diluent during network formation will be briefly discussed. The last part will deal with the present state of modelling of the structure growth by this mechanism.

2. NETWORK FORMATION MECHANISMS

From the point of view of elementary reaction steps, the free-radical crosslinking polymerization qualitatively does not differ from the linear polymerization of a monounsaturated monomer: It starts with initiation, proceeds by propagation, in which the

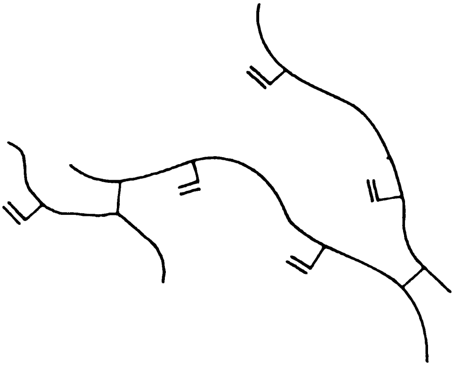


FIG. 1
Structure of an ideal vinyl–divinyl copolymer

monomers are added to the active ends of growing chains, accompanied by chain transfer, and the active chain ends are deactivated by termination reactions. The difference is in the presence of a multiunsaturated (e.g. bisunsaturated) monomer. If the bisunsaturated monomer is incorporated into the growing chain, one of the two double bonds reacts and the other one becomes pendant. The pendant double bond also takes part in the copolymerization and units with pendant double bonds are gradually converted into units with both reacted double bonds – crosslinks. An ideal structure is seen in Fig. 1. It often happens that the chemical reactivity of a pendant double bond is equal to that in the bisunsaturated monomer. The reaction scheme for copolymerization is then the same as for a copolymerization of two monovinyl monomers (cf. e.g., Table I). For unequal reactivities (intrinsic or induced), the reaction scheme can be extended to correspond to a ternary, quaternary, . ., etc. copolymerizations.

Yet, the effective reactivity of a pendant double bond can be different from its "chemical" reactivity. This is due to spatial correlations resulting in cyclization and excluded volume. Spatial correlations make the effective reactivity of the pendant double bond to vary – typically, they make it first increase and then decrease.

2.1. *Cyclization*

The apparent increase in reactivity of the pendant double bond in the beginning is due to the fact that, in addition to intermolecular reaction, also an intramolecular reaction can take place with pendant double bonds on the same growing chain or on chains bonded chemically through crosslinks. That the intramolecular reaction can be very important at the beginning of the copolymerization follows from the following consideration (Fig. 2): The active end of the growing macroradical (*) can attack the

TABLE I

Typical elementary reactions considered in ideal vinyl monomer (1)–divinyl monomer (2) copolymerization (equal and independent reactivities of vinyl groups in the divinyl monomer)

Reaction	Reaction scheme
Dissociation of initiator	$I \rightarrow 2I^*$
Initiation	$I^* + M_x \rightarrow IM_x^*$
Propagation	$\ldots M_x^* + M_y \rightarrow \ldots M_xM_y^*$
Transfer to monomer	$\ldots M_x^* + M_y \rightarrow \ldots M_x + M_y^*$
Termination by recombination	$\ldots M_x^* + M_y^* \rightarrow \ldots M_x M_y \ldots$
Termination by disproportionation	$\ldots M_x^* + M_y^* \rightarrow \ldots M_x + M_y \ldots$

$x,y = 1,2$.

double bonds of the monomers (propagation); it also can attack pendant double bonds on other polymer molecules (intermolecular crosslinking) or pendant double bonds on the same molecule (intramolecular crosslinking). At the very beginning of polymerization, there exist only very few chains with pendant double bonds in the reaction system dissolved in monomers (only the growing macroradical itself in the limit of zero conversion), so that the chance the free radical meets such a pendant double bond is close to zero. The probability of the intramolecular reaction depending on the chain flexibility is finite, so that the ratio of the extents of the intra- to intermolecular crosslinking can initially be very high.

When the formation of a small ring by intramolecular crosslinking is easy, only small rings are formed and no intermolecular crosslinking occurs (cyclopolymerization). The result is a "linear" chain containing small rings. Monomers with strong tendency to cyclopolymerization are represented for example by diallylamines or divinyl formals[6].

The other extreme, when intramolecular crosslinking is weak, is represented by the case of a very stiff bridge connecting the double bonds in the bisunsaturated monomer and stiff backbone chain. A very stiff bridge may not be a sufficient condition for suppression of ring formation if the main chain is flexible. Then, "backbiting" becomes possible after addition of one or a few monomer units. Styrene–1,4-divinylbenzene copolymerization can serve as an example where cyclization within the divinyl unit is not possible but is observed during copolymerization. Cyclization is also difficult when the connecting bridge is very long because, in the ideal case, the cyclization probability is proportional to $N^{-3/2}$, where N is the number of monomer units in the connecting bridge. Thus, copolymers of α,ω-divinyl polyethers or polybutadienes of molecular weight of several thousands would hardly exhibit intramolecular crosslinking in bulk.

The overwhelming majority of crosslinking copolymerizations is the intermediate case between cyclopolymerization and essentially ring-free copolymerization, with varying but generally strong cyclization. It should be remembered, however, that cyclization is promoted by dilution and one can find strong evidence of cyclization for (dilute)

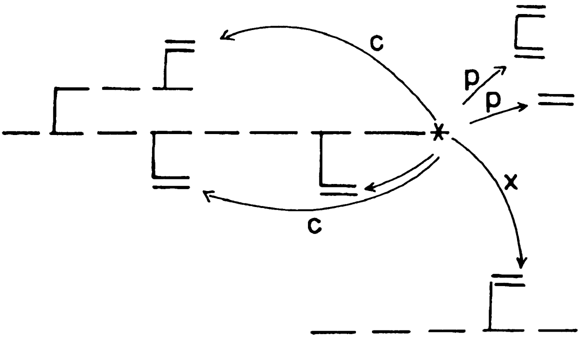


FIG. 2
Possible reactions of a macroradical end (p propagation, x crosslinking, c cyclization)

solution copolymerizations of systems that do not show up cyclization in bulk polymerization.

2.2. *Excluded-Volume Effects*

The decrease in the apparent reactivity of the pendant double bond in crosslinking copolymerizations is due to various kinds of steric hindrance for the pendant double bond which prevent it from either inter- or intramolecular crosslinking. These hindrances may cause a strong diffusion control of the reaction; the term "excluded volume" is associated with all these effects.

The excluded-volume effect on reactivity of a group can already exist at the pregel stage. A group located inside a branched polymer has certainly less opportunity to react than that at the periphery. In an intra- or intermolecularly crosslinked polymer, the mobility and accessibility of a group is even lower. As a rule, in vinyl–divinyl networks there exists always an appreciable proportion of pendant double bonds irrespective of the crosslinking conditions (see below).

2.3. *Experimental Evidence For Changes in Apparent Reactivity of Pendant Double Bonds*

There exists abundant experimental evidence from the studies of low-conversion as well as medium- and high-conversion copolymers about the changes in the apparent reactivity of the pendant double bond.

2.3.1. Composition of Low-Conversion Copolymers

For a ring-free copolymerization, the low conversion copolymers should contain units of bisunsaturated monomers bearing pendant double bonds. The fraction of crosslinked units (bisunsaturated monomer units with both reacted double bonds) is negligible. With increasing conversion, the fraction of crosslinked units increases and the shape of this dependence should depend on the reactivity ratios. Data on homopolymers and copolymers[7] of diallyl compounds, and on dimethacrylate[8] and divinylbenzene[9] copolymers show that, already at low conversions, the fraction of crosslinked units is much higher. This can be explained by cyclization. Polymers of diallyl phthalate contain less pendant double bonds than polymers of diallyl isophthalate because of higher cyclization tendency of the former[5].

There is a quantitative difference between the polymerization of diallyl and divinyl compounds due to the fact that the length of the primary chains in allyl polymerization is lower because of degradative chain transfer. The fraction of the units with pendant double bonds depends on the flexibility of the bridge connecting the allyl groups, and decreases with dilution. For divinyl copolymers of much higher molecular weight of primary chains, these dependences are less pronounced or absent.

Very interesting is the dependence of the composition of the low conversion ethylene dimethacrylate (EDMA)–styrene copolymers on the composition of the feed[8]. If the content of EDMA units with both reacted vinyls is plotted against the concentration of the EDMA monomer in the feed, one can see that their content in the copolymer is not zero (as it would be for a ring-free copolymerization). Initially, their content is roughly proportional to the EDMA concentration in the feed. However, by further increasing the amount of the EDMA monomer in the feed the content of doubly reacted EDMA units in the copolymer does not grow any more and all EDMA units are incorporated in the copolymer only as units with pendant vinyls (Fig. 3). Apparently, the reactivity of the pendant vinyls is initially enhanced by cyclization but it becomes low due to existing intramolecular crosslinking when additional portions of EDMA are introduced (excluded-volume effect).

2.3.2. Changes in Composition with Conversion

The decrease in the fraction of units with pendant double bonds from 1 to 0 with conversion increasing from 0 to 1 expected for the ideal case has never been found in reality. The real decrease is less steep starting with a value less than unity and reaching a value higher than zero at full conversion of the monomers. An example of styrene–divinylbenzene copolymers is seen in Fig. 4. The higher is the content of the crosslinker, the flatter is the conversion dependence and the higher is the residual unsaturation.

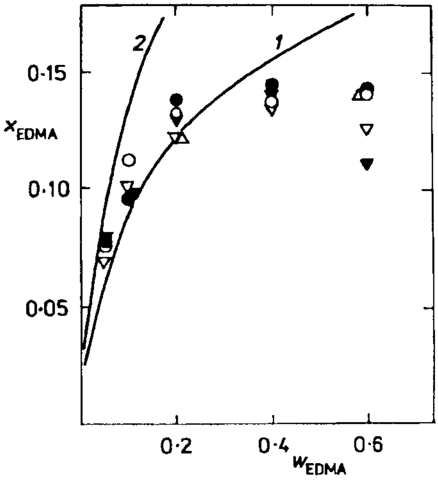


FIG. 3

Molar fraction (of all monomeric units) of ethylene dimethacrylate (EDMA) units with both reacted double bonds, x_{EDMA}, in low-conversion (soluble) styrene–EDMA copolymers[8] as a function of the weight fraction of EDMA in the feed, w_{EDMA}. Volume fractions of monomers in the feed v_0: ○ 1.0, ● 0.8, ▽ 0.6, ▼ 0.4, △ 0.2. The curves are calculated for the model taking into account cyclization: *1* $v_0 = 1.0$, *2* $v_0 = 0.25$

Important is the fact that for a high concentration of the crosslinker the composition of the formed copolymer with respect to the content of pendant vinyls is almost the same at the beginning as well as at the end of copolymerization! The existence of residual pendant double bonds in fully cured (or even postcured) vinyl–divinyl copolymers is a general phenomenon (cf. references in reviews[5,10] or refs[11,12]).

2.3.3. Crosslinking Efficiency

Another measure of wastage of pendant double bonds in intramolecular reactions is the determination of the fraction of crosslinks that are intermolecular. A crosslink is considered intermolecular if it contributes to the increase in the molecular mass in the pregel region, or to gelation.

The measurement of the molecular weight averages as a function of the conversion shows that the crosslinking efficiency (ratio of the effective number of crosslinks to the total number of crosslinks) is always lower than unity, decreases with decreasing conversion and, at low conversion it reaches the values of 0.1 – 0.01.

Another possibility of finding the crosslinking efficiency is the determination of the gel point conversion. The values calculated for a ring-free model yield values which are lower than the experimental ones by a factor of the order of 10^{-1} to 10^{-2}. For example, the gel point conversions in the polymerization of ethylene dimethacrylate vary between 1 – 2 wt.% (ring-free value about 0.01 wt.%). For polymerization of 1,3-divinylbenzene it was found to be 2 wt.% (ring-free value about 0.05 wt.%).

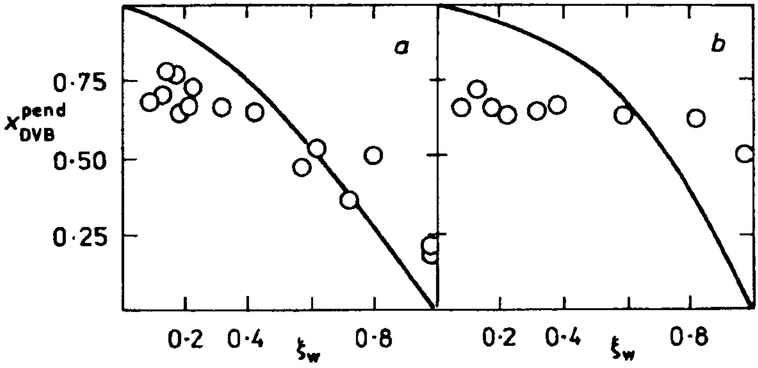


FIG. 4

Molar fraction (of all DVB units) of the units with pendant double bond, x_{DVB}^{pend}, in styrene–1,3-divinylbenzene copolymers as a function of weight conversion, ξ_w (ref.[9]): *a* 8 wt.% DVB, *b* 15 wt.% DVB. The curves are calculated for copolymerization without cyclization

Because the knowledge of the molecular mass of the primary chains is important in calculation of the crosslinking efficiency, a number of experiments have been performed with bisunsaturated monomers where the vinyls are connected with a bridge that can be split by hydrolysis, oxidation, etc.

2.3.4. Structure of the Pregel Copolymers

The structure and behaviour of the pregel polymers depends on the structure growth mechanism. Hydrodynamic and intramolecular dynamics behaviour depends on whether the molecules are just branched or also internally crosslinked. Viscometry of dilute solutions and NMR spectroscopy have been mainly used for this purpose.

It is known that the intrinsic viscosity of branched polymers is lower than that of linear polymers of the same molecular weight; in the case of the vinyl–divinyl copolymers, it was found to be even lower. This is due to intramolecular crosslinking[13]. The intrinsic viscosity of low-conversion vinyl–divinyl copolymers is the lower, the higher is the content of the divinyl monomer. With increasing conversion, the increase in viscosity is the steeper, the higher is the divinyl monomer content because these systems gel earlier on the conversion scale[14]. The intrinsic viscosity–molecular weight dependence of these polymers resembles that found for solution of crosslinked microgel particles prepared in microemulsions[15,16].

The NMR techniques can also bring evidence of the compactness of the molecules formed by crosslinking chain copolymerization. In high-resolution ^1H NMR of low-conversion soluble ethylene dimethacrylate–styrene copolymers only a part of the structure units could be seen[17]. This part (unconstrained) decreased from 100% at low concentrations of the crosslinker to low values at its high concentrations (Fig. 5). De-

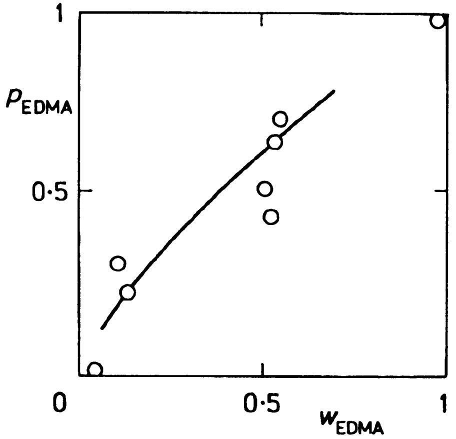
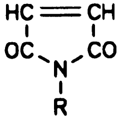


FIG. 5

Molar fraction of EDMA units with constrained (ex NMR) pendant double bonds p_{EDMA} in low-conversion styrene–ethylene dimethacrylate copolymers as a function of weight fraction of EDMA in the feed, w_{EDMA} (refs[8,17]) were obtained. These were characterized by permeabilities to oxygen and nitrogen and by selectivities. In addition, the phase structure of the membranes made from PPO and poly(*I*) was also subjected to examination.



I – V

I, R = 3-dimethylaminophenyl
II, R = 2,4,6-tribromophenyl
III, R = 2,3,4,5,6-pentabromophenyl
IV, R = 2,4,6-trichlorophenyl
V, R = 2,3,4,5,6-pentabromophenyl

EXPERIMENTAL

Materials

Substituted *N*-phenylmaleimides were prepared by the reaction of the corresponding aniline with maleic anhydride, followed by cyclodehydration of the maleamic acids obtained[6]. The following maleimides were obtained: *I*, m.p. 98 °C; *II*, m.p. 142 °C; *III*, m.p. 215 °C; *IV*, m.p. 131 °C; *V*, m.p. 150 °C. Acetone solutions of the imides (1.15 mol l^{-1}) and 2,2'-azobis(isobutyronitrile) (0.015 mol l^{-1}) were heated in sealed glass ampoules at 60 °C for 48 h; the polymaleimides were precipitated from solutions by a sixfold excess of ethanol. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was a commercial product (Spolana Neratovice, The Czech Republic).

Preparation of Membranes

The membranes were obtained by casting a chloroform solution (0.1 g ml^{-1}) of PPO or PPO/polyimide mixture on a glass plate to form a 0.35 mm layer. After solvent evaporation at room temperature, the membranes with a thickness of approximately 30 μm were released by immersing in water.

Methods

Number-average molecular weights $\overline{M}_n$ of poly(*N*-arylmaleimides) were measured on a Perkin–Elmer vapour pressure osmometer. The molecular weight of PPO was determined by GPC in toluene. In both cases, polystyrene standards were used for calibration.

Transport properties of the membranes were studied with the use of a laboratory-made apparatus[7] equipped with a thermal conductivity detector. The permeabilities, P, were determined from the amounts of O_2 and N_2 which passed through a membrane placed in the cell. The selectivity was expressed by the permeability ratio $\alpha_{O_2/N_2} = P_{O_2}/P_{N_2}$.

The phase structure of the membranes was examined by scanning electron microscopy (SEM) both from the membrane and the fracture surfaces. The samples were sputter-coated with a gold layer about 10 nm thick, observed and micrographed, using Jeol JSM 35 and JSM 6400 instruments.

the primary molecular weights as a function of the polymerization conversion hint at such mechanism[21].

Thus, gelation proceeds by mechanisms completely different from those leading to branching trees – the postulate of the classic Flory–Stockmayer branching theory. It may rather resemble some kind of chemical aggregation of colloidal particles. This is why gelation is so much delayed on the conversion scale. Thus, the structure near the gel point is rather heterogeneous. At higher conversions, the "void" space containing monomers is filled in by polymerization, so that the high-conversion structure appears to be more homogeneous.

The networks prepared with a low concentration of the crosslinking monomer (say 1% and below) do not exhibit such heterogeneous structure but they may contain cycles. Many of the hydrophilic gels developed and studied by Wichterle are from this category. However, polymerization in more dilute solutions enhances cyclization and a weak microgel-like structure may again be formed.

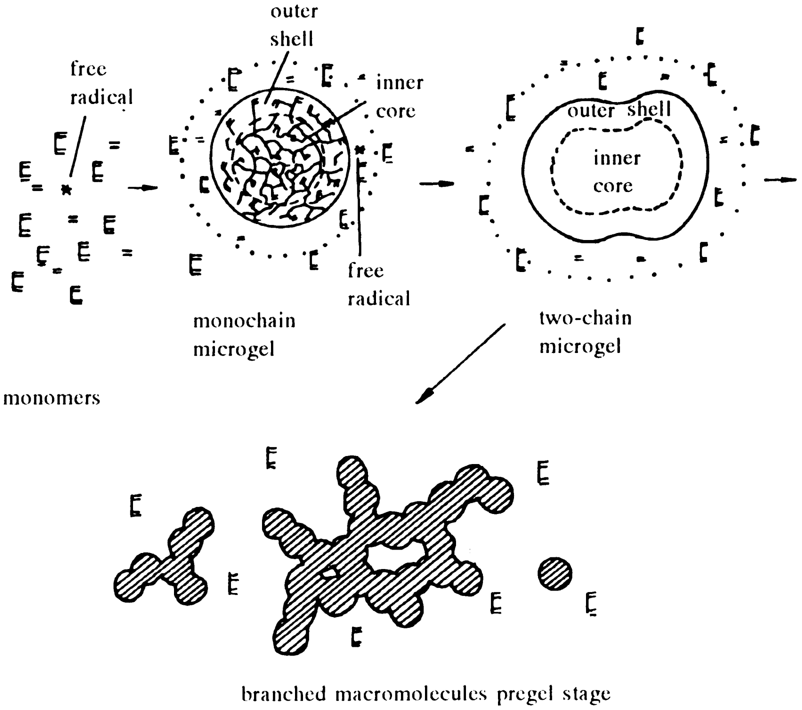


FIG. 6
Network formation in vinyl–divinyl copolymerization at higher concentrations of the divinyl monomer (microgelation)[20]

It should be noted that due to the non-ideal course of the free-radical crosslinking copolymerization the reactivity ratios for many vinyl–divinyl pairs published in the literature are to be taken with extreme caution because they have been calculated disregarding cyclization.

3. MODELLING OF FREE-RADICAL CROSSLINKING COPOLYMERIZATION

As the free-radical crosslinking copolymerization is the most complex way of preparation of polymer networks from the viewpoint of evolution of structure, also its theoretical modelling is rather complex. The complexity is twofold: (i) complex kinetically-controlled reaction mechanism, and (ii) strong spatial correlations and great difference from the branching-tree picture.

It is not the purpose of this article to discuss the present state and applicability of various branching theories and the reader is referred, for example, to a recent overview[20]. However, the application of the so-called statistical theories (the structures are generated from structure units in different reaction states) can be ruled out because these theories in the absence of spatial correlations, do not even describe correctly network formation determined by a complex reaction mechanism like that given in Table I.

The use of the kinetic (coagulation) theory or computer simulation in space are the other options. The former can treat the so-called time (stochastic) correlations rigorously whereas spatial correlations only as an approximation. The current methods of computer simulation (lattice or off-lattice percolation) can take spatial correlations into account, but their applicability is still limited by a full immobility of the structures during network formation (no diffusion). Under these conditions, it is not possible to take a complex reaction mechanism (like that given in Table I) into account. The only serious attempt to model free-radical polymerization of a tetrafunctional (e.g divinyl) monomer by percolation was made by Boots (cf., e.g. ref.[22]). The simulation consisted in distributing randomly the points of initiation on a lattice, from which the structure could grow with practically no termination. The clusters do not exhibit any translational movement and also its interior is immobile. Despite of these limitations, the qualitative picture resembles that drawn from the experimental results: an array of (poorly) interconnected clusters strongly intermolecularly crosslinked. Quantitative comparison fails because the calculated values of parameters depend on the type of lattice, are insensitive to many rate constants of elementary reaction steps, and the method cannot deal with copolymerizations. However, an improvement of the percolation models in general is under way.

It has been tempting to develop the kinetic methods that can deal rigorously with the details of the chemical mechanisms and that are able to account for the effects of spatial correlations: cyclization and excluded volume. A very brief explanation of the basis of the kinetic method may be worthwhile.

The structure growth process is described by a set of kinetic differential equations characterizing the time changes in concentration of each molecule, $c_{x,l}$, where x is the number of monomeric units and l is the number of unreacted functional groups. The quantities x and l can be vectors, i.e. a molecule can be composed of different monomeric units, and the groups can be different and can have different reactivity. For instance, for a bimolecular addition reaction

$$\mathrm{d}c_{x,l}/\mathrm{d}t \;=\; c_{x,l} \sum_{y,m} K(x,y;l,m) c_{y,m} \;+\; \sum_{y,m} K(x-y,y;l-m+1) c_{x-y,l-m+1}\, c_{y,m+1}\,,$$

where the positive term means the rate of formation of the given molecule and the negative one the rate of its transformation. The quantities $K(x,y;l,m)$ are effective rate constants (called kernels in Smoluchowski coagulation equations) dependent on the number of unreacted functional groups l and m but may also be dependent on the structure of the molecule given by x and y. With such a formulation, the evolution in time of concentration of each distinguishable molecule in the whole system, governed by elementary reactions given, e.g., in Table I, is described by several infinite sets of differential equation.

For the simplest case of chemical kinetics, $K(x,y;l,m) \propto lm$. There exist ways of solving these systems of differential equations numerically in terms of the moments of the molecular mass distribution and gelation, possibly including the Tromsdorff effect (depending only on the molecular mass average but the same for all molecular weights (cf., e.g. ref.[23]). More advanced variants can calculate also the sol fraction, crosslinking density, etc. (cf.refs[24,25] and an outline in review[20]).

The formulation of kinetics in terms of concentrations of molecules and numbers and reactivities of the groups is based on the postulate of equal accessibility of all groups irrespective of the size and shape of the molecule they are a part of. The cyclization reaction can be formally included if cyclization is considered uncorrelated, i.e. independent of the separation distance of the reacting groups in the molecule. This is, however, not realistic.

Within the framework of the kinetic theory, one can model the steric excluded volume effect, as schematically shown in Fig. 6, by a trick which makes the apparent reactivity dependent on the size (and structure) of the reacting molecule. Actually (Fig. 6), the reactivity of the groups decreases from the surface to the centre of the microgel molecule and more groups are thus affected in larger (and more compact) molecules than in the smaller ones. In the theory, this is taken equivalent to the case when all groups in the molecule have lower reactivity and the decrease in reactivity is higher for larger and more compact molecules.

Mathematically, these features are reflected in the functional dependence of the kernel. Whereas, for the conventional chemical kinetics (all groups equally accessible independently of the size of the molecule)

$$K(x,y;l,m) \propto lm$$

for a constrained reactivity

$$K(x,y;l,m) \propto l^{\sigma_x} m^{\sigma_y},$$

where the exponents σ_x and σ_y can be a function of the molecule structure, i.e. of x and l, and y and m, respectively. If the molecule is a sphere with reactive groups on the periphery $\sigma = 2/3$. The values of the exponents σ_x and σ_y are generally expected to decrease with increasing x or y. Likewise, for the cyclization process one can write down the following equations

$$\mathrm{d}c_{x,l}/\mathrm{d}t = -K_c(x,l)c_{x,l} + K(x,l+2)c_{x,l+2}$$

with

$$K_c(x,l) \propto l^{\rho}\, l = l^{1+\rho}$$

expecting the exponent ρ first to increase (more partner groups to react) and then to decrease (partner groups are less accessible).

If one visualizes the reacting molecules as (fractal) objects in which the surface is proportional to their reaction ability we have the situations given in Fig. 7.

A simple modification of the functional form of the kernel can thus account for a variety of spatial correlations. However, the departure from the simple exponents $\sigma_x = \sigma_y = 1$ makes the moment method for the solution of the kinetic differential equations inapplicable. Instead, one can use a Monte-Carlo method of simulation of processes described by the above differential equations with finite systems ($10^5 - 10^7$ monomeric units) developed by us[24 - 26].

The molecules are kept in the computer memory. A random number generator selects molecules or their pairs for reaction. The probability of finding them is weighted by the value of the respective kernels. If the system is sufficiently large, the largest molecule in the system suddenly steeply grows in size at the gel point and its mass becomes comparable with the rest of the distribution. The largest molecule represents the gel, the rest of the distribution the sol. Proper selection of the exponents and its functional dependence will make possible to simulate the structure evolution during free-radical crosslinking copolymerization under various conditions.

4. ROLE OF A DILUENT IN CROSSLINKING COPOLYMERIZATION

A diluent present during copolymerization can have several effects:

1) lowers the glass transition of the resulting network: the product is swollen (usually less than to equilibrium) and rubbery,

2) lowers the reaction rate,

3) increases cyclization,

4) may somewhat affect the chain conformation, but important is that after its removal, in the dry network, the network chains become supercoiled,

5) may bring about phase separation (macro- or microsyneresis).

The effect *1*) is very important for preparation of soft materials and has been utilized in Wichterle's spin casting of soft contact lenses.

Here, we will just briefly review effects *4*) and *5*) noting in passing that the increase in cyclization due to dilution can induce structural inhomogeneity (without phase separation) or make it stronger.

Normally, a possible (small) change in chain conformation by the presence of diluent, supercoiling of chains after the diluent removal, and a certain degree of their relaxation after reswelling influence somewhat the mechanical behaviour in the rubbery state which is accounted for in the rubber elasticity theories. No dramatic change is expected.

However, when the network is prepared in the presence of a large quantity of a diluent and the diluent is removed, the network chains become strongly supercoiled. When this network is reswollen in a poor solvent, the segment–segment contacts still

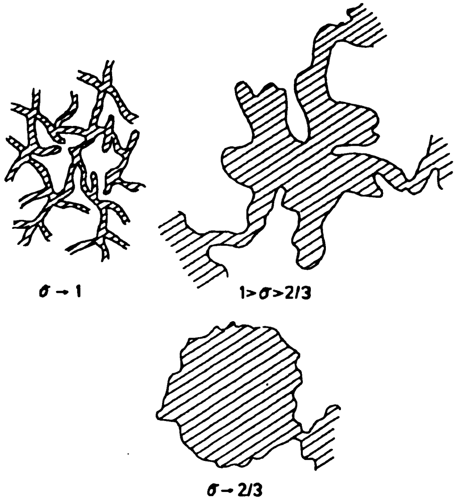


FIG. 7
Schematic shapes of structures with surfaces proportional to the number of accessible functional groups with the value of the exponent σ indicated

remain to be numerous and the degree of swelling is low. The tendency of the supercoiled chains to expand is compensated by the attractive segment–segment interactions. Now, if the number of these segment–segment contacts is slightly decreased, e.g. by a change in temperature (the sign depends on the temperature coefficient of the polymer–solvent interaction), the system may suddenly undergo a cooperative volume transition and expands; if the temperature is changed in the opposite direction, the gel collapses (Fig. 8). Conceptually, this transition resembles the liquefaction of a real (van der Waals) gas. This transition was predicted[27] in 1967 but it took another ten years before it was found experimentally[28]. The reason for such a time lag was the fact that the original theory was derived for non-ionic gels where the polymer–solvent interaction was governed by the Flory–Huggins interaction parameter with no or a slight concentration dependence. The transition was predicted to be possible for a gel prepared at a high dilution and simultaneously higher crosslinking density – two factors mutually

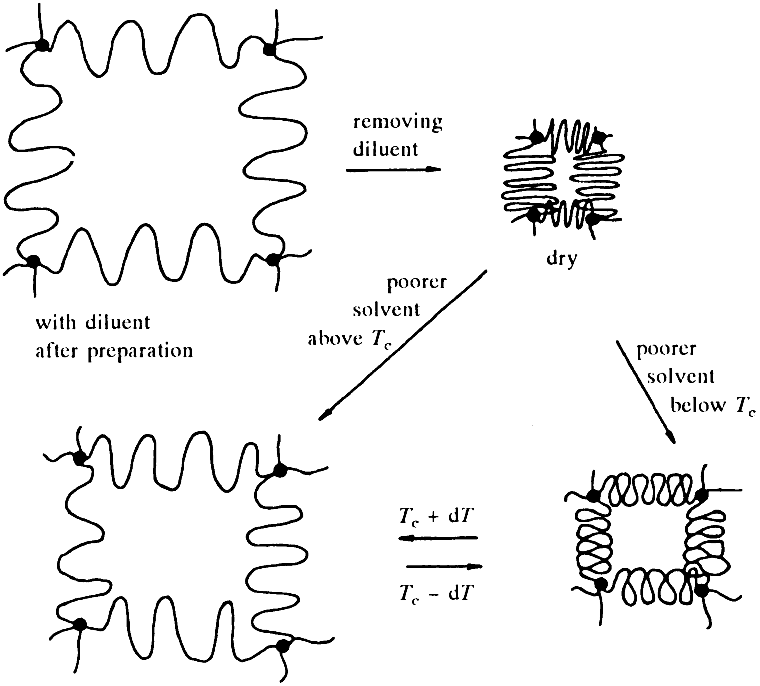


FIG. 8
Schematic representation of changes of the shape of network showing the temperature-induced volume phase transition and positive temperature coefficient of swelling for networks prepared in the presence of a diluent (T_c is critical temperature)

exclusive because they both assist solvent–gel phase separation during polymerization (see below) which is an unwanted phenomenon. Tanaka[28] in 1977 found that introduction of a few ionized groups in the gel structure makes the dilution – crosslinking degree conditions for phase transition much milder. This can be seen very well in the behaviour of the free-energy expression for the swollen system.

Since then, many new systems have been found (cf. e.g. ref.[29]) and also the phenomenon itself has grown from an interesting academic problem to challenging applications mainly in biosciences but not only there. Some of these applications are reviewed in a recent monograph[30]. The gels are called responsive or stimuli-sensitive where the stimuli mean not only changes in temperature, pH, salt concentration, but also light, enzymes, receptors, etc. which offers application in pharmacy and medicine not to mention one of the oldest application – concentration of solutions containing high-molecular-weight substances.

Much older than the volume phase transition, characterized by coexistence and transition between two swollen gel phases, is the phase separation by which a liquid phase (not containing a crosslinked polymer) is separated from a swollen gel. This kind of syneresis is as old as colloid science and syneresis manifested by deswelling or appearance of new phase dispersed in the gel was observed in many natural colloidal gels.

The phenomenon of phase separation during network formation is much newer. Theoretically, if taken as a kinetic process it has not yet been well described. Phase separation during network formation can occur for two main reasons[31]:

a) change of polymer–solvent interaction (χ-syneresis)

b) increase in molecular weights and beyond the gel point of the crosslinking density (ν-syneresis).

The onset of phase separation can be explained by the fact that the equilibrium degree of swelling decreases with increasing crosslinking density and the crosslinking density increases with increasing polymerization conversion. Phase separation sets in when the amount of the present diluent (diluent–monomer mixture) is equal to the equilibrium swelling capacity of the network.

With respect to the form of the separated phase, phase separation (syneresis) can occur as macrosyneresis and microsyneresis. The difference is schematically shown in Fig. 9. Macrosyneresis is close to equilibrium and can occur as a result of slow crosslinking processes after gel point when a coherent network exists. The onset of phase separation and phase equilibria changing with increasing conversion were treated theoretically by combining the swelling and network formation theories[32]. Since the ratio of phase volumes changes, the network and its response is more complex.

Microsyneresis is a more common form of phase separation occurring during network formation. It should be pointed out that microsyneresis often occurs in weak gels as a result of a change of polymer–solvent interaction: the gel just becomes turbid instead of shrinking and remaining transparent and homogeneous. Wichterle's water-swollen lightly crosslinked poly(2-hydroxyethyl methacrylate) gels are a striking example. The development of turbidity induced by temperature changes had been known perhaps since their discovery, but a systematic study by light-scattering and transmission methods was started by Sedláček[33] in 1967. During later studies, it was found that the turbidity developed by a temperature change is not stable in time and decreases until, after several months, a transparent gel of smaller volume is recovered. Non-equilibrium microsyneresis has passed into the stable form – macrosyneresis (Fig. 9). It was remarkable that the size of the separated particles (water droplets) did not essentially change but their number continuously decreased[34]. This could be explained by a theoretical model in which the network was locally deformed by the forming droplet. The constancy of the droplet diameter was explained by the existence of a minimum of free energy arising from the compensation of the energy change by network deformation (increasing with droplet size) and energy of the gel–water interface (increasing with decreasing diameter at constant separated volume)[34]. These phenomena are important for understanding phase separation during network formation. There, the turbidity developed during polymerization is fixed by subsequently formed crosslinks and becomes fully or partly permanent (Fig. 10).

The heterogeneous porous materials obtained by crosslinking copolymerization in the presence of a diluent were commercialized in the late fifties and early sixties (macroporous ion exchangers, sorbents, chromatographic separation materials, membranes).

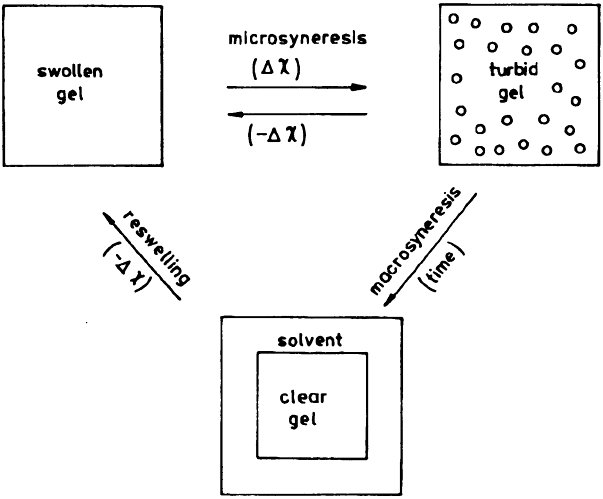


FIG. 9
Micro- and macrosyneresis in swollen gels induced by a change in polymer–solvent interaction parameter, $\Delta\chi$

The diluents used in polymerization range from poor to good solvents and linear oligomers and polymers soluble in the monomers[10]. The morphologies vary from droplets in the soft-gel type (low crosslinking densities) to two co-continuous phases and powder in the diluent type (not so much interesting commercially). Even more complicated structures are sometimes observed (skins on pore surfaces).

The basic driving mechanism in the formation of these porous structures is phase separation but the above discussed inhomogeneous nature of the free-radical crosslinking copolymerization is an important factor determining the morphology, particularly at higher crosslinking densities. Important is the moment at which phase separation starts and the phase volume ratio at this moment. If phase separation starts before the gel point, coalescence of separated microphase particles gives rise to coarse structure with large pores. This is, for example, the case of oligo(dimethysiloxane)s – strong precipitants – added to styrene and divinylbenzene. If phase separation starts farther beyond the gel point, the network is relatively dense and the excess liquid cannot form a microseparated phase and is rather squeezed out of the gel (macrosyneresis) (Fig. 10). The

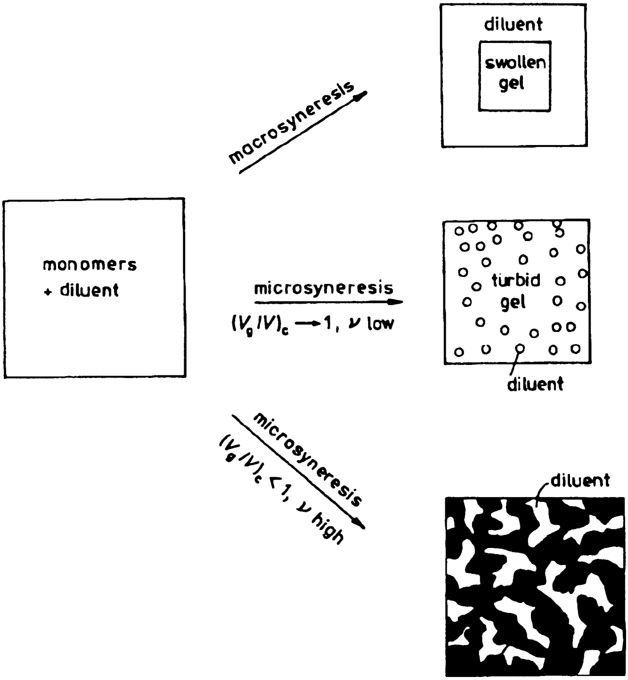


FIG. 10

Phase separation in the course of copolymerization ($(V_g/V)_c$ is critical relative volume of separated polymer phase, ν crosslink density) best moment for the phase separation to start is at or just beyond the gel point. The formed morphology is then fixed by continuous crosslinking.

Another important factor is that the actual diluent for the formed polymer is the monomer–diluent mixture. The monomer is usually a good solvent and it is being consumed as polymerization proceeds. The transfer of the monomer from the liquid phase to the polymer phase (formation of a kind of interpenetrating network) can have an interesting effect called inverse syneresis[10,35]. The uptake of the monomer by the separated network structure brings about its volume expansion, so that the volume of the porous copolymer is higher than the volume of the original monomer–diluent mixture (Fig. 11).

The dry and some swollen porous sorbent materials are usually in the glassy state at room temperature. It has been found that the morphology of pores depends on the history of the network transferred into the dry state. The transition into the glass can lock in the actual morfology of the polymer (cf. e.g. refs[36 - 39]). Thus, removal of the diluent by drying at elevated temperature (the polymer is rubbery during drying) yields a less porous structure than that obtained by a solvent exchange from good solvent to

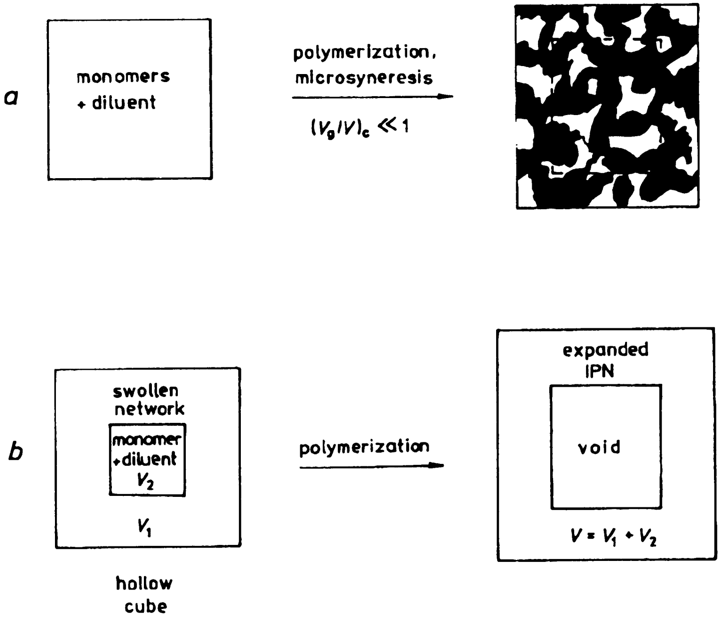


FIG. 11
Schematic representation of inverse syneresis: *a* during crosslinking copolymerization, *b* explanation of the volume expansion by a case of hollow cube swollen and filled with a diluent–monomer mixture leading to an expanded interpenetrationing network (IPN) and a void space

non-solvent. Hence, physical morphology is superimposed on chemical morphology and the systems undergo a slow physical aging. This aging is supposed to occur much faster because of a larger locked-in free volume. Thus, combination of copolymerization with phase separation and glass transition and possible fixation of the physical morphologies by crosslinking can be of use for preparation of a wide variety of porous structures.

REFERENCES

1. Wichterle O., Lím D.: Nature *186*, 494 (1960).
2. Chromeček R., Wichterle O., Gavrilova I., Kubín M., Špaček P.: Czech. 131 449 (1968); U.S. 3 497 577 (1970); Chem. Abstr. *72*, 112441 (1970).
3. Wichterle O., Chromeček R.: J. Polym. Sci., C *16*, 4677 (1967).
4. Chromeček R., Bohdanecký M., Kliment K., Otoupalová J., Stoy V., Štol M., Tuzar Z.: Czech. 141 101 (1971); S. African 67 03048 (1968); Chem. Abstr. *70*, 115716 (1969).
5. Dušek K. in: *Developments in Polymerisation 2.* (R. N. Haward, Ed.), p. 143. Applied Science Publishers, Barking 1982.
6. Corfield G. C., Butler R. A. in: *Developments in Polymerisation 3.* (R. N. Haward, Ed.), p. 1. Applied Science Publishers, Barking 1982.
7. Matsumoto A.: Eur. Polym. J. *25*, 385 (1989) and references cited therein.
8. Dušek K., Spěváček J.: Polymer *21*, 750 (1980).
9. Malinský J., Dušek K., Klaban J.: J. Macromol. Sci., Chem. A *5*, 1017 (1971).
10. Seidl J., Malinský J., Dušek K., Heitz W.: Adv. Polym. Sci. *5*, 113 (1967).
11. Rosenberg J. E., Flodin P.: Macromolecules *20*, 1518 (1987).
12. Kloosterboer H.: Adv. Polym. Sci. *84*, 1 (1988).
13. Galina H., Dušek K., Bohdanecký M., Štokr J., Tuzar Z.: Eur. Polym. J. *16*, 1043 (1980).
14. Shah A., Holdaway I., Parsons I. W., Haward R. N.: Polymer *19*, 1067 (1978).
15. Hoffmann M.: Makromol. Chem. *175*, 613 (1974).
16. Antonietti M., Bremser W., Schmidt M.: Macromolecules *23*, 3796 (1990).
17. Spěváček J., Dušek K.: J. Polym. Sci., Polym. Phys. Ed. *18*, 2027 (1980).
18. Allen P. E. M., Bennett D. J., Hagias S., Hounslow A. M., Ross G. S., Simon G. P., Williams D. R. G., Williams E. H.: Eur. Polym. J. *25*, 785 (1989).
19. Shea K. J., Stoddard G. J.: Macromolecules *24*, 1207 (1991).
20. Dušek K., Šomvársky J. in: *Synthesis, Characterization, and Theory of Polymeric Networks and Gels* (S. M. Aharoni, Ed.), p. 283. Plenum Press, New York 1992.
21. Fernandez A. M., Widmaier J. M., Sperling L. H., Wignal G. D.: Polymer *25*, 1718 (1984).
22. Boots H. M., Kloosterboer J. G., van den Hei G. M.: Br. Polym. J. *17*, 219 (1985).
23. Tobita H., Hamielec A. E.: Macromolecules *22*, 3098 (1989).
24. Dušek K., Šomvársky J., Braam A. W. M.: *NETWORKS 92 Conference, San Diego 1992*; Abstracts, p. 35.
25. Šomvársky J., Dušek K., Braam A. W. M., Tiemersma-Thoone G. P. J. M.: Presented at *4th European Polymer Federation Symposium on Polymeric Materials, Baden-Baden 1992*, Abstr. 058.
26. Mikeš J., Dušek K.: Macromolecules *15*, 93 (1982).
27. Dušek K., Patterson D.: J. Polym. Sci., A *26*, 1209 (1968).
28. Tanaka T.: Phys. Rev. Lett. *40*, 820 (1978).
29. Ilavský M., Hrouz J., Bouchal K.: Polym. Bull. *14*, 301 (1985).

30. Dušek K. (Ed.): *Responsive Gels – Volume Phase Transition*; Adv. Polym. Sci., in press.
31. Dušek K. in: *Polymer Networks. Structure and Mechanical Properties* (A. J. Chompff and S. Labana, Eds), p. 245. Plenum Press, New York 1972.
32. Dušek K.: J. Polym. Sci., C *16*, 1289 (1967).
33. Sedláček B.: Collect. Czech. Chem. Commun. *32*, 1398 (1967).
34. Dušek K., Sedláček B.: Collect. Czech. Chem. Commun. *36*, 1569 (1971).
35. Dušek K., Seidl J., Malinský J.: Collect. Czech. Chem. Commun. *32*, 2766 (1967).
36. Hauptke K., Pientka V.: J. Chromatogr. *102*, 117 (1974).
37. Wieczorek P. P., Ilavský M., Kolarz B. N., Dušek K.: J. Appl. Polym. Sci. *27*, 277 (1982).
38. Okay O.: J. Appl. Polym. Sci. *32*, 5533 (1986).
39. O'Kane J. M., Sherrington D. C.: Macromolecules *23*, 5286 (1990).

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