RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

September 1962

GRAFT POLYMERS

G. S. Kolesnikov and Tsêng Han-ming

I. Introduction 485

II. Carbon-chain graft polymers 486

1. Grafting by radical polymerisation 486

A. Chain transfer reaction 486

B. Methods based on the presence in the polymer of groups capable of breaking down to form active centres which initiate monomer polymerisation 488

C. Copolymerisation across double bonds in the macromolecule 489

2. Grafting by ionic polymerisation 490

A. Cationic polymerisation 490

B. Anionic polymerisation 490

3. Grafting by chemical reaction 490

III. Carbon-hetero-chain graft copolymers 490

IV. Hetero-chain graft copolymers 491

V. Hetero-carbon-chain graft copolymers 492

I. INTRODUCTION

The properties of high-molecular-weight compounds can be modified by grafting side chains on the polymer backbone, the nature of the side chains being either similar to the backbone or entirely different. Whereas some properties of graft copolymers are determined by those of the constituent backbone and side chains, others are not shown by any of the constituent polymers. An example of this is the graft copolymers which contain hydrophilic and hydrophobic chains (*e.g.* polystyrene on starch). Graft copolymers can also emulsify "oil–water" systems when none of the constituent polymers is an emulsifying agent.

The number of publications dealing with the preparation and properties of graft polymers is growing yearly and there is now a need both for a systematic treatment of the literature and for classification of graft polymers. Several surveys have been published[1-27] in which the material is arranged according to the methods of synthesis. We suggest that classification of graft polymers be considered from two viewpoints: first, from the position of all graft polymers within the series of other high-molecular-weight compounds and second, from the inter-relations of the individual members of the graft polymer series. This can be achieved by various means but the most rational one, in our view, is that adopted by Korshak whose classification is based on chemical structure[28]. We used the same principle for suggesting[29] the division of graft polymers into four types:

I. Homo-chain polymer backbone with grafted homo-chain branches (homo-chain graft polymers).

II. Homo-chain polymer backbone with grafted hetero-chain branches (homohetero-chain graft polymers).

III. Hetero-chain polymer backbone with grafted hetero--chain branches (hetero-chain graft polymers).

IV. Hetero-chain polymer backbone with grafted homo--chain branches (heterohomo-chain graft polymers).

The constituent polymer fragments in a graft copolymer can form either regular or random structures depending on the conditions of synthesis. The same polymer chains can be more or less regular or completely random in structure depending on the conditions of preparation. If the former are referred to as "crystalline" and the latter as "amorphous" the graft polymers of each of the above four types can be divided into four groups: (*a*) amorphous backbone and side chains (amorphous graft copolymers); (*b*) amorphous backbone, crystalline side chains (amorphous–crystalline graft copopolymers); (*c*) crystalline backbone and

side chains (crystalline graft copolymers); and (*d*) crystalline backbone, amorphous side chains (crystalline–amorphous graft copolymers).

The above division into types and groups makes it possible to include the structural and chemico-structural properties in the nomenclature of graft copolymers. This classification can embrace both organic and inorganic copolymers; we believe that it can not only group systematically the already known graft polymers but also reveal new groups of these substances.

The methods of preparation of graft copolymers include mechanical–chemical, irradiation–chemical, and various chemical ones. This review will be limited to the chemical methods of synthesis. Only polymers having carbon chains for the backbone and side chains have been considered as an example of homo-chain polymer constituents. The review does not include the formation of graft copolymers from naturally-occurring polymers. The literature references to graft polymers are arranged according to the chemical–structural principle mentioned above.

II. CARBON-CHAIN GRAFT POLYMERS (CARBON-CHAIN POLYMER BACKBONE WITH GRAFTED CARBON-CHAIN BRANCHES)

Much has been published on the synthesis of this type of graft polymers. The methods vary with respect both to the nature of the starting materials and the mechanism of the grafting reaction. The most widely used synthesis is based on free radical polymerisation; it is the most important method of preparation and gives graft polymers of different composition with diverse properties, but the spacing of the grafts and the length of the side chains are not easy to control. Another method of preparation is ionic polymerisation.

1. GRAFTING BY RADICAL POLYMERISATION

Despite the general nature of such polymerisation, various paths have to be followed for the formation of the radicals required for grafting. These include chain transfer during polymerisation of monomers in the presence of polymers, copolymerisation of monomers with polymers containing double bonds and the so-called "two-step method" based on the introduction into the polymer of groups able to break down under the polymerisation conditions to form active centres at which side chain grafting occurs.

A. Chain Transfer Reaction

This widely used method is based on chain transfer which occurs on polymerisation of monomer B in the presence of an initiator and previously introduced carbon-chain polymer AAAAA, which is either in solution or in a swollen state [30–32]. The reaction can be carried out in the block† in solution, in emulsion, and in latex. Growing chains begin to form from monomer B as the initiator breaks down. The growing polymer radicals react with molecules of the previously introduced AAAAA polymer and detach from it hydrogen or other labile atoms with consequent formation of free radicals on the polymer chains. These newly formed radicals initiate polymerisation of monomer B and side chains BBBBB are formed which are chemically bound to the polymer backbone. The number of grafted side chains depends both on the nature and molecular weight of polymer AAAAA and on the nature of the attacking radicals.

Omitting the stage of formation of the growing polymer radical, the process can be represented as follows:

$$\dot{R}+\cdots CH_2CHXCH_2CHX\cdots \rightarrow RH+\cdots CH_2\dot{C}XCH_2CHX\cdots \quad (1)$$

$$\cdots-(CH_2CHY)_nCH_2\dot{C}HY+\cdots CH_2CHXCH_2CHX\cdots \rightarrow$$

$$\rightarrow \cdots(CH_2CHY)_nCH_2CH_2Y+\cdots CH_2\dot{C}XCH_2CHX\cdots \quad (2)$$

$$\cdots-CH_2\dot{C}XCH_2CHX\cdots+mCH_2=CHY \rightarrow \cdots CH_2CXCH_2CHX\cdots$$
$$\cdots YCHCH_2CHYCH_2CHYH_2C \quad (3)$$

$$\cdots CH_2\dot{C}XCH_2CHX-\cdots+\dot{C}HYCH_2(CHYCH_2)_n-\cdots \rightarrow$$

$$\rightarrow \cdots-CH_2CXCH_2CHX-\cdots$$
$$\quad\quad CHYCH_2(CHYCH_2)_n-\cdots \quad (4)$$

where CH_2CHX = A and CH_2CHY = B.

Eqns. (1) and (2) express the chain transfer reaction involving primary radicals (1) and growing polymer radicals (2). The graft copolymer (3) is formed by addition of monomer to the polymer radicals. Recombination of polymer radicals (4) is theoretically possible but not highly probable. Houtz and Adkins [33] first reported the increase in size of polystyrene macromolecules obtained by polymerisation of styrene in the presence of polystyrene dissolved in it. Flory [34] has suggested that in this case branching occurs as the result of chain transfer by the polymer.

Korshak [13] has shown that the overwhelming majority of copolymers formed by radical copolymerisation of two monomers (the chain transfer being effected by the polymer molecules) are graft copolymers since their backbone and side chains are of different composition. This difference can be extremely marked if the relative activity of one monomer is substantially greater than that of the other. The backbone in such cases can be expected to contain more residues of the more active monomers and the side chains more of the less active ones. The first synthesis of a copolymer by the radical mechanism can thus be regarded also as the first synthesis of a graft polymer.

It had been thought that macroradicals could only be formed by reaction (2) since primary radicals would react more readily with monomer molecules than with polymer ones, the hypothesis being based on the activation energy of the chain transfer reaction being higher than that of the addition reaction. However, Smets [32] showed that reaction (1) did actually occur, but that its rate depended on the nature of the monomer–polymer–initiator system. Thus methyl methacrylate in the presence of polystyrene gives a high yield of the graft polymer when the reaction is initiated by benzoyl peroxide, but only an insignificant amount of the graft polymer when azoisobutyric acid dinitrile or tertiary butyl peroxide is used as initiator. At the same time appreciable and roughly similar amounts of graft copolymers are formed independently of the nature of the initiators when vinyl acetate is polymerised in the presence of poly(methyl methacrylate). The same results have been reported for the vinyl acetate–poly(ethyl α-chloroacrylate)

† Solid state. The terms "block" and "graft" polymer are often used to distinguish between addition at the end of an existing chain and addition as a side chain (Ed. of Translation).

stem[35]. Benzoyl peroxide is an effective graft initiator for rubber, whereas azoisobutyric acid dinitrile fails to give a graft copolymer[36-38].

Schulz *et al.*[39] determined the chain transfer constants‡ during the formation of graft copolymers by polymerisation of monomers in the presence of low-molecular-weight polymers. This is the first and therefore a very interesting attempt to investigate the mechanism of graft polymer synthesis by the chain transfer method.

The role of the chain transfer through the polymer is enhanced by a rise in temperature since the energy of activation of the chain transfer reaction is greater than that of the growth reaction. The rate of chain transfer also depends on the polymer : monomer ratio, the lability of the atom being detached and the reactivity of the polymer radical[8,9]. As expected, graft polymers are usually obtained more readily by increasing the polymer : monomer ratio[40]. But when the polymer concentration is very high the grafting may be complicated by the increasing viscosity of the system which may alter the chain transfer constant and by the graft polymer forming a new phase which would lower the graft polymer yield and reduce the number and length of grafted side chains. Hayes[41] and Berlin *et al.*[42] also observed that the yield of graft polymers declined with increasing concentration of polymer in the system.

When the polymer contains highly reactive centres (bromoethyl[43], bromophenyl[44-47], or thiol groups[48-49]) the high rate constants for chain transfer by these groups ensure the formation of side chains. Thus when thioglycollic acid or hydrogen sulphide acts on the copolymer of methyl methacrylate with glycidyl methacrylate the number of SH-groups formed in the copolymer depends on the number of glycidyl methacrylate residues in the copolymer. Side chains can be grafted at the sites of the SH groups[48,49]. Fox, Gluckman, and others[48,49] have devised an equation, based on the kinetic reaction scheme, for determining the effectiveness of grafting§ in a system where the grafting is achieved by chain transfer by the SH-groups joined to the backbone. They postulated that the molecular weight of the side chains was independent of the degree of grafting and that all the free radicals, including the sulphur ones, react at the same rate. Their equation is given below:

$$E \cong \left[\frac{(1-\Phi)}{1-\Phi-y_0 \ln \Phi}\right]\left[1+\frac{(1+r)\,y_0^2}{(\Phi+y_0)(1+y_0)}\right],$$

where Φ is the unreacted fraction of the chain transfer centres, *i.e.* $[SH]_{final}/[SH]_{initial}$, y_0 is the initial ratio of the number of chain terminations effected by radicals to the number of chain terminations effected by chain transfer by the polymercaptan, *i.e.*

$$y_0 = \frac{\left(\frac{k_{term}}{k^2_{growth}}\right) \times \text{initial rate of polymerisation}}{C_s\,[SH]_0},$$

C_S being the chain transfer constant and r the fraction of chain terminations occurring by disproportionation, *i.e.*

$$r = \frac{k_{term\ disproport}}{k_{total\ term}}.$$

In one instance the observed value of E was 0.79 and that calculated from the equation was 0.86.

‡ The chain transfer constant is the ratio of the rate constant of chain transfer to the rate constant of chain growth.

§ The effectiveness of grafting is the fraction by weight of the polymer grafted on the backbone relative to the total weight of the newly formed polymer (grafted branches + new homopolymer).

Some functional groups in a chain are sometimes characterised by an enhanced rate constant for chain transfer, *e.g.* the methyl and phenyl groups in poly(vinyl acetate) and poly(vinyl benzoate)[50-52]. Polymer chains containing labile atoms can be obtained by copolymerisation with either a monomer containing labile atoms or one capable of acquiring such atoms by additional chemical treatment when already in the copolymer. Thus saponification of the styrene–allylydene diacetate copolymer yields a copolymer which contains CHO groups whose hydrogen atoms participate readily in chain transfer. Polymerisation of any vinyl monomer in the presence of a saponified copolymer gives graft copolymers[53].

Chain transfer reactions are important in the synthesis of graft polymers in the case of rubber and synthetic polydienes and occur simultaneously with direct addition across double bonds[54-57]. In these cases the dinitrile of azoisobutyric acid is, unlike benzoyl peroxide[58-60], practically unable to initiate grafting. When poly(methyl methacrylate) and polystyrene are grafted on rubber the side chains are short and small amounts of homopolymers are formed, *i.e.* the grafted monomer is used up almost entirely in forming the graft copolymer[38,62-65].

Other factors, besides the conditions of the chain transfer reaction, which are extremely important in the synthesis of graft copolymers by radical polymerisation of the monomer in the presence of a polymer are steric hindrances and the chemical nature of the polymer and the monomer, which determines their polarity and reactivity. The monomers and polymers can be graded as follows according to ease of graft copolymer formation: vinyl chloride > > vinyl acetate > styrene and poly(vinyl chloride) > polyacrylonitrile > poly(vinyl acetate) > polystyrene[41].

Chain transfer has often been used for the preparation of graft polymers[40,50,66-102]. Thus Roland and Richards[50] polymerised ethylene under pressure in the presence of poly(vinyl acetate) and ethyl peroxide and they obtained a graft polymer which contained polyethylene side chains and polyethylene fragments in the backbone.

Miller[98] grafted polyacrylonitrile on polyacrylamide and found that all the initial polyacrylamide participated in the formation of the graft polymer. The softening point of graft polymers drops with increasing number of grafted side chains and approaches, within limits, the softening point of the random copolymer containing an equal number of acrylamide and acrylonitrile residues.

Polyampholytes have been obtained by polymerisation of 2-vinyl pyridine in the presence of poly(ethyl acrylate) (initiator: dinitrile of azoisobutyric acid) with subsequent acid hydrolysis[86]. The following grafts have also been effected: poly(vinyl acetate), poly(vinyl chloride), poly(vinyl formate), and polystyrene on polyethylene[40]; acrylic acid on polyacrylamide[101]; poly(vinyl chloride) on the copolymer of butyl methacrylate and methacrylic acid[42,102]; poly(vinyl acetate) on poly(ethyl α-chloroacrylate)[35]; poly(vinyl acetate) on poly(vinyl chloride)[41]; and poly(vinyl acetate) and poly(methyl methacrylate) on poly(vinyl benzoate)[51].

Pure copolymers cannot be obtained by the chain transfer reaction but it has the advantage of simplicity, and hence is widely used industrially. Rubber-like graft copolymers are prepared by polymerisation of monomers (styrene, methyl methacrylate, acrylonitrile) in the latex of natural or synthetic rubber in the presence of water-soluble initiators or by polymerisation of monomers in

the presence of rubber which has been dissolved or allowed to swell in them [93,103]; when vulcanised these rubbers show enhanced durability, resistance to atmospheric effects and to friction and are suitable for the preparation of gas-filled elastomers.

Graft polymers suitable for the production of plastics can be synthesised from the appropriate monomer and rubber, the amount of the latter usually constituting no more than 10% of the former, but the yield is, as a rule, low. The graft polymer obtained by polymerisation of styrene in the presence of 30% rubber shows good impact strength but reduced hardness and marked residual deformation (compared to polystyrene) following compression and stretching [102]. Berlin and Khanukaeva [104] found that the graft polymers prepared by polymerisation of styrene in the presence of 5–10% rubber are hard, elastic, and able to withstand impacts 3–5 times greater than those withstood by polystyrene or styrene–acrylonitrile copolymers.

The graft polymers prepared by polymerisation of vinyl chloride in the latex of butyl methacrylate and acrylic acid copolymer and by polymerisation of a mixture of butyl methacrylate and acrylic acid in a poly(vinyl chloride) latex show good adhesive properties, photostability as well as resistance to abrasion and to the effect of water, solvents, and many chemical compounds [42,102].

B. Methods Based on the Presence in the Polymer of Groups Capable of Breaking Down to Form Active Centres which Initiate Monomer Polymerisation

Introduction of groups into polymer macromolecules which readily form active polymerisation centres (polymer initiators) is another important method of preparation of graft polymers. These include peroxide and hydroperoxide [105–114], diazo- [115], diazoimino- [116], and dithiocarbonic [117] groups.

The peroxide and hydroperoxide groups are used most frequently. They are usually formed in the polymers by oxidation [75,118,199], ozonation [58,120–127], action of peroxide compounds (*e.g.* on the acid chloride of poly(acrylic acid) [118,128–130] and on polyaldehydes [131]), irradiation by X-rays or γ-rays in the presence of air [24,25,132], electrolysis of aqueous solutions of poly(acrylic acid) or other polymers containing the carboxyl group [133,134] and other methods used in the synthesis of low-molecular-weight peroxides and hydroperoxides.

Homolytic breakdown of peroxide and hydroperoxide groups leads to a simultaneous formation of macro- and micro-radicals which initiate polymerisation of the monomer present to give a graft copolymer and homopolymer respectively. These can be separated by fractionation of the graft reaction products and the relative reactivities of the radicals can be compared. Smets *et al.* [134] fractionated the product of polymerisation of styrene in dioxan in the presence of a copolymer of methyl acrylate and t-butyl peracrylate and found that the ratio of graft polystyrene and homopolystyrene depended largely on the viscosity of the solution and increased with increase in viscosity. This ratio is a function of monomer concentration and is inversely related to it. Riess and Banderet [135] confirmed these results.

The difference in lability of micro- and macro-radicals is also important in the synthesis of graft polymers. Microradicals and the chains formed from them are much more labile than macro-radicals and the chains which they enter. The rate of termination of the more labile chains is considerably higher than that of the less labile ones so that less homopolymer is formed.

The ability to form polymer peroxides depends on the structure of the macromolecules. Mark [136,137] had suggested that polystyrene would readily give a hydroperoxide since its chains contained tertiary carbon atoms similar to those of the cumene side chain. However, this only occurs extremely slowly and with great difficulty [75,110,118,138–141]. Metz and Mesrobian [75,110,140] and others [47,109,118] have suggested that polystyrene be converted to poly-*p*-isopropylstyrene in which the isopropyl group is easily oxidised to give a hydroperoxide.

Poly-α-olefines and α-olefine copolymers which contain tertiary carbon atoms form hydroperoxide groups on atmospheric oxidation under relatively mild conditions ($\sim 70^\circ$ and 3 atm pressure) [119]. Isotactic polymers react only on the surface or in the amorphous regions close to the surface; with atactic polymers the hydroperoxide groups are formed within the whole bulk of the polymer although here, too, the surface area subjected to the action of ozone is very important, the rate of peroxide formation dropping with diminution of the "surface : volume" ratio [142,143]. Grafting of poly(methyl methacrylate) on polypropylene reduces the tensile strength somewhat but enhances the elongation. Polystyrene grafted on polypropylene and on polybutene gives copolymers of great impact strength unaffected by aging [119]. Ozonisation of polypropylene and polyethylene and subsequent polymerisation of vinyl monomers in their presence have been used to obtain graft copolymers by other authors as well [144–150]. The gas permeability of polyethylene can be markedly reduced and its photostability increased by grafting polyacrylonitrile on crystalline polyethylene [144]; grafting of 15% acrylic acid on polyethylene fibres and films gives strong, hydrophilic materials which can be dyed by basic dyes [145,146].

Grafting of poly(vinyl chloride) on polypropylene and polybutene enhances elasticity [119]. The plasticising effect of the hydrocarbon component of such graft copolymers differs from that of the normal plasticisers used for poly(vinyl chloride); these contain polar groups which associate with the polar groups of the polymer and act as solvents. Poly-α-olefines do not combine with poly(vinyl chloride) and the macromolecules of the latter cannot associate with one another; consequently the temperature of the second order transformation does not drop as occurs when ordinary plasticisers are used.

A graft copolymer which showed highly-elastic deformation between 85° and 235° was obtained by polymerising polystyrene in the presence of ozonised isotactic polystyrene. This graft copolymer shows transformation points characteristic for each individual copolymer [124,151,152]. Graft copolymers of different degrees of crystallinity can be obtained by varying the ratio of the initial substances and the degree of ozonisation. Such graft copolymers are formed by polymeric chains consisting of chemically homogeneous links of different spatial configuration. Ozonisation followed by decomposition of the peroxide groups gives graft copolymers from polyvinyl chloride and various monomers (ethyl acrylate, vinylidene chloride, methyl methacrylate, acrylonitrile, styrene and vinyl acetate) [153], from polystyrene and poly(acrylic acid) [127], and from other substances [154].

The random copolymer of methyl methacrylate and isopropenyl acetate gives on hydrolysis a copolymer which contains tertiary OH groups oxidised by hydrogen peroxide to hydroperoxide groups. Methyl methacrylate polymerised (thermally or by oxidation–reduction) in the presence of such a macrohydroperoxide yields graft copolymers [130]. The rate of the grafting reaction is proportional to the square root of the concentration of the macrohydroperoxide.

Electrolysis of partially neutralised polymeric carboxylic acids gives free radicals at the anode which are simultaneously oxidised by the oxygen formed to hydroperoxides with a yield of 1%. Such hydroperoxides have been used by Smets for initiation of acrylamide polymerisation in an aqueous solution [134].

Formation of homopolymers is an undesirable side reaction in grafting by monomer polymerisation in the presence of macroperoxides. This can be practically completely suppressed by ferrous ions [111,155–158]. The ·OH radicals formed by the decomposing macrohydroperoxides are converted into OH^- anions and no homopolymers are formed. The reaction must be carried out in emulsion and has yielded graft polymers from styrene and polystyrene or the copolymer of styrene and 4-vinyl cyclohex-1-ene [111]. A very promising but little investigated synthesis of graft copolymers is based on an oxidation–reduction reaction between certain cerium salts (such as cerium ammonium nitrate) and compounds containing the OH, SH, CHO, or NH_2 groups [159]. Polyacrylonitrile, poly(methyl acrylate) and polyacrylamide have been successfully grafted on poly(vinyl alcohol) [16,159,160] by this method.

$$Ce^{4+} + \sim\sim CH_2CH(OH) \sim\sim \rightarrow [\text{complex}] \rightarrow$$
$$\rightarrow Ce^{3+} + H^+ + \sim\sim CH_2\dot{C}(OH) \sim\sim (\text{or } \sim\sim CH_2\dot{C}H \sim\sim).$$

Graft polymers so obtained are not contaminated by homopolymers since the initiating centres are only formed on the polymer chain.

Graft polymers can be obtained from polymers and copolymers containing aromatic amino-groups. When such high-molecular-weight compounds are diazotised a polymeric diazonium salt is formed which reacts with Fe^{II} to form a polymeric polyradical able to initiate polymerisation of vinyl monomers. This method has been used for the preparation of a graft copolymer of polyaminostyrene and acrylamide [161].

As already mentioned, graft polymers can be obtained from high-molecular-weight compounds containing peroxide-ether and peroxide-anhydride groups [128–130,134]. Such polymers are formed by the action of t-butyl hydroperoxide or perbenzoic acid hydroperoxide on polymers and copolymers containing acid chloride groups. The rate of formation of the graft copolymers is proportional to the square root of the macroinitiator concentration.

C. Copolymerisation across Double Bonds in the Macromolecule

a. Double bonds within the main chain of carbon-chain macromolecules. When graft copolymers are synthesised by the addition of radicals, formed from monomers, across the double bonds in polymers the side chains grow by polymerisation of monomers. The reaction takes place at lower temperatures and polymer concentrations than those needed for the chain transfer reaction. The process is, however, often complicated by gel formation and chain transfer reaction involving hydrogen atoms in the α-position with respect to the double bond. Synthetic rubbers are the most typical representatives of synthetic polymers containing double bonds in the chain and were naturally the first and main substances used in this synthesis of graft polymers. Butadienestyrene rubber has been copolymerised with styrene both in the mass in the presence of peroxides [162] and in emulsion [102]. The thermomechanical curves for block graft copolymers show two inflections, at about 100°, which is characteristic for polystyrene, and at about -40°, which is characteristic for rubber; the initial rubber had a glass point ranging from -65° to -70°. The thermomechanical behaviour of these graft copolymers was like that of a mixture of two polymers [162]. Vulcanised graft copolymers containing poly(methyl methacrylate) side chains branching from the main butadienestyrene chains have greater abrasion and flex-cut resistance than soot-filled vulcanised butadienestyrene rubbers [163].

When aniline–formaldehyde resins are prepared in the presence of butadienestyrene rubber the tensile strength of the vulcanised graft copolymers formed first increases with increasing resin content and then begins to diminish [164]. Copolymerisation of styrene with butadieneacrylonitrile rubber in emulsion in the presence of potassium persulphate gives a graft polymer whose glass point is 15° lower than that of polystyrene [102].

Polystyrene brominated with *N*-bromosuccinimide in the presence of benzoyl peroxide and then dehydrobrominated with sodium butoxide gives a polymer [46] with double bonds in the backbone; this unsaturated polymer was copolymerised with vinyl acetate in the presence of benzoyl peroxide both in the mass and in benzene solution to give a mixture of graft copolymers and poly(vinyl acetate). Synthesised graft copolymers have been hydrolysed to graft copolymers with poly(vinyl alcohol) side chains which are reconverted by acetic anhydride into poly(vinyl acetate).

b. Double bonds in the side chains of the macromolecules. Soluble copolymers with double bonds in the side chains can be prepared by copolymerisation of monovinyl monomers (styrene, methyl methacrylate and others) with low concentrations of divinyl monomers such as ethylidene dimethacrylate, divinyl benzene, and allyl methacrylate [165]. Copolymerisation of these with vinyl monomers gives graft copolymers. Graft copolymers based on polyacrylonitrile have been obtained [166,167] in which poly(acrylic acid) or poly(vinyl acetate) formed the side chains. The initial copolymer was prepared by polymerisation of acrylonitrile containing 0.007–0.028 mole % *N,N'*-methylenebisacrylamide. Copolymers formed at these concentrations have unsaturated side groups and it is at these sites that grafting of side chains occurs. When the concentration of *N,N'*-methylenebisacrylamide exceeds 0.028 mole %, the copolymers no longer dissolve completely in dimethyl formamide, evidently because of the formation of copolymers with a reticular structure. Crouch and Shotton [168] found that liquid polybutadiene ($M \simeq 1300$) containing ~60% of vinyl side groups copolymerised with maleic anhydride and with drying oils. In this case, too, three-dimensional structures were formed. The probability of such an occurrence should always be considered in graft copolymer syntheses based on the use of unsaturated side chains.

2. GRAFTING BY IONIC POLYMERISATION

A. Cationic Polymerisation

Descriptions of ionic polymerisation often employ the terminology used for radical polymerisation (initiation, chain growth, chain termination, chain transfer) although the mechanisms of the two types of polymerisation are entirely different. The synthesis of graft polymers by copolymerisation of styrene in carbon tetrachloride or other solvents, in which poly-*p*-methoxystyrene is dissolved, in the presence of BF_3 or $SnCl_4$ at 0°–20° can be regarded as based on a chain transfer reaction although the mechanism of this reaction has not yet been finally elucidated. The rate of styrene polymerisation is independent of, and the composition of the graft copolymer almost independent of the concentration of poly-*p*-methoxystyrene [169]. Styrene does not polymerise when the molar ratio styrene : poly-*p*-methoxystyrene is less than 1.65 : : 0.377. Attempts to prepare graft polymers from poly-*p*-methoxystyrene and n-butyl vinyl ether, ethyl vinyl ether, pinene, isobutene, or *N*-vinylpyrrolidone failed. The authors [169] concluded that the number of polymer–monomer combinations was limited because: (1) the polymer must react with the attacking carbonium ions, (2) the polymer must be soluble in a solvent suitable for cationic polymerisation, and (3) the difference in solubility must be sufficient for separation of homopolymers from graft copolymers.

Graft copolymers have been obtained [170] by polymerisation of styrene in the presence of aluminium chloride and poly(vinyl chloride), polystyrene forming the side chains; homopolymerisation of styrene and destruction of poly(vinyl chloride) also occur in this reaction. Styrene and indene branches are easily grafted on poly(vinyl chloride) and the copolymer of vinyl chloride with vinylidene chloride; this also applies to *trans*-stilbene and indole. Destruction of graft copolymers is considerably reduced at lower polymerisation temperatures when titanium tetrachloride is used instead of aluminium chloride. The same method has been used to obtain a graft copolymer from poly(chloromethyl) styrene and isobutene in the presence of aluminium bromide [171].

B. Anionic Polymerisation

Polybutadiene and its copolymers containing double bonds react with styrene, acrylonitrile, and α-methacrylonitrile in the presence of sodium or sodium hydride to form graft copolymers with branches starting from the backbone at the sites of unsaturation. It is desirable to use no solvent since a high concentration of monomer favours the formation of graft copolymers [172].

Recently [173] graft copolymers have been obtained in which poly(methyl methacrylate) forms the main chain and polystyrene the side ones. Their synthesis is based on the reaction between the polystyrene carbanions and the ester groups of poly(methyl methacrylate). Benzylsodium and phenylisopropylpotassium were used as catalysts; they are ionised in tetrahydrofuran to form reddish violet solutions. The colour changes to reddish orange after the addition of the first few drops of styrene, which indicates the formation of styrene anion and its polymerisation. When concentrated poly(methyl methacrylate) in tetrahydrofuran is added at a low temperature the colour begins to change as the polystyrene monocarbanion disappears by reacting with the ester groups to form side chains.

3. GRAFTING BY CHEMICAL REACTION

Graft copolymers in which the carbon-chain backbone and the carbon-chain branches are linked by non-carbon-to-carbon bonds can, provisionally, be regarded as carbon-chain graft polymers. The relative proportion of such hetero-chain links can be extremely small and their presence will then have no effect on the properties of the graft polymers. The latter are obtained by interaction of polystyrene with an end amino-group (such polystyrene is formed by polymerising styrene in the presence of sodium in liquid ammonia) with copolymers containing small amounts of β-isocyanatoethyl methacrylate [174]; in these graft polymers the side chains and the backbone are joined by urea-groups. The initial copolymers were those of β-isocyanatoethyl methacrylate with methyl methacrylate, butyl methacrylate, lauryl methacrylate, butyl acrylate, acrylonitrile, styrene, and vinyltoluene. The grafting reaction could be followed by the disappearance of titratable amino-groups in time. The most studied system was the graft of styrene on the copolymer of methyl methacrylate and β-isocyanatoethyl methacrylate.

III. CARBON-HETERO-CHAIN GRAFT COPOLYMERS (HETERO-CHAIN BRANCHES GRAFTED ON CARBON-CHAIN POLYMER BACKBONE)

These graft copolymers are most frequently prepared from carbon-chain polymers containing reactive side atoms and groups (NH_2, OH, SH, Cl, COOH, COCl, COOR, $CONH_2$, SOCl, CHO, and others [11,26,136,175–199]). They can also be prepared by copolymerisation of vinyl monomers with hetero-chain polymers with an unsaturated end group [196,197,200,201]. Another method involves the simultaneous polymerisation and polycondensation which occur when mixtures of a vinyl monomer containing an ester or carboxyl group and an ω-hydroxycarboxylic acid or its polyester are heated [196,197,202–204]. The polyester of an ω-hydroxycarboxylic acid can be replaced by polyesters of dicarboxylic acids and glycols, but the reaction is complicated by the formation of three-dimensional structures [203].

Recently [205] graft carbon-hetero-chain copolymers have been prepared by interaction of phenol–formaldehyde resins with the acid chlorides of dicarboxylic acids and bis-phenols at their interface. This method yields products whose properties vary depending on the nature and ratio of the starting materials.

Several works are devoted to grafting polyoxyethylene on various polymers and copolymers by reacting the latter with ethylene oxide. Polyoxyethylene grafted on poly(vinyl alcohol) reduces the rigidity and hardness of poly(vinyl alcohol) films and enhances their thermoplastic and adhesive properties. The graft copolymers so obtained remain readily soluble in water and can be used in various reactions since they contain primary OH groups in the side chains and secondary OH groups in the backbone [178]. Polyoxyethylene side chains can be grafted on copolymers of styrene and vinyl alcohol obtained by saponification of styrene copolymers with small amounts of vinyl acetate. The resultant graft copolymers contain hydrophobic backbones and hydrophilic side chains [136]. Copolymers of styrene and acrylic acid also react with ethylene oxide, forming graft copolymers with polyoxyethylene side chains [179]. These adhere well to glass and can be used to prevent the accumulation of static electric charge on polymeric materials. Three-dimensional elastic products

result from the action of 2:4 diisocyanatotoluene on such graft copolymers. The ester groups in the copolymer of styrene and dimethyl moleate were converted into β-hydroxyethylamide groups and graft copolymers with polyoxyethylene side chains were obtained on reaction with ethylene oxide[175]. When the copolymer of styrene with allyl acetate was hydrolysed to the corresponding allyl alcohol copolymer the latter reacted with ethylene oxide, the side chains grafting on at the sites of the OH groups[175]. Ethylene oxide reacts with polyacrylamide to give graft copolymers with a low coefficient of side chain polymerisation[180] and simultaneous formation of cross-linked polymers. Condensation of polyacrylamide or copolymers of acrylamide with polyethylenechlorohydrin also forms graft copolymers[181].

Carbon-hetero-chain graft copolymers with polyester side chains can be prepared both by trans-esterification of polyesters with polymers containing ester or carboxyl groups and by copolymerisation of vinyl monomers with polyesters of ω-hydroxycarboxylic acids with an unsaturated end group; they are also formed by simultaneous polymerisation and polycondensation of vinyl monomers with the ester groups of ω-hydroxycarboxylic acids or their esters[189,204]. When hetero-chain polyesters able to form ordered structures are grafted on poly(methyl methacrylate) the graft copolymers formed also have such an ordered structure[175,189-193,195-197,199,203,204] that spherulites could be seen by polarised light[197,198,200,203,204].

Studies of trans-esterification between poly(methyl methacrylate) and various hetero-chain polyesters showed that grafting of side chains from polyesters able to form ordered structures led to: (1) folding of the macromolecules in solution into more symmetrical globules, reflected in lowered intrinsic viscosity and simultaneous increase of the Huggins constant; (2) change in physical properties, in particular a reduction in the tensile strength and a considerable increase in the elongation at rupture (up to 200–240%); (3) rise of softening point for a definite optimal ratio between the side chains and the backbone. The structure and properties of graft copolymers given by trans-esterification depend not only on the ratio of the initial substances and their nature but also on the duration of the trans-esterification reaction[195]. If the optimal time is exceeded esterolysis of the polyester side chains by the ester groups of poly(methyl methacrylate) occurs, with loss of structural order and change in the physical properties, which then approach those of poly(methyl methacrylate).

One of the present authors and Gurgenidze had shown that graft copolymers of ordered structure could also be formed by the reaction of isotactic poly(methyl methacrylate) with poly(ethylene azelate)[192].

Graft copolymers containing side chains of polyesters of ω-hydroxycarboxylic acids have been obtained from ω-hydroxypelargonic acid and a copolymer of styrene with maleic anhydride, under conditions ensuring polycondensation of the hydroxycarboxylic acid, and from styrene–maleic anhydride copolymer and polyesters of ω-hydroxyenanthic, ω-hydroxypelargonic, and ω-hydroxyundecanoic acids[197,198]. In this case also ordered graft copolymers able to form spherulites can be obtained. The thermomechanical properties of the graft copolymers are intermediate between those of the polyesters and the styrene–maleic anhydride copolymer. Grafting of polyesters to the latter gives products which are highly elastic at high temperatures, similar to graft polymers of polyacrylic acid and polystyrene[127]. The infra-red spectra of the graft copolymers given by the styrene–maleic anhydride copolymer and polyesters differ from that of the initial copolymer in having absorption bands at 1700–1750 and 1200 cm^{-1} characteristic of ester groups and an absorption band at 3000 cm^{-1} characteristic of the COOH group[198].

Graft copolymers of ordered structure have also been obtained by copolymerisation of methyl methacrylate and acrylonitrile with polyesters of ω-hydroxypelargonic and ω-hydroxyenanthic acids; the polyesters contained a terminal methacrylic group which was introduced by treating the polyesters with the acid chloride of methacrylic acid[175,197,200]. Copolymerisation with methyl methacrylate was carried out in the bulk phase[175,197] and with acrylonitrile in the bulk phase and in an emulsion[200].

Graft copolymers with hydrophobic and hydrophilic properties were obtained by simultaneous polymerisation and polycondensation of methacrylic and ω-hydroxypelargonic acids, the former constituting the backbone and the polyester of the latter the side chains. These graft polymers are, unlike polymethacrylic acid, elastic at high temperatures and have an ordered structure when the ω-hydroxypelargonic acid content of the initial mixture is 50 wt. % and over. Spherulites were formed in this case also[203]. The same method was used to prepare graft copolymers from methyl methacrylate and ω-hydroxypelargonic acid and from methyl methacrylate and ω-hydroxyenanthic acid.

Several publications are devoted to the grafting of polyamide side chains to carbon-chain polymers[182-188,197,205]. Graft copolymers can be obtained from ε-caprolactam with (i) polyacrylic acid, (ii) poly(methyl acrylate)[182], or (iii) copolymers of styrene with acrylic acid, methyl acrylate, and maleic anhydride[183,188]. The reaction is limited by a number of factors: loss of amino-groups, cross-linking, heterogeneity of the molten reaction mixture, etc. An important factor is the compatibility of the starting materials. Wichterle and Gregor[184] attempted to react ε-caprolactam and styrene–*N*-methacrylcaproamide copolymer in the presence of Na-caprolactam but, despite the low temperature (70°–80°), the reaction mixture began to gel at the outset because cross-linking occurred by the Claisen reaction between the diacyl imide groups belonging to different polymer chains. Dogadkin and his coworkers found that when butadienestyrene rubbers containing carboxylic groups were heated at 200°–220° with ε-caprolactam the latter slowly added on to the rubber. The reaction was accelerated by using sodium and boron trifluoride–diethyl ether[185,186]. Valentine[187] obtained graft copolymers from poly(methyl methacrylate) and caprolactam.

We have prepared graft copolymers with polyenanthamide side chains by polycondensation of aminoenanthic acid in the presence of styrene–maleic anhydride copolymer or in the presence of polyacrylic acid when hydrophobic–hydrophilic products were obtained[197,206]. The solid-phase reaction at 185° gives either amorphous or ordered graft copolymers depending on the ratio of the initial substances.

IV. HETERO-CHAIN GRAFT COPOLYMERS (HETERO-CHAIN BRANCHES GRAFTED ON HETERO-CHAIN POLYMER BACKBONE)

Hetero-chain polymers with reactive groups (CONH, SO_2NH, NHCONH, NHCOO, etc.) in the chain can be con-

verted into hetero-chain graft copolymers either by reaction with substances which can yield hetero-chain polymers (*e.g.* alkylene oxides) or with already formed polymers [207].

The application of polyamide synthetic fibres used in modern textiles is limited by their poor hydrophilic properties. Grafting of polyoxyethylene side chains on the polyamides (at the nitrogen atom) has given the most promising results in attempts to synthesise high-melting hydrophilic polyamides.

Haas *et al.*[208] investigated polyoxyalkylation of a number of polyamides (polycaprolactam, polyhexamethyleneadipamide, mixed polyamides, methoxymethylated polyamides, polyamides containing sulphamide groups in the chain, polyurea synthesised from 2,4-diisocyanotololuene and hexamethylenediamine). Ethylene oxide, propylene oxide, ethylene carbonate, and epichlorohydrin have been tried as oxyalkylating agents, but satisfactory results were obtained only with ethylene oxide. The synthesised graft copolymers with polyoxyethylene side chains had almost the same melting points, crystallinity, and solubility as the original polyamides; thus, grafting of ~60% polyoxyethylene on polyhexamethyleneadipamide lowers the m.p. to ~220°. Since polyoxyethylene branches act as internal plasticisers the graft copolymers are more elastic than the original polyamides; they are not, however, as strong. Introduction of polyoxyethylene side chains affects markedly the vapour permeability of the polyamides: the figure for polyhexamethyleneadipamide is 3.13 g m^{-2} h^{-1} but when 50% polyoxyethylene is grafted on it, rises to 52.8 g m^{-2} h^{-1}.

Sonnerskog [209] has also described the preparation of graft copolymers with polyoxyethylene branches by the action of ethylene carbonate on polyamides.

The grafting of polyoxyethylene on caprone powders, films, and fibres [180,210,211], and on films of polyhexamethylenethiodivaleramide and of mixed polyamide anid G-669 [180,210] have also been investigated and the reaction was found to occur not only at the surface but also within the substance of the films, fibres, and powders. The products were a polyoxyethylated polycaprolactam, which was readily soluble in alcohol, and polyoxyethylated anid G-669, which was water-soluble. Graft polymers in which polyacrylic acid branches were grafted on the polyamide backbone have also been prepared [212].

Coleman [213] prepared graft copolymers of polyethyleneterephthalate which were high melting, possessed good physical properties, and gave fibres which could be more readily dyed; his starting materials were the sodium derivative of the dimethyl ester of hydroxyterephthalic acid and polyoxyethylene whose terminal OH group was replaced by chlorine atoms followed by trans-esterification with ethylene glycol.

Amino-acid graft polymers have been prepared by polymerisation of *N*-carboxy-α-amino-acid anhydrides in the presence of polylysine or polyornithine used as macroinitiators [214]. A water-soluble graft copolymer has been prepared from trypsin and *N*-carboxytyrosine anhydride. Enzymes modified in this way with 5 to 10% grafted tyrosine fully retain their proteolytic activity [215]. It has been suggested that linear side chains could be grafted on the biologically least important functional groups in enzymes, antibodies, and antigens to give modified biologically active proteins; these could then be linked by covalent bonds to water-insoluble polymers.

V. HETERO–CARBON-CHAIN GRAFT COPOLYMERS (CARBON-CHAIN BRANCHES GRAFTED ON HETERO--CHAIN POLYMER BACKBONE)

These are prepared by polymerisation of vinyl monomers in the presence of hetero-chain polymers making use of either peroxide groups or chain transfer reactions.

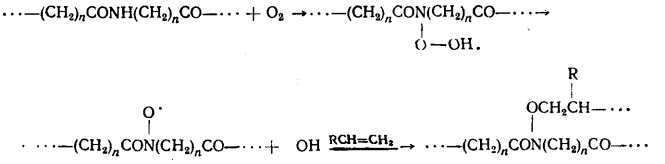
Hetero-chain polymer compounds containing peroxide groups are formed when such polymers are treated with ozone or atmospheric oxygen at high temperatures. They initiate polymerisation of vinyl monomers and so lead to the formation of hetero-carbon-chain graft copolymers. This method is being thoroughly investigated by Korshak and his coworkers [216-226]. They have succeeded [216-221] in grafting polystyrene, poly(methyl methacrylate), poly(vinyl acetate), poly(vinylidene chloride), and polyacrylonitrile on fibres and films of caprone, anid, enanth, mixed polyamide anid G-669, and poly(ethylene terephthalate) (Lavsen) by ozonising hetero-chain polymers and then polymerising the vinyl monomers. Styrene showed the greatest reactivity under the conditions adopted by them. The yield of graft copolymers is inversely related to the degree of orientation of the polyamide; under similar conditions of ozonisation and grafting, the increase in weight following grafting of styrene on anid G-669 is several times greater than that observed in the case of caprone [220]. If the optimum ozonisation period is exceeded, the mechanical strength of the graft copolymers diminishes but even after treatment for 6 h and subsequent grafting of polystyrene the caprone film strength amounted to 72% of that of the original film.

Poly(ethylene terephthalate) has demonstrated that hetero-chain polyesters can yield graft copolymers with carbon-chain branches when preliminary ozonisation is used to create polymerisation centres [221]. Of the monomers tried (styrene, vinylidene chloride, acrylonitrile, and vinyl acetate) styrene gives graft copolymers most readily; as in the case of the polyamides, the yields of graft copolymers drop with increasing orientation of the material (film, fibre) undergoing grafting.

Brief ozonisation and subsequent copolymerisation of poly(ethylene terephthalate) with styrene increases the elongation but this is accompanied by a decrease in tensile strength. The same method has been used for the preparation of graft copolymers from poly(ethylene terephthalate) and acrylic acid [154].

Korshak and his coworkers have suggested activating polyamides and polyesters by heating films and fibres made of these polymers in an atmosphere of air or nitrogen [222-226] instead of ozonisation. Such activated films and fibres form graft copolymers in their surface layers when they are heated with vinyl monomers.

The authors suppose that polyamide and polyester products (films, fibres, powders) contain some sorbed air, which reacts during storage with polyamides or polyesters to form peroxide centres. When such materials are heated even in the absence of oxygen the peroxide centres break down and free radicals are produced, which initiate copolymerisation with vinyl monomers. They suggest the following mechanism of initiation:



Such thermal treatment does not lower the strength of the original polymers and enhances that of the graft copolymers. Grafting of polystyrene on caprone fibre gives a polystyrene layer amounting to 23.6% of the fibre weight. When the fibre carrying the grafted polystyrene layer was treated with acid the polystyrene was stripped as a hollow tube; the molecular weight of grafted polystyrene can reach 60 000–80 000.[225] Grafting of acrylic acid on poly(ethylene terephthalate) films[226] increases the adhesion of photographic emulsions to the poly(ethylene terephthalate) base, which is of great practical interest since it makes it possible to reduce the weight of photographic and cinematographic films without impairing their mechanical properties (as compared to films based on cellulose triacetate).

The chain transfer reaction has been used to obtain graft copolymers of styrene and polyester synthesised from adipic acid and pentaerythrol dibromide [2,2-di(bromomethyl)propan-1,3-diol]. Polymerisation of styrene in the presence of this polyester and benzoyl peroxide gives a mixture of the original polyester, polystyrene, and graft copolymer[43] which is separated by selective solution: the polystyrene dissolves in cyclohexane and the polyester in acetone. The graft polystyrene branches are detached from the main polyester chain by esterolysis with ethyl acetate. The molecular weight of the isolated polystyrene was determined and it was found that the particular specimen of graft copolymer contained one polystyrene chain per 23 000 elementary ester units, with a degree of polymerisation of 600. The transfer reaction constant was 40.5×10^{-5} at 60°. Hurd and Roedel[227] copolymerised vinyl monomers (methyl methacrylate, styrene, dichlorostyrene, etc.) with polysiloxanes containing vinyl or allyl groups in the presence of peroxides (the vinyl-containing polysiloxanes are prepared by hydrolysis of methyl vinyl dichlorosilane and the allyl-containing ones are obtained similarly).

This literature survey indicates the extensive interest in the synthesis of graft polymers. Most of the chemical methods used, however, are based on either the chain transfer reaction or the presence (or introduction) of active groups in the main polymer which can initiate the growth of side chains. Other chemical methods have not been sufficiently investigated and we believe that extension of the methods of synthesis of graft polymers will be fruitful, both theoretically and practically in enlarging the range of new polymer materials with the desired properties.

1. N.G.Gaylord, Interchemical Rev., 15, 91 (1956).
2. N.G.Gaylord, Interchemical Rev., 16, 3 (1957).
3. R.Hart, Ind.chim.belge, 21, 1053 (1956).
4. R.Hart, Ind.chim.belge, 21, 1193 (1956).
5. R.Hart, Ind.chim.belge, 21, 1309 (1956).
6. R.Hart, Ind.chim.belge, 22, 39 (1957).
7. E.H.Immergut and H.F.Mark, Makromol.Chem., 18/19, 322 (1956).
8. G.Smets, Ind.plast.mod., 9, No.4, 43 (1957).
9. G.Smets, Ind.plast.mod., 9, No.4, 52 (1957).
10. G.Smets, Coll.Czech.Chem.Comm., 22, Spec.Issue, 264 (1957).
11. A.A.Berlin, "Uspekhi Khimii i Tekhnologii Polimerov" (Advances in Polymer Chemistry and Technology), Vol.2, Goskhimizdat, Moscow, 1957, p.13.
12. A.N.Pravednikov and Yu.S.Lipatov, "Metody Polucheniya i Svoistva Privitykh Blok-Polimerov" (Methods of Preparation and Properties of Graft Block Polymers), VINTI, 1958.
13. V.V.Korshak, Uspekhi Khim., 29, 569 (1960) [Russ.Chem. Rev., 269 (1960)].
14. M.S.Akutin, Khim.Nauka i Prom., 2, 585 (1957).
15. I.I.Radchenko, Kauchuk i Rezina, No.7, 16 (1957).
16. G.Smets, Khim i Tekhnol.Polimerov, Nos.7-8, p.186 (1960). (Translated into Russian).
17. A.A.Berlin, Uspekhi Khim., 27, 94 (1958).
18. G.L.Slonimskii, Khim.Nauka i Prom., 4, 73 (1959).
19. A.Chapiro, Ind.plast.mod., 8, No.9, 67 (1956).
20. A.Chapiro, Ind.plast.mod., 9, No.1, 41 (1957).
21. A.Chapiro, Ind.plast.mod., 9, No.2, 34 (1957).
22. G.Smets and R.Hart, Fortschr.Hochpolym.-Forsch., 2, 173 (1960).
23. A.Chapiro, Chimie et Industrie, 76, 754 (1956).
24. A.Chapiro, J.Polymer Sci., 29, 321 (1958).
25. A.Chapiro, J.Polymer Sci., 34, 439 (1959).
26. A.A.Berlin, Uspekhi Khim., 29, 1189 (1960) [Russ.Chem. Rev., 541 (1960)].
27. W.J.Burlant and A.S.Hoffman, "Block and Graft Polymers", Reinhold, New York, 1960.
28. V.V.Korshak, "Khimiya Vysokomolekulyarnykh Soedinenii" (The Chemistry of High Molecular Weight Compounds), Izd. Akad.Nauk SSSR, 1950, p.339.
29. G.S.Kolesnikov and Tsêng Han-ming, Vysokomol.Soed., 3, 475 (1961).
30. R.B.Carlin and H.Shakespeare, J.Amer.Chem.Soc., 68, 876 (1946).
31. R.B.Carlin and D.L.Hufford, J.Amer.Chem.Soc., 72, 4200 (1950).
32. G.Smets and M.Claesen, J.Polymer Sci., 8, 289 (1952).
33. R.Houtz and H.Adkins, J.Amer.Chem.Soc., 55, 1609 (1933).
34. P.Flory, J.Amer.Chem.Soc., 59, 241 (1937).
35. G.Smets, L.Convent, and X Van der Borght, Makromol. Chem., 23, 162 (1957).
36. F.M.Merrett, Trans.Faraday.Soc., 50, 759 (1954).
37. P.W.Allen, G.Ayrey, C.G.Moore, and J.Scanlan, J.Polymer Sci., 36, 55 (1959).
38. Y.Minoura, Y.Mori, and M.Imoto, Makromol.Chem., 24, 205 (1957).
39. G.V.Schulz, G.Henrici, and S.Olive, J.Polymer Sci., 17, 45 (1955).
40. J.Potts *et al.*, Paper presented at American Chemical Society Meeting-in-Minature, Jan.1957. See Ref.27.
41. R.A.Hayes, J.Polymer Sci., 11, 531 (1953).
42. A.A.Berlin, L.V.Stupen', B.I.Fedoseeva, and D.M. Yanovskii, Dokl.Akad.Nauk, 121, 644 (1958).
43. E.Schonfeld and I.Waltcher, J.Polymer Sci., 35, 536 (1959).
44. G.Smets and J.Schmets, Bull.Soc.chim.belges, 62, 358 (1953).
45. J.Schmets and G.Smets, Bull.Soc.chim.belges, 63, 58 (1954).
46. T.Saigusa and R.Oda, Bull.Inst.Chem.Res., Kyoto Univ., 33, 126 (1955).
47. M.H.Jones, H.W.Melville, and W.G.P.Robertson, Nature, 174, 78 (1954).
48. T.G.Fox *et al.*, J.Polymer Sci., 37, 397 (1959).
49. M.S.Gluckman *et al.*, J.Polymer Sci., 37, 411 (1959).
50. J.R.Roland and L.M.Richards, J.Polymer Sci., 9, 61 (1952).
51. G.Smets and A.Hertoghe, Makromol.Chem., 17, 189 (1956).
52. A.Vrancken and G.Smets, Makromol.Chem., 30, 197 (1959).
53. T.Saigusa and R.Oda, Bull.Inst.Chem.Res., Kyoto Univ., 34, 56 (1956).
54. J.Le Bras and P.Compagnon, Rev.gén.caoutchouc, 24, 241, 281 (1947).
55. J.Scanlan, Trans.Faraday Soc., 50, 756 (1954).

56. P.W.Allen, F.M.Merrett, and J.Scanlan, Trans.Faraday Soc., 51, 95 (1955).
57. P.W.Allen and F.M.Merrett, J.Polymer Sci., 22, 193 (1956).
58. A.Banderet and W.Kobryner, Compt.rend., 244, 604 (1957).
59. W.Kobryner and A.Banderet, Compt.rend., 245, 689 (1957).
60. W.Kobryner and A.Banderet, Rev.gén.caoutchouc, 34, 1017 (1957).
61. W.Kobryner and A.Banderet, J.Polymer Sci., 34, 381 (1959).
62. W.Cooper, G.Vaughan, and R.W.Madden, J.Appl.Polymer Sci., 1, 329 (1959).
63. D.Barnard, J.Polymer Sci., 22, 213 (1956).
64. Y.Mori, Y.Minoura, and M.Imoto, Kagaku (Tokyo), 27, 415 (1957); Chem.Abs., 51, 17230 (1957).
65. P.W.Allen, G.Ayrey, C.G.Moore, and J.Scanlan, J.Polymer Sci., 36, 55 (1959).
66. A.A.Berlin *et al.*, Author's Cert.No.70763 (1946).
67. A.A.Berlin *et al.*, Author's Cert.No.73031 (1946).
68. A.A.Berlin *et al.*, Author's Cert.No.68062 (1946).
69. A.A.Berlin *et al.*, Author's Cert.No.72663 (1947).
70. A.A.Berlin *et al.*, Author's Cert.No.123312 (1948).
71. T.G.Fox and S.Gratch, Ann.N.Y.Acad.Sci., 57, 367 (1953).
72. H.W.Coover and J.B.Dickey, U.S.P.2649434 (1953); Chem.Abs., 47, 10862 (1953).
73. H.Jones *et al.*, B.P.71594 (1954); Chem.Abs., 49, 2748 (1955).
74. T.E.Stanin and J.B.Dickey, U.S.P.2649435 (1953); Chem.Abs., 47, 10862 (1953).
75. D.J.Metz and R.B.Mesrobian, J.Polymer Sci., 16, 345 (1955).
76. R.Hayes, J.Polymer Sci., 13, 583 (1954).
77. T.Alfrey and C.Lewis, J.Polymer Sci., 4, 767 (1949).
78. J.F.Voeks, J.Polymer Sci., 18, 123 (1955).
79. A.A.Berlin and I.F.Bogdanov, Zhur.Obshch.Khim., 17, 1699 (1947).
80. A.A.Berlin and T.A.Makarova, Zhur.Obshch.Khim., 21, 1267 (1951).
81. M.Magat, Paper presented at International Symposium on Macromolecular Chemistry, Milan, 1954; Ricerca sci., 25, Supplement, 503 (1955).
82. K.Noma, K.Nagai, and O.Nishiura, Chem.High Polymers (Japan), 6, 479 (1949); Chem.Abs., 46, 1291 (1952).
83. S.Okamura, S.Ohara, and E.Nakanishi, Chem.High Polymers (Japan), 1, 79 (1944); Chem.Abs., 44, 5145 (1950).
84. M.C.de Wilde, Ind.chim.belge., 20, No.Special, 374 (1955).
85. G.Tasset and G.Smets, J.Polymer Sci., 12, 517 (1954).
86. G.van Paesschen and G.Smets, Bull.Soc.chim.belges, 64, 173 (1955).
87. F.M.Merrett, Paper presented at International Symposium on Macromolecular Chemistry, Milan, 1954; Ricerca sci., 25, Supplement, 279 (1955).
88. G.F.Bloomfield and P.M.Swift, J.Appl.Chem., 5, 609 (1955).
89. R.Hill, Rubber and Plastics Age, 35, 170 (1954).
90. C.C.Menon and S.L.Kapur, J.Appl.Polymer Sci., 1, 372 (1959).
91. A.A.Berlin, A.F.Kronman, D.M.Yanovskii, and V.A.Kargin, Vysokomol.Soed., 2, 1188 (1960).
92. P.W.Allen *et al.*, J.Polymer Sci., 36, 55 (1959).
93. P.M.Swift, J.Appl.Chem., 8, 803 (1958).
94. G.L.Yukhnovskii and A.V.Chernobai, Author's Cert. No.118976.
95. V.N.Kotrelev and M.S.Akutin, Plast.Massey, No.3, 5 (1959).
96. A.A.Berlin and I.A.Khanukaeva, Kauchuk i Rezina, No.6, 20 (1960).
97. O.Seizo and Y.Takao, Chem.High Polymers (Japan), 15, 165 (1958).
98. M.L.Miller, Canad.J.Chem., 36, 303 (1958).
99. E.H.Gleason, M.L.Miller, and G.F.Sheats, J.Polymer Sci., 38, 133 (1959).
100. V.E.Shashoua and K.E.van Holde, J.Polymer Sci., 28, 395 (1958).
101. M.Miller and C.Rauhut, J.Colloid Sci., 14, 524 (1959).
102. A.A.Berlin, J.Polymer Sci., 34, 371 (1959).
103. S.H.Pinner and V.Wicherley, Plastics, 22, 27, 242, 456, 503 (1957).
104. A.A.Berlin and I.A.Khanukaeva, Tyazhelaya Promyshlennost' Podmoskov'ya, 3, 14 (1959).
105. Y.Landler and P.Lebel, French P.1101682; Chem.Abs., 53, 14569 (1959).
106. B.P.791453 (1958); Chem.Abs., 52, 14210 (1958).
107. Ital.P.530825.
108. Ital.P.581077.
109. J.Hicks and H.Melville, J.Polymer Sci., 12, 461 (1954).
110. D.J.Metz and R.B.Mesrobian, Paper presented at International Symposium on Macromolecular Chemistry, Milan, 1954; Ricerca sci., 25, Supplement, 291 (1955).
111. J.A.Manson and L.H.Cragg, Canad.J.Chem., 36, 858 (1958).
112. P.Lebel, J.Polymer Sci., 34, 458 (1959).
113. G.Riess and A.Banderet, Kunststoffe–Plastics, 5, No.1, 5 (1958).
114. French P.1175699 (1959); Chem.Abs., 54, 16027 (1960).
115. L.Valentine and B.Chapman, Paper presented at International Symposium on Macromolecular Chemistry, Milan, 1954; Ricerca sci., 25, Supplement, 276 (1955).
116. W.Hahn and A.Fischer, Makromol.Chem., 21, 77 (1956).
117. T.Otsu, J.Polymer Sci., 26, 236 (1957).
118. W.Hahn and H.Lechtenböhmer, Makromol.Chem., 16, 50 (1955).
119. G.Natta, G.Beati, and F.Severini, J.Polymer Sci., 34, 685 (1959).
120. P.Lebel, Thesis, Paris, 1957.
121. P.Lebel, Rubber Age, 82, 692 (1958).
122. P.Lebel, Rubber and Plastics Age, 39, 65 (1958).
123. Y.Landler and P.Lebel, Simposium über Makromoleküle, Wiesbaden, Oktober 1959, Kurzmitteilungen, IV, A2.
124. N.A.Plate, V.P.Shibaev, T.I.Patrikeeva, and V.A.Kargin, Vysokomol.Soed., 3, 292 (1961).
125. V.A.Kargin *et al.*, Vysokomol.Soed., 1, 114 (1959).
126. V.A.Kargin, N.A.Plate, and E.P.Rebinder, Vysokomol. Soed., 1, 1547 (1959).
127. P.V.Kozlov, M.M.Iovleva, and N.A.Plate, Vysokomol. Soed., 1, 1101 (1959).
128. T.Saigusa, T.Nozaki, and R.Oda, J.Chem.Soc.Japan, Ind. Chem.Sect., 57, 233 (1954).
129. T.Saigusa, T.Nozaki, and R.Oda, J.Chem.Soc.Japan, Ind. Chem.Sect., 57, 243 (1954).
130. V.Hahn and A.Fischer, Makromol.Chem., 16, 36 (1955).
131. G.Delzenne and G.Smets, Makromol.Chem., 18/19, 82 (1956).
132. W.J.Burlant and D.H.Green, J.Polymer Sci., 28, 252 (1958).
133. M.Magat, A.Chapiro, and J.Sebban, J.Chem.Phys., 52, 709 (1955).
134. G.Smets, A.Poot, M.Miller, and J.P.Bex, J.Polymer Sci., 34, 287 (1959).
135. G.Riess and A.Banderet, Bull.Soc.chim., 51, 733 (1959).
136. H.Mark, Textile Res.J., 23, 294 (1954).
137. H.Mark, Angew.Chem., 67, 53 (1955).
138. J.A.Manson and L.H.Gragg, Angew.Chem., 67, 332 (1955).
139. M.H.Jones, H.W.Melville, and W.G.P.Robertson, Paper presented at International Symposium on Macromolecular Chemistry, Milan, 1954; Ricerca sci., 25, Supplement, 271 (1955).
140. D.J.Metz and R.B.Mesrobian, U.S.Government Research Report available as P.B.118306 (1954).

141. S.Axelrod, available as P.B.131 295, September 1956. See Ref.27.
142. M.Lazar, Yu.Pavlinets, Z.Manyasek, M.Michko, and D.Berek, Vysokomol.Soed., 3, 943 (1961).
143. Z.Manysek, D.Berek, M.Michko, M.Lazar, and Yu.Pavlinets, Vysokomol.Soed., 3, 1104 (1961).
144. W.Burlant and C.Taylor, SPE Journal, 14, N10, 49 (1958).
145. Y.Landler and P.Lebel, Khim.i Teknol.Polimerov, No.1, 101 (1960) (Translated into Russian).
146. Y.Landler and P.Lebel, French P.1161824 (1956); Chem. Zentr., 17527 (1959).
147. French P.1172920; Bull.offic.propriété industr., No.3890 (1958).
148. French P.1177898; Bull.offic.propriété industr., No.3897 (1959).
149. K.Wasaburo and T.Shigeru, J.Chem.Soc.Japan, Pure Chem. Sec., 80, 780, 57A (1959).
150. M.Lazar, R.Rado, and Yu.Pavlinets, "Simpozium po Makromolekulyarnoi Khimii" (Symposium on Macromolecular Chemistry), Moscow, June 1960, Section III, p.214.
151. N.A.Plate, Candidate's Thesis (Ph.D.Equivalent), Lomonosov Moscow State University, 1960.
152. V.A.Kargin, V.P.Shibaev, and N.A.Plate, Vysokomol. Soed., 3, 299 (1961).
153. Y.Landler and P.Lebel, "Simpozium po Makromolekulyarnoi Khimii" (Symposium on Macromolecular Chemistry), Moscow, June 1960, Section III, p.191.
154. P.V.Kozlov, M.M.Iovleva, A.Kh.Khakimova, and A.B. Zezin, Vysokomol.Soed., 2, 1575 (1960).
155. R.J.Orr and H.L.Williams, J.Amer.Chem.Soc., 78, 3273 (1956).
156. J.R.Urwin, J.Polymer Sci., 27, 580 (1958).
157. F.T.Wall and T.J.Swoboda, J.Amer.Chem.Soc., 71, 919 (1949).
158. R.J.Orr and H.L.Williams, J.Amer.Chem.Soc., 79, 3137 (1957).
159. G.Mino and S.Kaizerman, J.Polymer Sci., 31, 242 (1958).
160. French P.1174149; Bull.offic.propriété industr., No.3892 (1958).
161. L.Valentine and B.Chapman, Paper presented to International Symposium on Macromolecular Chemistry, Milan, 1954; Ricerca sci., 25, Supplement, 278 (1955).
162. J.Blanchette and L.Nielsen, J.Polymer Sci., 20, 317 (1956).
163. G.S.Whitby, Ind.Eng.Chem., 47, 806 (1955).
164. J.van Alphen, Proc.Third Rubber Tech.Conf., 670 (1954). See Ref.18.
165. J.Schmets and G.Smets, Bull.Soc.chim.belges, 63, 59 (1954).
166. A.Hunyar and H.Reichert, Faserforsch.und Textiltechnik., 6, 442 (1955).
167. A.Hunyar and A.Rothe, Faserforsch.und Textiltechnik., 8, 99, 143, 179 (1957).
168. W.Crouch and J.A.Shotton, Ind.Eng.Chem., 47, 2091 (1955).
169. H.C.Haas, P.M.Kamath, and N.W.Schuler, J.Polymer Sci., 24, 85 (1957).
170. P.H.Plesch, Chem.and Ind., 954 (1958).
171. G.Kockelbergh and G.Smets, J.Polymer Sci., 33, 227 (1958).
172. W.Jurgleit and R.Freeman, ASTIA Report, AD 226101, July 1959. See Ref.27.
173. P.Rempp, V.I.Volkov, Zh.Parro, and Sh.Sadron, Vysokomol. Soed., 2, 1521 (1960).
174. R.Graham, J.Polymer Sci., 24, 367 (1957).
175. P.Weiss, J.F.Gerecht, and I.J.Krems, J.Polymer Sci., 35, 343 (1959).
176. W.Kern, R.C.Schulz, and D.Braun, Khim.i Tekhnol. Polimerov., Nos.7–8, 166 (1960) (Translated into Russian).
177. R.C.Schulz, Kunststoffe–Plastics, 6, 32 (1959).
178. S.G.Cohen, H.C.Haas, and H.Slotnick, J.Polymer Sci., 11, 193 (1953).
179. B.A.Ripley-Duggan, B.P.771926; Chem.Abs., 51, 10960 (1957).
180. S.R.Rafikov, G.N.Chelnokova, I.V.Zhuravleva, and P.N. Gribkova, "Simpozium po Makromolekulyarnoi Khimii" (Symposium on Macromolecular Chemistry), Moscow, June 1960, Section III, p.184.
181. R.Stroh and J.Ebersberger, German P.925130 (1955); Chem.Abs., 50, 12545 (1956).
182. P.J.Flory, U.S.P.2524045 (1950); Chem.Abs., 45, 901 (1951).
183. C.B.Chapman and L.Valentine, J.Polymer Sci., 34, 319 (1959).
184. O.Wichterle and V.Gregor, J.Polymer Sci., 34, 309 (1959).
185. I.A.Tutorskii, Z.Smelyi, and B.A.Dogadkin, "Simpozium po Makromolekulyarnoi Khimii" (Symposium on Macromolecular Chemistry), Moscow, June 1960, Section III, p.224.
186. I.A.Tutorskii, Z.Smelyi, and B.A.Dogadkin, Vysokomol. Soed., 1, 1652 (1959).
187. L.Valentine, Fibres, 16, 12 (1955).
188. German P.925130 (1955); Chem.Abs., 50, 12545 (1956).
189. G.S.Kolesnikov and Tsêng Han-ming, Izv.Akad.Nauk USSR, Otd.Khim.Nauk, 1336 (1959).
190. G.S.Kolesnikov and Tsêng Han-ming, Acta Chim.Sinica, 25, 124 (1959).
191. G.S.Kolesnikov and Tsêng Han-ming, Vysokomol.Soed., 1, 1566 (1959).
192. G.S.Kolesnikov and Tsêng Han-ming, Vysokomol.Soed., 1, 1733 (1959).
193. G.S.Kolesnikov and Tsêng Han-ming, Vysokomol.Soed., 2, 947 (1960).
194. Tsêng Han-ming and G.S.Kolesnikov, Vysokomol.Soed., 2, 1010 (1960).
195. G.S.Kolesnikov and Tsêng Han-ming, Vysokomol.Soed., 2, 1717 (1960).
196. G.S.Kolesnikov and Tsêng Han-ming, "Simpozium po Makromolekulyarnoi Khimii" (Symposium on Macromolecular Chemistry), Moscow, June 1960, Section III, p.236.
197. Tsêng Han-ming, Thesis, Institute of Organoelemental Compounds, Academy of Sciences of the USSR, 1961.
198. Tsêng Han-ming and G.S.Kolesnikov, Vysokomol.Soed., 3, 1415 (1961).
199. G.S.Kolesnikov and G.T.Gurgenidze, Vysokomol.Soed., 4, 452 (1962).
200. Tsêng Han-ming and G.T.Kolesnikov, Vysokomol.Soed., 3, 919 (1961).
201. G.S.Kolesnikov and G.T.Gurgenidze, Soobshch.Akad.Nauk Gruz.SSR, 28, 297 (1962).
202. Tsêng Han-ming and G.S.Kolesnikov, Vysokomol.Soed., 2, 1870 (1960).
203. G.S.Kolesnikov and Tsêng Han-ming, Vysokomol.Soed., 3, 1210 (1961).
204. G.S.Kolesnikov and Tsêng Han-ming, Vysokomol.Soed., 3, 637 (1961).
205. V.V.Korshak, S.V.Vinogradova, and A.S.Lebedeva, Vysokomol.Soed., 3, 1117 (1961).
206. Tsêng Han-ming and G.S.Kolesnikov, Vysokomol.Soed., 4, 130 (1962).
207. Polaroid Corp., Belg.P.538048 (1955); Chem.Zentr., 10084 (1960).
208. H.C.Haas, S.G.Cohen, A.C.Oglesby, and E.R.Karlin, J.Polymer Sci., 15, 427 (1955).
209. S.Sonnerskog, Acta Chem.Scand., 10, 467 (1956).
210. S.R.Rafikov, G.N.Chelnokova, and P.N.Gribkova, Vysokomol.Soed., 1, 378 (1959).
211. B.V.Petukhov and A.B.Pakshver, Kolloid.Zhur., 18, 741 (1956).
212. A.Nuessle and R.Crawford, Textile Res.J., 23, 462 (1953).
213. D.Coleman, J.Polymer Sci., 14, 15 (1954).

214. M.Sela, E.Katchalski, and M.Gehatia, J.Amer.Chem.Soc., 78, 746 (1956).
215. E.Katchalski, Khim.i Tekhnol.Polimerov, Nos.7-8, 49 (1960) (Translated into Russian).
216. V.V.Korshak and K.K.Mozgova, Author's Cert.No.116 268 (1959).
217. V.V.Korshak and K.K.Mozgova, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 651 (1958).
218. V.V.Korshak, K.K.Mozgova, and M.A.Shkolina, Dokl. Akad.Nauk, 122, 609 (1958).
219. V.V.Korshak, K.K.Mozgova, and M.A.Shkolina, Vysokomol.Soed., 1, 1364 (1959).
220. V.V.Korshak, K.K.Mozgova, and M.A.Shkolina, Vysokomol.Soed., 1, 1573 (1959).
221. V.V.Korshak, K.K.Mozgova, and M.A.Shkolina, Vysokomol.Soed., 1, 1604 (1959).
222. V.V.Korshak, K.K.Mozgova, and M.A.Shkolina, Vysokomol.Soed., 2, 957 (1960).
223. V.V.Korshak, K.K.Mozgova, and M.A.Shkolina, Author's Cert.No.131 084 (1960).
224. V.V.Korshak, K.K.Mozgova, and M.M.Shkolina, Vysokomol.Soed., 3, 1462 (1961).
225. V.V.Korshak, K.K.Mozgova, and M.M.Shkolina, Vysokomol.Soed., 3, 1655 (1961).
226. V.V.Korshak, K.K.Mozgova, M.A.Shkolina, *et al.*, Vysokomol.Soed., 4, 1462 (1961).
227. D.T.Hurd and G.T.Roedel, Ind.Eng.Chem., 40, 2078 (1948).

Institute of Organoelemental Compounds,
Academy of Sciences of the USSR

PRESENT STATE OF ION-EXCHANGE CATALYSIS

N.G.Polyanskii

CONTENTS

1. Concept of ion-exchange catalysis and its terminology 496
2. Ion exchangers as catalysts in hydration 498
3. Ion exchangers as catalysts in hydrolysis 500
4. Ion exchangers as catalysts in esterification 501
5. Ion exchangers as catalysts in dehydration 503
6. Use of ion exchangers as catalysts in alkylation 503
7. Ion exchangers as catalysts in polymerisation 505
8. Ion exchangers as catalysts in condensation reactions 506
9. Ion exchangers as catalysts in certain other reactions 509

1. CONCEPT OF ION-EXCHANGE CATALYSIS AND ITS TERMINOLOGY

Like the corresponding ions in homogeneous media, the counter-ions of the high-molecular-weight polyelectrolytes are capable of catalysing many organic reactions of varying character.

This new application of ion exchangers, which can be termed ion-exchange catalysis, is now being developed and our knowledge is still incomplete. Nevertheless, the results of both laboratory studies and industrial applications of ion exchangers as catalysts are encouraging for the future prospects of ion-exchange catalysis.

The catalytically active counter-ions of ion exchangers are in a solvated state, and in this respect are similar to the so-called free ions in ordinary electrolyte solutions. For that reason both the reactions catalysed in solution by ions and those catalysed by counter-ions of ion-exchange resins are able to proceed in accordance with the same mechanism, and are of the same kinetic order. The rate of a given reaction depends, however, on whether a given amount of catalytically active ions is present in the form of a soluble electrolyte, or in the form of an ion exchanger.

As suggested by Haskell and Hammett[1], the ratio of the reaction rate in a heterogeneous system to that in a homogeneous system, at equivalent concentrations of catalyst ions, is termed the efficiency of the ion exchanger. The efficiency of the ion exchanger q may be equal to, larger than, or smaller than unity, and depends on the properties of the catalyst itself, as well as on those of the solvent.

The essence of this concept may be exemplified by the irreversible first-order reaction of decomposition of AB into A and B, using Q_{AB} moles of the starting compound.

The rate of the reaction in a homogeneous system is $dQ_{AB}/dt = k_h.Q_{AB}$, where k_h is the velocity constant of a homogeneous reaction. For the corresponding heterogeneous reaction, carried out in the presence of an ion exchanger $dQ_{AB}/dt = k_{het}Q_{AB}$. The efficiency of the ion exchanger, *i.e.* the ratio between the velocity constants of the heterogeneous and homogeneous reaction is $q = k_{het}/k_h$. The relationship of the efficiencies of an ion exchanger for two compounds belonging to the same chemical class, is termed the specificity ratio[2]. If the reactants, *e.g.* esters, are simultaneously placed in contact with the catalyst, the value $r = q_1/q_2$ is a measure of the selectivity of the transformation of one component with respect to the other. This value is quantitatively related to the standard free energies of four intermediate states:

$$RT \ln q_1/q_2 = (F_{R_1} - F_{H_1}) - (F_{R_2} - F_{H_2}),$$

the subscript H corresponds to the reaction under homogeneous, and the subscript R to the same reaction under heterogeneous conditions of catalysis.

By changing the reaction conditions the efficiency of the ion exchanger with respect to different components in the mixture may be altered, and by changing the specificity ratio a more extensive conversion of one compound relative to another may be caused.

The efficiency of ion exchangers depends on the following factors: (*a*) the properties of the catalyst and the reactants, which determine the activation energy of the reaction; (*b*) the distribution constant of reactants between the solution and the catalyst; (*c*) the nature of the solvent.