Translated from *Uspekhi Khimii*, 53, 370-397 (1984) U.D.C. 542.971.2:542.952:655.552

Modern Problems of Homolytic Telomerisation

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The results of studies in homolytic telomerisation during the last decade at the Institute of Organoelemental Compounds of the USSR Academy of Sciences are surveyed. The synthetic possibilities which have arisen as a result of initiation by metal carbonyls are demonstrated. The prospects for the practical utilisation of telomerisation are discussed.
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I. INTRODUCTION

Telomerisation is understood as a radical chain process in which a molecule of any kind of saturated compound (telogen) combines with several molecules of an olefin or another unsaturated compound. Formally, the reaction can be expressed by Eqn.(2) of Scheme 1; it fills the "gap" between addition and polymerisation:

Scheme 1

(1) $X-Y + C=C \longrightarrow X-C-C-Y$ (*addition*),

(2) $X-Y + n\,C=C \rightarrow X-(C-C)_n-Y$ (telomerisation; $n = 2$-20)

Telomers

(3) $X-Y + n\,C=C \rightarrow X-(C-C)_n-Y$ (polymerisation; $n \rightarrow \infty$).

This comparatively new field began to develop in the postwar years. At the present time systematic and extensive researches into telomerisation are prosecuted in the USSR, the USA, Japan, Italy, the Federal Republic of Germany, and France.

Telomerisation is a typical organic reaction; it makes it possible to synthesise under similar conditions homologous series of polyfunctional compounds of different classes by selecting appropriate telogen–monomer pairs. The studies by Soviet investigators, and in particular by the team at the Institute of Organoelemental Compounds of the USSR Academy of Sciences, have in many respects enriched the theoretical and practical aspects of telomerisation and have led to its transformation from a purely laboratory reaction into a process suitable for technological application[1-3].

Two monographs and a number of reviews[1,4], among which we shall mention only those published in recent years[5-12], have been devoted to telomerisation. The concept of telomerisation has been included in an encyclopaedia[13] and in textbooks of organic chemistry[14]. The rate of development of researches in this field is so great that it has now become necessary to write new reviews and monographs.

New important branches of telomerisation have developed extensively in recent years and its applications in organic synthesis, in the study of general problems of radical chemistry, and in practice have been greatly expanded. This includes the discovery of fundamentally new initiators and initiating systems which made it possible to involve in telomerisation many new types of telogens and monomers as well as their new combinations which had been previously believed to be ineffective in this process. Instances of telomerisation accompanied by the rearrangement of growing radicals have been extensively studied. Investigations have been developed into stepwise telomerisation and the cotelomerisation of two monomers with one telogen. Practical applications in which telomerisation makes it possible to solve important problems have been found. New methods have been developed for the isolation of telomers as well as schemes for demonstrating their structure by methods of physical organic chemistry. The most important advances achieved in the field of telomerisation during the last decade are considered in this review.

II. GENERAL PROBLEMS OF TELOMERISATION

Monomers. In principle any unsaturated compound capable of radical polymerisation can be used in free-radical telomerisation; ethylene, alk-1-enes, vinyl chloride, vinylidene chloride, perfluoroethylene, chlorofluoroethylenes, allyl and acrylic compounds, and diene hydrocarbons and their derivatives have been studied in greatest detail and are frequently used.

Telogens. Substances containing bonds which readily undergo homolytic dissociation are used as telogens:



The types of such bonds whose dissociation leads to telomerisation are presented below:

C—H	B—H	SO_2—Hal
C—C	N—Hal	Si—H
C—Cl	P—H	Sn—H
C—Br	S—H	Cl—H
C—I	S—Hal	Br—H
	S—S	I—H

Reaction mechanism. The generally accepted mechanism of telomerisation initiated by radical-forming substances is presented in Scheme 2.

Scheme 2

(1) Initiator $\rightarrow$ R$^{\cdot}$
(2) R$^{\cdot}$ + X—Y $\rightarrow$ RX + Y$^{\cdot}$ } (initiation)

(3) Y$^{\cdot}$ + CH_2 = CHR $\rightarrow$ $YCH_2\dot{C}HR$
(4) $YCH_2\dot{C}HR + n CH_2 = CHR \xrightarrow{k_p} Y(CH_2CHR)_nCH_2\dot{C}HR$ } (growth of radical)

(5) $Y(CH_2CHR)_nCH_2\dot{C}HR$ + X—Y $\xrightarrow[\text{telomers}]{k_{tr}}$ $Y(CH_2CHR)_{n+1}X$ + Y$^{\cdot}$ (chain transfer)

(6) Radicals $\rightarrow$ inactive products (chain termination)

Here k_p and k_{tr} are the chain propagation and chain transfer constants respectively and $n = 1,2,3, \ldots$

In most instances the telomerisation reactions initiated by peroxides, azo-compounds, and light proceed in accordance with this scheme in which chain transfer directly to the telogen [stage (5) of scheme 2] takes place. However, many examples of telomerisation in which Scheme 2 does not hold have now accumulated. The importance of Scheme 2 consists in the fact that in many cases of smooth telomerisation under rigorously controlled conditions it is possible, knowing the distribution of the telomers in terms of the number of monomer units to estimate comparatively simply the relative rates of the intermediate stages—for example, the partial chain transfer constants C_n can be determined from the Mayo equation[15]:

$$C_n = k_{tr}/k_p = Q \cdot \left(T_n \Big/ \sum_{n+1}^{\infty} T_i \right) ,$$

where Q is the molar ratio of the monomer and the telogen and T_n the molar yield of the telomer incorporating n monomer units. A characteristic feature of the partial constants C_n, in contrast to the general chain transfer constants C_∞ determined from radical polymerisation data, consists in the fact that they reflect the influence of the fragment Y of the telogen on the radical centre in the telomer-radicals $Y(CH_2CHR)_n^{\cdot}$. For many telomerisation processes, the constants C_n increase as n increases from 1 to 4–5 (Table 1) and only then assume constant values. They make it possible to estimate the reactivities of the intermediate radicals, telogens, and monomers.

Initiation. The independence of C_n on the nature of the radical-forming compound and, within certain limits, of its concentration (at the same temperature) shows that the initiator is not involved in the chain propagation and transfer stages. The initiation of telomerisation by radical-forming substances such as acyl and alkyl peroxides, azo-compounds, and similar compounds is restricted to a fairly narrow class, since the reaction proceeds only with telogens containing an *E–E'* bond readily susceptible to homolytic dissociation. For example, peroxides and azobisisobutyronitrile successfully initiate the telomerisation of olefins with CCl_4 but are incapable of initiating the analogous reactions involving the C–Cl bond with compounds of the type RCH_2CCl_3.[9] On the other hand, the major influence of polar affects on the course of telomerisation has been discovered. When the polar effects of the telogen and the monomer are of the same kind, even extremely reactive compounds do not react via the telomerisation mechanism under the conditions of the method of initiation indicated. Thus, on initiation with peroxides, azo-compounds, or ultraviolet light, acrylic monomers are not telomerised by the esters of α-bromo-substituted acids, chloroform, and carbon tetrachloride[10]; instead of undergoing telomerisation, the monomer polymerises. Nevertheless, these initiation methods retain fully their importance for telomerisation, particularly telomerisation involving the dissociation of a C–H bond.

A new important procedure involves the use of metal carbonyls for the initiation of telomerisation. Carbonyls were employed for this purpose for the first time in the Laboratory of Organoelemental Synthesis at the Institute of Organoelemental Synthesis of the USSR Academy of Sciences in 1959–1961.[13] As will be shown below, when halogen-containing telogens are used, the initiation of the telomerisation by mononuclear metal carbonyls can be described by Scheme 3:

Scheme 3

$$M(CO)_n \rightleftarrows M(CO)_{n-1} + CO ;$$

$$\rangle C—Hal + M(CO)_{n-1} \rightarrow \underset{\text{(A)}}{\rangle C^{\cdot}} + HalM(CO)_{n-1} .$$

Next the reaction proceeds via stages (3)–(6) of Scheme 2 (Y = $\rangle C^{\cdot}$) or, in contrast to the initiation of the telomerisation by radical-forming substances, the intermediate metal carbonyl halide (A) participates in the chain transfer stage, transferring the halogen to the growing radical via Scheme 4 (where $m = 0,1$):

Scheme 4

$$(A) + Y(CH_2CHR)_m CH_2\dot{C}HR \rightarrow Y(CH_2CHR)_{m+1}Hal + M(CO)_{n-1} .$$

The metal-containing species $M(CO)_{n-1}$ arising in this stage participates in the transfer of the kinetic chain, abstracting the halogen from the telogen, as shown in Scheme 3.

This is a very flexible initiation procedure, since, by varying the nature of the metal carbonyl, it is possible to achieve reactions which proceed with very great difficulty. It has now been found that the complexes of metal carbonyls with various ligands, i.e. $M(CO)_{n-1}L$, as well as the combination of the metal carbonyl and the ligand taken separately, i.e. $M(CO)_n$ + L are even more active telomerisation initiators. Subsequently, both in the studies in the Laboratory of Organoelemental Synthesis at the Institute of Organoelemental Synthesis of the USSR Academy of Sciences and in the studies by foreign investigators, a wide range of initiating systems were applied, including various transition metal compounds (carbonyls, halides, chelates, and π-complexes) in combination with various activating additives (co-initiators)—alcohols, amines, amine hydrochlorides, nitriles, carboxylic acid esters, phosphorous acid esters, dimethylformamide (DMF), etc.[13]

Chain transfer. A wide variety of forms of chain transfer in telomerisation have now been discovered. Apart from the reactions with chain transfer by the growing radicals to the telogen [stage (5) of Scheme (2)]. reactions have been found in which chain transfer proceeds via the fragmentation of the growing radical (Scheme 5), via the oxidation of the growing radical (Scheme 6), and via the transfer of the halogen from metal carbonyl halides (Scheme 4). For example, for the telomerisation of ethylene by tetrachloroethylene (initiator—t-butyl peroxide (TBP)], we suggested[16] that chain transfer takes place via the fragmentation of the growing radical in accordance with Scheme 5:

Scheme 5

$$CCl_2{=}CCl_2 + n CH_2{=}CH_2 \xrightarrow{\text{TBP}} Cl(CH_2CH_2)_nCCl{=}CCl_2 ;$$

(1) (TBP) $\rightarrow$ 2R$^{\cdot}$;

(2) R$^{\cdot}$ + $CCl_2{=}CCl_2 \rightarrow RCCl_2\dot{C}Cl_2 \rightarrow RCCl{=}CCl_2 + Cl^{\cdot}$;

(3) Cl$^{\cdot}$ + n $CH_2{=}CH_2 \rightarrow Cl(CH_2CH_2)_n^{\cdot}$;

(4) $Cl(CH_2CH_2)_n^{\cdot} + CCl_2{=}CCl_2 \rightarrow Cl(CH_2CH_2)_n CCl_2\dot{C}Cl_2$ (B) ;

(5) $Cl(CH_2CH_2)_nCCl_2\dot{C}Cl_2 \xrightarrow{\text{fragmentation}} Cl(CH_2CH_2)_nCCl{=}CCl_2 + Cl^{\cdot}$.

There is no doubt that the chain transfer by the radical (B) to the telogen does not occur both as a consequence of the low reactivity and considerable stability of this radical and owing to the low probability of the abstraction of a chlorine atom from tetrachloroethylene. The radicals (B) undergo fragmentation with formation of the final products and the elimination of the chain propagating chlorine atom. Such telomerisation is accompanied by the formation of a number of side products; in particular, extensive chlorination takes place with evolution of hydrogen chloride, which is also consistent with the hypothesis of the intermediate formation of atomic chlorine.

A new type of telomerisation, in which there is undoubtedly no usual chain transfer to the telogen, has been found[17-21]; it was shown that contrary to the literature data, under the conditions of the Meerwein reaction it is possible to achieve the telomerisation of ethylene, acrylonitrile, and vinylidene chloride by arenediazonium chlorides (Scheme 6):

Scheme 6

$$ArN_2Cl + nCH_2=CHX \xrightarrow[CH_3COONa]{CuCl_2/CuCl} Ar(CH_2CHX)_nCl + N_2 ;$$

(1) $ArN_2Cl \xrightarrow{CuCl} Ar^{\cdot}$;

(2) $Ar^{\cdot} + CH_2=CHX \rightarrow ArCH_2\dot{C}HX$;

(3) $ArCH_2\dot{C}HX + nCH_2=CHX \rightarrow Ar(CH_2CHX)_n^{\cdot}$;

(4) $Ar(CH_2CHX)_n^{\cdot} + ArN_2Cl \not\rightarrow$ (do not react);

(5) $Ar(CH_2CHX)_n^{\cdot} + CuCl_2 \rightarrow Ar(CH_2CHX)_nCl + CuCl$;

Ar = C_6H_5, *n*-$NO_2C_6H_4$, *o*-$CH_3C_6H_4$; X = H, CN, $COOCH_3$; $n = 1, 2$.

All the stages of this reaction, except stage (3), had been proposed earlier. We were able to obtain telomers and demonstrate thereby that stage (3) can take place[21]. In this case direct chain transfer via stage (4) is undoubtedly ruled out; the growing radical is stabilised in the oxidation-reduction reaction with $CuCl_2$ via stage (5).

Certain examples in which the telomerisation does not obey the usual mechanism with chain transfer to the telogen were enumerated above. However, the reactions of the usual type (Scheme 2) have been most thoroughly investigated, including investigations by kinetic methods.

Chain termination is the least investigated stage in the telomerisation mechanism. It has been frequently suggested that chain termination takes place as a result of the dimerisation or disproportionation of radicals. However, tests in relation to the telomerisation of cyclohexene, heptene, and propene by trifluoroiodomethane[22] and carbon tetrachloride[23] did not confirm this hypothesis. In the case of carbon tetrachloride[23] the formation of hexachloroethane was not observed, but the hydrides of the intermediate radicals, obtained as a result of the "allyl termination", were found. Instances (for example, in the telomerisation of isobutene by aliphatic acids[24]) where the recombination and cross-recombination reactions of radicals play a significant role and the yield of the corresponding compound is comparable to that of the telomers have been discovered in recent years.

Thus a wide variety of reactions with different types of initiation and chain transfer and termination mechanisms, depending on the structure of the telogen and the monomer and also on the nature of the initiating system, can be achieved at the present time by the telomerisation method. This has greatly extended the scope of the utilisation of telomerisation for synthetic purposes.

III. METAL CARBONYLS AS INITIATORS OF A NEW TYPE

Interesting features have been discovered in telomerisation using initiators of a new type—variable valence compounds and carbonyls of Group VI–VIII metals. Freidlina and Belyavskii showed in 1959[25,26] that iron, chromium, molybdenum, and tungsten carbonyls effectively initiate the homolytic telomerisation of ethylene with CCl_4, $CHCl_3$, and CCl_3COOR. Since then initiating systems based on transition metal carbonyls have been widely used in homolytic chain reactions involving both telomerisation[9,10,12,27] and polymerisation[28,29]. The data accumulated suggest that in this case we are dealing with a new branch of homogeneous catalysis—the metal carbonyl-initiated homolytic chain reactions. The study of the application of redox initiators (the character of the initiating action of which resembles in many respects that of metal carbonyls), mainly iron and copper halides and complex cyanides[30-32] as well as chlorine-containing iron complexes of the type $[L_4Fe^{III}Cl_2]_2[Fe^{II}Cl_4]$, where L = DMF or dimethyl sulphoxide (DMSO), and $[(CH_3CN)_6Fe^{II}][Fe^{III}Cl_4]_2$ in telomerisation was prosecuted simultaneously[33]. Both these large groups of metal-containing initiators are combined[12] in the broad concept of coordination initiators, whose application significantly expands the synthetic scope of telomerisation, namely (1) it makes it possible to regulate the composition of the telomerisation mixture, driving the telomerisation reaction towards the formation of lower telomers up to 70–80% yield of the adduct relative to the sum of the telomers, (2) it directs telomerisation selectively to the C–Hal bond in the presence of reactive C–H and C–Hal bonds in the telogen, (3) it makes it possible to introduce into the telomerisation reaction telogens with the trichloromethyl group which is inert under the conditions of peroxide initiation, (4) it permits the telomerisation of readily polymerisable monomers such as acrylic compounds, styrene, and vinyl chloride, (5) it leads to a simple way of synthesising branched telomers in accordance with a stepwise telomerisation scheme (see Section VI), and (6) it increases the selectivity of the photoinitiation driving the reaction towards the rupture of the C–Hal bond.

Metal carbonyls are the most promising initiators. Differing appreciably (depending on the metal) in their activity in the initiation stage and in their ability to participate in the chain transfer stage, suitably selected metal carbonyls make it possible to achieve any of the synthetic possibilities in telomerisation enumerated above or to obtain a combined result.

In terms of their interaction with the telogen, the monomer, the co-initiator, and finally the growing radical, metal carbonyls effective in telomerisation can be divided into three groups. The first group includes carbonyls capable of abstracting a halogen atom from the telogen in the initiation stage and of transferring it to the growing telomer radical, regenerating at the same time the halogen abstracting species. In other words, these carbonyls are capable of participating in the chain transfer stage without interrupting the kinetic chain. This group includes $Fe(CO)_5$ and its derivatives with the ligand L in the coordination sphere of iron $[L_nFe(CO)_{5-n}]$.

The second group comprises carbonyls capable of abstracting a halogen atom from the telogen in the initiation stage but incapable of transferring it to the growing telomer radical. It includes chromium, molybdenum, and tungsten hexacarbonyls.

The third group is made up of dinuclear carbonyls with a metal–metal bond, for the initiating capacity of which the conditions in the homolytic dissociation of the metal–metal

bond are of decisive importance; their interrelations with the components of the reaction mixture are frequently manifested in an extremely complex manner. This group includes $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$, and $[Cp_2Fe(CO)_2]_2$, as well as, apparently, $[CpW(CO)_3]_2$ and $[CpMo(CO)_3]_2$, which are capable of forming metal-centred radicals[34].

The addition of chloroform to alk-1-enes can serve as a test reaction for the classification of metal carbonyls[35-38]. Chloroform is able to react with dissociation of both C–Cl and C–H bonds in different sequences depending on the character of the initiation (Scheme 7).

Scheme 7

(1) $CCl_3{-}H \rightarrow \dot{C}Cl_3 \xrightarrow{-C=C-} CCl_3\dot{C}{-}\dot{C}- \xrightarrow{CCl_3{-}H} CCl_3C{-}\dot{C}H$;

(2) $Cl\,CH{-}Cl \rightarrow \dot{C}HCl_2 \xrightarrow{-C=C-} CHCl_2\dot{C}{-}\dot{C}- \xrightarrow{CCl_3{-}H} CHCl_2C{-}\dot{C}H$;

(3) $Cl_3CH{-}Cl \rightarrow \dot{C}HCl_2 \xrightarrow{-C=C-} CHCl_2\dot{C}{-}\dot{C}- \xrightarrow{CHCl_2{-}Cl} CHCl_2C{-}CCl$.

Eqn.(1) represents the peroxide type of initiation: the C–H bond is dissociated in the initiation and chain transfer stages and the initiator is not involved in the chain transfer stage. Eqn.(2) represents a mixed type of initiation: the metal carbonyl participates in initiation but not in chain transfer; the initiation involves the C–Cl bond and the chain transfer involves the C–H bond. Eqn.(3) represents metal carbonyl initiation where the carbonyl participates in the initiation and chain transfer stages; the initiation and chain transfer take place with dissociation of the C–Cl bond.

In the case of iron pentacarbonyl, which, depending on the conditions, can either react directly via reactions of types (2) and (3) of Scheme 7 or indirectly via a reaction of type (1) (forming a radical $R^{\cdot}$ capable of abstracting a hydrogen atom from chloroform), in each specific reaction it is necessary to take into account the tendency of $Fe(CO)_5$ to form complexes with the monomer[39] and the co-initiator[40-42]. In the case of a weakly polar monomer exhibiting a small capacity for complex formation with iron carbonyl (for example, ethylene), the metal carbonyl is not involved in the chain transfer stage when $Fe(CO)_5$ is used in small amounts (< 5 mole %) without an initiator and the distribution of the telomer homologues in the telomerisation of CCl_4 or $CHCl_3$ with C_2H_4 does not differ from their distribution in peroxide initiation[26,27].

It has been shown for monomers forming comparatively stable complexes with $Fe(CO)_5$ (propene and specially vinyl chloride) in relation to telomerisation with CCl_4 and $CHCl_3$[39,40] that, at a low $Fe(CO)_5$ concentration and for a long kinetic chain, only the initiating activity of the carbonyl is manifested in the reaction, i.e. it is able to generate $\dot{C}Cl_3$ radicals and the chain transfer constants do not differ from those in the peroxide initiation. With increase of the $Fe(CO)_5$ concentration, the content of the adduct in the mixture of telomers increases appreciably and C_1 can be significantly greater than in the peroxide initiation, i.e. the involvement of the initiator in the chain transfer stage becomes appreciable (a halogen atom is transferred from the telogen to the growing radical via an iron carbonyl intermediate—see Table 1). It has been found[39] that in the initiation by $Fe(CO)_5$, the reactivity of olefins in telomerisation with CCl_4 varies in parallel with the thermal stability of the complexes (C=C). .$Fe(CO)_4$ (C=C is the monomer). Apparently a maximum $Fe(CO)_5$ concentration exists above which C_1 and C_2 no longer increase[43] and in addition self-inhibiting properties of the carbonyl make an appearance[27]. Accordingly the content of the adduct in the mixture of telomers passes through a maximum as a function of both the $Fe(CO)_5$ concentration and the reaction time at $[Fe(CO)_5]_0 = const$.[42,44,45]

The character of the initiation of the telomerisation by iron pentacarbonyl changes sharply in the presence of a nucleophilic co-initiator—an alcohol, a tertiary amine, DMF, DMSO, hexamethylphosphoramide (HMP), and *N,N*-dichloramide[27]. The first two members of the series predominate in the mixture of telomers. The chain transfer rate constant C_1 increases greatly (Table 1), which can be explained by the fact that, in the presence of a nucleophilic co-initiator incorporated in the coordination sphere of iron (this has been demonstrated by EPR[46,47]), the iron-containing species $(Fe)^nCl$, formed as a result of the abstraction of a chlorine atom from the chlorine-containing telogen (CCl_4), transfers the chlorine atom to the growing radical at a much higher rate than in the direct interaction of the growing radical with the telogen.

Table 1. The telomerisation of ethylene by carbon tetrachloride with different methods of initiation[5]*

$CCl_4 + C_2H_4 \rightarrow CCl_3(CH_2CH_2)_nCl$

Initiator	Composition of mixture of telomers, mole %					C_n			
	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	C_1	C_2	C_3	C_4
Azobisisobutyronitrile	3.1	36.2	30.9	17.2	12.5	0.15	2.8	4.9	5.5
$Fe(CO)_5$	5.4	47.3	29.0	12.7	5.9	0.20	3.6	5.7	7.9
$Fe(CO)_5 + CH_3OH$	66.7	23.7	7.8	1.8	0	6.0	7.7	13.3	—

* Temperature 100 °C; $[C_2H_4]_0/[CCl_4]_0 \cong 4$.

The rate constant for chain transfer via $Fe(CO)_4Cl$ for the adduct-radical in the telomerisation of CCl_4 with C_2H_2 and C_3H_6 using CH_3OH as the co-initiator proved to be 100 times higher than in the peroxide initiation, i.e. than in the direct interaction of the growing radical with the telogen[48,49]:

$$CCl_4 + Fe(CO)_{5-n}(CH_3OH)_n \rightarrow \dot{C}Cl_3 + ClFe(CO)_{4-n}(CH_3OH)_n + CO \ ;$$
$$\dot{C}Cl_3 + CH_2 = CH_2 \rightarrow CCl_3CH_2\dot{C}H_2 \ ;$$

$$CCl_3CH_2\dot{C}H_2 + ClFe(CO)_{4-n}(CH_3OH)_n \xrightarrow{k_{tr} \geqslant 4 \times 10^5 \text{ litre mol}^{-1}\,s^{-1}}$$
$$\rightarrow CCl_3CH_2\dot{C}H_2Cl + \dot{F}e(CO)_{4-n}(CH_3OH)_n \ ;$$
$$CCl_3CH_2\dot{C}H_2 + CCl_4 \xrightarrow{k_{tr} = 0.39 \times 10^4 \text{ litre mol}^{-1}\,s^{-1}} CCl_3CH_2CH_2Cl + \dot{C}Cl_3 \ .$$

Nucleophilic co-initiators act in two ways. On the one hand, they increase the overall rate of reaction, the rate constant increasing in parallel with the increase of their dielectric constants; on the other hand, they influence C_1, i.e. they facilitate the involvement of the initiator in the stage where the halogen is transferred from the telogen to the growing radical and can be arranged in a sequence corresponding to the increase of their electron-donating capacity[45].

The majority of systems based on $Fe(CO)_5$ effectively initiate telomerisation by chlorine-containing telogens at a temperature above 100 °C[12]. However, there exist co-initiators which significantly reduce the initiation temperature. Thus, in the presence of *N,N*-dichlorosulphonamides $XC_6H_4SO_2NCl_2$, iron pentacarbonyl effectively initiates the reaction of CCl_4 with alk-1-enes at a temperature as low as 50 °C and at 25 °C the reaction proceeds to the extent of 1–2% in 6 h.[50] In certain cases when the dissociation of the C–Hal bond is sufficiently easy, as, for example, in the case

of CBr_4 and CCl_3Br, the reaction with acrylic monomers in the presence of the usual $Fe(CO)_5$ + DMF system begins already at room temperature and takes place exothermically[51]:

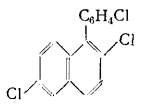
$$CCl_3Br + CH_2{=}CHCOOCH_3 \xrightarrow[20-80^\circ]{Fe(CO)_5+C_6H_5N(CH_3)_2} CCl_3(CH_2CH)_nBr \quad ;$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad COOCH_3$$
$$n = 1\,(37\%);\ n=2\,(12\%)\ .$$

It may be that in this case the carbonyl is activated by the telogen incorporated at the same time in the coordination sphere of the iron.

The use of initiating systems of the type of $Fe(CO)_5^+$ co-initiator made it possible to introduce into telomerisation compounds with the CCl_3 group[9,12,52] and benzyl chloride (via the C–Cl bond)[55]. These systems are effective in the initiation of telomerisation with participation of compounds having a CCl_2 group activated by electron-accepting substituents[53,54] and compounds with the CBr_3 and CBr_2 groups[10,56–58].

Using initiating systems based on $Fe(CO)_5$, it is possible to telomerise by polychloro- and polybromo-derivatives polymerisable monomers such as acrylic compounds[10,53,59,60], vinyl chloride[43,55,57,61], vinylidene chloride[62], and 1,3-dienes[63,64]. The familiar ability of $Fe(CO)_5$ to promote dehalogenation and dehydrohalogenation has been used in telomerisation to convert linear chain compounds into cyclic and aromatic compounds. Such are, for example, the lactonisation reactions in the telomerisation of unsaturated compounds by esters of α-halogeno-substituted acids[10] and the formation of ring-chlorinated phenylnaphthalenes in the telomerisation of DDT with vinyl chloride[65]:

$$(ClC_6H_4)_2CHCCl_3 + CH_2{=}CHCl \xrightarrow[\text{coinitiator}]{Fe(CO)_5}$$



Substituted 2,2,6-trichloro-1-(chlorophenyl)tetrahydronaphthalenes are formed in the telomerisation of ethylene, methyl acrylate, and styrene with DDT[66–68]. Thus initiators based on $Fe(CO)_5$ lead to extensive possibilities in telomerisation (see Table 6 for further details).

The representatives of the second group of metal carbonyls–chromium, molybdenum, and tungsten hexacarbonyls–give rise to an initiating metal-centred radical $\dot{M}(CO)_5$ or $L_n\dot{M}(CO)_{5-n}$; the latter abstracts a halogen atom from the telogen in the initiation stage and produces a species [for example, $ClM(CO)_5$], which is not involved in the subsequent development of telomerisation. The partial chain transfer constants C_n for the reactions of CCl_4 with ethylene and propene hardly change on passing from peroxide initiation to initiation by the carbonyls $Cr(CO)_6$, $Cr(CO)_5[P(C_6H_5)_3]$, $Mo(CO)_6$, or $W(CO)_6$[69–72] (Table 2). The formation of $\dot{C}Cl_3$ radicals in the photochemical interaction of chromium, molybdenum, and tungsten hexacarbonyls with polychloroalkanes has been demonstrated by EPR using spin trapping agents[74]. The formation of the radicals $Cl\dot{C}r(CO)_5$ by the abstraction of chlorine from CCl_4 under the influence of $Cr(CO)_6$ has also been reliably established by EPR[75,76]. The co-initiators which usually facilitate the involvement of the carbonyl-containing species in the chain transfer stage naturally do not influence the proportions of the telomers in the mixture in the given instance (where such involvement does not occur).[71] The chain transfer constants C_n are in such cases close to the "cross" constant (Table 2).

The use of co-initiators in combination with $Cr(CO)_6$ does not affect appreciably the yield of adducts and telomers in the reactions of CCl_4 and $CHCl_3$ with olefins[71,77], although the rate of initiation in the presence of a co-initiator increases (for low degrees of conversion of the telogen)[70–72]. The insertion of an active ligand of the type of $P(C_6H_6)_3$ in the ligand sphere of the metal carbonyl can increase significantly the initiating activity of the carbonyl, as has been observed for $Cr(CO)_5[P(C_6H_5)_3]$.[70] The insertion of HMP in the coordination sphere of chromium with displacement of CO and the formation of the complex $ClCr(CO)_3$(HMP) in the presence of CCl_4 has been observed by EPR[76]. Apparently metal carbonyls of this type are most effective in the initiation of telomerisation reactions which are distinguished by a long kinetic chain, because these carbonyls do not regenerate the initiating species during telomerisation.

Table 2. Partial chain transfer constants C_n for the telomerisation of propene by carbon tetrachloride with different methods of initiation (at 120 °C)[69–72].

Initiator	C_1	C_2
Peroxide*	2.65	33.0
$Cr(CO)_6$	2.63	34.9
$Mo(CO)_6$	2.03	39.2
$Mn_2(CO)_{10}$	1.79	26.4
$Cr(CO)_6$ + HMP	1.51	26.7
$Cr(CO)_6$ + DMF	1.60	28.2
$Cr(CO)_6 + CH_3CN$	1.59	22.3
$Cr(CO)_6 + CH_3OH$	1.51	23.2
$Mn_2(CO)_{10}$ + DMF	1.95	27.2

* The values obtained by interpolating the data for 95°, 105°, and 145 °C.[73]

Among the representatives of dinuclear metal carbonyls, $Mn_2(CO)_{10}$ has been studied in greatest detail in telomerisation[38,59,78–82]. The stage preceding initiation (and possibly determining the rate of reaction as a whole[27,34]) is in this instance the dissociation of the metal carbonyl at the metal–metal bond, which takes place either thermally (120–130 °C) or under the influence of ultraviolet light. The metal-centred $\dot{M}n(CO)_5$ radicals formed are capable of abstracting a chlorine atom from the telogen and of initiating telomerisation. The formation of $\dot{C}Cl_3$ from CCl_4 and of $\dot{C}Cl_2CCl_2H$ under the influence of $\dot{M}n(CO)_5$ has been demonstrated by EPR[74]. The radicals $Mn(CO)_5$ cannot then be attached to a spin trapping agent, which indicates a high reactivity in the abstraction of chlorine from the telogen[74]. The partial chain transfer constants for the telomerisation of ethylene and propene with CCl_4, initiated by $Mn_2(CO)_{10}$, are close in magnitude to the chain transfer constants for the same reaction initiated by peroxides[82] (Table 2). The relative isomerisation constant in the reaction of methyl chloroacetate with ethylene, initiated by $Mn_2(CO)_{10}$, is almost the same as under the conditions of peroxide initiation[38]. The main process stabilising the growing adduct and telomer radicals is abstraction of hydrogen by the latter from the components of the medium [pathway (2), Scheme 2].

Thus the available data show that $Mn_2(CO)_{10}$ does not participate in the stage involving the transfer of the halogen from the telogen to the growing radical[38,59,80–82]. It does not initiate the addition of CH_3OCOCH_2R to hex-1-ene which takes place effectively in the presence of peroxides[81] whence it follows that $\dot{M}n(CO)_5$ does not participate in the transfer of hydrogen from the substrate to the growing radical, accompanied by the dissociation of a C–H bond. (This does not apply to processes involving the homolysis of other E–H bonds, for example Si–H.) It has been found that $Mn_2(CO)_{10}$ initiates fairly readily reactions with both CCl_4 and $RCCl_3$[59,79,80], since in its presence telomers with the CCl_3 group are

capable of further reactions of the type of stepwise telomerisation (see Section VI). This property of $Mn_2(CO)_{10}$ apparently explains the maxima on the curve describing the time variation of the yields of the lower telomers[80].

A characteristic feature of $Mn_2(CO)_{10}$ as an initiator is that nucleophiles not only do not activate it but in many instances actually reduce the effectiveness of initiation[79,80]. Microadmixtures of iron compounds exert a considerable influence; therefore, when telomerisation initiated by $Mn_2(CO)_{10}$ is carried out in metallic reactors, i.e. under conditions close to those obtained in the industrial process, one can obtain a mixture of telomers with an increased content of lower telomers, which is reflected in the chain transfer constant determined[36,83].

It is noteworthy that, in the telomerisation of ethylene by methyl chloroacetate, initiation proceeds with abstraction of the chlorine atom by the $Mn(CO)_5$ radicals, but the overall reaction product is almost wholly a mixture of telomers formed as a result of the dissociation of a C–H bond in the telogen[38]:

$$\left.\begin{array}{l} CH_3OCOCH_2Cl \xrightarrow{Mn_2(CO)_{10}} CH_3OCO\dot{C}H_2 \xrightarrow{nC_2H_4} \dot{T}_n \\ \dot{T}_n \xrightarrow{CH_3OCOCH_2Cl} CH_3OCO\dot{C}HCl \end{array}\right\} \text{(initiation);}$$

$$\left.\begin{array}{l} CH_3OCO\dot{C}HCl + n\,H_2C{=}CH_2 \rightarrow CH_3OCOCHCl(CH_2CH_2)_n^{\cdot} \\ CH_3OCOCHCl(CH_2CH_2)_n^{\cdot} + ClCH_2COOCH_3 \rightarrow \\ \rightarrow CH_3OCOCHCl(CH_2CH_2)_nH + CH_3OCO\dot{C}HCl \end{array}\right\} \text{(main kinetic chain).}$$

The telomerisation of ethylene[38,80–82] and propene[82] with CCl_4, of ethylene with CCl_3COOCH_3[38] and $ClCH_2COOCH_3$[38,81], and of 1,1,1,3-tetrachloropropane with methyl acrylate[59] can be initiated with the aid of $Mn_2(CO)_{10}$.

IV. STEPWISE TELOMERISATION

A telomer having a group reactive in telomerisation (CCl_3, CBr_3) can play the role of a telogen, having entered into a secondary reaction with the monomer. Such a process has come to be called stepwise[12] or secondary[4] telomerisation, in contrast to the usual chain telomerisation. The products of the stepwise telomerisation can have the same structure as the telomers obtained by the usual (chain) telomerisation if the carbon atom which carries the unpaired electron in the growing radical is attacked in the secondary reaction[84]:

$$CH_3I \xrightarrow{C_2H_4} CH_3CH_2CH_2I \xrightarrow{C_2H_4} CH_3(CH_2)_4I \text{ etc.}$$

The synthetic value of this reaction consists in the fact that any telomer-homologue can be obtained from preceding members of the series by consecutive monomer addition steps.

The structure of the product of the stepwise telomerisation can, however, differ from that of the telomers obtained by the usual telomerisation when there are several reactive centres in the telomer and the radical attack is not directed to the carbon atom carrying the unpaired electron in the growing radical[85]:

$$CH_3OCOCH\underset{\downarrow}{Br}_2 \xrightarrow{CH_2{=}CHCl} CH_3OCOCH\underset{\downarrow}{Br}CH_2CHClBr \xrightarrow{CH_2{=}CHCl} \rightarrow CH_3OCOCH(CH_2CHClBr)_2 .$$

(The arrow indicates the point of attack.) This version of the stepwise telomerisation makes it possible to synthesise branched telomers†. The greatest synthetic possibilities in this version arise from the application of coordination initiators (including metal carbonyls), which initiate selectively the reaction at the most reactive C–Hal bond in the telogen[12]. However, stepwise telomerisation is also not ruled out for peroxide initiation[56,86]:

$$CBr_4 \text{ (or } CHBr_3) \xrightarrow[BP]{C_2H_4} CBr_3CH_2CH_2Br \xrightarrow[BP]{C_2H_4} (BrCH_2CH_2)_2CBr_2 ,$$

where BP is benzoyl peroxide. 1,1,1,3-Tetrachloroalkanes enter into the stepwise telomerisation initiated by the $Fe(CO)_5$ + co-initiator systems[9,87,88], for example:

$$ClCH_2CH_2CCl_3 + C_2H_4 \rightarrow (ClCH_2CH_2)_2CCl_2 .$$

When the esters of α-halogeno-substituted acids are used as telogens, the stepwise telomerisation makes it possible to obtain α-substituted lactones[89], including spiro-dilactones, which are difficult to obtain by other procedures[90]:

$$CHCl_2COOCH_3 + 2\,C_2H_4 \rightarrow \begin{array}{l} H_2C\text{——}CClCH_2CH_2Cl \\ \quad\vert\qquad\quad\vert \\ H_2C\quad C{=}O \\ \quad\backslash O/ \end{array} ;$$

$$(C_2H_5OCO)_2CBr_2 + 2\,RCH{=}CH_2 \rightarrow \begin{array}{l} \quad\quad\quad\quad\quad\quad\quad\quad O \\ \quad\quad\quad\quad\quad\quad\quad\quad\vert \\ \quad\quad\quad\quad H_2 \quad\quad\quad O\text{—}C \\ \quad\quad\quad\quad\vert \quad\quad\quad\quad\vert \\ RHC\text{—}C \quad C \quad\quad C\text{—}CHR \\ \quad\quad\quad\quad\vert\quad\vert\quad\quad\quad\quad\vert\quad\quad\quad\quad\vert \\ \quad\quad\quad O\text{—}C \quad\quad C\text{—}O \quad\quad (\quad) \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad H_2 \\ \quad\quad\quad\quad\quad\quad\quad\quad O \end{array} .$$

Thus the stepwise scheme expands the synthetic possibilities of telomerisation.

1. Determination of the Structure of Halogen-containing Telomers

In all cases of telomerisation with participation of polyhalogeno-telogens, it is necessary to solve problems involving the determination of the structure of the telomers, which are sometimes by no means simple, bearing in mind the possibility of rearrangements in the growing radicals, of the disproportionation of the halogens in the chlorine- and bromine-containing adducts and telomers[91], and the probability of stepwise telomerisation. Studies in the Laboratory of Organoelemental Synthesis at the Institute of Organoelemental Synthesis of the USSR Academy of Sciences[92–99] have established that ^{13}C NMR is a reliable method for the determination of the structures of polyfunctional halogen-containing telomers. The regions in which the signals of various polychloro-groups[92–95] and polybromo-groups[95–97] appear have been investigated in detail, the characteristic interactions of the vicinal and geminal halogen atoms have been discovered, and a scheme has been developed using the additive increments due to chlorine and bromine in the chlorine- and bromine-containing fragments[98,99], which makes it possible to calculate the chemical shifts of the polyhalogeno-groups in the ^{13}C NMR spectra.

V. TELOMERISATION ACCOMPANIED BY THE REARRANGEMENT OF THE RADICALS

Oxygen-containing telogens reacting as a result of the dissociation of a C–H bond are of special interest in the telomerisation reaction. These include carboxylic acids, alcohols, ketones, and their various derivatives (Table 3). These telogens have been investigated in reactions with a wide range of monomers, which has led to the discovery of the characteristics of the telomerisation with their participation, involving the rearrangement of the growing radicals.

† In this case the usual telomers have the structure $CH_3OCOCHBr(CH_2CHCl)_nBr$.

As a result, the growing radical in this group of reactions participates simultaneously in three competing processes—chain propagation, chain transfer, and isomerisation. The study of the characteristics of such reactions has demonstrated extensive possibilities in their employment for research and synthetic purposes[11,100,101].

Table 3. The telomerisation of unsaturated compounds by carboxylic acids and their derivatives, alcohols, ketones, and acetals.

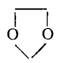
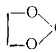
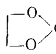
No.	Telogen	Identified telomers*	n, m	$10^2\ C_{n\geq 3}$	C_i (type of migration)	Refs.
		Monomer $CH_2{=}CH_2$; $R{=}C_4H_9$				
1	HCO_2CH_3	$H(CH_2CH_2)_nCO_2CH_3$	1—4	17	—	[111]
		$HO_2CCH_2(CH_2CH_2)_nH$	1—3	15	—	
		$H(CH_2CH_2)_mCH(CH_2R)CO_2CH_3$	1—2	8	0.4 (1.6-H)	
2	CH_3CO_2H	$H(CH_2CH_2)_nCH_2CO_2H$	1—4	—	—	[102]
		$H(CH_2CH_2)_mCHRCO_2H$	1—2	—	(1.5-H)	[104]
3	$CH_3CO_2CH_3$	$H(CH_2CH_2)_nCH_2CO_2CH_3$	1—6	4	—	
		$CH_3CO_2CH_2(CH_2CH_2)_nH$	1—3	—	—	
		$H(CH_2CH_2)_mCHRCO_2CH_3$	1—3	6	1.5 (1.5-H)	
4	CH_3CN	$H(CH_2CH_2)_nCH_2CN$	1—4	4	—	[109]
		$H(CH_2CH_2)_mCHRCN$	1—2	3	0.9 (1.5-H)	
5	$ClCH_2CO_2CH_3$	$H(CH_2CH_2)_nCHClCO_2CH_3$	1—4	20	—	[105]
		$H(CH_2CH_2)_mCClRCO_2CH_3$	1—2	16	3.6 (1.5-H)	
6	$BrCH_2CO_2CH_3$	$Br(CH_2CH_2)_nCH_2CO_2CH_3$	1—4	120	0	[108]
7	$CH_3CH_2CO_2H$	$H(CH_2CH_2)_nCH(CH_3)CO_2H$	1—5	15	—	[107]
		$H(CH_2CH_2)_mCR(CH_3)CO_2H$	1—2	19	6.5 (1.5-H)	
8	$CH_3CH_2CO_2CH_3$	$H(CH_2CH_2)_nCH(CH_3)CO_2CH_3$	1—4	12	—	[106]
		$H(CH_2CH_2)_mCR(CH_3)CO_2CH_3$	1—2	13	5.2 (1.5-H)	
9	CH_3CH_2CN	$H(CH_2CH_2)_nCH(CH_3)CN$	1—4	8	—	[103]
		$H(CH_2CH_2)_mCR(CH_3)CN$	1—2	11	2.9 (1.5-H)	
10	$C_4H_9CH_2CO_2CH_3$	$H(CH_2CH_2)_nCH(C_4H_9)CO_2CH_3$	1—4	14	—	[103]
		$H(CH_2CH_2)_mCR(C_4H_9)CO_2CH_3$	1—2	12	2.0 (1.5-H)	
11	$C_4H_9CH_2CN$	$H(CH_2CH_2)_nCH(C_4H_9)CN$	1—3	—	—	[132]
		$CH_3CH_2CR(C_4H_9)CN$	1		(1.5-H)	
12	$CH_3COCH_2CO_2CH_3$	$H(CH_2CH_2)_nCH(COCH_3)CO_2CH_3$	1—2	—	—	[133]
		$CH_3CH_2CR(COCH_3)CO_2CH_3$	1	—	(1.5-H)	
13	ClCOCOCl	$Cl(CH_2CH_2)_nCOCl$	1—3	700	(1.5-Cl)	[134]
14	$CH_2(CO_2CH_3)_2$	$H(CH_2CH_2)_nCH(CO_2CH_3)_2$	1—2	—	—	[135]
		$H(CH_2CH_2)_mCR(CO_2CH_3)_2$	1—2	—	(1.5-H)	
15	$NCCH_2CO_2CH_3$	$H(CH_2CH_2)_nCH(CN)CO_2CH_3$	1—6	—	—	[136]
		$H(CH_2CH_2)_mCR(CN)CO_2CH_3$	1—4	—	43 (1.5-H)	
16	$CH_3O_2C(CH_2)_kCO_2CH_3$ (k=2,4)	$H(CH_2CH_2)_nCH(CO_2CH_3)(CH_2)_{k-1}CO_2CH_3$	1—2	—	—	[137]
		$CH_3CH_2CR(CO_2CH_3)(CH_2)_3CO_2CH_3$	1	—	(1.5-H)	
17	CH_3COCH_3	$CH_3COCH_2(CH_2CH_2)_nH$	1—4	—	—	[138]
		$CH_3COCHR(CH_2CH_2)_mH$	1—3	—	(1.5-H)	
18	$CH_3CH(OCH_3)_2$	$CH_3CH(OCH_3)OCH_2(CH_2CH_2)_nH$	1—3	—	—	[124, 126]
		$CH_3O_2CCH_2(CH_2CH_2)_mH$	1	—	(1.5-H)	
		ditto	3	—	(1.9-H)	
		$CH_3CO(CH_2CH_2)_nH$	1—3	—	—	
19		 $CH(CH_2CH_2)_nH$	1—3	—	—	[139]
		 $C(C_4H_9)(CH_2CH_2)_mH$	1—2	—	(1.5-H)	
		$HOOCCH_2(CH_2CH_2)_nH$	1—3	—	—	
20	CH_3CH_2OH	$H(CH_2CH_2)_nCH(CH_3)OH$	1—4	4	—	[110]
		$H(CH_2CH_2)_mCR(CH_3)OH$	1—3	7	1.3 (1.5-H)	
21	cyclo-C_6H_{12}	cyclo-$C_6H_{11}(CH_2CH_2)_nH$	1—3	9	2.4	[140]
		cyclo-$C_6H_{10}(R)(CH_2CH_2)_mH$	1—2	—	(1.5-H)	
		Monomer $CH_3CH{=}CH_2$; $R{=}C_3H_7$				
22	$HCO_2C_2H_5$	$H(CH_3CHCH_2)_nCO_2C_2H_5$	1—4	—	—	[141]
		$HO_2CCH(CH_3)CH_2CH_2CH_3$	1	—	—	
		$H(CH_3CHCH_2)_2CH(CH_3)CHRCO_2C_2H_5$	3	—	(1.6-H)	
23	$CH_3CO_2CH_3$	$H(CH_3CHCH_2)_nCH_2CO_2CH_3$	1—3	—	—	[115]
		$H(CH_3CHCH_2)_mCHRCO_2CH_3$	1—2	—	**(1.3-H)**	
		$[CH_3CH_2CH_2CH(CH_3)CH_2]_2CHCO_2CH_3$	4	—	**(1.5-H)**	
		Monomer $CH_3CH{=}CH_2$; $R{=}C_3H_7$				
24	$ClCH_2CO_2CH_3$	$H(CH_3CHCH_2)_nCHClCO_2CH_3$	1—2	—	—	[112, 114, 116]
		$H(CH_3CHCH_2)_mCRClCO_2CH_3$	1—3	70	(1.3-H)	
		$[CH_3CH_2CH_2CH(CH_3)CH_2]_2CClCO_2CH_3$	4	—	(1.5-H)	
25	$CH_3CH_2CO_2H$	$H(CH_3CHCH_2)_nCH(CH_3)CO_2H$	1—2	—	—	[142]
		$H(CH_3CHCH_2)_mCR(CH_3)CO_2H$	1—2		(1.3-H)	
26	$CH_3CH_2CO_2CH_3$	$H(CH_3CHCH_2)_nCH(CH_3)CO_2CH_3$	1—2		—	[113]
		$(CH_3CH_2CH_2)_2C(CH_3)CO_2CH_3$	2	—	(1.3-H)	

Table 3 (contd.)

No.	Telogen	Identified telomers*	n, m	$10^2 C_{n\geqslant 3}$	C_i (type of migration)	Refs.
Monomer $CH_2{=}CHCl$						
27	$ClCH_2CO_2CH_3$	$H(CHClCH_2)_nCHClCO_2CH_3$	1–3	—	—	[117]
		$ClCH_2O_2CCH_2(CH_2CHCl)_mH$	1–2	—	0	
28	$CH_3CH_2CO_2CH_3$	$H(CHClCH_2)_nCH(CH_3)CO_2CH_3$	1–2	—	0	[118]
Monomer — $(CH_3)_2C{=}CH_2$						
29	$ClCH_2CO_2CH_3$	$H[(CH_3)_2CCH_2]_nCHClCO_2CH_3$	1–2	—	—	[123]
		$H[(CH_3)_2CCH_2]_2CClCO_2CH_3$ with $CH_2C(CH_3){=}CH_2$ on the C	2	—	(1,5-H)	
		$CH_2{=}C(CH_3)CH_2[(CH_3)_2CCH_2]_mCHClCO_2CH_3$	0–1		—	
30	$CH_3CH_2CO_2CH_3$	$H[(CH_3)_2CCH_2]_nCH(CH_3)CO_2CH_3$	1–2	—	—	[24]
		$H[(CH_3)_2CCH_2]_2C(CH_3)CO_2CH_3$ with $CH_2C(CH_3){=}CH_2$ on the C	2	—	(1,5-H)	
Monomer $C_4H_9CH{=}CH_2$						
31	$ClCH_2CO_2CH_3$	$H(C_4H_9CHCH_2)_nCHClCO_2CH_3$	1–2	—	—	[121]
		$(C_4H_9CH_2CH_2)_2CClCO_2CH_3$	2	—	(1,3-H)	
32	$CH_3CH_2CO_2CH_3$	$H(C_4H_9CHCH_2)_nCH(CH_3)CO_2CH_3$	1–2	—	—	[121]
		$(C_4H_9CH_2CH_2)_2C(CH_3)CO_2CH_3$	2	—	(1,3-H)	
Monomer $CH_3CO_2CH{=}CH_2$						
33	$CH_3CH_2CO_2CH_3$	$H(CH_3CO_2CHCH_2)_nCH(CH_3)CO_2CH_3$	1–3	—	—	[119]
		$H(CH_3CO_2CHCH_2)_2CX(CH_3)CO_2CH_3$ ($X{=}CH_3CO_2CH_2CH_2$, $CH_3CHCO_2CH_3$)	2	—	(1,5-H)	
Monomer $CH_3CO_2CH_2CH{=}CH_2$						
34	$CH_3CH_2CO_2CH_3$	$H(CH_3CO_2CH_2CHCH_2)_nCH(CH_3)CO_2CH_3$	1–3	—	—	[120]
		$(CH_3CO_2CH_2CH_2CH_2)_2C(CH_3)CO_2CH_3$	2	—	(1,3-H)	
Monomer $(CH_3)_3SiCH{=}CH_2$						
35	$CH_3CH_2CH_3$	$H[(CH_3)_3SiCHCH_2]_nCH(CH_3)CO_2CH_3$	1–2	—	—	[122]
		$[(CH_3)_3SiCH_2CH_2]_2C(CH_3)CO_3CH_3$	2	—	(1,3-H)	

* Here R is an alkyl group appearing in the α-position relative to the functional group as a result of the rearrangement of the radicals and chain propagation in accordance with Scheme 8.

1. Reaction Conditions

The low effectiveness of the telogens reacting as a result of the dissociation of a C–H bond as chain transfer agents in the reaction makes it necessary to employ as initiators mainly alkyl or acyl peroxides, which give rise to $R\dot{O}$ radicals on decomposition (t-butyl peroxide, dicyclohexyl peroxydicarbonate) in the temperature range 50–150 °C. These reactions are characterised by relatively low degrees of conversion of the telogen (1–10%) and sometimes the formation of a considerable amount (15–60%) of unidentified higher telomers. In order to reduce the content of the latter, the telomerisation must be carried out at comparatively low pressures (25–50 atm). Analytical and preparative gas–liquid chromatography and ^1H and ^{13}C NMR spectroscopy are widely used to analyse the mixtures, to obtain the telomers in a pure form, and to demonstrate their structure.

2. Telomerisation of Ethylene

It was demonstrated for the first time in 1964 that the telomerisation of ethylene by acetic acid (Table 3, No.2) is accompanied by a rearrangement of the growing radicals with 1,5-migration of the hydrogen atom, which leads to the formation of two series of telomers[102]. Subsequently, it was possible to show in relation to a wide range of reactions with ethylene that such rearrangement is a fairly common phenomenon for reactions with comparatively ineffective telogens[103] (Scheme 8). The radicals (C) formed in the initiation stage react with ethylene to produce the growing radicals (D), which are converted into telomers of the non-rearranged series T_n, having transferred the chain to the telogen:

Scheme 8

$$\underset{(T_0)}{RCH_2CO_2CH_3} + R'O^{\cdot} \rightarrow \underset{(B)}{R\dot{C}HCO_2CH_3}\ ;$$

$$(C) + n\,CH_2{=}CH_2 \rightarrow \underset{(D)}{{}^{\cdot}(CH_2CH_2)_n\,CHRCO_2CH_3}\ ;$$

$$(D) \xrightarrow{T_0} \underset{T_n}{H(CH_2CH_2)_nCHRCO_2CH_3}\ ;$$

$$\underset{(E)}{\dot{C}H_2CH_2CH_2CH_2CHRCO_2CH_3} \xrightarrow{\text{1,5-H-rearrangement}} \underset{(F)}{CH_3CH_2CH_2CH_2\dot{C}RCO_2CH_3} \rightarrow$$

$$\xrightarrow{C_2H_4} CH_3(CH_2)_3\underset{(CH_2CH_2)_m^{\cdot}}{CRCO_2CH_3} \xrightarrow{T_0} \underset{T_m}{H(CH_2CH_2)_m}\,\underset{C_4H_9}{CRCO_2CH_3}\ .$$

Radicals with two monomer units (E) rearrange to the radicals (F) from which a second series of telomers T'_m having a branched structure is formed after chain propagation and transfer.

It has been shown[103] that in the given system the growing radical (D) ($n = 1$) does not rearrange with 1,3-migration of hydrogen. It might have been supposed that telomers with a branched structure T'_m are obtained via the stepwise telomerisation mechanism from the telomers formed (see Section IV). However, detailed investigations yielded much evidence showing that here we are in fact dealing with a rearrangement of radicals[11]. One of the most convincing pieces of evidence is the high process selectivity—only one series of branched telomers containing the butyl group in the α-position is formed. Special tests demonstrated the absence of comparable amounts of α-ethyl-substituted telomers, which should have been produced as a result of the secondary reaction of the first telomer $CH_3CH_2CHRCO_2CH_3$ with ethylene[11].

The influences of various factors on the course of telomerisation and on the degree of rearrangement have been estimated quantitatively in relative terms and compared using the method of relative kinetics, within the framework of which the partial chain transfer constants $C_n = k_{tr}/k_p$ and the relative isomerisation constants $C_i = k_i/k_p$ have been estimated (Table 3).[103] For the same monomer, when the radical centre is sufficiently remote from the functional group and the substituent R, the reactivity of the radicals $\dot{C}(CH_2CH_2)_nCHRCO_2CH_3$ is independent of the nature of R. The difference between the values of C_n with $n \geq 3$ for reactions involving different telogens $RCH_2CO_2CH_3$ is then determined solely by the difference between the efficiencies of the telogens as chain transfer agents for the reaction (Table 3). Thus $C_{n\geq 3}$ can serve as a relative measure of the efficiency of the given telogen in the chain transfer stage. The data in Table 3 show that the telogens investigated in telomerisation with ethylene, which react at the C–H bond, are characterised by extremely low values of $C_{n\geq 3}$ (from 0.04 to 0.20) and only methyl bromoacetate (Table 3, No.6), which reacts as a result of the dissociation of the C–Br bond, can be classified as an extremely effective telogen.

The corresponding radicals differ much more as regards the degree of rearrangement C_i. $C_i = 0$ has been obtained for methyl bromoacetate, which is highly effective in telomerisation. Comparison of data for methyl acetate and methyl bromoacetate (Table 3, Nos.3 and 6 respectively), where the growing radicals are the same, has shown that a higher value of C_i corresponds to the less effective methyl acetate. Thus the comparatively low efficiency of the telogen in the chain transfer reaction constitutes an important condition for the rearrangement of the radicals.

However, this is a necessary but not a sufficient condition. Thus the values of $C_{n\geq 3}$ for methyl chloroacetate (No.5) and methyl propionate (No.8) are higher than for methyl acetate (No.5) and the degree of rearrangement is in this case also higher (see Table 3). In the given instance, the difference between the stabilities of the initial and rearranged radicals plays a significant role and it is naturally higher in the presence of a substituent R = Cl or CH_3, different from hydrogen, at the radical centre of the rearranged radical (F) (Scheme 8). Here the polar nature of the substituent R does not play a fundamental role: for both electron-donating (CH_3) and electron-accepting (Cl) substituents, the degree of rearrangement is higher than for R = H.

On the other hand, the increase of the chain length of the substituent in the α-position relative to the carboxy-group (Table 3, No.10) results in a decrease of the degree of rearrangement, which can be explained by the appearance of steric hindrance in the intramolecular chain transfer stage. At the same time the nature of the initiating system [peroxides and complex initiators based on $Mn_2(CO)_{10}$ and $Fe(CO)_5$] hardly affects the rearrangement with migration of hydrogen in the telomerisation reaction[36,62,82].

3. Telomerisation of Propene

The replacement of ethylene by propene led to new prospects for the investigation of telomerisation (Scheme 9). In the study of the telomerisation of propene by carboxylic acids and their derivatives, it was shown[11] that, together with the 1,5-migration of hydrogen in the radical (H), there is also a high degree of the 1,3-migration of hydrogen in the radical (G) containing one monomer unit. This results in a sharp increase of the content of telomers with two substituents in the α-position and among the higher telomers there are virtually no compounds of the non-rearranged series[112–114] (Table 3, Nos.23, 24, and 26).

Scheme 9

$$\underset{(G)}{CH_3\dot{C}HCH_2CHRCOOCH_3} \xrightarrow{1,3\text{-H}} \underset{(G')}{CH_3CH_2CH_2\dot{C}RCOOCH_3}\ ;$$

$$\underset{(H)}{CH_3\dot{C}HCH_2\overset{CH_3}{\overset{|}{C}}HCH_2CHRCOOCH_3} \xrightarrow{1,5\text{-H}} \underset{(H')}{CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2\dot{C}RCOOCH_3}.$$

Comparison of data for the reactions of propene with various telogens of the type $RCH_2CO_2CH_3$ (R = H, Cl, or CH_3)[112,113,115] shows that in this series too the lowest relative degree of rearrangement corresponds to methyl acetate (R = H), where the difference between the stabilities of the rearranged (H′) and non-rearranged (H) radicals is smallest (see Scheme 9). It has been shown in relation to the telomerisation of propene by methyl chloroacetate (Table 3, No.24)[114,116] that the decrease of the reaction temperature from 150 °C to 25 °C results in the disappearance of the telomers whose formation is associated with the 1,3-migration of hydrogen, while the 1,5-migration of a hydrogen atom, which is more favourable from the standpoint of the conformation of the transition state, proved to be much less affected by the change of temperature. This is yet another piece of evidence showing that we are in fact dealing with the migration of hydrogen, since in the case of the secondary reaction of telomers T_n of the type $H[CH(CH_3)CH_2]_nCHRCO_2.CH_3$ with propene there are no grounds for expecting markedly different reactivities for T_1 and T_2.

The rearrangement of the radicals with 1,3-migration of hydrogen in the case of propene is associated, in our view, with a favourable combination of polar factors—the nucleophilic radical centre attacks the electrophilic component of the radical in the intramolecular transfer range.

4. Other Monomers

The significant role of the polar characteristics of the growing radical in the rearrangement has been confirmed in the study of the telomerisation of vinyl chloride (Table 3, Nos.27 and 28), where the growing radicals have a pronounced electrophilic character. In this case the rearrangement of the radicals $ClCHCH_2(CHClCH_2)_nCHRCO_2CH_3$, where $n = 0$, 1, does not occur[117,118].

The influence of the nature of the monomer on the reaction has been manifested also in the comparison of the results obtained in the reactions of methyl propionate with vinyl acetate[119] and allyl acetate[120] (Table 3, Nos.33 and 34). In the former case only the 1,5-migration of a hydrogen atom takes place, while in the reaction with $CH_2{=}CHCH_2CO_2CH_3$, which can be regarded as a substituted analogue of propene,

the 1,3-migration of hydrogen takes place. The formation of two telomers with different structures containing two monomer units was also noted for the telomerisation of hex-1-ene[121] (Table 3, Nos.31 and 32) and trimethylvinylsilane[122] (No.35).

A number of interesting features distinguish the telomerisation of isobutene[24,122]. In this case there is no 1,3-migration of hydrogen in the radical $(CH_3)_2\dot{C}CH_2CHRCO_2CH_3$, although polar factors favour it (see Scheme 10). The absence of the rearrangement is apparently associated with the steric hindrance, which has a particularly marked effect in the stage involving the formation of the energetically unfavourable four-membered transition state, while the 1,5-migration of hydrogen in the radical (I) proceeds to a high extent:

Scheme 10

$$(CH_3)_2\dot{C}CH_2C(CH_3)_2CH_2CHRCO_2CH_3 \xrightarrow{1,5\text{-}H} (CH_3)_2CHCH_2C(CH_3)_2CH_2\dot{C}RCO_2CH_3$$

(I) (I')

$$(CH_3)_2C{=}CH_2 \longrightarrow CH_3C(\cdot)(=CH_2)(=CH_2) \quad ;$$

$$(I') + CH_3C(\cdot)(=CH_2)(=CH_2) \longrightarrow (CH_3)_2CHCH_2C(CH_3)_2CH_2CRCO_2CH_3 \longrightarrow$$

$$\longrightarrow (CH_3)_2CHCH_2C(CH_3)_2CH_2CRCO_2CH_3 \quad .$$

$$CH_2CH(CH_3)_2$$

Here the behaviour of the radical (I') is unusual. By virtue of the characteristic features of its structure, it is hardly involved in the chain propagation and transfer reactions and mainly recombines with the isobutenyl radicals, giving rise to an unsaturated compound. Subsequently the hydrogenation of the double bond makes it possible to obtain readily the saturated analogue.

5. Telomerisation of Olefins by Acetals

The study of the telomerisation of ethylene[124] and propene[125] by linear acetals led to the discovery of a new combination of rearrangements with 1,5- and 1,9-migrations of a hydrogen atom (Table 3, No.18). The reaction develops via the C–H bond of the methoxy-group with formation of long-chain acetals T_n. The intermediate growing radicals (Scheme 11) with one and three monomer units rearrange respectively with 1,5- and 1,9-migration of hydrogen. On the other hand, the radical with two monomer units does not rearrange with 1,7-migration of hydrogen. Such selectivity constitutes important evidence in support of an intramolecular character of the migration of hydrogen, because all three telomers T_n, where n = 1, 2, and 3, can participate to equal extents in secondary reactions. We may note that the 1,9-migration of hydrogen corresponds to two 1,5-transitions as regards the conformation of the transition state, which probably actually facilitates the occurrence of this rearrangement[126]:

Scheme 11

$$CH_3CH(OCH_3)_2 \xrightarrow{R\dot{O}} CH_3\dot{C}H(OCH_3) \quad ;$$

$$(T_0)$$

$$CH_3\dot{C}H(OCH_3) + n\,CH_2{=}CH_2 \xrightarrow{T_0} CH_3CH(OCH_3)\underset{(T_n)}{CH_2(CH_2CH_2)_nH} \quad ;$$

$$CH_3CH(OCH_3)CH_2(CH_2CH_2)_n \xrightarrow[1,9\text{-}H(n=3)]{1,5\text{-}H(n=1)} CH_3\dot{C}(OCH_3)CH_2(CH_2CH_2)_nH \quad ;$$

$$CH_3\dot{C}(OCH_3)CH_2(CH_2CH_2)_nH \xrightarrow{-CH_3\dot{O}} CH_3C(O)OCH_2(CH_2CH_2)_nH \quad .$$

6. The Use of ^{13}C NMR for the Investigation of the Structure of Telomers

The processes described above and analogous reactions always result in the formation of extremely complex compounds having a branched structure and belonging to different classes—carboxylic acids and their esters, nitriles, halogeno-derivatives, substituted cyclic and linear acetals and their hetero-analogues, etc. ^{13}C NMR has been used widely and successfully to determine the structures of such compounds[121,127–131]. The characteristic groups and the corresponding chemical shifts of the signals as well as the rules governing the variation of the chemical shifts as a function of the structure of neighbouring units have been discovered for a large number of model compounds. For example, the ^{13}COO and $^{13}CH_3$–C signals are displaced downfield with increase of the number of substituents at the neighbouring carbon atom; the accumulation of substituents at the β-carbon atom leads to an upfield shift of the $^{13}CH_3$.CH_2C signal. Calculations based on an additive scheme taking into account corrections[128] and the regression equation proposed by ourselves, with the corresponding coefficients, which relates the chemical shifts of the key signals of the test compounds, in particular, the esters of polybranched acids, to the chemical shifts of the signals of the corresponding carbon atoms in isostructural hydrocarbons, have been widely used to assign the signals[121,129].

VI. COTELOMERISATION OF TWO MONOMERS WITH ONE TELOGEN

Cotelomerisation may imply the reactions of two monomers with one telogen, of two telogens with one monomer, or of two monomers with two telogens[4,12]. The study of cotelomerisation was begun only in recent years and concerns mainly different versions of the reactions of monomers with one telogen. The difficulties in the study of a complex mixture of homo- and co-telomers limit the development of this field. Examination of the simplest cotelomerisation scheme

$$\underset{\text{telogen}}{X-Y} + \underbrace{mA + nB}_{\text{monomers}} \xrightarrow{\text{initiator}} \underset{\text{cotelomers}}{XA_mB_nY} \quad ,$$

shows that, for each value of the sum $m + n$, one may expect the formation of 2^{m+n} different structures if the growth of the radical chain takes place only via the "head to tail" mechanism. When $m + n = 1$–3, there is a possibility of the formation of 14 compounds; the absence of asymmetric atoms in the molecules of the products is then assumed.

Table 4. The cotelomerisation of two monomers* with one telogen.

No.	Monomer	Telogen	Initiator	Identified cotelomers T_n		Refs.
				$n=2$	$n=3,4$	
1	$CH_2=CH_2+CH_2=CHCH_3$	CCl_4	$(C_6H_5CO)_2O_2$	T_2^{PE}, T_2^{EP}	$T_3^{PEE}, T_3^{EEP}, T_3^{PEP}$	[143]
2	$CH_2=CH_2+CH_2=CHCH_3$	$(CH_3)_2CHCOOCH_3$	$[(CH_3)_3C]_2O_2$	T_2^{PE}, T_2^{EP}	**	[144]
3	$CH_2=CH_2+CH_2=C(CH_3)_2$	$(CH_3)_2CHCOOCH_3$	$[(CH_3)_3C]_2O_2$	T_2^{EI}, T_2^{IE}	**	[145]
4	$CH_2=CH_2+CH_2=CHCl$	CCl_4	$(C_6H_5CO)_2O_2$	T_2^{VE}, T_2^{EV}	T_3^{VEE}, T_3^{EVE}	[146, 147]
5	$CH_2=CHCH_3+CH_2=CHCl$	$CHCl_3$	$(C_6H_5CO)_2O_2$	T_2^{VP}, T_2^{PV}	T_3^{VPV}, T_3^{PVP}	[148]
6	$CH_2=CHCH_3+CH_2=CHCl$	CCl_4	$(C_6H_5CO)_2O_2$	T_2^{VP}, T_2^{PV}	$T_3^{PVP}, T_3^{PPV}, T_3^{VVP}, T_3^{VPV}$	[149, 150]
7	$CH_2=CHCH_3+CH_2=CCl_2$	CH_3CCl_3	$Fe(CO)_5$ + DMF	T_2^{VP}	Not investigated	[151]
8	$CH_2=CHCH_3+CH_2=CHCN$	CCl_4	$[(CH_3)_3C]_2O_2$	T_2^{PA}, T_2^{AP}	Not investigated	[152]
9	$CH_2=CH_2+CF_2=CFCF_3$	FSO_2Cl	$(C_6H_5CO)_2O_2$	Not formed	T_3^{EFE}, T_4^{EFEE}	[153]

* Conventional notation: $E = CH_2CH_2$, $P = CH_2CHCH_3$, $I = CH_2C(CH_3)_2$, $V = CH_2CHCl$, $V' = CH_2CCl_2$, $A = CH_2CHCN$, $F = CF_2CFCF_3$.
** All possible telomers have been obtained.

In view of the difficulties in the investigation, cotelomerisation was initially used only to obtain mixtures of oligomers with useful properties—fire resistance, thermal stability, high covering power, and compatibility with polymers. Numerous examples of the preparation of such oligomers have been published[4]; the molecular weights of a series of these, which varies in the range from 400 to 10000, were indicated.

The study of the structure of the lower cotelomers and the determination of the ratio of their yields and the yields of homotelomers as a function of the reaction conditions and the nature of the components are of great theoretical interest. Such study makes it possible to investigate the comparative reactivities of the monomers and radicals in competing reactions, to determine the sequence in which the monomer units are incorporated in the radical chain, and to observe the influence of the polar properties of the monomers, telogens, and growing radicals on the reactions. Cotelomerisation can apparently be used as a model for the solution of certain problems in copolymerisation.

The cotelomerisation of different pairs of monomers with telogens reacting both via a C–Cl bond (Table 4, Nos.1, 4, 6, 7, and 8), via a C–H bond (Nos.2, 3, and 5), or via an S–Cl bond (No.9) was investigated for the first time in the Laboratory of Organoelemental Synthesis at the Institute of Organoelemental Compounds of the USSR Academy of Sciences in relation to nine examples (Table 4) with identification of all the homotelomers and cotelomers formed, containing between one and three monomer units in the molecules. In examples 1–3 both monomers are olefins and are characterised by a polar effect of the same kind; in the remaining examples each two monomers differ markedly as regards the polar effect.

Table 4 shows that in all cases, except for Nos.7 and 9, both possible cotelomers, containing two monomer units, were obtained; the cotelomer whose formation is favoured by the polar effect in the chain transfer stage and by the higher reactivity of the radical centre in T_2 is then formed in a higher yield. When the polar effects of the two monomers act in the same direction and when the telogen is weakly electrophilic, all six possible cotelomers, containing three monomer units, are formed (Nos.2 and 3). In all the remaining cases the cotelomers T_2, for which the polar effect is unfavourable in the chain propagation or chain transfer stage (Nos.1 and 4–6), are not formed. Example 9 is a special case where the two monomers not only differ in their polarity but one of them ($CF_2=CF-CF_3$) is extremely inert in radical reactions; nevertheless it has been possible to involve perfluoropropene in this process. Here it is easy to observe the influence of the polar effects—the absence of groups of the type FSO_2F_n and FSO_2EFF.

VII. PROSPECTS FOR THE PRACTICAL APPLICATION OF TELOMERISATION

The study of the chemical reactions of the tetrachloroalkanes $CCl_3(CH_2CH_2)_nCl$ demonstrated the possibility of using them for the synthesis of ω-chlorocarboxylic acids on the basis of which methods have been developed for the preparation of a new polyamide fibre and synthetic perfumes[1,154]. The reaction of ethylene with tetrachloroethylene made it possible to synthesise 1,1,2-trichlorobutadiene, which readily polymerises via a radical mechanism; its polymers are readily soluble in organic solvents, are resistant to the action of inorganic acids in the cold, and are incombustible; their films exhibit an effective adhesion to metals, rubber, and synthetic materials[155].

The telomerisation of ethylene via the esters of halogenoacetic acids has served as the basis of a method for the synthesis of γ-aminobutyric and ε-aminocaproic acids; the former is an active psychotropic preparation (Gammalon) and the latter is an agent arresting the flow of blood (ε-Capron)[156,157].

The telomerisation of DDT in the presence of complex initiators with formation of derivatives of tetra- and dihydronaphthalenes constitutes one of the possible procedures for the chemical treatment of DDT.[158] Alkyl chlorides, which are essential for the manufacture of biologically degradable surfactants, are obtained by the telomerisation of ethylene by hydrogen chloride. Preparations have been made for the industrial application of this process[159].

The combination in a single process of telomerisation and the rearrangement of radicals made it possible, after a suitable selection of the monomers, telogens, and process parameters, to devise a simple single-stage method of synthesis of branched and polybranched monocarboxylic acids (VIK, PORK), which produce no chemical waste or waste water. The method makes it possible to obtain acids with a wide variation of their structures within the framework of a single universal technology. The preparation of branched

Table 5. Examples of the telomerisation of unsaturated compounds by halogen-containing telogens initiated by organic radical-forming agents.

No.	Telogen (bond dissociated)	Monomer	Initiator and reaction conditions	Identified telomers and (C_n)	n	Refs.
1	$CHCl_3$(C—Cl, C—H)	CH_2=CHC_3H_7	TBP; 3 h 130—150°	$CCl_3(CH_2CHC_3H_7)_nH$	1—2	[166]
				$CCl_3CH_2CHClC_3H_7$	—	
				$CHCl_2CH_2CH_2C_3H_7$	—	
				$CHCl_2CH_2CHClC_3H_7$	—	
2	$CHBr_3$(C—Br)	CH_2=CH_2	BP; 4 h, 100°	$CHBr_2(CH_2CH_2)_nBr$	1—2	[56]
3	$CHBr_3$(C—Br)	CH_2=$CHCl$	BP; 4 h, 100°	$CHBr_2(CH_2CHCl)_nBr$ (C_1=0.74; C_2=1.77)	1—3	[57]
4	$CHCl_2COOCH_3$ (C—H, C—Cl)	CH_2=$CHCH_3$	TBP; 1 h, 150°	$H(CH_2CHCH_2)_n$× ×$CHClCOOCH_3$	1—3	[168]
				$H(CH_2CHCH_2)_n$× ×CCl_2COOCH_3	1—3	
				$Cl(CH_2CHCH_2)_n$× ×CCl_2COOCH_3	1—3	
				$Cl(CH_2CHCH_2)_n$× ×$CHClCOOCH_3$	1—3	[169]
5	CCl_2COOCH_3 (C—Cl)	CH_2=$CHCH_3$	TBP; 1 h, 150°	$Cl(CH_2CHCH_2)_n$ CCl_2COOCH_3 (C_1=2.1; C_2=29.1; C_3=28.2)	1—3	[169]
6	$CCl_2(COOC_2H_5)_2$ (C—Cl)	CH_2=CH_2	BP; 5 h, 100° TBP; 5 h, 130°	$Cl(CH_2CH_2)_n$× ×$CCl(COOC_2H_5)_2$	1—4	[54]
7	FSO_2Cl(S—Cl)	CH_2=CH_2	BP; 25 min, 90°	$FSO_2(CH_2CH_2)_nCl$	1—4	[170]
8	FSO_2Cl(S—Cl)	CH_2=$CHCl$	BP; 45 min, 90°	$FSO_2(CH_2CHCl)_nCl$	1—3	[171]
9	FSO_2Cl(S—Cl)	CH_2=CF_2	BP; 2.5 h, 90°	$FSO_2(CH_2CF_2)_nCl$	1—3	[171]
				$FSO_2CH_2CF_2CF_2CH_2CH_2$× ×$CF_2Cl$	—	

acids by the telomerisation method has been achieved on an industrial scale[160,161].

The VIK acids are highly effective substitutes of dietary and technical plant oils in the paint and varnish industry and other branches of the national economy. Fully oil-free high-quality ML-1121 autoenamels have been devised on their basis at the GIPI LKP, one tonne of VIK replacing up to one tonne of plant oils[162]. Oil-free drying agents have been obtained on an industrial scale on the basis of VIK[161]; the use of VIK makes it possible not only to save up to four tonnes of dietary oils per tonne of VIK but also to increase significantly the activity of the drying agents as a result of the higher concentration of the metal salt and hence their consumption can be reduced.

The VIK and PORK acids are also effective extractants for non-ferrous and rare metals. They make it possible to increase significantly the productivity of extraction processes in hydrometallurgy[163]. The higher fractions of the VIK and PORK acids constitute the basis for the preparation of foam fire extinguishers and de-emulsifying agents[164] and also serve as flotation agents, whereby one can increase by 3—4% the extraction of valuable components from mineral ores, which is extremely important bearing in mind the scale of the mining products processing industry[165]. The main effect of these studies has been the development of a simple technology, the high quality of the telomerisation products obtained, and the possibility of economising on large amounts of dietary and imported technical plant oils.

Table 6. Examples of telomerisation initiated by metal carbonyls.

No.	Telogen (bond dissociated)	Monomer	Initiator and reaction conditions	Identified telomers	n	Refs.
1	CCl_4	CH_2=CH_2	$Mn_2(CO)_{10}$; 2 h, 120°	$CCl_3(CH_2CH_2)_nCl$	1—3	[80]
2	CCl_4	CH_2=CH_2	$Cr(CO)_6$ or $Cr(CO)_5[P(C_6H_5)_3]$; 1 h, 120°	$CCl_3(CH_2CH_2)_nCl$	1—5	[70]
3	CCl_4	CH_2=$CHCH_3$	$Mo(CO)_6$, $W(CO)_6$; 120°	$CCl_3(CH_2CHCH_3)_nCl$	1—3	[69]
4	CCl_4	CH_2=$CHCH_3$	$Cr(CO)_6$**; 1 h, 120-140°	$CCl_3(CH_2CHCH_3)_nCl$	1—3	[71]
5	CCl_4	CH_2=$CHCH_3$	$Fe(CO)_5$, $Cr(CO)_6$; 1 h, 120°	$CCl_3(CH_2CHCH_3)_nCl$	1—3	[72]
6	CCl_4	CH_2=$CClCH_3$	$Fe(CO)_5$ + iso-C_3H_7OH; 4 h, 120°	$CCl_3(CH_2CClCH_3)_nCl$	1—3	[172]
				$CCl_3(CH_2CClCH_3)_2$	—	
7	$CHBr_3$(C—Br)	CH_2=CH_2	$Fe(CO)_5$ + DMF, HMP; 4 h, 100°	$CHBr_2(CH_2CH_2)_nBr$	1—2	[56]
8	$CHBr_3$(C—Br)	CH_2=$CHCl$	$Fe(CO)_5$; 4 h, 80°	$CHBr_2(CH_2CHCl)_nBr$	1—3	[57]
9	$CHBr_3$(C—Br)	CH_2=$CHCl$	$Fe(CO)_5$ + DMF; 4 h, 60°	$CHBr_2(CH_2CHCl)_nBr$	1—2	[57]
10	CH_3CCl_3(C—Cl)	CH_2=CCl_2	$Fe(CO)_5$ + iso-C_3H_7OH; 30 min, 130-140°	$CH_3CCl_2(CH_2CCl_2)_nCl$	1—2	[62]
11	$C_2H_5CCl_3$(C—Cl)	CH_2=$CHCl$	$Fe(CO)_5$ + iso-C_3H_7OH; 3 h, 145°	$C_2H_5CCl_2(CH_2CHCl)_nCl$	1—2	[61]
12	$ClCH_2CH_2CCl_3$(C—Cl)	CH_2=CH_2	$Mn_2(CO)_{10}$ + HMP; 2 h, 120°	$Cl(CH_2)_2CCl_2(CH_2CH_2)_nCl$	1—2	[80]
13	$ClCH_2CH_2CCl_3$(C—Cl, C—H)	CH_2=CCl_2	$Fe(CO)_5$ + HMP; 1 h, 130-135°	$Cl(CH_2)_2CCl_2(CH_2CCl_2)_nCl$	1—2	[62]
				$Cl(CH_2)_2CCl_2(CH_2CCl_2)_nH$	1—2	
				$CCl_3CH_2CHCl(CH_2CCl_2)_nH$	1—2	
14	$ClCH_2CH_2CCl_3$(C—Cl)	CH_2=$CHCOOCH_3$	$Fe(CO)_5$ + DMF; $Fe(CO)_5$ $Mo(CO)_6$, $Mn_2(CO)_{10}$***	$Cl(CH_2)_2CCl_2(CH_2CHCOOCH_3)_nCl$	1—2	[59]
				$Cl(CH_2)_2CCl_2(CH_2CHCHOOCH_3)_nH$	1—2	
15	$C_6H_5CH_2Cl$(C—Cl)	CH_2=CH_2	$Fe(CO)_5$ + HMP, DMF; 4 h, 145°	$C_6H_5CH_2(CH_2CH_2)_nCl$	1—2	[55]
16	$C_6H_5CH_2Cl$	CH_2=$CHCl$	$Fe(CO)_5$ + DMF; 4 h, 145°	$C_6H_5CH_2(CH_2CHCl)_nCl$	1—4	[173]
17	$ClCH_2COOCH_3$(C—H)	CH_2=CH_2	$Mn_2(CO)_{10}$; 2 h, 120°	$H(CH_2CH_2)_nCHClCOOCH_3$	1—3	[81]
				$H(CH_2CH_2)_nC(C_4H_9)ClCOOCH_3$	—	
18	CCl_3COOCH_3(C—Cl)	CH_2=CH_2	$Mn_2(CO)_{10}$, $Mn_2(CO)_{10}$ + DMF; 1 h, 140°	$Cl(CH_2CH_2)_nCCl_2COOCH_3$	1—4	[38]
19	$CCl_2(COOC_2H_5)_2$ (C—Cl)	CH_2=CH_2	$Fe(CO)_5$ + DMF; 5 h, 100-125°	$Cl(CH_2CH_2)_nCCl(COOC_2H_5)_2$	1—2	[54]
20	$CCl_2(COOC_2H_5)_2$(C—Cl)	CH_2=CH_2	$Fe(CO)_5$ + DMF; 4 h, 175°	$Cl(CH_2CH_2)_nCCl(COOC_2H_5)_2$	1—2	[54]
				$CH_2CH_2CClCOOC_2H_5$ | | O——CO	—	
				CH_2CH_2 | | O—CO $\diagdown$ C $\diagup$ CO—O | | CH_2CH_2	—	
21	FSO_2Cl(S—Cl)	CH_2=$CHCl$	$Fe(CO)_5$ + DMF; 1 h, 90°	$FSO_2(CH_2CHCl)_nCl$	1—4	[170]

* Without co-initiator or in combination with iso-C_3H_7OH, DMF, or HMP (HMP = hexamethylphosphoramide and DMF = dimethylformamide).

** Without co-initiator or in combination with HMP, DMF, or CH_3CN.

*** In combination with cyclohexanol.

As a typical organic reaction, telomerisation gives rise to extensive synthetic possibilities. Tables 5 and 6 present examples of telomerisation, involving halogen-containing telogens and initiators of different kinds, achieved in the Laboratory of Organoelemental Synthesis at the Institute of Organoelemental Compounds of the USSR Academy of Sciences in 1977–1982.

Further study of this productive reaction will undoubtedly lead to the development of its new practical applications.

REFERENCES

1. R.Kh.Freidlina and Sh.A.Karapetyan, "Telomerizatsiya i Novye Sinteticheskie Materialy" (Telomerisation and New Synthetic Materials), Izd.Akad.Nauk SSSR, Moscow, 1961.
2. S.K.Velichko, in "Razvitie Organicheskoi Khimii v SSSR" (The Development of Organic Chemistry in the USSR), Izd.Nauka, Moscow, 1967, p.303.
3. R.Kh.Freidlina and A.B.Terent'ev, Vestnik Akad. Nauk SSSR, 1980, (9), 32.
4. C.Starks, "Free Radical Telomerisation", Acad. Press, New York–London, 1974.
5. R.Kh.Freidlina, "Proceedings of the VIIth World Petroleum Congress, Mexico, 1967", p.33.
6. I.B.Afanas'ev and G.I.Samokhvalov, Uspekhi Khim., 1969, **38**, 687 [Russ.Chem.Rev., 1969, **38**(4)].
7. R.Kh.Freidlina, F.K.Velichko, and E.Ts.Chukovskaya, "Metody Elementoorganicheskoi Khimii. Khlor. Alifaticheskie Soedineniya" (Methods of Organoelemental Chemistry. Chlorine. Aliphatic Compounds), Izd.Nauka, Moscow, 1973, Chapter 5.
8. K.Plochocka, Wiad.chem., 1973, **27**, 45.
9. R.Kh.Freidlina and E.C.Chukovskaya, Synthesis, 1974, 477.
10. R.Kh.Freidlina and F.K.Velichko, Synthesis, 1977, 145.
11. R.Kh.Freidlina and A.B.Terent'ev, Acc.Chem.Res., 1977, **10**, 9.
12. F.K.Velichko, T.T.Vasil'eva, R.G.Petrova, and A.B.Terent'ev, Zhur.Vses.Khim.Obshch.im Mendeleeva, 1979, **24**, 181.
13. R.Kh.Freidlina, A.B.Terent'ev, and F.K.Velichko, in "Entsiklopediya Polimerov" (The Encyclopaedia of Polymers), Izd.Sovetskaya Entsiklopediya, Moscow, 1977, **3**, p.590.
14. A.N.Nesmeyanov and N.A.Nesmeyanov, "Nachala Organicheskoi Khimii" (Principles of Organic Chemistry), Izd.Khimiya, Moscow, 1974, **2**, p.509.
15. F.R.Mayo, J.Amer.Chem.Soc., 1948, **70**, 3689.
16. A.V.Belyavskii and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1961, 838.
17. R.Kh.Freidlina, B.V.Kopylova, and L.V.Yashkina, Dokl.Akad.Nauk SSSR, 1968, **183**, 1113.
18. B.V.Kopylova, L.V.Yashkina, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1971, 179.
19. B.V.Kopylova, L.V.Yashkina, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 976.
20. B.V.Kopylova, V.I.Dostovalova, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1971, **201**, 612.
21. R.Kh.Freidlina, N.A.Kuz'mina, L.V.Yashkina, B.V.Kopylova, V.I.Dostovalova, and E.Ts.Chukovskaya, Dokl.Akad.Nauk SSSR, 1977, **236**, 637.
22. R.Haszeldine, J.Chem.Soc., 1953, 3761.
23. E.Kooiman and E.Farenhorst, Rec.Trav.chim., 1950, **70**, 867.
24. A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 1539.
25. R.Kh.Freidlina and A.B.Belyavskii, USSR P.126 493 (1959); Byul.Izobret., 1960, No.5, 17.
26. R.Kh.Freidlina and A.B.Belyavskii, Dokl.Akad. Nauk SSSR, 1959, **127**, 1027.
27. E.Ts.Chukovskaya, R.G.Gasanov, I.I.Kandror, and R.Kh.Freidlina, Zhur.Vses.Khim.Obshch.im Mendeleeva, 1979, **24**, 161.
28. C.H.Bamford, Symposium, "Reaktsionnaya Sposobnost', Mekhanizmy Reaktsii i Struktura v Khimii Polimerov" (Reactivity, Reaction Mechanism, and Structure in Polymer Chemistry) (Translated into Russian), Izd.Mir, Moscow, 1977, p.67.
29. B.A.Dolgoplosk and E.I.Tinyakova, "Generirovanie Svobodnykh Radikalov i Ikh Reaktsii" (The Generation of Free Radicals and Their Reactions), Izd.Nauka, Moscow, 1982.
30. M.Asscher and D.Vofsi, J.Chem.Soc., 1961, 2261, J.Chem.Soc., 1963, 1887.
31. Sh.A.Karapetyan, A.V.Belyavskii, and N.A.Kuz'mina, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 1272.
32. Y.Pietrasanta and B.Bontevin, Double Liaison, 1980, **22**, 305.
33. I.P.Lavrent'ev, L.G.Korableva, A.I.Kuzaev, Yu.M.Shul'ga, and M.L.Khidekel', Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1995.
34. H.B.Abramson and M.S.Wrighton, J.Amer.Chem. Soc., 1977, **99**, 5510.
35. E.Ts.Chukovskaya, A.A.Kamyshova, R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1965, **164**, 602.
36. R.Kh.Freidlina, F.K.Velichko, and R.A.Amriev, Dokl.Akad.Nauk SSSR, 1969, **187**, 350.
37. A.A.Kamyshova and L.V.Ivanova, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1677.
38. M.A.Moskalenko, A.B.Terent'ev, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 1260.
39. R.Kh.Freidlina, N.A.Grigor'ev, T.A.Onishchenko, and B.A.Englin, Dokl.Akad.Nauk SSSR, 1972, **205**, 602.
40. R.Kh.Freidlina, E.Ts.Chukovskaya, and B.A.Englin, Dokl.Akad.Nauk SSSR, 1964, **159**, 1346.
41. R.Kh.Freidlina, E.Ts.Chukovskaya, N.A.Kuz'mina, and A.A.Kamyshova, Izv.Akad.Nauk SSSR, Ser. Khim., 1968, 1319.
42. T.A.Onishchenko and B.A.Englin, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 1770.
43. A.A.Kamyshova, B.N.Osipov, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 60.
44. R.Kh.Freidlina, B.N.Osipov, and B.A.Englin, Izv.Akad.Nauk SSSR, Ser.Khim., 1970, 2511.
45. R.Kh.Freidlina, N.A.Grigor'ev, T.A.Onishchenko, and B.A.Englin, Dokl.Akad.Nauk SSSR, 1972, 205, 602.
46. R.G.Gasanov and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1977, **235**, 1309.
47. R.G.Gasanov, T.T.Vasil'eva, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 817.
48. R.G.Gasanov, L.V.Ivanova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 1011.
49. R.G.Gasanov, L.V.Ivanova, N.A.Grigor'ev, A.L.Tumanskaya, and R.Kh.Freidlina, Dokl.Akad. Nauk SSSR, 1983, **273**, 1441.
50. N.A.Rybakova, E.Ts.Chukovskaya, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 249.
51. F.K.Velichko, L.V.Vinogradova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 181.

52. N.A.Grigor'ev, N.A.Kuz'mina, E.Ts.Chukovskaya, A.N.Tumanskaya, and R.Kh.Freidlina, Izv.Akad. Nauk SSSR, Ser.Khim., 1980, 1333.
53. F.K.Velichko, L.V.Vinogradova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 1410.
54. L.V.Vinogradova, F.K.Velichko, R.A.Amriev, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 203.
55. T.T.Vasil'eva, R.G.Gasanov, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 1290.
56. T.T.Vasil'eva, G.A.Trapeznikova, and B.V.Nelyubin, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 635.
57. T.T.Vasil'eva, G.A.Trapeznikova, V.I.Dostovalova, B.V.Nelyubin, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1584.
58. T.T.Vasil'eva, L.F.Germanova, V.I.Dostovalova, B.V.Nelyubin, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 2759.
59. E.Ts.Chukovskaya, M.A.Rozhkova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 1582.
60. E.Ts.Chukovskaya, M.A.Rozhkova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 1782.
61. R.Kh.Freidlina, N.A.Kuz'mina, A.A.Kamyshova, S.D.Polishchuk, and E.Ts.Chukovskaya, Izv.Akad. Nauk SSSR, Ser.Khim., 1977, 174.
62. N.A.Kuz'mina, E.Ts.Chukovskaya, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 921.
63. A.B.Belyavskii, E.Ts.Chukovskaya, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1972, **202**, 589.
64. E.Ts.Chukovskaya and R.Kh.Freidlina, Izv.Akad. Nauk SSSR, Ser.Khim., 1972, 468.
65. R.Kh.Freidlina, N.A.Kuz'mina, and E.Ts.Chukovskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 588.
66. M.A.Rozhkova, E.Ts.Chukovskaya, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1973, **212**, 382.
67. N.A.Kuz'mina, E.Ts.Chukovskaya, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 489.
68. R.Kh.Freidlina, M.A.Rozhkova, N.A.Kuz'mina, and E.Ts.Chukovskaya, Izv.Akad.Nauk SSSR, Ser. Khim., 1975, 374.
69. N.A.Grigor'ev, A.L.Tumanskaya, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 2583.
70. N.A.Grigor'ev, A.L.Tumanskaya, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 199.
71. N.A.Grigor'ev, A.L.Tumanskaya, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 1515.
72. N.A.Grigor'ev, A.L.Tumanskaya, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1673.
73. R.Kh.Freidlina, F.K.Velichko, and E.Ts.Chukovskaya, see Ref.7, p.229.
74. R.G.Gasanov and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1979, **246**, 111.
75. R.G.Gasanov and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1977, **235**, 1309.
76. R.G.Gasanov and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1980, **254**, 113.
77. A.A.Kamyshova and L.V.Ivanova, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1677.
78. A.B.Terent'ev, M.A.Moskalenko, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1406.
79. E.Ts.Chukovskaya, N.A.Kuz'mina, M.L.Rozhkova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser. Khim., 1982, 1345.
80. M.A.Moskalenko, A.B.Terent'ev, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 637.
81. A.B.Terent'ev, M.A.Moskalenko, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 374.
82. N.A.Grigor'ev, A.L.Tumanskaya, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 1122.
83. M.A.Moskalenko, A.B.Terent'ev, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 877.
84. V.Ya.Katsobashvili, E.D.Safronenko, and I.B.Afanas'ev, Vysokomol.Soed., 1965, **7**, 823.
85. R.Kh.Freidlina, F.K.Velichko, and L.V.Vinogradova, Dokl.Akad.Nauk SSSR, 1975, **223**, 625.
86. A.B.Belyavskii and V.N.Kost, Izv.Akad.Nauk SSSR, Ser.Khim., 1963, 1514.
87. L.O.Moore, J.Org.Chem., 1972, **37**, 2633.
88. Y.Nakada, Y.Yura, and K.Murayama, Bull.Chem. Soc.Japan, 1976, **49**, 1072.
89. R.Kh.Freidlina, E.Ts.Chukovskaya, and A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1967, 2474.
90. F.K.Velichko, R.A.Amriev, T.A.Pudova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 369.
91. T.T.Vasil'eva and F.K.Velichko, "The IIIrd International Symposium on Organic Free Radicals. Abstracts of Papers. Freiburg, 1981", p.254.
92. F.K.Velichko, V.I.Dostovalova, N.A.Kuzmina, E.I.Fedin, and R.Kh.Freidlina, Org.Magn.Reson., 1975, **7**, 46.
93. F.K.Velichko, E.C.Chukovskaya, V.I.Dostovalova, N.A.Kuzmina, and R.Kh.Freidlina, Org.Magn.Reson., 1975, **7**, 361.
94. F.K.Velichko, E.Ts.Chukovskaya, V.I.Dostovalova, N.A.Kuz'mina, T.T.Vasil'eva, and R.Kh.Freidlina, "Tezisy Dokladov I Vsesoyuznoi Nauchno-Tekhnicheskoi Konferentsii 'Sostoyanie i Perspektivy Razvitiya Teoreticheskikh Osnov Proizvodstva Khlororganicheskikh Produktov', Baku, 1975" (Abstracts of Reports at the Ist All-Union Scientific and Technical Conference on 'The State and Prospects for the Development of a Theoretical Basis for the Manufacture of Organochlorine Products', Baku, 1975", p.148.
95. F.K.Velichko, E.C.Chukovskaya, V.I.Dostovalova, T.T.Vasil'eva, N.A.Kuzmina, and R.Kh.Freidlina, "VI Tagung Physical Gesellschaft DDR, 'Polymerphysik 1978', Leipzig, 1978", KVL 9, p.74.
96. F.K.Velichko, V.I.Dostovalova, L.V.Vinogradova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser. Khim., 1978, 734.
97. F.K.Velichko, V.I.Dostovalova, L.V.Vinogradova, and R.Kh.Freidlina, Org.Magn.Reson., 1980, **13**, 442.
98. V.I.Dostovalova, F.K.Velichko, T.T.Vasil'eva, N.V.Kruglova, and R.Kh.Freidlina, Org.Magn. Reson., 1981, **16**, 251.
99. V.I.Dostovalova, F.K.Velichko, T.T.Vasil'eva, N.V.Kruglova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 213.
100. R.Kh.Freidlina and A.B.Terent'ev, in "Advances in Free-Radical Chemistry", Heiden, London, 1980, **6**, p.1.
101. R.Kh.Freidlina, A.B.Terent'ev, M.Ya.Khorlina, and S.N.Aminov, Zhur.Vses.Khim.Obshch.im Mendeleeva, 1966, **11**, 211.
102. R.Kh.Freidlina, S.N.Aminov, and A.B.Terent'ev, Dokl.Akad.Nauk SSSR, 1964, **156**, 1133.
103. R.Kh.Freidlina, A.B.Terent'ev, N.S.Ikonnikov, and M.A.Churilova, Dokl.Akad.Nauk SSSR, 1973, **208**, 1366.

104. N.S.Ikonnikov, A.B.Terent'ev, M.A.Churilova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 2497.
105. R.Kh.Freidlina, A.B.Terent'ev, and N.S.Ikonnikov, Dokl.Akad.Nauk SSSR, 1970, **193**, 605.
106. A.B.Terent'ev, N.S.Ikonnikov, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1971, **196**, 1373.
107. R.Kh.Freidlina, P.A.Zagorets, I.N.Bryantsev, and A.B.Terent'ev, Dokl.Akad.Nauk SSSR, 1971, **197**, 105.
108. N.S.Ikonnikov, A.B.Terent'ev, M.A.Churilova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser. Khim., 1972, 2479.
109. A.B.Terent'ev, M.A.Churilova, V.I.Dostovalova, and V.A.Svoren', Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 1814.
110. A.B.Terent'ev and M.A.Churilova, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 2593.
111. P.A.Zagorets, I.N.Bryantsev, and A.B.Terent'ev, 1976, 909.
112. A.B.Terent'ev, N.S.Ikonnikov, V.I.Dostovalova, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1973, **213**, 1354.
113. A.B.Terent'ev, M.A.Churilova, N.S.Ikonnikov, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 439.
114. N.S.Ikonnikov and A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 371.
115. A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2614.
116. N.S.Ikonnikov and A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 2148.
117. N.S.Ikonnikov and A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 2813.
118. A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 2537.
119. M.A.Moskalenko, V.I.Dostovalova, and A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1327.
120. A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 1670.
121. A.B.Terent'ev, N.S.Ikonnikov, and V.I.Dostovalova, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 1546.
122. A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 2645.
123. A.B.Terent'ev, N.S.Ikonnikov, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1978, **238**, 870.
124. O.G.Safiev, U.B.Imashev, and A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 2499.
125. O.G.Safiev, U.B.Imashev, and A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1590.
126. A.B.Terent'ev, O.G.Safiev, and U.B.Imashev, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 2643.
127. R.Kh.Freidlina, A.B.Terent'ev, and V.I.Dostovalova, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 2125.
128. A.B.Terent'ev, V.I.Dostovalova, and R.Kh.Freidlina, Org.Magnet.Reson., 1977, **9**, 301.
129. V.I.Dostovalova, A.B.Terent'ev, N.S.Ikonnikov, and R.Kh.Freidlina, Org.Magn.Reson., 1983, **21**, 11.
130. A.B.Terent'ev, V.I.Dostovalova, N.S.Ikonnikov, M.A.Moskalenko, and R.Kh.Freidlina, Izv.Akad. Nauk SSSR, Ser.Khim., 1980, 558.
131. A.V.Germash, V.V.Zorin, V.I.Dostovalova, and A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 173.
132. A.B.Terent'ev, M.A.Churilova, V.I.Dostovalova, and V.A.Svoren', Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 1814.
133. A.B.Terent'ev, Yu.P.Chizhov, and P.Brahme, Izv.Akad.Nauk SSSR, Ser.Khim., 1970, 176.
134. D.R.Napier, J.Org.Chem., 1965, **30**, 1305.
135. A.B.Terent'ev, S.N.Aminov, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1965, 2042.
136. P.Kaefer, A.Saus, and B.Dederichs, Z.Naturforsch., 1977, **32b**, 53, 58.
137. A.B.Terent'ev and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 1527.
138. O.N.Petrenko, M.G.Vinogradov, S.P.Verenchikov, A.Ya.Shteinshneider, A.B.Terent'ev, and G.I.Nikishin, Zhur.Org.Khim., 1978, **14**, 1386.
139. V.P.Nayanov, V.V.Zorin, A.B.Terent'ev, S.S.Zlotskii, and D.L.Rakhmankulov, Zhur.Org.Khim., 1976, **12**, 461.
140. C.Huggett, T.R.Walton, and C.R.Midkiff, Polymer Prepr., Amer.Chem.Soc., Div.Polymer Chem., 1964, **5**, 106.
141. M.A.Churilova, A.B.Terent'ev, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 121.
142. M.A.Churilova and A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 2497.
143. N.A.Grigor'ev and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 625.
144. N.S.Ikonnikov, N.I.Lamova, A.B.Terent'ev, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2751.
145. N.S.Ikonnikov, A.B.Terent'ev, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 137.
146. T.A.Onishchenko, B.L.Zhuk, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2297.
147. V.L.Zhuk, T.T.Miftakhov, T.A.Onishchenko, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1976, **226**, 581.
148. R.Kh.Freidlina, T.A.Onishchenko, B.L.Zhuk, and O.A.Eletskaya, Dokl.Akad.Nauk SSSR, 1976, **227**, 108.
149. T.A.Onishchenko, B.L.Zhuk, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 1374.
150. R.Kh.Freidlina, T.A.Onishchenko, and B.L.Zhuk, Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 2250.
151. N.A.Grigor'ev, N.A.Kuz'mina, E.Ts.Chukovskaya, A.L.Tumanskaya, and R.Kh.Freidlina, Izv.Akad. Nauk SSSR, Ser.Khim., 1980, 1333.
152. T.A.Onishchenko, N.P.Plekhanova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1351.
153. N.A.Grigor'ev, L.S.German, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 809.
154. A.N.Nesmeyanov, R.Kh.Freidlina, V.N.Belov, and Sh.A.Karapetyan, USSR P.113687 (1956); Byul. Izobret., 1958, (6), 26.
155. A.P.Suprun and T.A.Soboleva, USSR P.439493 (1972); Byul.Izobret., 1974, (30), 56.
156. R.Kh.Freidlina, T.T.Vasil'eva, F.K.Velichko, and A.B.Terent'ev, USSR P.545635 (1975); Byul. Izobret., 1977, (5), 89.
157. A.B.Terent'ev, F.K.Velichko, and T.T.Vasil'eva, USSR P.540861 (1975); Byul.Izobret., 1976, (48), 69.
158. N.A.Kuz'mina, Sh.A.Karapetyan, E.Ts.Chukovskaya, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser. Khim., 1979, 1814.
159. E.S.Povolotskaya and L.I.Kheifets, Khim.Prom., 1983, **13** (141).
160. R.Kh.Freidlina, A.B.Terent'ev, Yu.P.Chizov, and N.S.Ikonnikov, USSR P.633854 (1966); Byul. Izobret., 1978, (43), 76.

161. R.Kh.Freidlina, D.I.Povolotskii, A.B.Terent'ev, and V.M.Mikhailov, USSR P.615059 (1975); Byul. Izobret., 1978, (26), 74.
162. R.Kh.Freidlina and A.B.Terent'ev, French P.2091907/74.
163. N.N.Aslanov, K.F.Barysheva, R.Kh.Freidlina, and A.B.Terent'ev, USSR P.392126 (1971); Byul. Izobret., 1973, (32), 60.
164. S.N.Aminov, R.Kh.Freidlina, and A.B.Terent'ev, USSR P.445444 (1972); Byul.Izobret., 1974, (37), 16.
165. V.I.Sokolova and V.A.Rygalov, USSR P.818654 (1979); Byul.Izobret., 1981, (13), 26.
166. N.V.Kruglova and T.N.Skokova, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 867.
167. R.Kh.Freidlina, T.T.Vasil'eva, G.A.Trapeznikova, and B.V.Nelyubin, Dokl.Akad.Nauk SSSR, 1979, **247**, 1429.
168. M.A.Moskalenko and A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2150.
169. M.A.Churilova and A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 1167.
170. N.A.Grigor'ev, L.S.German, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 865.
171. N.A.Grigor'ev, L.S.German, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 918.
172. R.Kh.Freidlina, E.Ts.Chukovskaya, and A.A.Kamyshova, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 1903.
173. T.T.Vasil'eva, V.I.Dostovalova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 2541.

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