21. Z.K. Maizus, N.M. Emanuel', and V.A. Yakovleva, Dokl. Akad. Nauk SSSR, 143, 366 (1962).
22. J. Bateman, Quart. Rev., 8, 147 (1954).
23. D.G. Knorre, Z.K. Maizus, and N.M. Emanuel', Dokl. Akad. Nauk SSSR, 123, 123 (1958).
24. J.R. Thomas and O.L. Harle, J. Phys. Chem., 63, 1027 (1959).
25. W.T. Miller and A.L. Dittman, J. Amer. Chem. Soc., 78, 2793 (1956).
26. W.T. Miller, S.D. Koch, and T.W. McLafferty, J. Amer. Chem. Soc., 78, 4992 (1956).
27. W.T. Miller and S.D. Koch, J. Amer. Chem. Soc., 79, 3084 (1957).
28. W.T. Miller, J.O. Stopper, G. Fuller, and A.C. Currie, J. Amer. Chem. Soc., 86, 51 (1964).
29. G.A. Kapralova and A.E. Shilov, Kinetika i Kataliz, 2, 362 (1961).
30. G.A. Kapralova, L.Yu. Rusin, A.M. Chaikin, and A.E. Shilov, Dokl. Akad. Nauk SSSR, 150, 1282 (1963).
31. G.A. Kapralova, A.M. Chaikin, and A.E. Shilov, Kinetika i Kataliz, in the press.
32. A.S. Rodgers, J. Phys. Chem., 67, 2799 (1963).
33. A.S. Rodgers, J. Phys. Chem., 69, 254 (1965).
34. G.C. Fettis, J.H. Knox, and A.F. Trotman-Dickenson, J. Chem. Soc., 1064 (1960).
35. P.C. Anson, P.S. Fredericks, and J.M. Tedder, J. Chem. Soc., 918 (1959).
36. P.S. Fredericks and J.M. Tedder, J. Chem. Soc., 144 (1960).
37. N.N. Semenov and A.E. Shilov, Kinetika i Kataliz, 6, 3 (1965).
38. G.A. Kapralova, E.M. Trofimova, L.Yu. Rusin, A.M. Chaikin, and A.E. Shilov, Kinetika i Kataliz, 4, 653 (1963).
39. L.Yu. Rusin, A.M. Chaikin, and A.E. Shilov, Kinetika i Kataliz, 5, 1121 (1964).
40. G.A. Kapralova, E.M. Trofimova, and A.E. Shilov, Kinetika i Kataliz, 6, 977 (1965).
41. N. Semenoff, Chem. Rev., 6, 347 (1929).
42. N.N. Semenov, "Tsepnye Reaktsii" (Chain Reactions), Goskhimizdat, 1934.
43. N.N. Semenov, "Transfert d'Énergie dans les Gaz", Interscience, 1962, p. 183.
44. P.J. Slootmakers and A. Van Tiggelen, Bull. Soc. chim. belges, 67, 135 (1958).
45. M. Boudart, "Eighth Symposium (International) on Combustion", 1962, p. 42.
46. R.S. Brokaw, J. Phys. Chem., 69, 2488 (1965).
47. V.I. Vedeneev, L.V. Gurvich, V.N. Kondrat'ev, V.A. Medvedev, and E.L. Frankevich, "Energiya Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu" (Dissociation Energy of Chemical Bonds. Ionisation Potentials and Electron Affinities), Izd. Akad. Nauk SSSR, Moscow, 1962.
48. K. Ziegler, Ber., 55, 2257 (1922).
49. D. Coffman, C. Marvel, and F. Hager, J. Amer. Chem. Soc., 49, 2293 (1927).
50. H. Gilman, J. Amer. Chem. Soc., 51, 2840 (1929).
51. H. Gilman and F.W. Moore, J. Amer. Chem. Soc., 62, 1842 (1940).
52. K. Ziegler and E. Eimers, Annalen, 567, 43 (1950).
53. K. Ziegler and H. Colonius, Annalen, 479, 135 (1930).
54. D. Bryce-Smith, J. Chem. Soc., 1603 (1956).
55. L.T. Zakharkin, O.Yu. Okhlobystin, and K.A. Bilevich, J. Organometal. Chem. (Amsterdam), 4, 341 (1965).
56. L.I. Zakharkin, K.A. Bilevich, and O.Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 152, 338 (1963).
57. L.T. Zakharkin, O.Yu. Okhlobystin, and K.A. Bilevich, J. Organometal. Chem. (Amsterdam), 2, 309 (1964).
58. O.Yu. Okhlobystin, K.A. Bilevich, and L.T. Zakharkin, J. Organometal. Chem. (Amsterdam), 2, 281 (1964).
59. A.K. Zefirova and A.E. Shilov, Dokl. Akad. Nauk SSSR, 136, 599 (1961).
60. H. De Vries, Rec. Trav. chim., 80, 866 (1961).
61. N.G. Gaylord and H.F. Mark, "Linear and Stereoregular Addition Polymers — Polymerisation with Controlled Propagation" (Translated into Russian), Inostr. Lit., Moscow, 1962.
62. F.S. D'yachkovskii, N.N. Bubnov, and A.E. Shilov, Dokl. Akad. Nauk SSSR, 123, 870 (1958).
63. F.S. D'yachkovskii and A.E. Shilov, Zhur. Obshch. Khim., 33, 406 (1963).
64. F.S. D'yachkovskii, G.A. Kapralova, and A.E. Shilov, Trudy Khim. i Khim. Tekhnol., 1, 81 (1961).
65. F.S. D'yachkovskii and A.E. Shilov, "Trudy Konferentsii po Probleme Primeneniya Korrelyatsionnykh Uravnenii v Organicheskoi Khimii" (Proceedings of the Conference on the Application of Correlation Equations in Organic Chemistry), Vol. 1, Tartu, 1962, p. 126.
66. F.S. D'yachkovskii, A.E. Shilov, and L.I. El'terman, Kinetika i Kataliz, 4, 644 (1963).
67. F.S. D'yachkovskii and A.E. Shilov, Kinetika i Kataliz, 4, 919 (1963).
68. F.S. D'yachkovskii, N.N. Bubnov, and A.E. Shilov, Dokl. Akad. Nauk SSSR, 122, 629 (1958).
69. R. West and W. Glaze, J. Amer. Chem. Soc., 83, 3580 (1961).
70. J. Berkowitz, D.A. Bafus, and T.L. Brown, J. Phys. Chem., 65, 1380 (1961).
71. T.L. Brown, D.W. Bickerhoff, and D.A. Bafus, J. Amer. Chem. Soc., 84, 1371 (1962).
72. T.L. Brown and J.A. Ladd, J. Organometal. Chem. (Amsterdam), 2, 373 (1964).
73. I.V. Golovanov and A.K. Piskunov, Zhur. Fiz. Khim., 38, 2268 (1964) [Russ. J. Phys. Chem., 1225 (1964)].
74. A.D. Stepukhovich and V.A. Ulitskii, Zhur. Fiz. Khim., 35, 2569 (1961) [Russ. J. Phys. Chem., 1270 (1961)].
75. Yu.A. Lebedev, E.A. Miroshnichenko, and A.M. Chaikin, Dokl. Akad. Nauk SSSR, 145, 1288 (1962).
76. H. Hartel and M. Polanyi, Z. phys. Chem., B11, 97 (1930).
77. A.G. Evans and H. Walker, Trans. Faraday Soc., 40, 384 (1944).
78. W.G. Alcock and E. Whittle, Trans. Faraday Soc., 61, 244 (1965).
79. D.H.R. Barton and A.J. Head, J. Chem. Soc., 3695 (1952).
80. A.E. Shilov and R.D. Sabirova, Kinetika i Kataliz, 5, 40 (1964).
81. E.W.R. Steacie, "Atom and Free Radical Reactions", New York, 1954.

Institute of Chemical Physics,
USSR Academy of Sciences

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CHAIN TRANSFER WITH FISSION

N.S. Enikolopyan, V.I. Irzhak, and B.A. Rozenberg

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1. INTRODUCTION

Processes leading to the formation of macromolecules can be divided into two classes — chain reactions, which include many different methods of polymerisation, and non-chain reactions, which include condensation polymerisation and stepwise reactions.

As early as 1934 Semenov defined [1] polymerisation as a non-branching chain process, and predicted the possibility of chain transfer in a polymerisation system in general, and through a polymer in particular.

More recently, as a result of advances in the chemistry of hetero-chain polymers, various highly specific — both chemically and kinetically — phenomena have been discovered.

In 1940 Flory recognised the degradation caused by the starting materials on a polymer formed by condensation polymerisation [2]. Subsequently, Korshak and his coworkers [3-5] showed that considerable interchain exchange by transesterification and transamidation occurs during the formation of polyesters and polyamides by condensation polymerisation. This phenomenon has been put to use for the synthesis of mixed polymers of the polyester, polyamide, and polyamidoester types.

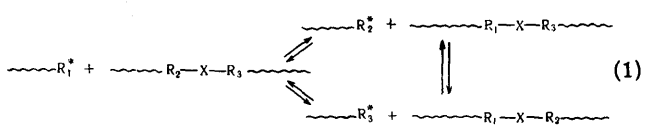
The possibility of interchain exchange was ascribed initially to condensation polymerisation processes only [3-5], and was even taken to be one of the fundamental differences between polycondensation and polymerisation processes.

However, interchain exchange is governed only by the structure of the macromolecule and by the type of active centre, and is evidently a characteristic of all hetero-chain polymers irrespective of the method of preparation. Such exchange can therefore occur in both polycondensation and polymerisation, and also with the resulting hetero-chain polymeric molecules, independently of their method of preparation.

Studies of the polymerisation and copolymerisation of trioxan [6-12] have led to the conclusion that an interchain exchange of a similar type, proceeding by a transacetalation mechanism, occurs in this system.

In 1962 Enikolopyan [8] demonstrated the possibility of interchain exchange during polymerisation by a mechanism which was subsequently called chain transfer through the polymer with fission (CTF).

Chemically, the CTF reaction consists in the exchange interaction of two molecules — one of which is an active centre and the other an inactive macromolecule — by a homolytic or heterolytic substitution mechanism. In general, the mechanism of the CTF reaction can be written



(1)

where X is a hetero-atom (O, S, N, P, Si, metal, etc.) and $\sim R_i^*$ is an active macromolecule (cation, anion, or radical).

The mechanism suggested is fairly universal, and we may assume that it applies to interchain exchange and also to the so-called "degradation" reactions between a polymer chain and the starting materials (or materials of similar nature) during condensation polymerisation. As shown by Korshak and coworkers [3,4], who made a systematic and extensive study of this reaction, interchain exchange proceeds much faster in the presence of catalysts of an acidic or basic nature. The end-groups of the starting material may have a catalytic effect on the process, but the rate of interchain exchange in this case is lower than with specially added catalysts. The exchange reaction is very strongly inhibited when it occurs between macromolecules with blocking end-groups (e.g. alkylated end-groups).

These facts strongly suggest that the reactions in question occur via some ionic states, probably as nucleophilic substitution reactions according to scheme (1).

It can be seen from the scheme that the CTF reaction should produce, during homopolymerisation, a redistribution in size of the growing macromolecules [9], and during the interaction of chemically different polymeric chains, block copolymers [10]. This reaction is one of the most general methods for modification of the main chain and side-chains of a polymer. It can be used to prepare mixed hetero-chain and carbon–hetero-chain macromolecules.

If $\sim R_i^*$ is a compound of low molecular weight the result of the CTF reaction should be a polymer with specified end-groups. This opens up wide possibilities for the synthesis of polymers and oligomers with reactive end-groups. The great practical importance of the CTF reaction in which $R_i^* \sim$ is a material of low molecular weight arises also from the possibility of synthesising thermostable polymers having a lower temperature limit of polymerisation. This method has been successfully applied to the problem of producing thermally stable polyoxymethylene.

An interesting feature of the CTF reaction is the ability of the active centre of the macromolecule to attack its own chain:

$$R_i - R_j - R_k^* \rightleftarrows R_i^* + \binom{R_k}{R_j}. \qquad (2)$$

In this case a cyclic macromolecule may be formed [12]. We may also expect the formation of some very peculiar polymers having a "ring within a ring" structure (polycatenanes). If two polymers of different composition take part in a CTF reaction, copolymers will be formed without a chemical bond being involved.

The most essential feature of polymeric systems in which CTF reactions are proceeding is, as scheme (1) shows, the fact that every "dead" polymeric chain can become "alive". Also, a "dead" polymeric system can be "revived" by introducing a suitable activator. Of all the reactions known in polymer chemistry, CTF alone can bring "dead" chains into the polymerisation process without significant modification. Thus, the concept of a "live" system is more general than the definition of Szwarc [13] implies.

A detailed thermodynamic, kinetic, and chemical analysis of the CTF reaction, made in the Polymerisation Kinetics Laboratory of the Institute of Chemical Physics of the USSR Academy of Sciences, has established the uniqueness of the process, which can therefore be considered to be a new, fifth elementary act among polymerisation processes.

The present review aims to systematise and summarise existing data on the CTF reaction, and to discuss the potential applications of this reaction to polymer modification.

2. KINETIC AND THERMODYNAMIC FEATURES OF CHAIN TRANSFER WITH FISSION (CTF)

The specific feature of polymeric systems as compared with chemical substances of low molecular weight, is from the thermodynamic standpoint, their statistical nature, i.e. the existence of a definite distribution in size and composition of the macromolecules. This must undoubtedly be reflected in the nature of the processes occurring in polymer systems.

Thus, the size distribution alone will alter the entropy of the system, irrespectively of the nature of the polymeric molecules, of their state in the system, and of their interactions with each other and with the medium. Consider a reaction leading to a change in the size distribution of the macromolecules. We shall assume that the change involves only equivalent bonds: since the internal energy of the system depends on the total energy of the bonds, which is assumed to remain unchanged, and also on the interaction of the macromolecules with each other and with the medium (which depends on the total number of segments, again assumed unchanged), the reaction does not affect the internal energy of the system.

$$R_i + R_j \rightarrow R_{i+k} + R_{j-k}. \qquad (3)$$

The total entropy of the system can be split into the configurational entropy, the entropy of the segments, and the entropy of interaction of the macromolecules with each other and with the medium; the statements made above in relation to the enthalpy of the system apply also to the entropy, with the exception of the configurational entropy, whose value depends on the length of the macromolecule according to the expression

$$S_{R_j} = R \ln (a^j), \qquad (4)$$

where j is the length of the macromolecule, and a is the number of possible positions in space of a segment with one end fixed.

Since the entropy of the system is equal to the sum of the entropies of the components, the configurational entropy also must be unaffected by our reaction.

It follows from the statistical nature of a polymeric system that we must take the distributional entropy of the system into account. Strictly speaking, any physical system can be regarded as statistical from the point of view of the distribution of the various forms of energy. However, energy redistribution occurs so rapidly that, with few exceptions, the energy can be assumed to adopt an equilibrium (Boltzmann) distribution. This is not so in polymeric systems, where the distribution concerns units in macromolecules. Obviously, a redistribution of this type cannot occur unless a kinetically favourable mechanism is available. If such a mechanism is possible, the reaction will lead to the establishment of an equilibrium distribution, whose nature can be readily inferred on the hypothesis of maximum entropy. Thus, the driving force of exchange reactions of this type is an entropic one.

Taking the distributional entropy into account, we obtain for the reaction

$$\Delta S = R\left\{\ln \frac{(i+j)!}{(i+k)!\,(j-k)!} - \ln \frac{(i+j)!}{i!\,j!}\right\} = R \ln \frac{j!\,i!}{(i+k)!\,(j-k)!}. \qquad (5)$$

Solving the problem of maximum distributional entropy [14] for the conditions

$$\sum_j R_j = N; \quad \sum_j j R_j = M,$$

we find, as for the Boltzmann distribution,

$$R_j = \frac{N^2}{M}\left(1 - \frac{N}{M}\right)^{j-1} \simeq \frac{N^2}{M} e^{-\frac{N(j-1)}{M}}. \qquad (6)$$

The composition distribution of the macromolecules presents a more complicated problem, because the structure of the copolymer must affect both the internal energy of a macromolecule and its entropy. Thus, even in the presence of a mechanism leading to redistribution, maximum distributional entropy may not be achieved owing to the increase in internal energy or to the decrease in entropy of the macromolecules themselves.

Clearly, redistribution of the sequences A...A and B...B within a chain involves breaking A–A and B–B bonds and the creation of two A–B bonds, or *vice versa*. For each exchange of this kind the expenditure (or gain) of energy is given by

$$\Delta E = 2\left(\epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2}\right), \qquad (7)$$

so that the redistribution will be influenced not only by the distributional entropy but also by the change in internal energy. In the limiting case when

$$\epsilon_{AB} \ll \frac{\epsilon_{AA} + \epsilon_{BB}}{2}, \qquad (8)$$

there will obviously be no redistribution at all, in spite of the evident loss of distributional entropy.

Chain transfer with fission is the kinetic mechanism which allows attainment of the most probable distribution, corresponding to maximum entropy. Alternative mechanisms are possible, of course, but the reactions encountered in polymer chemistry either involve fundamental changes in the system [15-17] or operate only on macroradicals or macroions, i.e. on the "live" part of the macromolecule, without affecting the "dead" parts (reversible polymerisation).[18]

The special kinetic status of CTF was first pointed out by Enikolopyan and his coworkers [8,9]. From a study of interchain exchange in a system consisting of R molecules of mean degree of polymerisation $\bar{P}$ with all end-groups active, i.e. of the reaction

$$R_i + R_j \rightarrow R_{i+e} + R_{j-e}, \qquad (9)$$

they arrived [9] at the kinetic equation for the concentration of the $j$mer

$$\frac{dR_j}{dt} = -2kR_jR - 2kR_j\sum_1^N iR_i + 2k\sum_{i=j}^N\sum_{e=j}^N R_iR_e + 2k\sum_1^j\sum_{j-i}^j R_iR_e + 4k\sum_{i=j}^N\sum_1^N R_iR_e, \qquad (10)$$

the coefficient k being independent of j, i, and e.

At equilibrium

$$\frac{dR_j}{dt} = 0. \qquad (11)$$

The equation gives for R_j

$$R_j = \frac{R}{\bar{P}}\, e^{-j/\bar{P}}. \qquad (12)$$

This implies that, independently of the initial distribution, CTF leads to a Semenov–Flory distribution [1,21]

as calculated for equilibrium polymerisation and polycondensation. It can be shown that under these conditions

$$\frac{\overline{P}_w}{\overline{P}_N} = 2.$$

The attainment of this distribution was experimentally demonstrated by studying the cationic exchange between low-molecular-weight dimethyl ethers of poly(oxymethylene glycol)[19], because the molecular-weight distribution is difficult to determine for high-polymer samples.

Disproportionation of the dimethyl ether of dioxymethylene glycol (degree of polymerisation $P = 2$) on treatment with 0.06% sulphuric acid at 120° causes the appearance of a whole series of oligomers, beginning with dimethoxymethane, in amounts independent of both catalyst concentration and temperature. The fact that the resulting composition is independent of the experimental conditions suggests that the observed distribution is an equilibrium one.

The distribution obtained cannot be compared with the function (5), because the latter was derived for the case of $j \gg 1$; in the case of oligomers we cannot ignore the length of one of the two monomeric units in comparison with the length the entire molecule.

The distribution function for oligomers of low molecular weight was obtained by a statistical method, which led to expression (6), obtained previously by a thermodynamic method (p. 309):

$$R_n = \left(\frac{1}{2}\right)^n = e^{-0.69n}. \qquad (13)$$

This equation satisfactorily describes the experimental results.

Thus, it has been shown both theoretically and experimentally that CTF leads to the most probable molecular-weight distribution.

It should be noted that these results have been obtained on the assumption that the rate constant of CTF is independent of the degree of polymerisation of the attacking active molecule and of the molecule being attacked, i.e. that it does not depend on the site of attack. This assumption can be unambiguously substantiated only on the basis of kinetic data. To this end, the kinetics of the establishment of equilibrium was investigated[20] for the disproportionation of the dimethyl ether of dioxymethylene glycol, using the boron trifluoride–ether complex as catalyst.

Evaluation of the kinetics based on a scheme analogous to (3)

$$R_e^* + R'_m{-}O{-}R'_n \rightarrow R_m^* + R'_e{-}O{-}R'_n,$$

where R'_i is a free-radical residue of structure $CH_3{-}[OCH_2]_i{-}$ and R_i^* is a carbonium ion of corresponding structure or a radical forming part of an oxonium ion

$$R'_i{-}\overset{+}{O}\!\!<\!\!\begin{matrix}R'_m\\R'_n\end{matrix}.$$

The set of kinetic equations corresponding to the proposed scheme is

$$\frac{dR_n}{d\tau} = R\sum_{i=1}^{n} R_i^* - \sum_{e=1}^{n-1}\sum_{i=1}^{n-e} R_i R_e^* - nR_n R^*, \qquad (14)$$

$$\frac{dR_n^*}{d\tau} = \left(R - \sum_{i=1}^{n-1} R_i\right) R^* - \bar{n} R R_n^*,$$

$$d\tau = 2k dt$$

where R_i is the concentration of $CH_3{-}[OCH_2]_i{-}OCH_3$ molecules,

R is the total concentration of all molecules,

R_j^* is the concentration of active centres,

n is the mean number of $-OCH_2-$ groups per molecule,

and k is the rate constant for interaction between an active centre and a neutral molecule (assumed independent of R_e^*, R'_m, and R'_n).

This system can be solved step by step. The following expressions are obtained for the first three terms (n = = 1, 2, 3)

$$R_1 = R\left(\frac{1}{2} - \frac{1}{2}e^{-R^*\tau}\right),$$

$$R_2 = R\left(\frac{1}{4} + \frac{1}{2}e^{-R^*\tau} + \frac{1}{4}e^{-2R_\tau^*}\right),$$

$$R_3 = R\left(\frac{1}{8} + \frac{1}{8}e^{-R^*\tau} - \frac{1}{8}e^{-2R^*\tau} - \frac{1}{8}e^{-3R^*\tau}\right). \qquad (15)$$

The following formula gives the total concentration of the remaining molecules

$$R_{\text{rem}} = R\left(\frac{1}{8} - \frac{1}{8}e^{-R^*\tau} - \frac{1}{8}e^{-2R^*\tau} + \frac{1}{8}e^{-3R^*\tau}\right). \qquad (16)$$

These equations fully represent the experimental results, the best agreement being obtained with a rate constant of $k = 0.021$ litre mole^{-1} s^{-1}. The agreement between theory and experiment confirms the authors' original assumption of the equivalence of all the acetal bonds.

The role of CTF in the various stages of the process is one of the most important problems in polymerisation kinetics. It is obvious that, in the absence of a chain-growth reaction, CTF must lead to a Semenov–Flory distribution[1,21], but chain growth will perturb this distribution in such a way that at very low rates of CTF (in the absence of chain termination and chain transfer, and with instantaneous initiation) the molecular-weight distribution will be described by Poisson's law[18]

$$R_j = \frac{\overline{P}^j}{j!} e^{-\overline{P}}. \qquad (17)$$

We shall estimate the relative velocities of these reactions.

The rate of the growth reaction is

$$w_{gr} = k_{gr} R M_0 (1 - \alpha), \qquad (18)$$

where α is the extent of reaction, R the concentration of active centres, and M_0 is the initial concentration of monomer.

The rate of the CTF reaction is

$$w_{CTF} = k_{tr} R M_0 \alpha. \qquad (19)$$

The closeness with which the molecular-weight distribution in the system approaches an exponential distribution will be determined by the ratio of the velocities:

$$\frac{w_{CTF}}{w_{gr}} = \frac{k_{tr}}{k_{gr}} \frac{\alpha}{1-\alpha}. \qquad (20)$$

We must remember, however, that the chain growth reaction alters the length by one unit, whereas the CTF reaction alters it by an amount of the same order as the chain length, so that the velocity ratio should be multiplied by the mean degree of polymerisation $\overline{P}$. Thus the transfer intensity factor is

$$\varphi = \varepsilon \overline{P} \frac{\alpha}{1-\alpha}.$$

It is evident that the relative intensity of CTF increases sharply towards the end of the polymerisation process. A study of the polymerisation of tetrahydrofuran has, indeed, shown that the role of CTF, detected by the increase in viscosity of the system, is particularly

noticeable at the very end of the polymerisation, when the growth reaction has practically ceased[22].

Berlin and his coworkers [12] have considered theoretically the possibility of cyclisation by scheme (2) during CTF. They have derived an equation for the molecular-weight distribution in the system with allowance for the formation of cyclic structures

$$h_j = \frac{\alpha}{\beta} \cdot \frac{1}{j^{5/2}} e^{-j/l}, \qquad (21)$$

$$N_j = \frac{N}{l} e^{-j/l},$$

where l is the mean degree of polymerisation of linear molecules, h_j and N_j are the concentrations of cyclic and of linear molecules of length j, and α and β are the rate constants for cyclisation and interchain exchange respectively.

Analysis of the equations yields a number of interesting conclusions. Fig. 1 shows the variation of the mass of cyclic macromolecules for different values of the parameter

$$\varepsilon = \frac{mN}{h_0}, \qquad (22)$$

where

$$h_0 = \lim_{l\to\infty} \int_m^\infty e^{-j/l} \frac{dj}{j^{5/2}} = \frac{\alpha}{\beta} \frac{2}{\sqrt{m}},$$

is the limiting amount of monomer in the cyclic molecules.

From Fig. 1 it is evident that for $M_0 < h_0$ practically the whole of the polymer is cyclic and for $M_0 > h_0$ the mass of cyclic polymer is practically constant. Estimated values of h_0 and ϵ are 4×10^{21} cm^{-3} and 10^{-3} respectively. Thus, in some cases the polymer can be almost completely converted into a cyclic state.

Consideration of the overall molecular-weight distribution gives for $\overline{P}_w/\overline{P}_N$ the expression

$$\frac{\overline{P}_w}{\overline{P}_N} = \frac{2}{3}\left(1 - \frac{h_0}{M_0}\right)^2 \frac{1}{\varepsilon}, \qquad (23)$$

which shows that cyclisation may be a possible cause of the great polydisperseness of polymerisation products.

Recent experimental studies of the polymerisation of heterocyclic compounds [23-27], and earlier work on condensation polymerisation [28-31], have shown that large rings can be formed under these conditions.

The possibility of CTF in a system leads to redistribution of the macromolecules with respect to composition as well as to length. Plechova et al.[10] discuss the influence of CTF on the composition of copolymers.

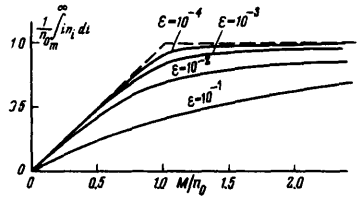


Fig. 1. Variation of mass of cyclic macromolecules with polymer concentration for different values of the parameter ϵ.[12]

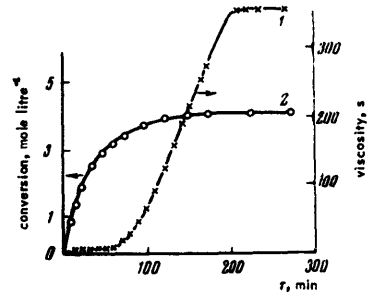


Fig. 2. Dependence of the viscosity of the polymerisation medium (1), and of the extent of reaction (2), on the duration of polymerisation of tetrahydrofuran in diethyl ether at 20° in the presence of the catalytic system

$(C_2H_5)_2O.BF_3$ —— $CH_2-CH-CH_2Cl$ (O)

with $[M]_0$ = 7.0 M, $[cat]_0$ = 0.02 M (after Rozenberg [22]).

The CTF reactions occurring in the case of a binary copolymer can be summarised as follows:

$$\sim\!\sim A^* + \sim\!\sim A\!-\!B \sim\!\sim \xrightarrow{k_1} \sim\!\sim A\!-\!A \sim\!\sim + \sim\!\sim B^*$$
$$\sim\!\sim A^* + \sim\!\sim B\!-\!B \sim\!\sim \xrightarrow{k_2} \sim\!\sim A\!-\!B \sim\!\sim + \sim\!\sim B^* \qquad (24)$$
$$\sim\!\sim B^* + \sim\!\sim A\!-\!B \sim\!\sim \xrightarrow{k_3} \sim\!\sim B\!-\!B \sim\!\sim + \sim\!\sim A^*$$
$$\sim\!\sim B^* + \sim\!\sim A\!-\!A \sim\!\sim \xrightarrow{k_4} \sim\!\sim A\!-\!B \sim\!\sim + \sim\!\sim A^*$$

It is clear that the composition of the copolymer undergoes a change: sequences (blocks) of units of a given kind can be split, and conversely separate blocks of a given unit can become "fused" into a single block. Thus, CTF can cause redistribution of the units of a copolymer among blocks and affect the number of blocks in the macromolecule.

By analogy with the number average degree of polymerisation, we can introduce the parameters S_A and S_B, the mean lengths of the blocks ~A...A~ and ~B...B~. If the average number of blocks of a given type in the macromolecule is l, it readily follows that

$$S_A = \frac{m_A}{l}, \quad S_B = \frac{m_B}{l},$$

where m_A and m_B are the respective numbers of A and B units in the molecule.

Solving the set of differential equations for the variation in l and $[A^*]$, we obtain for equilibrium the following equation

$$l^2 - \kappa[m_A - l][m_B - l] = 0, \qquad (25)$$

where

$$\kappa = \frac{k_2 k_4}{4k_1 k_3}.$$

When κ = 1 the expression for l takes the form

$$l = \frac{m_A m_B}{m_A + m_B} \qquad (26)$$

and

$$\overline{S}_A = 1 + \frac{m_A}{m_B}, \quad \overline{S}_B = 1 + \frac{m_B}{m_A}. \qquad (27)$$

This means that monomer units in the copolymer which are present in small numbers as compared with the other component are distributed singly.

Eqn. (26) can be obtained by a purely statistical approach[32,33].

Thus the occurrence of CFT in a system must cause a redistribution of the monomer units in the system irrespective of the initial distribution.

In the absence of CTF the average length of the blocks is completely determined by the copolymerisation constants according to the formulae

$$\bar{S}_A = r_1 e + 1; \quad \bar{S}_B = \frac{e}{r_2} + 1. \qquad (27')$$

Discrepancies between the experimental composition of a copolymer and that calculated from the formulae (27') have been reported in papers on the copolymerisation of dioxolan with styrene[34] and of 3,3-bischloromethyl--oxacyclobutane with β-propiolactone[35]: obviously, this can be ascribed to the occurrence of CTF in these systems.

Analysis of copolymerisation kinetics with allowance for CTF leads to expressions for the rate and for the composition of the copolymer which differ from the classical expressions.

For small extents of reaction, when the consumption of monomer can be ignored, and $k_2 = 0$, we obtain

$$\alpha + \frac{k_{12}e}{k}\left(1 - \frac{k_{21}}{K_{11}}\right)\ln\left\{1 + \frac{k_1 x}{k_{21} + k_{12}n\,\frac{k_{21}}{k_{11}}}\right\} = K_{11}C_0 t, \qquad (28)$$

where

$$\alpha = \frac{m_A}{A}; \quad n = \frac{B}{A}.$$

In the absence of CTF, the parameter α varies linearly with time:

$$\alpha = k_{11}Ct_0\,\frac{1 + k_{12}/k_{11}\cdot n}{1 + k_{12}/k_{21}\cdot n}, \qquad (29')$$

whereas if transfer through the polymer is substantial

$$\alpha = k_{11}kC_0 t. \qquad (29'')$$

The physical significance of these relationships is clear: CTF leads to a greater number of active centres of type A* than in the case of ordinary copolymerisation; this increases or decreases the rate of accumulation of the component A according as $k_{11} \gtrless k_{21}$, since

$$\frac{1 + k_{12}/k_{11}\,n}{1 + k_{12}/k_{21}\,n} \gtrless 1.$$

It is evident that the change in the rate of polymerisation of each of the components in the presence of CTF (as compared with the classical scheme of copolymerisation) will cause departures from the Mayo–Lewis composition equation[36,37].

Thus the instantaneous composition of the copolymer in the presence of CTF is given by the equation[36]

$$n = \frac{1}{2}\left[\frac{er_1r_3 - r_2r_4}{r_3} - \frac{e + r_2}{r_3}\left(\frac{1}{\alpha} - 1\right) + \sqrt{\left[\frac{er_1r_3 - r_2r_4}{r_3} - \frac{e + r_2}{r_3}\left(\frac{1}{\alpha} - 1\right)\right] + 4\left[\frac{r_4}{r_3} + \frac{r_1 e}{r_3}\left(\frac{1}{\alpha} - 1\right)\right]}\right], \qquad (30)$$

where r_1 and r_2 are the copolymerisation constants, and

$$r_3 = \frac{k_1}{k_{21}}; \quad r_4 = \frac{k_2}{k_{12}}; \quad n = \frac{m_A}{m_B}; \quad e = \frac{A_0}{B_0}, \alpha = \frac{m_B}{B_0}.$$

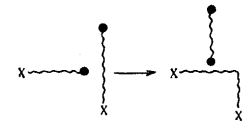
In the absence of CTF ($r_3 = r_4 = 0$) Eqn. (30) becomes identical with the classical equation for the instantaneous composition of a copolymer. If either of the parameters r_3 and r_4 is non-vanishing, the composition given by formula (30) can deviate very significantly from the classical composition. The difference increases with increase in α.

A remarkable consequence of the occurrence of CTF in a system is the special form of the "live" state of the system. The "live" state of polymers, discovered and investigated by Szwarc[13], depends on the absence of any reactions which destroy active centres or cause chain limitation in general, and thus can occur only in absolutely pure systems. This state is characterised by a molecular-weight distribution of the Poisson type[18], a linear increase in degree of polymerisation with extent of reaction, and rigid adherence to the expression

$$\bar{P}_N = \frac{\Delta M}{C}, \qquad (31)$$

where C is the total quantity of active centres, ΔM the amount of polymerised material, and $\bar{P}_N$ the mean degree of polymerisation.

As was stated above, CTF leads to an exponential molecular-weight distribution irrespective of the detailed mechanism of polymerisation. The broken macromolecules take part in CTF without disturbing the distribution, as is the case with normal "live" polymers. Molecules having "dead" end-groups on both sides can acquire active terminations as a result of CTF. As can readily be shown, this should produce chains both ends of which are active:



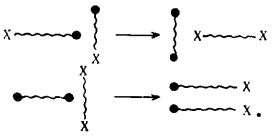
(32)

Therefore, all molecules, both "live" and "dead", will take part in reactions of chain growth, since there will be a constant exchange of end-groups between the macromolecules. Thus, in a way, all molecules in the system are "live", whatever the nature of their end-groups.

Studies of the variation in molecular weight with extent of reaction in the polymerisation of trioxan[38,39] have shown that the viscosity molecular weight increases linearly with extent of conversion, suggesting that the polyoxymethylene molecules are live[38]. However, later experiments revealed a temperature dependence of the slope of the linear plot of $\bar{M}_w$ against extent of reaction, which was unrelated to differences in the degree of initiation[38]. This provides unambiguous proof of the presence of chain--limiting reactions in the system, probably by transfer to impurities with a rate constant much higher than the growth rate constant. The linear variation of the viscosity--average molecular weight with extent of reaction can be retained only in the presence of intense CTF, which allows all the molecules to take part in chain growth and maintains proportionality between number-average and weight--average molecular weights. Thus, this special form of the "live" state of the molecules manifests itself in the polymerisation of trioxan.

It is interesting to consider the nature of the distribution of end-groups among the chains. If the macromolecules can have only two types of end-groups (active and inactive), the system will be composed of three types of molecule: — both end-groups active (A), only one active (B),

and both inactive (C) — transition of molecules of one type into another type occurring by the scheme



(32′)

The set of equations describing this process is

$$\frac{dA}{dt} = \frac{dC}{dt} = -2\frac{dB}{dt} = \frac{1}{2}kB\Sigma jB_j - 2kA\sum_j jC_j,$$
$$2A + B = a;$$
$$2C + B = b, \qquad (33)$$

where a is the total concentration of active groups, and b of inactive groups.

Assuming that CTF results in the establishment of an equilibrium molecular-weight distribution, and also an equilibrium distribution of end-groups, the former being observed not only in the system as a whole but also in each group of molecules, we obtain

$$\frac{A}{A+B+C} = \frac{a^2}{(a+b)^2};\quad \frac{B}{A+B+C} = \frac{2ab}{(a+b)^2};\quad \frac{C}{A+B+C} = \frac{b^2}{(a+b)^2}. \qquad (34)$$

It should be noted that this distribution of end-groups can be obtained from purely statistical considerations, by assuming that the probability of finding any group at one end of a chain is equal to its fraction of the total number of ends, whilst the probability of finding any two groups at the two ends of a chain is equal to the product of the separate probabilities for each of the groups. The fraction of macromolecules of a given type is determined by the probability of their formation.

A kinetic analysis of the exchange between molecules having more than two types of end-group is fairly complicated, but it leads to a similar result.

As the above considerations show, the kinetic and the probability approaches to the distribution of macromolecules with respect to length, composition, and type of end-groups give identical results, because of the entropic nature of CTF.

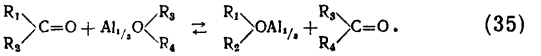
3. CTF AS AN EXCHANGE REACTION

It is possible to set up a simple and convenient model of CTF reactions on the basis of low-molecular-weight compounds simulating the functional groups which can undergo CTF (fragments of the main chain or of a side-chain of the polymer). These model exchange reactions must satisfy a number of requirements arising from the specific chemical features of CTF reactions in macromolecular compounds.

The reactions must be reversible. This is because a necessary condition for this reaction to occur during polymerisation is that the new active centre formed after the act of transfer must be able to carry on the polymerisation and CTF process. When CTF occurs, the rate constants for M_1^* with respect to M_1–M_1 and M_2–M_2, and also for M_2^* with respect to M_1–M_1 and M_2–M_2, will be different for the different homopolymers, but it is necessary that all these reactions should take place — which means, in practice, that the reaction must be reversible — in order that CTF can occur.

A second important requirement of the model reactions of exchange interaction is adherence to the principle of conservation of functional groups. This means that the functional groups initially present must not undergo any chemical change during the reaction: only radicals bound to the functional groups are exchanged.

In view of the latter requirement, we must exclude those exchange reactions which, though formally resembling model exchange reactions, follow a quite different mechanism, involving changes in the functional groups during the process. For example, reactions which do not satisfy the above conditions, although formally very similar to model reactions for CTF, are the Meerwein–Ponndorf–Verley reaction of ketones and the Oppenauer oxidation of alcohols [40]

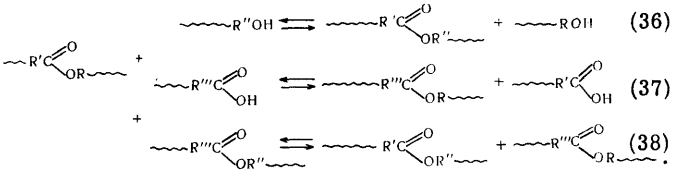


(35)

Another example of a reaction of this type is transamination, discovered by the Soviet biochemists Braunshtein and Kritsman [41].

At the present time, hardly any papers have been published on the detailed mechanism of exchange reactions, but some general features observed in studies of transesterification processes and in particular the alcoholysis of carboxylic esters [42–58] justify the statement that these are fairly typical of nucleophilic substitution processes at a carboxy-group [59,60].

We shall consider some model reactions of exchange interaction. The examples below are given merely as an illustration, and are by no means comprehensive. One of the most thoroughly investigated model reactions is transesterification. It can be conducted in three ways — (1) by reaction between an ester and an alcohol (alcoholysis), (2) by reaction between an ester and an acid (acidolysis), and (3) by reaction between two esters (esterolysis):



(36)

(37)

(38)

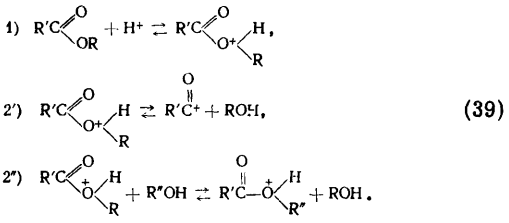
Reactions (36) and (37) simulate the reaction between a polyester macromolecule and a low-molecular-weight impurity (acid or alcohol); reaction (38) simulates the interchain exchange of two polyester macromolecules.

The rate of reactions (36) and (37) is considerably increased by acidic or basic additives [44,46,61], while reaction (38) is accelerated by acidic catalysts [45,61]. Studies of alcoholysis have shown [49] that a heavier hydrocarbon radical displaces a lighter one, but on occasions a heavier alcohol radical is displaced by a lighter one in fairly high yield, as in the alcoholysis of bornyl acetate by ethanol and by butanol [47]. The structure of the radical R′ has a major effect on the rate of exchange. Thus, the exchange is strongly retarded by the presence of double bonds in the α and β positions with respect to the carboxy-group, as in crotonic and cinnamic esters [44]. Conversely, electron-acceptor groups in the α position to the carboxyl increase the rate of exchange [44].

It has recently been shown [56] that the yield of alcoholysis products is practically unaffected by the number and complexity of the substituents in the acid part of malonic esters.

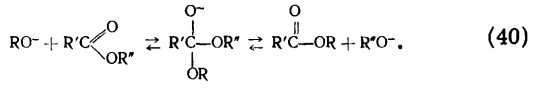
The relative reactivity of various radicals in the alcoholysis of acetates has been measured[50]. As was to be expected, primary alcohols are the most reactive, followed by secondary alcohols.

Korshak and Vinogradova[61] studied the kinetics of alcoholysis in the exchange between ethyl stearate and cetyl alcohol. The reaction takes place even in the absence of catalysts, but very high temperatures are then necessary. Alkaline (sodium hexadecyloxide) and particularly acid (concentrated sulphuric acid) catalysts allow the temperature to be lowered appreciably whilst increasing the velocity above that of the uncatalysed reaction. The mechanism of the uncatalysed (or acid-catalysed) alcoholysis, like that of the thoroughly investigated hydrolysis of esters under analogous conditions[62], appears to consist in the rapid formation of an acylalkyloxonium ion, which subsequently decomposes to form an acylium cation or reacts with the alcohol:



(39)

The mechanism of alkaline alcoholysis involves initial attack by an alkoxy-anions on the carboxyl carbon atom, which has a partial positive charge as a result of the electron-acceptor effect of the carbonyl group. The resulting anionic intermediate can decompose in two ways — to regenerate the starting compounds or to form the exchange products[59]:



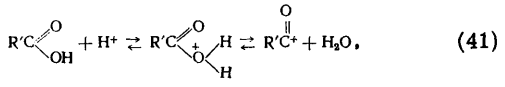
(40)

Some unusual features were observed in a study of the alcoholysis between ethyl stearate and acetic acid[63]. It was shown that the order of the reaction changes from first to second during the course of the reaction.

Acidolysis is accelerated by protonic and aprotic acids[64]. It is very important in synthetic chemistry, and is widely used for the preparation of vinyl esters of carboxylic acids from vinyl acetate[65].

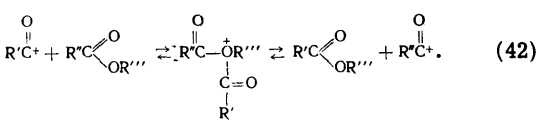
As in the previous systems, the uncatalysed exchange between two esters occurs very slowly and only at sufficiently high temperatures[66]. The reaction becomes much faster in the presence of alkaline, and even more so in the presence of acidic, catalysts[66-68]. The rate of the reaction is proportional to the concentration of the reagents[66].

The mechanism of acid-catalysed acidolysis evidently involves initial formation of an acylium cation



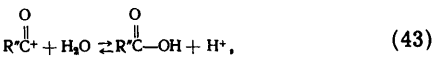
(41)

which can then attack a molecule of the ester with exchange of the ester group:



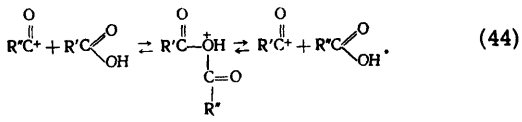
(42)

Regeneration of $O{=}C^{+}R'$ can occur either through the interaction of $O{=}C^{+}R''$ with water



(43)

followed by reaction (41), or directly by reaction between $O{=}C^{+}R''$ and the acid



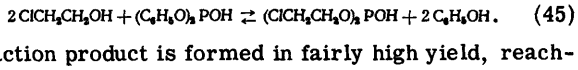
(44)

In addition to the Soviet work discussed above[61,63,66], we must mention that papers of Flory[2,69], who showed that the alcoholysis of poly(decamethyleneadipate) under the influence of small amounts of an alcohol or a glycol (decamethylene glycol or dodecan-1-ol) follows first-order kinetics in the presence of an acid catalyst. The reaction velocity is proportional to the concentration of the acid catalyst. The activation energy of the alcoholysis is 11.5 kcal mole^{-1}. It was also shown that the exchange reaction in question is approximately 11 times as slow as the polyesterification of decamethylene glycol and adipic acid.

Various workers[70-72] have found that these exchange reactions follow second-order kinetics, the activation energy of the uncatalysed exchange being 20–30 kcal × × mole^{-1} higher than that of the acid- or base-catalysed reaction by factors of 2–3.

On the basis of the kinetic results obtained in their study of transesterification on model compounds, Korshak and Vinogradova[73,74] arranged the reactions in order of increasing relative reaction rate as follows: esterolysis < < alcoholysis < acidolysis. We should note, however, that in the condensation polymerisation process used in the synthesis of polyesters the relative importance of acidolysis and alcoholysis decreases as the reaction proceeds, owing to the loss of functional groups, while esterolysis becomes increasingly important as a result of the accumulation of polymeric products.

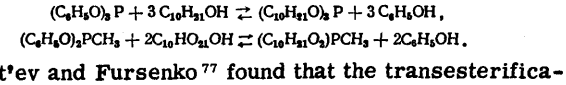
Transesterification occurs readily also with the esters of phosphoric, phosphorous, and phosphonic acids[75-80]. The preparation of dialkyl phosphites from diphenyl phosphites by an exchange reaction between the latter and aliphatic alcohols was worked out by Petrov et al.[75] The reaction proceeds by the scheme



(45)

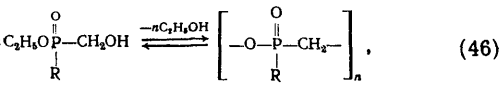
The reaction product is formed in fairly high yield, reaching 93%.

Good yields of exchange products have been obtained also in the transesterification of aromatic esters of phosphoric and phosphonic acids with aliphatic alcohols[76]. The reaction is catalysed by alkali-metal alkoxides and is represented by the equations



Nifant'ev and Fursenko[77] found that the transesterification of phosphites and phosphonites, a very important synthetic reaction used in the preparation of many phosphorus derivatives, can be carried out under much milder conditions (20–40°) and without a catalyst if the 2-fluoroethyl esters of tervalent phosphorus acids are used as starting compounds.

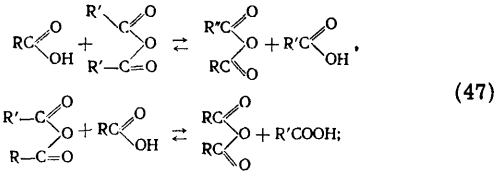
Pudovik and Evstaf'ev[78,79] used transesterification to prepare polyphosphites and polyphosphinites by the reaction of phosphinic and phosphinous esters with glycols. In a recent paper[80], these authors have extended this method to the preparation of phosphorus-containing polymers by homopolyesterification:



(46)

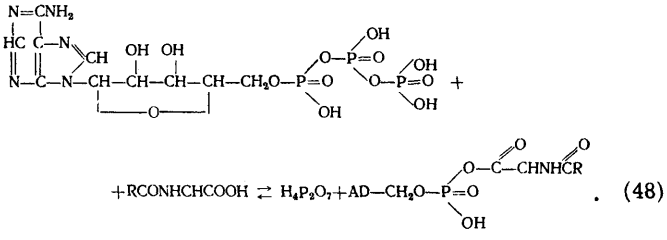
where R = OC_2H_5, C_2H_5, C_6H_5. The kinetics of this reaction is described by a second-order equation, with an activation energy of 23 kcal mole^{-1}.

A very important reaction in synthetic chemistry is the exchange interaction of carboxylic acids with acid anhydrides[81-85], leading to formation of the anhydrides of the corresponding acids or to mixed anhydrides:



(47)

The formation of a mixed anhydride is thought[86] to be one of the essential intermediate stages in the synthesis of polypeptides and proteins. Adenosinetriphosphoric acid, which can be said to contain an inorganic acid anhydride group, exchanges with an acylamino-acid to form a mixed anhydride — the acyladenylate of the amino-acid, which can then be used *in vivo* or *in vitro* to construct a peptide link:



(48)

The transetherification of an ether or acetal linkage also has great practical importance in the synthesis of various ethers and acetals[87-94]. These reactions, which proceed according to the scheme

$$ROR + R'OR' \rightleftarrows 2ROR',$$

are catalysed as a rule by acid substances — protonic[94] and aprotic[89] acid, ion-exchange resins[91], and other compounds[89,90] — being particularly important in the synthesis of natural products, especially polysaccharides, in which interchain exchange occurs through the splitting of a glucoside link under the influence of specific enzymes[86].

Exchange reactions between the amide group and acids, amides, esters, and amines are quite rapid. These reactions are of the utmost importance in biosynthesis, and will be dealt with separately.

The disulphide group, and polysulphide groups in general[95], are very reactive towards a number of exchange interactions. The most typical exchanges of this type are the thiol–disulphide and disulphide–disulphide, which can be represented by the general equations

$$RSSR + R'SH \rightleftarrows RSSR' + RSH; \quad (49)$$

$$RSSR + R'SSR' \rightleftarrows 2R'SSR. \quad (50)$$

It is interesting to note that these reactions can be initiated both by anionic and by cationic catalysts. In a few cases the exchange can occur also by a radical mechanism. Thus, for example, exchange was reported[96] between dodecanethiol and propyl disulphide merely on heating, without the addition of any activators.

The thiol–disulphide exchange is very strongly accelerated in the presence of alkaline catalysts[97]. The polarity of the solvent has a considerable effect on the rate of exchange. It has been shown[98] that an exchange which is slow in absolute methanol is accelerated by aqueous methanol, and goes very rapidly in the presence of alkali. The rate of the thiol–disulphide exchange in methanol at 0–35° is proportional to the concentration of disulphide and the alkyl sulphide ion, and the activation energy[99] is 15 kcal × × mole^{-1}. Reactants containing sterically hindered groups, such as 2-methylpropane-2-thiol reacting with di-t-butyl disulphide, exchange very slowly, with an activation energy of ~ 22 kcal mole^{-1}.

Entirely different behaviour is observed when the thiol–disulphide exchange is carried out in non-polar media. The exchange interaction between aliphatic thiols and disulphides in an aromatic hydrocarbon medium is very slow even at 200°. Its activation energy is 28 kcal mole^{-1}. Yet the exchange of aromatic thiols and disulphides under similar conditions is quite fast even at much lower temperatures, and has an activation energy of ~ 10 kcal mole^{-1}. The reaction rate is proportional to the square root of the concentration of disulphide, and is independent of the thiol concentration. Gur'yanova and her coworkers[100] proposed a radical exchange mechanism in non-polar media to explain these facts

$$\begin{aligned} RSSR &\rightleftarrows 2RS^{\cdot}, \\ RS^{\cdot} + R'SH &\rightleftarrows R'S^{\cdot} + RSH, \\ R'S^{\cdot} + RS^{\cdot} &\rightleftarrows R'SSR; \end{aligned} \quad (51)$$

The presence of radicals was demonstrated by the accelerating effect of ultraviolet radiation and by reaction with 2,2-diphenyl-1-picrylhydrazyl. The exchange is catalysed by peroxides and azoisobutyronitrile[95]. The decomposition of acyl peroxides occurs in a similar way[34]. A radical mechanism has been postulated also for the exchange of disulphides[101]: unsymmetrical aromatic disulphides undergo rearrangement to symmetrical disulphides in boiling dioxan solutions, under ultravoilet irradiation, or on heating to 170°.

Disulphides exchange very readily in polar media in the presence of hydrogen sulphide or alkyl sulphide anions[97,102,103]. Disulphide exchange can occur also in the presence of protonic or aprotic acids[97,104,105]. The sulphonium ion is assumed to be active species.

Space does not allow us to discuss all the many exchange interactions which can be applied to polymeric molecules for the purpose of modifying them. We shall point out only that the use of nuclear magnetic resonance methods in recent years has helped to demonstrate the occurrence of exchange reactions in the most varied systems[106-109].

4. METHODS OF DETECTING CTF

Exchange reactions involving macromolecular compounds occur by essentially similar processes. Just as with other chemical transformations of macromolecular

compounds [110], the morphology of the polymer plays an important part. This is obviously a highly significant factor in reactions of this type, and exerts a strong influence on the reactivity of polymers.

The occurrence of CTF in a system can be detected in a number of ways. For a CTF reaction to manifest itself in the synthesis of a polymer by condensation or addition polymerisation, the rate constant of the CTF step must be comparable with the rate constant of the polymer formation reaction. This criterion becomes less essential when we are dealing with CTF between two existing homopolymers, since in this case the exchange can be considerably intensified by raising the temperature.

A strict chemical proof of the presence of CTF may be provided by the very fact that block and graft copolymers are formed under conditions offering no conceivable mechanism for their formation other than CTF.

Two methods of synthesis of block copolymers based on CTF have been developed. In the first method the block copolymer is synthesised by the polymerisation of one monomer in a medium of the other homopolymer [111,112], when polymerisation is accompanied by CTF. Block copolymers synthesised by this method and the methods used to identify them are listed in Table 1.

In the second method, block copolymers are synthesised by initiating CTF between the two homopolymers. It is evident that in this case we have no polymerisation as such, and that only CTF processes take place according to the scheme

$$\sim\!\sim R_jOR_i\sim\!\sim + \sim\!\sim R_kOR_l\sim\!\sim \longrightarrow \sim\!\sim R_jOR_k\sim\!\sim + R_iOR_l\sim\!\sim \quad (52)$$

The results of these syntheses [113] are set out in Table 2.

Pairs of homopolymers were chosen such that one of the polymers was insoluble in the solvent used, thus enabling the occurrence of CTF to be detected visually by the gradual swelling followed by dissolution of the insoluble polymer. Blank experiments without the catalyst (to check whether the insoluble homopolymer was soluble in a solution of the other homopolymer) and without the soluble homopolymer (to check whether the polymer was soluble when degraded by the catalyst) gave no such effect. In both cases, the insoluble polymer was regenerated in almost quantitative yield.

TABLE 1. Preparation of copolymers by cationic polymerisation of a monomer in the presence of other polymers [11].

Monomer	Polymer	Type of polymer formed	Method of identification
Trioxan	polydioxolan	block copolymer	kinetic
Formaldehyde	»	ditto	»
Trioxan	poly(ethylene oxide)	»	spectral
»	poly(propylene oxide)	»	»
»	poly(tetramethylene oxide)	»	»
»	poly(ethylene adipate)	»	»
Styrene	polydioxolan	»	spectral
Trioxan	dimethyl ethers of poly(oxymethylene glycol)	homopolymer	kinetic
Formaldehyde	ditto	»	»
Trioxan	poly(methyl methacrylate)	graft copolymer	spectral

TABLE 2. Preparation of block copolymers by the interaction of homopolymers [113].

Soluble polymer	Insoluble polymer
Polydioxolan	polyoxymethylene
Poly(tetramethylene oxide)	polyoxymethylene
Polydioxolan	poly-3,3-bischloromethyloxacyclobutane

Obviously, graft copolymers also can be synthesised by a similar procedure, if the functional group by which the chain is transferred is located in a side-branch of the homopolymer. Again, two methods of synthesis are possible — (1) the polymerisation of one monomer in a medium of the other homopolymer, and (2) reaction between the two homopolymers — results of the synthesis of graft polymers by the second method being listed in Table 3 [113].

It might be thought that block and graft copolymers are formed not as a result of CTF but by the copolymerisation of pairs of monomers produced during the establishment of equilibrium with an active polymer chain, which is itself formed by the action of the catalyst on the polymers. However, the results of the third experiment in Table 2 and of the experiments summarised in Table 3 show unambiguously that the block and graft copolymers were formed by a CTF reaction, since the starting homopolymers used could not act as monomer donors under the conditions of the experiments.

Thus, the synthesis of block and graft copolymers by the methods described is a rigorous chemical proof of the reality of CTF as an elementary act.

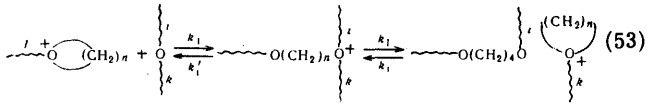
This act can be quite clearly identified even in homopolymerisation processes. A universal method of identification is the change in the molecular-weight distribution of the polymer during polymerisation. Some difficulties in the identification of this elementary act may arise when the polymerisation process is reversible, because under these conditions, too, the most probable molecular-weight distribution will establish itself in the system. These difficulties can be readily overcome by noting that in the case of reversible polymerisation the most probable distribution occurs only in the "live" part of the polymer.

An interesting effect is observed in the cationic polymerisation of oxygen-containing cyclic compounds. Thus, in the polymerisation of tetrahydrofuran [22] or trioxan [114], and perhaps also of other analogous compounds, a large increase in the viscosity of the reaction medium is found towards the end of the polymerisation process. Fig. 2 shows the variation in viscosity of the medium and in the extent of conversion as a function of time during polymerisation. This effect is not difficult to explain on the basis of CTF concepts.

TABLE 3. Preparation of graft copolymers by the interaction of homopolymers [113].

Soluble polymer	Insoluble polymer
Poly(butyl vinyl ether)	polyoxymethylene
Poly (butyl vinyl ether)	poly-3,3-bischloromethyloxacyclobutane

Thus, as was shown above (p. 310), the relative contribution of CTF to the polymerisation process should increase continuously as the reaction proceeds. Since a cyclic ether (acetal) is considerably more basic than a linear polyether, the rate of chain growth is higher, as a rule, than the rate of CTF. In this case the mechanism of CTF is complex, consisting of two consecutive acts: an active centre attacks the polymeric macromolecule with formation of an oxonium ion, and the resulting polymeric oxonium ion then decomposes:


(53)

The rate of the CTF process depends on the ratio of the constants for these elementary reactions: clearly, all the active centres should be in the form of polymeric oxonium ions towards the end of the reaction, so that the reaction medium consists of an aggregated system with labile bonds between polymer chains. Of course, this effect must cause a substantial increase in the viscosity of the medium. The viscosity of a system undergoing polymerisation drops to the normal value on treatment with a nucleophilic reagent[22], i.e. when the labile bonds are broken. The occurrence of this effect during homopolymerisation can itself be taken as evidence for CTF in the system under study.

Clear indications of interchain exchange and related interactions between a polymer chain and the starting materials or compounds of similar chemical nature have been obtained in the study of reactions leading to the formation of macromolecules by condensation polymerisation. As already pointed out, these reactions appear to proceed by a mechanism analogous to CTF. We shall call these reactions interchain exchange reactions in the case of condensation polymerisation.

Since fairly high temperatures are normally used for condensation polymerisation, the contribution of interchain exchange to the formation of macromolecules is considerably increased. We shall consider a few examples which illustrate interchain exchange processes occurring in condensation polymerisation reactions. These relate mainly to interchain exchange reactions of ester and amide groups.

We know from the theory of condensation polymerisation[3,4] that equivalent amounts of reactants are of great importance in the preparation of polymers of high molecular weight. Since functional groups of a single type do not interact, we can expect that a twofold excess, say, of one of the reactants will make it impossible to obtain a high-molecular-weight polymer: only low-molecular-weight reaction products should form in this case. Actually, however, it is possible to obtain products of fairly high molecular weight even in this case[115-117].

Thus, in the preparation of a polyester from a dicarboxylic acid and a diol with a twofold excess of one of the components, HOR'OOCR"COOR'OH or HOOCR"COOR'OOCR"COOH respectively are formed in the early stages of the reaction. Growth of the resulting "intermediates" becomes possible if exchange reactions by a transesterification mechanism (acidolysis or alcoholysis) take place:

$$2\,\mathrm{HOOCR''COOR'OOCR''COOH} \xrightleftharpoons{-R''(COOH)_2} \mathrm{HOOCR''[COOR'OOCR'']_2COOH},$$

$$2\,\mathrm{HOR'OOCR''COOR'OH} \xrightleftharpoons{-R'(OH)_2} \mathrm{HOR'[-OOCR''COOR'-]_2OH}. \quad (54)$$

The dicarboxylic acid or diol evolved is removed in a vacuum at a high temperature in order to displace the equilibrium. In practice, as a rule, a slight excess of diol is used, since this is the more volatile constituent and is more easily removed from the reaction medium.

The exchange interaction between amides and acids (or esters) can be used for the synthesis of polyamides.

Rafikov et al.[118] observed the formation of a polyamide from *NN'*-diacetylhexamethylenediamine and adipic acid:

$$n\mathrm{CH_3ONH(CH_2)_6NHCOCH_3} + n\mathrm{HOOC[CH_2]_4COOH} \rightleftarrows \mathrm{[-NH[CH_2]_6NHCO[CH_2]_4CO-]_n} + 2n\mathrm{CH_3COOH}. \quad (55)$$

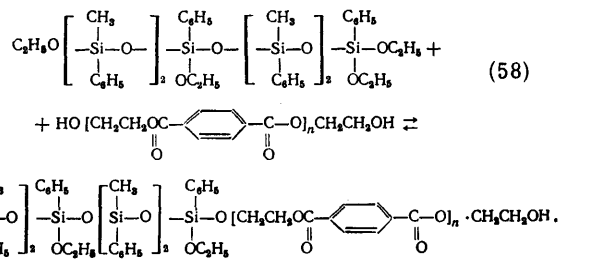
They also studied[118] the reaction between *NN'*-diacetylhexamethylenediamine and diethyl adipate. As before, the product of the reaction is polyhexamethyleneadipamide:

$$n\mathrm{CH_3CONH[CH_2]_6NHCOCH_3} + n\mathrm{C_2H_5OOC[CH_2]_4COOC_2H_5} \rightleftarrows \mathrm{[-NH[CH_2]_6NHCO(CH_2)_4CO-]_n} + 2n\mathrm{CH_3C(=O)OC_2H_5}. \quad (56)$$

Lastly, polyamides can be prepared by the exchange interaction of two diamides. Thus, Beste and Houtz[119] observed the formation of a polyamide from diacetylhexamethylenediamine and the diamide of sebacic acid:

$$n\mathrm{CH_3CONH[CH_2]_6HNCOCH_3} + n\mathrm{H_2NCO[CH_2]_8CONH_2} \rightleftarrows \mathrm{[-NH[CH_2]_6NHCO[CH_2]_8CO-]_n} + 2n\mathrm{CH_3CONH_2}. \quad (57)$$

The alcoholysis of polyesters has been suggested as a practical reaction for the regeneration of dimethyl terephthalate from poly(ethylene terephthalate) by treating the polymer with methanol[120]. Andrianov and his coworkers[121] demonstrated the interesting potential uses of alcoholysis in synthetic chemistry by preparing block and graft copolymers of poly(ethylene terephthalate) and polyorganosiloxanes:


(58)

The inclusion of ethoxy end-groups and side-groups in the polyorganosiloxane molecule leads to the formation of a mixed block-graft copolymer. The resulting copolymer has superior mechanical and dielectric properties and reasonably high thermal stability.

Kursanov et al.[122] demonstrated the occurrence of exchange interaction between two polyesters by an isotopic method. They studied the reaction between diethyl 2,3-dideuterosuccinate and poly(hexamethylene sebacate). The presence of deuterium in the polyester after reaction with the deuterated succinic ester is a proof of the occurrence of interchain exchange between polyester molecules.

A direct proof of ester exchange was given by Goodman and Nesbitt[123], who studied the interaction of poly(ethylene terephthalate) with tetramethylene dibenzoate and of poly(tetramethylene terephthalate) with ethylene dibenzoate. As a result of interchain exchange, they obtained ethylene and tetramethylene dibenzoates respectively.

The same workers showed that the cyclic trimer of ethylene terephthalate polymerises with formation of a linear polymer of high molecular weight. However, the reaction does not occur if the material is thoroughly dried. This suggests that the active initiator of the reaction is a hydroxy-acid, a hydrolysis product of the cyclic trimer. The mechanism of chain growth is an unusual trans-esterification reaction (acidolysis or alcoholysis) between the hydroxy-acid and the cyclic trimer.

The so-called hydrolytic polymerisation of lactams [4] involves a similar mechanism (transamidation). In general, from the point of view of the present Review, the polymerisation of any heterocycle can be treated as an exchange interaction irrespective of the type of active centre involved in the polymerisation.

Yet another general method of demonstrating the reality of interchain exchange reactions during condensation polymerisation depends on the formation of, say, a polyester from substances which contain neither free carboxyl nor free hydroxyl groups. Thus, a method of preparation of poly(ethylene terephthalate) from bis-2-acetoxyethyl terephthalate or bis-2-benzoyloxyethyl terephthalate has been described in the patent literature [124].

Several methods for identifying interchain exchange reactions are based on studies of the molecular weight, the molecular-weight distribution, or some other physical property of the products of condensation polymerisation [125]. Thus, when two samples of poly(decamethylene glycol) are mixed and heated [19], a fall in viscosity is observed: this is because the weight-average molecular weight decreases, although the number-average molecular weight remains constant under these conditions.

Using a very similar experimental approach, Rafikov et al.[126] separated by fractionation a narrow fraction of poly(ethylene adipate) from an unfractionated specimen. When this narrow fraction was heated in a sealed bulb at 170° the molecular-weight distribution became the same as in the original, unfractionated sample.

It is evident from the scheme discussed above that the acids and alcohols of low molecular weight generated by transesterification should lower the molecular weight of the polyester. Indeed, these phenomena have been thoroughly investigated in numerous publications by Korshak and his coworkers [125-136] and by others [69,137].

As in the case of polyesters, the exchange reactions accompanying the interaction between a polyamide and substance of a low molecular weight cause a lowering of the molecular weight of the former. Fig. 3 illustrates the results of the exchange reaction between polyhexamethyleneadipamide and adipic acid [128]. Similar results were obtained on reaction of this polymer with stearic acid [128] and of polycaprolactam with *p*-chlorobenzoic acid [138].

Korshak and Gribova [132] observed the aminolysis of polyurethane on heating it with aniline. They also showed that polyurethanes, like polyamides, can undergo, as well as aminolysis, exchange reactions with carboxylic acids, alcohols, and isocyanates [139].

A considerable lowering of molecular weight and softening temperature is observed when a polymer containing polysulphide links is treated with a thiol. Thus a liquid polymer of molecular weight ~ 5000 is formed when 5 mole % of butanethiol is added to an alkaline aqueous

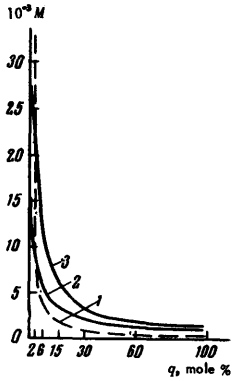


Fig. 3. Acidolysis of polyhexamethyleneadipamide by adipic acid (*q* mole %). Molecular weight:
1) calculated; 2) determined from viscosity;
3) determined from end-groups.

suspension of a macromolecular polysulphide [140]. Similar behaviour is observed with other substances which can denote alkyl sulphide ions, such as low-molecular-weight disulphides. Aromatic thiols, in particular thiophenols and mercaptobenzothiazole are effective donors [95]. Aliphatic thiols are less effective. Thiols with branched radicals have a very low activity [141] because of steric hindrance.

An interesting method, based on the change in physical properties of the resulting polymer, was used by Korshak and his coworkers [142] to demonstrate the occurrence of interchain exchange in condensation polymerisation. A polyamidoester of the composition

$$[-OCH_2CH_2NHCO[CH_2]_8CO-]_n, \quad (I)$$

was obtained by the condensation polymerisation of 2-aminoethanol with sebacic acid. Condensation polymerisation of *NN'*-bis-2-hydroxyethylsebacamide with sebacic acid was also carried out. The product in this case should have had the structure

$$[-OCH_2CH_2NHCO[CH_2]_8CONHCH_2CH_2OCO[CH_2]_8CO-]_n. \quad (II)$$

The two polymers were examined by electron diffraction, and found to have exactly the same identity period of 17 Å. This corresponds to the polyamidoester structure given by formula (I), whence we may conclude that polymer (II) has been converted into polymer (I) as a result of interchain exchange.

Kresse [143] used the lowering of the melting point of a copolyester (as compared with that of a mechanical mixture of the two separate polyesters) to detect interchain exchange. In exactly the same way, a copolymer was prepared from a mixture of three polyamides — poly(hexamethyleneazelaamide), polyhexamethyleneadipamide, and polycaprolactam — formation of the copolymer being demonstrated by monitoring the gradual fall in the melting point of the mixture of polyamides on heating [144]. The melting point continues to change until an equilibrium distribution of monomer units is established in the copolymer, as is clearly shown in Fig. 4, which is a plot of the flow temperature of the three-component system as a function of time of heating [144]. The authors also suggested [144] that

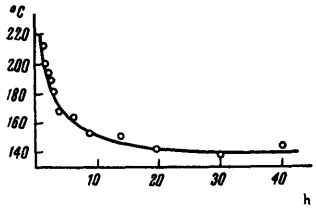


Fig. 4. Variation of the flow temperature of polyhexamethyleneazelaamide–polyhexamethyleneadipamide–polycaprolactam copolymers as a function of time of heating of the homopolymers [144].

the stability of solution of the resulting products can be used to characterise structural changes in the polyamide macromolecules during heating of the homopolyamides.

Technically valuable products have been obtained through the preparation of a copolyamide by heating a mixture of the two homopolyamides polyhexamethyleneadipamide and polycaprolactam [145,146]. It is interesting to compare the difference in melting point between copolymers of a given composition prepared either from the corresponding monomers or from the homopolymers [146,147]. As can be seen from Fig. 5, the melting points of the copolymers differ quite markedly, indicating that the distribution of monomer units is different in the two cases.

Results in good qualitative agreement with this conclusion have been obtained [148] from a study of the tensile strength of mixtures of homopolyamides as a function of time of heating, i.e. essentially as a function of the extent of interchain exchange. As shown in Fig. 6, progress of the reaction is accompanied by a gradual decrease in the tensile strength of the copolyamide. On the basis of the mechanism suggested above for CTF, we may assume that the high initial strength of the copolyamide stems from the large blocks formed in the block copolymer in the initial stages of the reaction; as the reaction proceeds, these blocks are broken up, and this appears to lower the tensile strength of the copolymer.

Thus, as shown by Korshak and his coworkers [149], a block copolymer is formed rapidly on heating mixtures of homopolyamides, the size of the blocks decreasing as interchain exchange proceeds. The system ultimately reaches an equilibrium state characterised by the appropriate distribution of monomer units in the copolymer. The

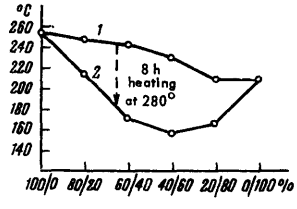


Fig. 5. Variation with composition in melting points of:
1) mixtures of polyhexamethyleneadipamide and polycaprolactam; 2) copolyamides.

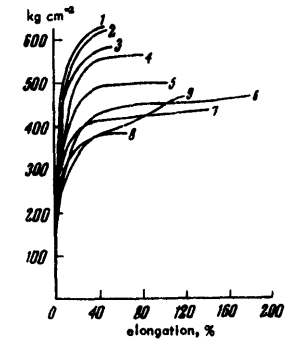


Fig. 6. Variation of the tensile strength of a mixture of polyhexamethyleneadipamide and polycaprolactam with time of heating (h):
1) 0.5; 2) 1; 3) 1.5; 4) 2; 5) 4; 6) 6; 7) 12; 8) 20; 9) 30.

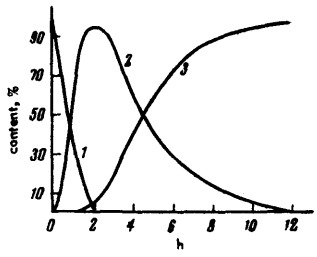


Fig. 7. Change in composition of a mixture of polyamides with heating [148]:
1) content of homopolymers; 2) content of block copolymers; 3) content of copolyamide.

change in composition of a mixture of polyamides is shown in Fig. 7.[148]

The progress of interchain exchange between two homopolymers can be followed by choosing a solvent in which one of the homopolyamides is insoluble. Thus it was found [149] in a study of the reaction between polyhexamethyleneadipamide and polyhexamethyleneisophthalamide that the latter polymer is insoluble in formic acid. When this mixture was heated, the usual fall in melting point was observed, and at the same time the amount of insoluble polyhexamethyleneisophthalamide decreased with time, as shown in Fig. 8. It is evident from these results that only a relatively crude indication of the extent of interchain exchange can be obtained from the change in melting point of a mixture of polymers, particularly in the initial stages, when the block copolymers formed consist of large blocks and have melting points little different from that of a mechanical mixture of the homopolymers.

Unambiguous evidence for the presence of interchain exchange was obtained in the study of naturally occurring molecules containing peptide links. A characteristic feature of these reactions is the fact that they proceed in aqueous media, where the peptide links can undergo hydrolytic reactions. These reactions occur under the influence of enzymes.

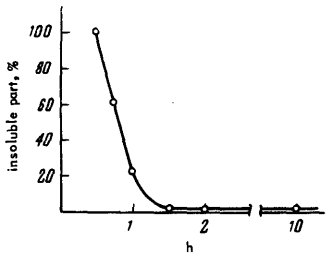
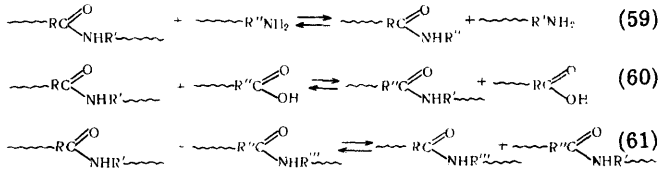


Fig. 8. Change in the relative amount of formic-acid-insoluble material in a polyhexamethylene-adipamide–polyhexamethyleneisophthalamide melt as a function of time of heating [149].

It was shown that various proteolytic enzymes, highly specific in action, can induce transpeptidation reactions as well as hydrolysis, whilst displaying their individual specificity. The term transpeptidation reaction refers to an interchain exchange reaction involving peptide links.

The discovery of transpeptidation is of the greatest interest, because these reactions can play an important role in the synthesis of proteins. In general, transpeptidation reactions can be represented by the following schemes



The earliest report of the possibility of reactions of this type is due to Bergmann [150], who discovered the reaction

$$\text{Hippuroylamine} + \text{Aniline} \xrightarrow{\text{papain}} \text{Hippuroylaniline} + NH_3. \quad (62)$$

It may be thought that the hippuroylaniline was formed by initial hydrolysis of the hippuroylamine followed by reaction between the free hippuric acid and aniline. However, special experiments showed that the rate of reaction (62) is greater than that of the analogous reaction in which hippuric acid was used as the substrate [150]. Therefore, hippuric acid is not an intermediate in this process. In this way a new type of reaction brought about by proteolytic enzymes — exchange interaction — was postulated.

These results were subsequently confirmed by a series of investigations by Fruton and his coworkers [151-153], who showed that papain, activated by cysteine, catalyses the replacement of the amide nitrogen in *N*-benzoylglycinamide or benzyloxycarbonyl-*L*-methioninamide by ^{15}N, introduced in the form of $^{15}NH_4^+$. Exchange of the amide group can occur also when the amide reacts with hydroxylamine, leading to the formation of the corresponding hydroxamic acid [152,153]. Preliminary hydrolysis of the amide, followed by reaction between the free hydroxyl and the hydroxylamine, is out of the question, since it has been shown experimentally that free amino-acids do not form hydroxamic acids with hydroxylamine to a significant extent. Similar results were obtained when different enzyme systems — ficin and chymotrypsin [154,155], and also cathepsin [152,155] — were used as exchange activators.

Many investigations showed that the ability to undergo exchange is an almost universal property of the amides of various amino-acids. The amide group has a general tendency to exchange with various compounds, in particular with hydroxylamine and ammonia, and the latter can be used in the form of nitrogen-labelled ammonium salts. The exchange reaction takes place in the presence of enzymes of vegetable [155,156] and animal [157,158] origin, and of bacteria [159,160].

Exchange of the amide group has been used in synthetic chemistry to build up polypeptide chains. It has been shown [161] that benzoyltyrosylglycinamide is formed when benzoyltyrosinamide reacts with glycinamide in the presence of chymotrypsin. In a similar way, benzyloxycarbonylglycyltyrosinamide can be obtained from benzyloxycarbonylglycinamide and tyrosyinamide in the presence of papain. The action of cathepsin on glycylphenylalaninamide was shown to yield a whole range of polypeptides of different molecular weights. Polypeptides are formed also from glycyltyrosinamide, alanylphenylalaninamide, and other amides [162,163] in the presence of this enzyme. Experiments by Orekhovich and Kaganova [164] provided additional suuport for the participation of amides in the biosynthesis of peptide links. By treating a tyrosine ester with glutamine or asparagine in the presence of crystalline chymotrypsin these workers obtained a peptide containing a tyrosine residue and glutamic or aspartic acid. If the amides are replaced by aspartic or glutamic acid, formation of a dipeptide does not occur. Many reactions of this type have been reported [165-173] and systematised in a number of reviews and monographs [53,86,174-180]. These include, for example, the formation of plasteins [169-173], which are insoluble peptides with molecular weights up to 400 000.

The examples given above clearly show that transpeptidation reactions are undoubtedly involved in the biosynthesis of peptide links, but their exact role in the general process of protein biosynthesis is still far from clear. Systematic quantitative experiments may, perhaps, solve this problem. This work should also go some way towards the solution of two other important aspects of the general problem of the biosynthesis of proteins: the influence of transpeptidation reactions on the sequence of amino-acid residues in the protein molecule and also the importance of these exchange interactions in the dynamic state of proteins, peptides, and amino-acids in the living organism.

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It is evident from what has been said above that reactions involving chain transfer with fission are of common occurrence in processes giving rise to the formation of heterochain polymers. Tney play a most important role in the formation of macromolecules, and they determine the properties of the resulting polymer to quite a large extent. Thus, they open up wide prospects for the controlled modification of heterochain polymers.

By including CTF among the primary steps in polymerisation, we gain a much deeper understanding of the thermodynamic and kinetic peculiarities of this process. Furthermore, many experimental facts could not be interpreted otherwise than in terms of CTF.

The discovery of transpeptidation justifies the hypothesis that interchain exchange reactions play an essential role in the biosynthesis of proteins.

The present Review will not have been written in vain if it can focus attention on the importance of CTF in processes leading to the formation of heterochain polymers, and on its potentialities in synthetic chemistry.

1. N. N. Semenov, "Tsepnye Reaktsii" (Chain Reactions), ONTI, Leningrad, 1934.
2. P. J. Flory, J. Amer. Chem. Soc., 62, 2261 (1940).
3. V. V. Korshak and S. V. Vinogradova, "Geterotsepnye Poliefiry" (Heterochain Polyesters), Izd. Akad. Nauk SSSR, Moscow, 1958.
4. V. V. Korshak and G. M. Frunze, "Sinteticheskie Geterotsepnye Poliamidy" (Synthetic Heterochain Polyamides), Izd. Akad. Nauk SSSR, Moscow, 1962.
5. V. V. Korshak, S. R. Rafikov, and V. A. Zamyatina, Collected Papers, "Issledovaniya v Oblasti Vysokomolekulyarnykh Soedinenii" (Research on Macromolecular Compounds), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1949, p. 3.
6. V. Jaacks and W. Kern, Makromol. Chem., 83, 71 (1965).
7. K. Weissermel, E. Fischer, K. Gutweisser, and H. D. Hermann, Kunststoffe, 54, 410 (1964).
8. N. S. Enikolopyan, J. Polymer Sci., 58, 1301 (1962).
9. V. V. Ivanov, A. A. Shaginyan, and N. S. Enikolopyan, Dokl. Akad. Nauk SSSR, 161, 154 (1965).
10. O. A. Plechova, V. V. Ivanov, and N. S. Enikolopyan, Vysokomol. Soed., in the press.
11. V. Jaacks, H. Baader, and W. Kern, Makromol. Chem., 83, 56 (1965).
12. Al. Al. Berlin, V. V. Ivanov, and N. S. Enikolopyan, Dokl. Akad. Nauk SSSR, in the press.
13. M. Szwarc, M. Levy, and R. Milkovich, J. Amer. Chem. Soc., 78, 2656 (1956).
14. V. G. Levich, "Vvedenie v Statisticheskuyu Fiziku" (Introduction to Statistical Physics), GINTI, Moscow, 1954.
15. S. E. Bresler, B. A. Dolgoplosk, V. A. Krol', and S. Ya. Frenkel', Zhur. Obshch. Khim., 26, 220 (1956).
16. B. A. Dolgoplosk, B. L. Erusalimskii, G. I. Kuren'gina, and E. I. Tinyakova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 311 (1960).
17. L. M. Pyrkov and S. Ya. Frenkel', "Mezhdunarodnyi Simpozium po Makromolekulyarnoi Khimii" (International Symposium on Macromolecular Chemistry), Moscow, 1960, Section II, p. 72.
18. W. Brown and M. Scwarc, Trans. Faraday Soc., 54, 416 (1958).
19. V. V. Ivanov, A. A. Shaginyan, V. P. Volkov, and N. S. Enikolopyan, Vysokomol. Soed., 7, 1833 (1965).
20. V. V. Ivanov, V. P. Volkov, V. N. Ivanov, and N. S. Enikolopyan, Kinetika i Kataliz, in the press.
21. P. J. Flory, "Principles of Polymer Chemistry", New York, 1953.
22. B. A. Rozenberg, E. B. Lyudvig, A. R. Gantmakher, and S. S. Medvedev, Vysokomol. Soed., 7, 188 (1965).
23. R. O. Colcleugh and K. Wilkinson, Khim. Tekhnol. Polimerov, No. 1, 45 (1964) (Translated into Russian).
24. A. M. Eastham, J. Amer. Chem. Soc., 79, 897, 900 (1957).
25. P. H. Plesh and P. H. Westermann, Paper Presented at International Symposium on Macromolecular Chemistry, Prague, 1965, Abstracts A 574.
26. K. S. Kazanskii, Candidate's Thesis, Institute of Chemical Physics of the USSR Academy of Sciences, Moscow, 1965.
27. M. Jacobson and W. H. Stockmayer, J. Chem. Phys., 18, 1600 (1950).
28. C. E. Bern, J. Polymer Sci., 15, 591 (1955).
29. S. D. Ross, E. R. Coburn, W. A. Weach, and W. B. Robinson, J. Polymer Sci., 13, 406 (1954).
30. M. Rothe, J. Polymer Sci., 30, 227 (1958).
31. I. Rothe, Angew. Chem., 71, 700 (1959).
32. A. Wald and J. Wolfowitz, Amer. Math. Soc. Coll. Publ., 11, 147 (1940).
33. W. L. Stevens, Ann. Eugenics, 9, 10 (1939).
34. M. Okada, J. Jamashita, and J. Ishii, Makromol. Chem., 80, 196 (1964).
35. K. Tada et al., Makromol. Chem., 71, 71 (1964).
36. F. R. Mayo and F. M. Lewis, J. Amer. Chem. Soc., 66, 1594 (1944).
37. C. Bamford, W. Barb, A. Jenkins, and P. Onyon, "Kinetics of Vinyl Polymerisation by Radical Mechanisms" (Translated into Russian), Inostr. Lit., Moscow, 1961.
38. G. V. Rakova and N. S. Enikolopyan, Dokl. Akad. Nauk SSSR, 156, 1167 (1964).
39. N. S. Enikolopyan, V. I. Irzhak, I. P. Kravchuk, G. V. Rakova, L. M. Romanov, O. A. Plechova, and G. P. Savushkina, see Ref. 25, Abstracts A 297.
40. A. Serrei, "Spravochnik po Organicheskim Reaktsiyam" (Handbook of Organic Reactions), Goskhimizdat, Moscow, 1962, p. 197.
41. A. E. Braunshtein and M. G. Kritsman, Biokhimiya, 8, 1 (1937).
42. O. Piele and G. Behen, Ber., 56, 562 (1923).
43. A. Grün, Ber., 54, 294 (1921).
44. P. Marschal, J. Chem. Soc., 53, 391 (1888).
45. A. Haller, Compt. rend., 143, 657 (1901).
46. R. Henignes, Angew. Chem., 1, 339 (1937).
47. S. Lel'chuk and A. Popova, Zhur. Obshch. Khim., 3, 148 (1937).
48. K. N. Kinzerskaya, Zhur. Prikl. Khim., 10, 1889 (1937).
49. E. Berner and A. Hjulstad, Ber., 71, 2052 (1938).
50. P. R. Fehlandt and H. Adkins, J. Amer. Chem. Soc., 57, 193 (1935).
51. M. Harfenist and R. Baltzly, J. Amer. Chem. Soc., 69, 362 (1947).
52. W. Farkas, O. Schächter, and B. H. Vromen, J. Amer. Chem. Soc., 71, 1991 (1949).
53. E. M. Kosower, "Molecular Biochemistry" (Translated into Russian), Izd. Mir, Moscow, 1964, p. 119.
54. W. E. Doering and H. H. Zeiss, J. Amer. Chem. Soc., 75, 4733 (1953).
55. L. S. Bondar' and R. A. Okulev, Izv. Akad. Nauk SSSR, Ser. Khim., 1996 (1965).
56. L. S. Bondar', P. T. Rodionov, and N. V. Pylina, Izv. Akad. Nauk SSSR, Ser. Khim., 1893 (1965).
57. A. Verley, Bull. Soc. chim. France, 41, 778 (1927).
58. A. R. Bader and H. A. Vogel, J. Amer. Chem. Soc., 74, 3992 (1952).
59. O. A. Reutov, "Teoreticheskie Osnovy Organicheskoi Khimii" (Theoretical Foundations of Organic Chemistry), Izd. Moskov. Gos. Univ., Moscow, 1964.
60. J. Mathieu and A. Allais, "Principes de la Synthèse organique" (Translated into Russian), Inostr. Lit., Moscow, 1962.
61. V. V. Korshak and S. V. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 63 (1951).
62. C. K. Ingold, "Reaction Mechanism and Structure of Organic Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1959.
63. V. V. Korshak and S. V. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 179 (1951).
64. F. Sowa, J. Amer. Chem. Soc., 60, 654 (1938).
65. G. N. Freidlin, A. A. Adamov, and A. A. Pershenkova, Collected Papers, "Problemy Organicheskogo Sinteza" (Problems in Organic Synthesis), 1965, p. 37.
66. V. V. Korshak and S. V. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 334 (1951).
67. G. Graves, U. S. P. 1 860 092.
68. R. Oda, J. Soc. Chem. Ind., Japan, 36, 33 (1933).
69. P. J. Flory, J. Amer. Chem. Soc., 62, 2255 (1940).
70. V. V. Korshak, N. N. Bekasova, and V. A. Zamyatina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 486 (1958).
71. T. Skwarski, Zeszyty Nauk. Politech. Lodz., Chem., 12, 41 (1956); Chem. Abs., 51, 1704 (1957).
72. G. Challa, Makromol. Chem., 38, 138 (1960).

73. V.V. Korshak and S.V. Vinogradova, Uspekhi Khim., 23, 314 (1954).
74. V.V. Korshak, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 753 (1951).
75. K.A. Petrov, E.E. Nifant'ev, R.G. Gol'tsova, A.A. Shchegolev, and B.V. Bushmin, Zhur. Obshch. Khim., 32, 3723 (1962).
76. K.A. Petrov, E.E. Nifant'ev, A.A. Shchegolev, M.M. Butilov, and I.F. Rebus, Zhur. Obshch. Khim., 33, 899 (1963).
77. E.E. Nifant'ev and I.V. Fursenko, Zhur. Obshch. Khim., 35, 1882 (1965).
78. A.N. Pudovik and G.I. Evstaf'ev, Vysokomol. Soed., 5, 886 (1963).
79. A.N. Pudovik and G.I. Evstaf'ev, Vysokomol. Soed., 6, 2139 (1964).
80. A.N. Pudovik and G.I. Evstaf'ev, Dokl. Akad. Nauk SSSR, 164, 1331 (1965).
81. R. Schiff, I.W. van Scheeren, and A.W. Stevens, Rec. Trav. chim., 84, 594 (1965).
82. T.G. Bonner, E.G. Gabb, P. McNamara, and B. Smethurst, Tetrahedron, 21, 463 (1965).
83. D.P. Minorov and V.V. Zharkov, Zhur. Org. Khim., 1, 1731 (1965).
84. L. Brown and J. Trotter, J. Amer. Chem. Soc., 73, 87 (1951).
85. H. Gault and E. Elkik, Compt. rend., 238, 2428 (1954).
86. D.L. Ferdman, "Biokhimiya" (Biochemistry), Izd. Vysshaya Shkola, Moscow, 1959, p. 418.
87. W. Theilheimer (Editor), "Synthetic Methods of Organic Chemistry", Vol. 6, Basle and New York, p. 272.
88. S.E. Forman, C.A. Erickson, and H Adelman, J. Org. Chem., 28, 2653 (1963).
89. S.M. Makin, B.K. Kruptsov, V.M. Medvedeva, and L.N. Smirnova, Zhur. Obshch. Khim., 32, 2527 (1962).
90. E.H. Pryde, D.J. Moore, H.M. Teeter, and I.C. Cowan, J. Org. Chem., 29, 2083 (1964).
91. C.E. Ham, J. Chem. Eng. Data, 8, 250 (1963).
92. F. Matsuda and M. Sugishita, Bull. Chem. Soc. Japan, 35, 1446 (1962).
93. See Ref. 87, Vol. 17, p. 231.
94. R. Grewe and A. Struve, Chem. Ber., 96, 2819 (1963).
95. M.B. Berenbaum, in "Chemical Reactions of Polymers" (Edited by E.M. Fettes), New York, 1964, p. 528.
96. G.G. Gorin, G. Dougherty, and A.V. Tobolsky, J. Amer. Chem. Soc., 71, 3551 (1949).
97. D.T. McAllan, T.V. Cullum, R.A. Dean, and F.A. Fidler, J. Amer. Chem. Soc., 73, 3627 (1951).
98. A. Fava and A. Iliceto, Ricerca sci., 23, 839 (1953); Chem. Abs., 47, 9814 (1953).
99. A. Fava, A. Iliceto, and E. Camera, J. Amer. Chem. Soc., 79, 833 (1957).
100. E.N. Gur'yanova, V.N. Vasil'eva, and L.S. Kuzina, Rubber Chem. Technol., 29, 534 (1956).
101. G. Leandri and A. Tundo, Ricerca sci., 23, 1646 (1953); Chem. Abs., 48, 12 699 (1954).
102. U.S.P. 2 521 870 (1950); Chem. Abs., 45, 8027 (1951).
103. U.S.P. 2 557 312 (1951); Chem. Abs., 46, 1579 (1952).
104. A.V. Tobolsky, F. Leonard, and G.R. Roeser, J. Polymer Sci., 3, 604 (1948).
105. R.E. Benesch and R. Benesch, J. Amer. Chem. Soc., 80, 1666 (1958).
106. H.H. Freedman, A.E. Young, and V.R. Sandel, J. Amer. Chem. Soc., 86, 4722 (1964).
107. M. Cocivera and E. Grunwald, J. Amer. Chem. Soc., 87, 2070 (1965).
108. H. Weingarten and I.R. Wazer, J. Amer. Chem. Soc., 87, 724 (1965).
109. J.R. Kennedy and F.P. Baldwin, Polymer, 6, 237 (1965).
110. L. Segal, in "Chemical Reactions of Polymers" (Edited by E.M. Fettes), New York, 1964, p. 528.
111. O.A. Plechova, G. Savushkina, I.F. Sanaya, N.F. Proshlyakova, B.A. Rozenberg, and N.S. Enikolopyan, Vysokomol. Soed., in the press.
112. V. Jaack, Doctoral Thesis, Mainz, 1957.
113. B.A. Rozenberg, A.I. Efremova, and N.S. Enikolopyan, Vysokomol. Soed., 7, 2172 (1965).
114. N.S. Enikolopyan, in "Khimicheskaya Kinetika i Tsepnye Reaktsii" (Chemical Kinetics and Chain Reactions), Izd. Akad. Nauk SSSR, 1966.
115. F. Davies, in "Chemical Reactions of Polymers" (Edited by E.M. Fettes), 1964, p. 501.
116. M. Levine and S.C. Temine, J. Polymer Sci., 28, 174 (1958).
117. V.V. Korshak and S.V. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 951 (1953).
118. S.R. Rafikov, V.V. Korshak, and G.N. Chelnokova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 743 (1953).
119. Z.F. Beste and R.C. Houtz, J. Polymer Sci., 8, 395 (1952).
120. B.P. 755 071 (1956); Chem. Abs., 51, 70 574 (1957).
121. K.A. Andrianov, O.I. Gribanova, A.G. Prelkova, and N.N. Sokolov, Vysokomol. Soed., 2, 521 (1960).
122. D.N. Kursanov, V.V. Korshak, and S.V. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 140 (1953).
123. I. Goodman and B.F. Nesbitt, Polymer, 1, 384 (1960).
124. B.P. 760 125 (1956); Chem. Abs., 51, 7733 (1957).
125. V.V. Korshak and S.V. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1109 (1952).
126. S.R. Rafikov, V.V. Korshak, and G.N. Chelnokova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 743 (1953).
127. V.V. Korshak, N.I. Bekasova, and V.A. Zamyatina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 614 (1958).
128. V.V. Korshak and V.A. Zamyatina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 609 (1945).
129. V.V. Korshak and V.V. Golubeva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 379 (1949).
130. V.V. Korshak and V.A. Zamyatina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 412 (1948).
131. V.V. Korshak and S.R. Rafikov, Dokl. Akad. Nauk SSSR, 48, 36 (1945).
132. V.V. Korshak and I.A. Gribova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 550 (1954).
133. S.R. Rafikov, V.V. Korshak, and L.N. Pinkina, Zhur. Obshch. Khim., 14, 1003 (1944).
134. V.V. Korshak and V.A. Zamyatina, Dokl. Akad. Nauk SSSR, 59, 909 (1948).
135. S.R. Rafikov, V.V. Korshak, and G.N. Chelnokova, Dokl. Akad. Nauk SSSR, 57, 357 (1947).
136. V.V. Korshak and S.V. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 756 (1951).
137. P.J. Flory, J. Amer. Chem. Soc., 64, 2205 (1942).
138. H. Staudinger and H. Schnell, Makromol. Chem., 1, 44 (1947).
139. V.V. Korshak and I.A. Gribova, Dokl. Akad. Nauk SSSR, 82, 397 (1952).
140. E.R. Bertozzi, F.O. Davies, and E.M. Fettes, J. Polymer Sci., 19, 17 (1956).
141. E.M. Fettes and H. Mark, J. Appl. Polymer Sci., 7, 2239 (1963).
142. V.V. Korshak, G.N. Chelnokova, and G.N. Distler, Dokl. Akad. Nauk SSSR, 82, 103 (1952).
143. P. Kresse, Faserforsch. Textiltech., 11, 853 (1960); Chem. Abs., 54, 23 340 (1960).
144. V.V. Korshak and G.M. Frunze, Dokl. Akad. Nauk SSSR, 97, 675 (1954).
145. Ya.E. Bernadskaya and G.I. Kudryavtsev, "Iskusstvennoe Volokno" (Artificial Fibres), Vol. 3, Gizlegprom, Moscow, 1952, p. 88.

146. C.J.Allen, J.Textile Inst., 44, 286 (1953).
147. H.Klare, "Technologie und Chemie der synthetischen Fasern aus Polyamiden", Verlag Technik, Berlin, 1954, p.21.
148. V.V.Korshak, T.M.Frunze, and Lu I-nan, Vysokomol. Soed., 2, 984 (1960).
149. T.M.Frunze, V.V.Korshak, and V.A.Makarkin, Vysokomol.Soed., 1, 500 (1959).
150. M.Bergmann and H.Fraenkel-Conrat, J.Biol.Chem., 119, 707 (1937).
151. J.S.Fruton, J.Biol.Med., 22, 263 (1950).
152. R.B.Johnston, M.J.Mycek, and J.S.Fruton, J.Biol. Chem., 185, 629 (1950).
153. J.Durell and J.S.Fruton, J.Biol.Chem., 207, 487 (1954).
154. R.B.Johnston, M.J.Mycek, and J.S.Fruton, J.Biol.Chem., 187, 205 (1950).
155. P.K.Stumpf, W.P.Loomis, and C.Michelson, Arch.Biochem., 30, 126 (1951).
156. C.C.Delwiche, W.D.Loomis, and P.K.Stumpf, Arch.Biochem.Biophys., 33, 333 (1951).
157. M.Schou, N.Grossowicz, A.Lajtha, and H.Waelsch, Nature, 167, 818 (1951).
158. H.Waelsch, Adv.Enzymol., 13, 237 (1952).
159. H.Waelsch, P.Owades, E.Borek, N.Grossowicz, and M.Schou, Arch.Biochem., 27, 237 (1950).
160. N.Grossowicz, E.Wainfan, E.Borek, and H.Waelsch, J.Biol.Chem., 187, 111 (1950).
161. J.S.Fruton, R.B.Johnston, and M.Fried, J.Biol.Chem., 190, 39 (1951).
162. J.S.Fruton, W.R.Hearn, V.M.Ingram, D.S.Wiggans, and M.Winitz, J.Biol.Chem., 204, 891 (1953).
163. M.E.Jones, W.R.Hearn, M.Fried, and J.S.Fruton, J.Biol.Chem., 195, 645 (1952).
164. V.N.Orekhovich and I.L.Kaganova, Dokl.Akad.Nauk SSSR, 95, 1259 (1954).
165. M.Bergmann and H.Fraenkel-Conrat, J.Biol.Chem., 124, 1 (1938).
166. M.Bergmann and J.S.Fruton, J.Biol.Chem., 124, 321 (1938).
167. M.Bergmann and O.K.Behrens, J.Biol.Chem., 124, 7 (1938).
168. E.Waldschmidt-Leitz and K.Kuhn, Z.physiol.Chem., 285, 22 (1950).
169. A.Ya.Danilevskii, "Organoplasticheskie Sily Organizma" (Organoplastic Forces of the Organism), Kharkov, 1886.
170. J.Wasteneys and H.Borsook, Physiol.Rev., 10, 110 (1930).
171. H.T.Tauber, J.Amer.Chem.Soc., 73, 1288, 4965 (1951).
172. W.T.Salter and C.M.Pearson, J.Biol.Chem., 112, 579 (1936).
173. H.Borsook, Physiol.Rev., 30, 206 (1950).
174. N.N.Lestrovaya, Collected Papers, "Uspekhi Biologicheskoi Khimii" (Advances in Biological Chemistry), Izd. Akad.Nauk SSSR, Vol.3, Moscow, 1958, p.97.
175. A.Meister, "Biochemistry of the Aminoacids" (Translated into Russian), Inostr.Lit., Moscow, 1961.
176. H.Neurath and K.Bailey (Editors), "Proteins — the Biochemistry of Protein Materials" (Translated into Russian), Vol.3, Part 1, Inostr.Lit., Moscow, 1958.
177. H.Neurath and K.Bailey, *ibid.*, Vol.3, Part 2, Moscow, 1959.
178. F.Haurowitz, "The Chemistry and Function of Proteins" (Translated into Russian), Izd.Mir, Moscow, 1965.
179. M.Dixon and E.Webb, "Enzymes" (Translated into Russian), Inostr.Lit., Moscow, 1961.
180. B.N.Zbarskii, I.I.Ivanov, and S.R.Mardashev, "Biologicheskaya Khimiya" (Biological Chemistry), Medgiz, Moscow, 1960.

Institute of Chemical Physics,
USSR Academy of Sciences

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CHEMICAL REACTIONS AT TEMPERATURES CLOSE TO 77°K

G. B. Sergeev

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I. INTRODUCTION

A new branch of chemistry, the study of chemical processes at low temperatures, close to the boiling point of liquid nitrogen, arose in recent years and has rapidly developed. Comparatively recently chemical reactions at low temperatures appeared to be unlikely. This view arose from the fact that the Arrhenius factor, which takes into account the necessity to overcome the activation barrier, increases sharply as the temperature is reduced. Furthermore, at low temperatures most substances are in the solid state where the mobility of the species is extremely low and molecular collision necessary for reaction is difficult to achieve.

Initially, the attention of chemists, who began to work at low temperatures, was drawn mainly to the problem of formation and stabilisation of radicals. Gradually the range of problems investigated widened and at present the study of the fundamental steps in the reaction of various species in the solid phase at low temperatures is one of the central problems of modern chemical kinetics. N.N.Semenov and his school and many other Soviet scientists have made a major contribution to the development of these studies.

The present review deals with certain results of studies on chemical reactions at low temperatures obtained in the Department of Chemical Kinetics at Moscow State University, directed by N.N.Semenov. In the course of these investigations the phenomenon of a spontaneous, explosive course of many chemical reactions at temperatures close to the boiling point of nitrogen and the effect of phase transitions on chemical processes were discovered, the possibility of chain reactions in the solid phase at this temperature was demonstrated, and the special role of unstable molecular complexes of the donor–acceptor type and their aggregates in low-temperature chemical reactions has been observed.

The Review consists of three principal parts. In the first section certain problems of the preparation and reactions of radicals in the solid phase are considered. The second section deals with the characteristic features of