Polymer Networks: A Challenge to Theorist and Technologist

Karel Dušek[a]

[a] Institute of Macromolecular Chemistry Czechoslovak Academy of Sciences, Prague 6, Czech and Slovak Federative Republic

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KAREL DUŠEK

Institute of Macromolecular Chemistry
Czechoslovak Academy of Sciences
162 06 Prague 6, Czech and Slovak Federative Republic

ABSTRACT

Polymer networks challenge a theorist to develop methods of their generation, describe their topology, and understand critical phenomena (gelation) during their formation. They challenge a technologist because of their unique properties based on their large-scale three-dimensional connectivity and their easy transformation of relatively low-viscosity liquids into crosslinked solids. Polymer networks challenge both, in that they are structurally very complex for the technologist who needs the theorist for understanding and controlling their structure and properties. Also, the theorist is challenged by problems appearing in technology which may initiate a basic reconsideration of the theories' assumptions. In this contribution, methods for modeling polymer network structures and their recent applications to relatively complex systems of technological importance are briefly discussed.

INTRODUCTION

It is difficult to define what a (polymer) network is. In materials science, it is understood to be a (very) large collection of material objects (atoms, molecules, aggregates, etc.) connected by a type of bonds into a (three-dimensional) array. If we do not specify the bonds (Van der

Waals, polar, hydrogen, ionic, covalent, etc.), any solid could be considered a network. From the experimental point of view, we can observe network properties if the bonds are permanent within the experimental window available. It is common sense to talk about a polymer network if the objects are held together by covalent bonds. However, even then, within the experimental window of years or decades, such networks can be considered (irreversibly) transient. On the other hand, some junctions resulting from cooperative action of relatively weak bonds (crystallites, multiple helices, etc.) may be quite strong, as many examples of biological and bioanalogical systems show. A gelatin gel can serve as one of them. This introduction is intended to show that methods of study developed for covalent networks can be used as well for other networks under appropriate experimental conditions.

The properties of a network are determined by its internal structure (connectivity pattern and spatial interactions) and the structure is determined by the structure growth processes. Therefore, it is clear that modeling network structures means modeling the structure growth. The resulting network structures may be very different. A classical structure of a lightly crosslinked rubber with long and interpenetrating network chains (Fig. 1) is very different from that of highly crosslinked system
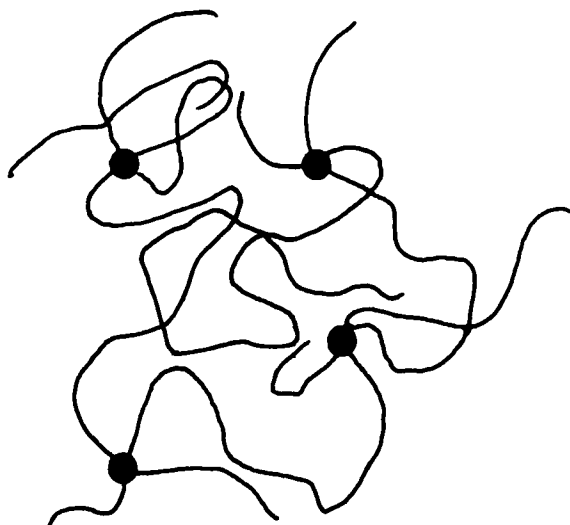
FIG. 1. Network obtained by crosslinking of primary chains.

$$\begin{array}{ccccccc}
| & & | & & | & \\
-\,\text{Si} & -\,0\, - & \text{Si} & -\,0\, - & \text{Si} & - \\
| & & | & & | & \\
0 & & 0 & & 0 & \\
| & & | & & | & \\
-\,\text{Si} & -\,0\, - & \text{Si} & -\,0\, - & \text{Si} & - \\
| & & | & & | & \\
0 & & 0 & & 0 & \\
| & & | & & | & \\
-\,\text{Si} & -\,0\, - & \text{Si} & -\,0\, - & \text{Si} & - \\
| & & | & & | & \\
\end{array}$$
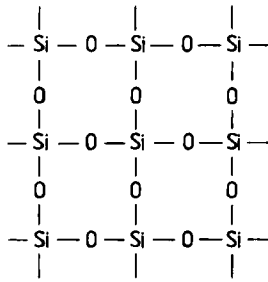
FIG. 2. Silicon oxide network.

formed from small units like silica gel (Fig. 2). In addition, silica gel micronetworks can form macronetworks by aggregation processes and can be of different structure (Fig. 3; [1]).

In polymer science, it is usually believed that gelation and network formation result from joining of molecules having functionality higher than two. A network structure always contains closed circuits; i.e., its cycle rank is larger than zero. However, one can show that there exist

SILICA AEROGEL: CAB−0−SIL:

FIG. 3. Silica gel macronetworks [1].

formation processes by which only treelike, dendritic structures are formed. Such structure growth has been observed experimentally [2]. It results from a multistep reaction: in each step, the reactant is monofunctional with respect to the groups already existing on the surface of the dendrite, but at least two other functional groups are added that are inactive in this step but become active in the next step. These "starburst" polymers have been synthesized and characterized [2] (Fig. 4).
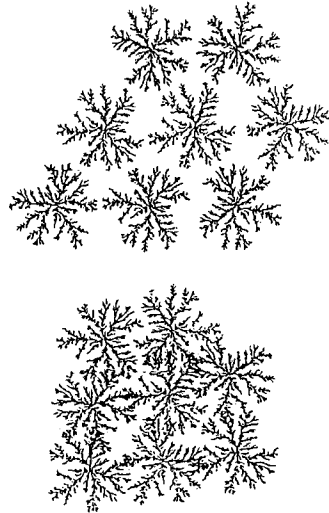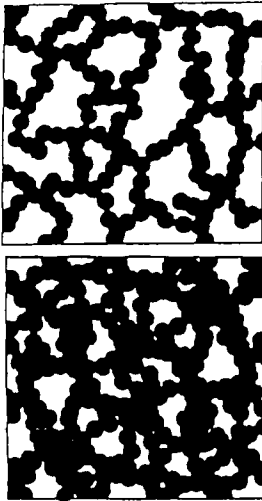
It is clear that a treelike structure cannot continue indefinitely because of the space-filling problem discussed by DeGennes and Hervet [3], and for a general multiplicative growth process by Gordon and Ross-Murphy [4]. In a simple case of random f-functional polycondensation, the number of units in generation g increases as $[(f - 1)\alpha]^g$ whereas the space available as g^3. If $(f - 1)\alpha > 1$ (α is the conversion of functional groups), the number of bound units increases more steeply than the space does and the growth becomes limited. In conventional crosslinking systems, the problem of overcrowding is circumvented by cycle (circuit) formation; the dendritic growth either stops or the functional groups react incompletely, which may give rise to side reactions. An interconnection of dendrites and formation of a macronetwork may be one of the consequences.

In this contribution, we will concentrate on classical ways of network formation by covalent bonds for which, at least beyond the gel point, ring formation is allowed.

MODELING OF NETWORK STRUCTURES

The existing network formation theories can be grouped in two categories: (a) off-space generation of essentially treelike structures below the gel point with uncorrelated circuit closing beyond the gel point; perturbation treatment of cyclization is possible; (b) generation of structure in n-dimensional space (percolation, off-lattice simulations). A brief account of these theories has been given elsewhere [5, 6].

The off-space generation can be performed by statistical methods by joining small units—usually monomer units, or parts of monomer units, or fragments larger than pregenerated units—clusters or superspecies—differing in their reaction states via their reacted functional groups participating in bonds of specified type. What develops in time for kinetically controlled structure growth is just distribution of these units. The reaction states of a unit differ in the number and type of reacted groups
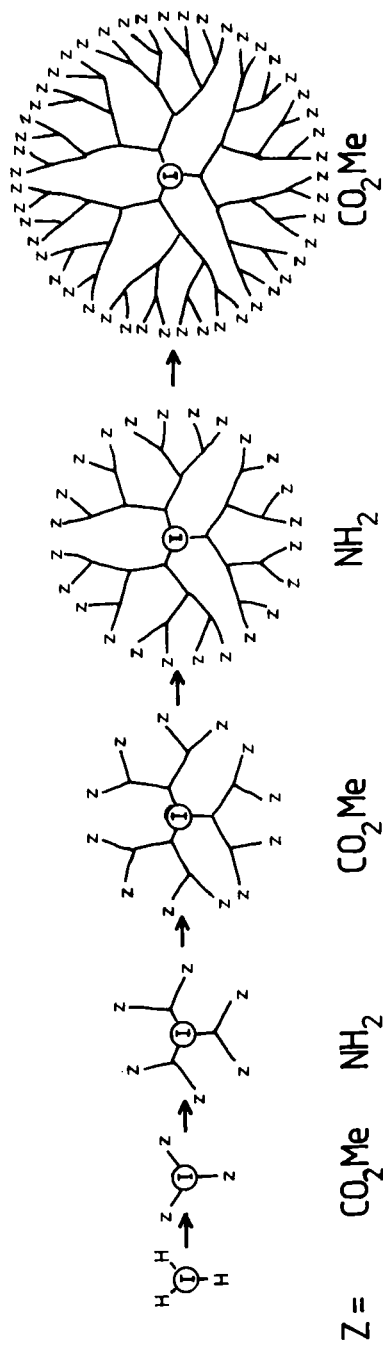
$Z = \quad CO_2Me \quad NH_2 \quad CO_2Me \quad NH_2 \quad CO_2Me$

FIG. 4. Schematic structure of "starburst" polymers [2].

and the type of bonds they are engaged in (Fig. 5). However, this struc-
ture generation process for the kinetically controlled structure growth is
in essence unnatural because it ignores the time (conversion) sequence of
bond arrangements in the structures.

Is this approximation serious? It was believed that it was not. This
belief was substantiated by the fact that the statistical generation by a
random growth process (f-functional polycondensation with no substitu-
tion effect) gave exactly the same results as the kinetic generation in
which the integrity of structures once formed remains preserved [7].
However, in the latter case the bonds are indistinguishable because the
same structure can result from an equilibrium-controlled growth process.
Later, it was found that structures formed from monomer units exhibit-
ing substitution effects (reactivity of a group is dependent on the state of
neighboring groups) differed depending on whether they were generated
by the statistical or kinetic methods [8, 9]. Within the framework of the
assumptions (no cycles below the gel point), the kinetic generation is
rigorous.

The differences were attributed to long-range stochastic correlations
[10] existing in systems with substitution effects, initiated structure
growths, and other complex structure growth mechanisms. The nature
of these correlations became clearer after a simple initiated structure
growth was examined [11]. The addition of monomer units to the grow-
ing structures is a simple first-order Markovian process, but the growing
processes of individual structures start at different times, i.e., at differ-
ent conditions for the structure growth, (e.g., the monomer:initiator
ratio). The statistical theory does not keep any record of the time (con-
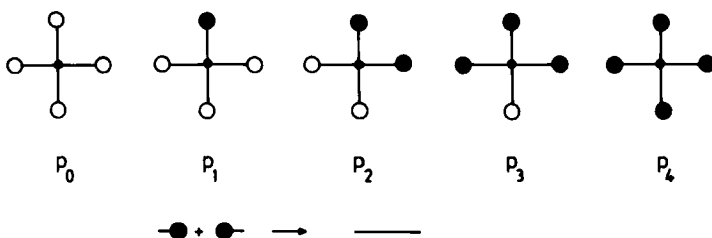version) sequence of bonds between units.

FIG. 5. Distribution of units of a tetrafunctional monomer in different reac-
tion states. p_i, number fraction of units; ●-reacted functional group, ○-unre-
acted functional group.

From what has been said above, it follows for a consumer of the branching theory (e.g., a technologist) that he should use the kinetic theory as much as possible. However, the kinetic method is technically more complex than the simple statistical theory. The former works with infinite sets of kinetic (nonlinear) differential equations, which usually have to be solved numerically. Using the method of moments, the computation should not represent any major problem up to the gel point. However, at the gel point many moments of the distribution diverge, so that the passage beyond the gel point is still an open problem. Moreover, the kinetic method works with covalently bound structures and is not able to describe the interior structure of the gel in contrast to the statistical method [12] except of the cycle rank equal to the difference between the number of bonds in the gel and number of bonds necessary for a connected treelike structure.

Therefore, a challenge to the theorist often imposed by the technologist is to modify the statistical theory, so that it is a good approximation for the exact solution. One way is to increase the size of the building units (superspecies) and apply methods of higher-order Markovian statistics: the reaction states of units are distinguished not only by the number and type of bonds they are engaged in, but also by the states of their nearest, second-nearest, . . . , neighbors (second-order, third-order, . . . , substitution effects). Another way is to differentiate between bonds formed within a time span Δt_i or conversion span $\Delta \alpha_i$ (i.e., α_1, α_2, . . .). This necessity followed from the analysis of multistage processes [13, 14] and was suggested for a general approximative treatment of the structure generation in case of substitution effects [15].

Both ways become increasingly complex when the states of units in more distant generations are taken into account as well as when Δt or $\Delta \alpha$ become smaller. It is evident that the solution must converge to the results of the kinetic theory if $n \rightarrow \infty$ or $\Delta \alpha \rightarrow 0$.

Whatever progress in the off-space network formation theories has been reached in recent years, one should not forget that in the rigorous treatment the long-range correlations like cyclization or fluctuations are absent. Any group in whatever structure has a chance to react, and this reaction chance is determined by its chemical reactivity and chance of meeting a proper partner (this chance is proportional to the density of groups — mean field approach). These limitations may seem to make the off-space generation models highly unrealistic and inapplicable to the real world.

However, it is not so. In many systems, these limitations may become

serious in the close vicinity of the critical point — gel point where the formation of an infinite structure is dominated by intermolecular reactions between very large branched molecules in competition with intramolecular reactions. Here, the mean-field approximation is invalid. For many polymer systems, the critical region dominated by fluctuations can be very small depending on the structure overlap. Outside this region below and beyond the gel point, the fluctuations may be unimportant.

Moreover, the long-range correlations can be treated within the off-space models by approximate methods. In treating the problem of cyclization, small cyclic structures can be used as building fragments and the effect of larger cyclic structures can be approximated by distinguishing between groups reacted inter- and intramolecularly (spanning-tree approximation). The different chances for reactions between and inside large molecules can perhaps be treated approximately within the framework of the kinetic theory. The experimental data accumulated over decades have evidenced that the mean-field approaches can give reasonable predictions for formation-structure-(properties) relations except for systems with extensive cyclization [16] and structure growth in the critical region. This is a strong justification for continuing development of this group of theories.

The major future development in network growth modeling is to be expected for the structure generation in space. At present, the lattice-based percolation techniques are relatively well known [17]. In polymer science, the random bond or site percolation and kinetic (initiated) percolation have been employed. The substitution effects can be taken into account. The percolation techniques have not been applied so far for multicomponent systems or more complex reaction mechanisms. Problems will be encountered with selection of reaction partners if they are not spatial neighbors. Off-lattice simulations are more sophisticated [18]: the reactants are dispersed in space and Cartesian coordinates are assigned to each of them or to their centers of gravity. If the reactants are oligomers with their own distribution of conformations, this component can be placed in space in different conformational states. The bond formation is effectuated by selecting at random reactive groups and assigning to them a reaction volume. If a partner group happens to be located inside this volume, a bond is considered to be formed. The reaction volume is gradually increased and more and more bonds are formed (Fig. 6).

The lattice percolation methods have been mainly used for the study of critical phenomena, particularly the critical exponents and scaling
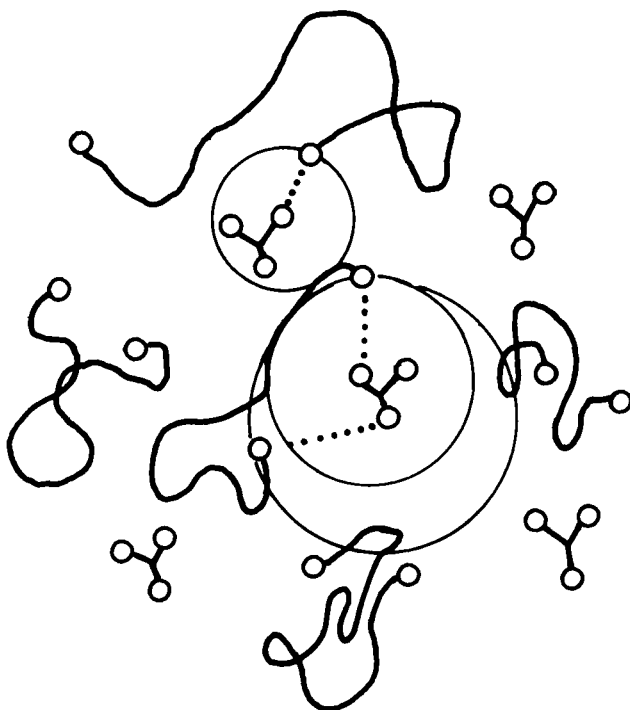
FIG. 6. Schematic representation of an off-lattice simulation of crosslinking of a bifunctional oligomer with a trifunctional crosslinking agent.

laws. The critical behavior of the models does not depend on the type of the lattice and depends only on the dimensionality of space. The values of some of the exponents obtained for the mean-field and percolation models are listed in Table 1. The majority of experimental critical exponents are close to the percolation ones [19]; however, sometimes they are not far from the mean-field ones. They also seem to depend on the conditions of preparation (dilution) (cf., e.g., Refs. [20, 21]).

Lattice percolation models are usually not good for description of structure over the whole range of structure buildup because the structural parameters (e.g., the degree of cyclization) depend on the lattice type. The main disadvantage of the present simulation techniques in space is a relative rigidity of the system during structure growth, which is in contrast with reality. In a real system, depending on the relative rate of

TABLE 1. Critical Coefficients

Parameter	Proportionality	Coefficient	Class. Perc. Theory	
Weight-average degree of polymerization	$P_w \propto |\epsilon|^{-\gamma}$	γ	1	1.74
z-average mean square radius of gyration	$\langle S^2 \rangle_z^{1/2} \propto |\epsilon|^{-\nu}$	ν	1/2	0.88
Weight fraction of gel	$w_g \propto |\epsilon|^{\beta}$	β	1	0.45
Mean-square radius of gyration of x-mer	$\langle S_x^2 \rangle^{1/2} \propto x^{\rho}$	ρ	1/4	0.40
Diffusion coefficient of x-mer	$D_x \propto x^{-y}$	y	1/4	0.28
Hydrodynamic radius of x-mer	$R_{xH}^{-1} \propto x^{-y}$	y	1/4	0.28
Number fraction of x-mers	$n_x \propto x^{-\tau}$	τ	5/2	2.20
z-average diffusion coefficient	$D_z \propto \langle R_H \rangle^{-1} \propto P_w^{-\kappa}$	κ	1/2	0.35
	$\langle S^2 \rangle_z^{1/2} \propto P_w^{\nu/\gamma}$	ν/γ	1/2	0.506

ϵ is the distance from the gel point, e.g., $\epsilon = (\alpha_g - \alpha)/\alpha_g$; α the is conversion of functional groups; coefficients calculated for $|\epsilon| \to 0$.

the network buildup, the formed crosslinks affect the existing chain conformation and the free energy of the system. By conformational rearrangements, the system tends to reach minimum energy. Modeling of such a structure growth would require minimization over all possible conformations of network structures commensurable with the space assigned to the model in the computer memory—a task for computers that will perhaps be available by the year 2000.

APPLICATION OF BRANCHING THEORIES TO COMPLEX TECHNOLOGICAL SYSTEMS

I am not going to discuss the challenges polymer networks offer to the technologist in various applications where their unique properties (including memory) can be exploited. I would rather concentrate on

challenges to the technologist that the network formation theories can offer by their structural information (for a partial list cf. Ref. [5]). The collection of structural information can then be used for understanding and predicting viscosity, viscoelasticity, equilibrium elasticity, radiation scattering, and other changes during and after network formation. They are also related to the problems of storage stability of various prereacted systems and safety during crosslinking.

In the literature, thousands of papers in the course of the last several decades have been devoted to experimental studies of network formation and structure, including tests of the applicability of network formation theories. Studies on epoxy or polyurethane networks (cf., e.g., Refs. [6, 22]) may serve as examples. These studies concentrated on model systems only partly of technological importance. They have been, however, extremely important as a gate to more complex systems.

Among more complex systems treated by the branching theories one can find polymers crosslinked by radiation (crosslinking and degradation), various epoxy resin–curing agent systems (amines, anhydrides, acids, phenols, ionic catalysts, etc.), polyisocyanate adducts (polyurethanes, polyureas, polyisocyanurates, etc.), polycyanates, melamine-formaldehyde resins, and, last but not least, polymer networks formed in multistage processes where the conditions in individual steps and the sequence of steps are of great importance for the structure of the products. The application to these more complex systems will be demonstrated on the examples of polyurethane networks composed of a number of different units formed by "side" reactions, interference of a "side" reaction in curing of epoxy resins with polycarboxylic acid, and a three-stage process of formation of a carboxyl-functionalized prepolymer and its subsequent crosslinking with a mixture of crosslinking agents.

The reaction of polyols with polyisocyanates resulting in polyurethanes may become quite complex, as the scheme in Fig. 7 shows. The urethane formed in the primary step can react with isocyanate under formation of a trifunctional allophanate; isocyanate can trimerize under formation of a trifunctional isocyanurate. Traces of water are usually present in commercial polyols, but due to the low molecular weight of water, tenths of weight percent of water represent tens of molar percent. Water readily gives urea groups that, in the presence of excess isocyanate, yield a trifunctional biuret. Thus, the side reactions give rise to some trifunctional crosslinks which either make gelation possible or increase the crosslinking density. As it is quite usual that real systems contain all or almost all these groupings, theoretical description of the

-NCO
(isocyanate)

+ H₂O

trimerization

-CO₂

+ HO-

-NH₂
(amine)

-NHCOO-
(urethane)

-N   CO   N-

OC   CO

N

(isocyanurate)

+ OCN-

+ OCN-

-NHCONH-
(urea)

-NCOO-

OCNH-
(allophanate)

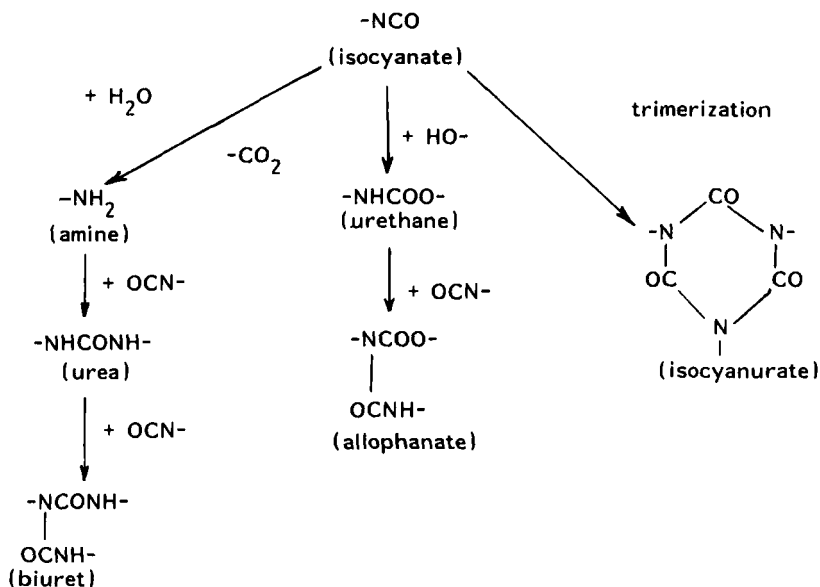+ OCN-

-NCONH-

OCNH-
(biuret)

FIG. 7. Reaction scheme for isocyanates in polyurethane formation.

network formation process seems hopeless. However, even such systems can be treated with a fair success [23]. For diisocyanate-polyol systems, the building blocks in the statistical theory are represented by the above-mentioned groupings, composed of halves of diisocyanate. The network is then generated by rejoining the halves of diisocyanate (bonds II) and by reconstituting the bonds to the hydroxyl groups of the polyol (bonds IH) (Fig. 8). The input information consists of the fractions of groupings (fragments), the determination of which represents a difficult analytical problem. However, even if the system is not analytically characterized in full, reasonable results can be obtained by the branching theory [23].

The theory predicts two gel points when the fraction of diisocyanate increases: one (sol → gel transition) occurs at a slight excess of isocyanate and can be explained by crosslinking of long polyurethane chains by a few trifunctional crosslinks. The second gel point (gel → sol transition) occurs at a high excess of isocyanate and can be interpreted as a lost of connectivity in a system heavily branched by side reactions with many dangling chains terminated by unreacted NCO groups. The gel → sol transition was possible because trimerization was absent. If it took place, "liquefaction" of the system would not have been possible. Of the collec-

unit	formula and types of bonds	designation	mole fraction
isocyanate	$\overset{\shortparallel}{<--}$ NCO	R	R
urethane	$\overset{\shortparallel}{<--}$ NHCO $\overset{|H}{-->}$ (O)	S	s
urea	$\overset{\shortparallel}{<--}$ NHCONH $\overset{\shortparallel}{-->}$	T	t
biuret	$\overset{\shortparallel}{<--}$ NHCO-N-CONH $\overset{\shortparallel}{-->}$	U	u
isocyanurate	(ring structure)	X	x
allophanate	$\overset{\shortparallel}{<--}$ NHCO-N-CO $\overset{|H}{-->}$ (O)	W	w
reacted hydroxyl	O $\overset{HI}{--->}$		α_H

XY
--> a bond X ---> Y

FIG. 8. Structural fragments for generation of polyurethane networks.

tion of results on sol fractions [23] and concentration of elastically active network chains, only one example is shown (Fig. 9). The agreement between the theory and experiments is reasonable. Thus, the technologist has in his hands a tool that can help him to predict, for instance, the stability of various prereacted systems containing excess isocyanate, predict the effect of traces of water on gelation and increase of crosslinking density, etc.

The curing of epoxy resins can also become complicated, as the scheme in Fig. 10 shows. The addition of an epoxy group to a carboxyl group results in the formation of a hydroxyester. However, if epoxy groups are in excess, they can react with OH groups of the hydroxyester under formation of a hydroxyl epoxy group and further gradual additions of epoxy groups (polyetherification). If carboxyl groups are in excess, the OH groups of the hydroxyester can be esterified and a diester is formed. However, even in the stoichiometric systems, a transesterification can occur yielding diester and glycol molecules. By this reaction the number of bonds does not change but they are only redistributed.

Thus, in a diepoxide–dicarboxylic acid system the diepoxide units are originally bifunctional. After transesterification they issue zero to four
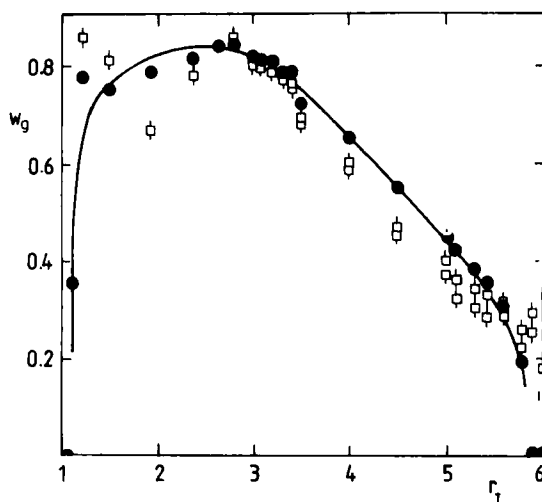
FIG. 9. Calculated ($\square$———$\square$) and measured gel fraction as a function of the initial molar ratio of NCO to OH groups, r_I, in a system poly(oxypropylene) diol-4,4'-diisocyanatodiphenylmethane at 90°C [23].

$$R^1COOH + CH_2\text{-}CHR^2 \\ \diagdown O \diagup$$

addition
esterification

$$R^1COOCH\ CH_2R^2 \\ |\\ OH$$

poly-
etherification

condensation
esterification

$$R^1COO\ CH\ CH_2R^2 \\ |\\ [OCHCH_2R^2]_x \\ |\\ OH$$

trans-
esterification

$$R^1COO\ CH\ CH_2R^2 \\ |\\ OCOR^1$$

$$R^1COO\ CH\ CH_2R^2 \\ |\\ OCOR^1$$
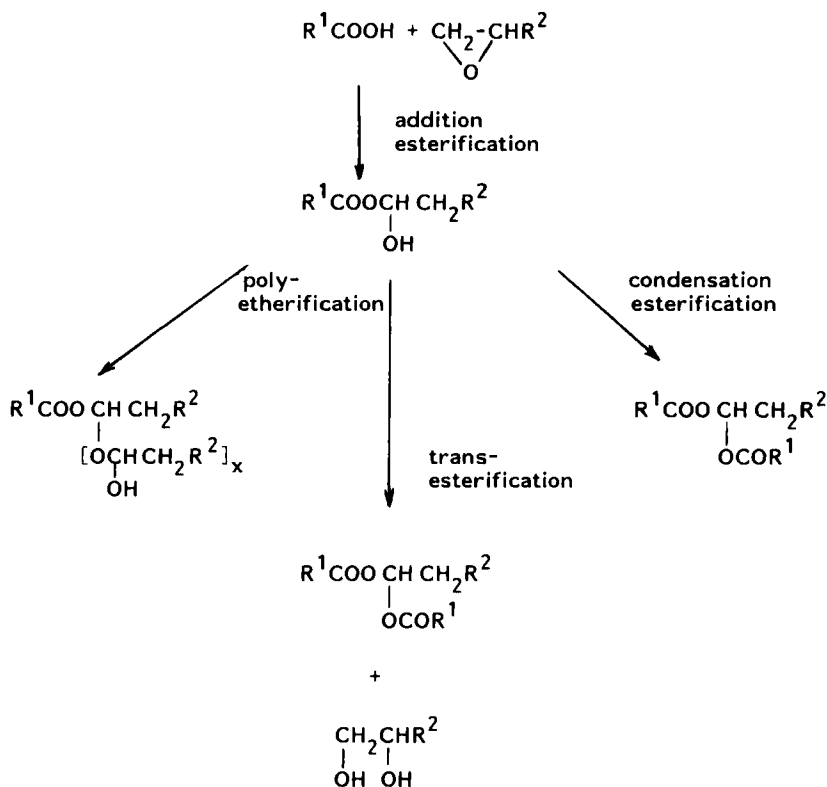
+

$$CH_2CHR^2 \\ |\quad| \\ OH\ OH$$

FIG. 10. Reactions between epoxy and carboxyl groups.

bonds instead of two, although the mean number of bonds remains two. Will this system gel? The branching theory gives a positive answer [14] and predicts the sol fraction and concentration of elastically active network chains. The dependence of the sol fraction on the transesterification conversion has been predicted to have a peculiar character: it never reaches zero and remains relatively high. This is explained by simultaneous crosslinking and "degradation" like that in radiation crosslinking. Indeed, gelation and the peculiar development of the sol fraction have been found experimentally (Fig. 11).

The third example is concerned with multistage processes (Fig. 12). Various industrial polymer products are often manufactured in several stages. The reasons are manifold: to increase the molecular weight and
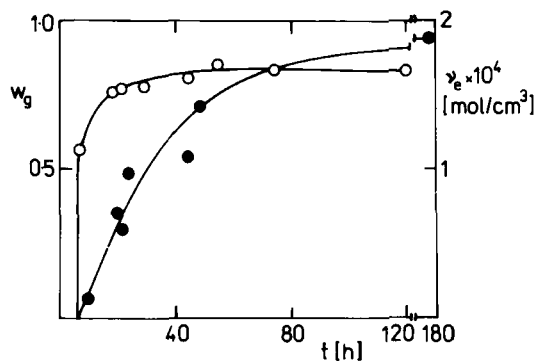
FIG. 11. Gel fraction development and increase of the concentration of elastically active network chains in the reaction of azelaic acid with diglycidyl ether of bisphenol A [24].

stage	components
1	monomers 1
	reactions 1
	products 1
2	products 1 + monomers 2
	reactions 2
	products 2
ℓ	products ℓ -1 + monomers ℓ
	reactions ℓ
	products ℓ

FIG. 12. Schematic representation of treatment of a multistage process [13].

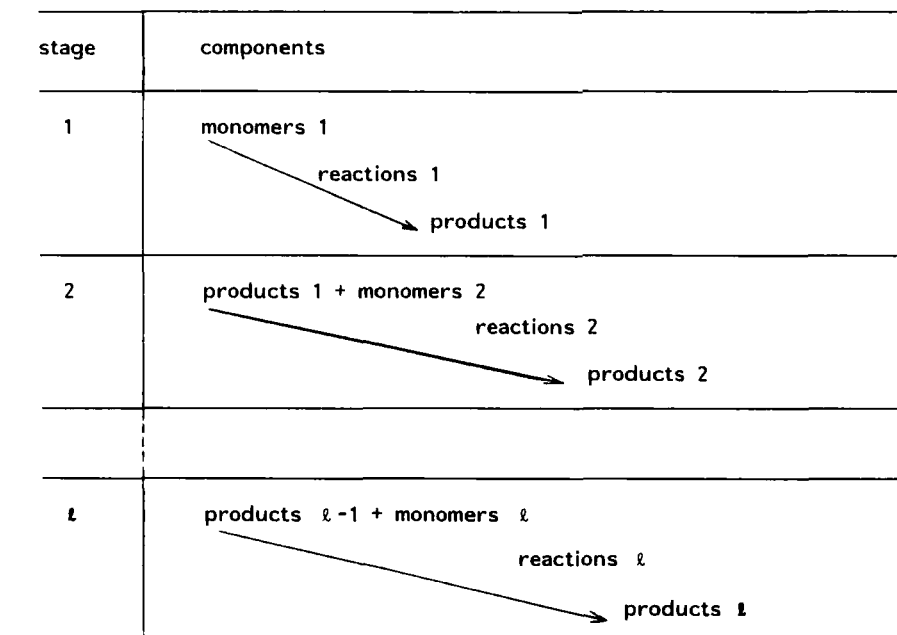prepare a prepolymer carrying appropriate reactive groups, so as to control the viscosity, T_g, crosslinking chemistry, and reactivity; to cope with limited solubility of some of the starting components; etc. Sometimes, it may be just because of technological convenience to add further components after certain reaction times. However, it is not always realized that multistaging has an effect on the resulting structure and properties. A two-stage process of preparation of polyurethanes in contrast to the one-stage process can serve as an example. The structure of the resulting polymer or network differs and may differ substantially — a fact not always recognized by those in the application field. A three-stage process by which branched prepolymers are prepared in two stages and cross-linked in the third stage is another example (Ref. [12] and references therein).

From the point of view of the branching theory, the description of a multistage process is a relatively complex problem. The product formed in the first stage has a certain degree-of-polymerization and compositional distribution; it also carries some reactive groups, possibly of different type. This product is used as one of the starting components in the next stage, and all information about this component must be available for treatment of the second stage. In the second stage, some of the reactive groups (not necessarily all) react, new reactive groups are introduced, the distributions change, etc.; in the third stage, some of the groups of the first and second stages may react as well and reactions with the newly introduced monomers (components) take place; and so on.

A rigorous simulation must take these features of the process into account. Within the formalism of the theory of branching processes [23], this task can be performed. A major problem exists, however: the theory generates a kind of weight fraction distribution of species in one stage which must be converted into a kind of number fraction distribution necessary for the treatment of the next stage. This transition can be formally obtained by integration of the respective probability-generating function. An analysis has shown that the integration can always be performed analytically if the individual stages are rigorously treated by the theory of branching processes. The analysis has also led to the conclusion that the whole process can be mathematically treated in one step if, and only if, the formed bonds are labeled by the stage in which they have been formed. This means that the number of the system variables increases. The additional input information must come from an analysis of the individual stages anyway, because no experimental method exists

that can distinguish between bonds of the same type formed at different conversions.

Analysis and understanding of the effect of multistaging have helped to elucidate the nature of non-Markovian distributions resulting from some relatively simple structure growth processes and of the effect of structure formation history. Application of these results helps the technologist substantially because he can then estimate the effect on the structure of changing such technological conditions that are easy to control: for example, time sequences of adding components and temperature regimes. In such systems the simple "rule of thumb" may not help much.

CONCLUSIONS

It can be concluded that both the theorist and technologist are challenged by the problems of polymer networks; moreover, they challenge each other and find their mutual usefulness. In the contemporary stage of development, the big industries find it important and profitable to give the chemists and technologists tools that bridge the technology with the end-user properties and the economy of the process. In the crosslinked polymer field, the branching theories play an important role. These represent the keystones of the packages of computer programs available to chemist and technologist and/or end-user. However, the branching theory and structural description is one step to reach the final goal. The structure generation must be bridged with packages relating the structure to physical and possibly other properties. This approach may be classified as "computer-assisted design" (CAD)—a term well known in many branches of technology. However, previous attempts to apply CAD had to rely on many empirical or semiempirical relations and represented at best a kind of optimization procedure. They could bring usable results only for a class of systems for which the relations have been determined and within a narrow range of variation of the input parameters.

HISTORICAL EPILOGUE

In the preceding paragraphs, the present state of the branching theory and its applications have been discussed with outlook to the future. On the occasion of the Herman Mark Symposium, it seems appropriate to glance back to the roots of the present theories.

The origin of branching theories was commonly identified with the Flory-Stockmayer classical theory initiated by Flory's publication in the *Journal of American Chemical Society* in 1941 [25] in which the critical gel point conversion had been predicted using a simple probabilistic approach. The same approach had already been used by Flory in 1936 [26] for the calculation of the degree of polymerization distribution of random linear polymers.

In 1962, the theory of branching processes (cascade theory), employing the cascade substitution and probability-generating functions as a tool for describing the distributions, was introduced into polymer science by Gordon and Good [27]. It enabled one to deal with chemically complex systems and to obtain a variety of structural parameters. However, this formalism has had deep roots. It was used more than 100 years ago to describe the birth and death processes. In 1874, Reverend H. Watson and F. Galton published an article entitled "The Problem of Extinction of Families" [28] where they discussed the laws controlling the extinction of family names in families of English peers.

Galton formulated the problem in *Educational Times* (April 1, 1873, p. 14) as follows:

> *Problem 4001:*
> A large nation, of whom we will concern only ourselves with adult males, N in number, and who each bear separate surnames colonise a district. Their law of population is such that, in each generation, a_0 per cent of the adult males have no male children who reach adult life; a_1 have one such child, a_2 have two, and so on up to a_5, who have five.
> Find (1) what proportion of the surnames will have become extinct after r generations; and (2) how many instances will be of the same surname being held by m persons.

We can see a close analogy with problems we have been faced with in network formation: the distribution of units in different reaction states and the distributions of units up to the *r*th generation obtained by cascade substitution.

Watson used the formalism of probability generating functions (now considered by some chemists too abstract) and obtained a recurrent equation for the extinction probability, from which a probability could be obtained that the family name disappears after a given number of generations. The same probability calculated essentially in the same way

tells us in network formation whether a bond has a finite continuation.

It is commonly accepted that the statistical-mechanical theory of the most characteristic property of polymer networks — equilibrium elasticity — originates from Flory and Rehner [29] in 1943. However, it should not be forgotten that the first molecular model of rubber elasticity based on statistical thermodynamics and statistics of an isolated polymer chain was developed by the *Geheimrat* in 1934 in Vienna [30].

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