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Organometallic Catalysis in Diene and Cyclo-olefin Polymerisation Processes. II. The Metathesis Reaction in Polymer Chemistry

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The development of ideas concerning the mechanism of the metathesis reaction and its employment in polymer chemistry are examined. The possible applications of the metathesis reaction in the synthesis of polymers by the polymerisation of cyclo-olefins and cyclodienes with ring opening and via the degradation of high-molecular-weight rubbers and their modification are discussed.
The bibliography includes 160 references.

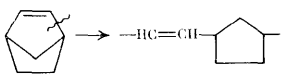
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I. THE MECHANISMS OF REACTIONS INVOLVING RING OPENING IN CYCLO-OLEFINS AND METATHESIS REACTIONS OF OLEFINS

The polymerisation of norbornene under the influence of the $TiCl_4$–$Al(C_7H_{13})_4$ catalytic system with formation of a polymer in which the double bonds of the initial monomer are fully retained was first carried out in 1955–1956.[1-3] Subsequently Natta and other investigators[4-8] demonstrated the possibility of synthesising analogous linear polymers from cyclopentene, cyclo-octadiene, and other cyclo-olefins with the aid of catalytic systems containing tungsten or molybdenum compounds and organoaluminium compounds. The compositions of the above systems resemble those of the Ziegler catalysts for the polymerisation of olefins and dienes.

Truett and co-workers[2,3], who investigated this reaction with respect to norbornene, concluded that the ring opening in the polymerisation of norbornene takes place at the C–C bond adjoining the double bond:



Natta and co-workers, who studied the polymerisation of a series of cyclo-olefins with ring opening, initially adopted an analogous view as to the reaction mechanism[9].

Studies on the redistribution of double bonds in olefins under the influence of catalysts containing molybdenum and tungsten compounds in combination with alkylating agents developed independently and simultaneously. In 1964 Banks and Bailey[10] demonstrated for the first time that, when propene is maintained over MoO_3 or WO_3 on Al_2O_3 at 120 °C and a pressure of 35 atm, small amounts of ethylene and butene are formed. Subsequently many other catalytic homogeneous and heterogeneous catalytic systems, incorporating tungsten, molybdenum, rhenium, or tantalum compounds in combination with alkylating agents (particularly with organoaluminium or organotin compounds) were put forward[11-22]. In homogeneous systems the reaction involving the redistribution of double bonds in many olefins takes place at very high rates without heat changes at normal temperatures[23,24].

In a number of studies[24-26] using ^{14}C-labelled and deuteriated olefins it was shown experimentally that the olefin disproportionation reaction proceeds via the direct rupture of the double bonds. For example, this has been demonstrated[24] for the cometathetical reaction of but-2-ene and perdeuterobut-2-ene:

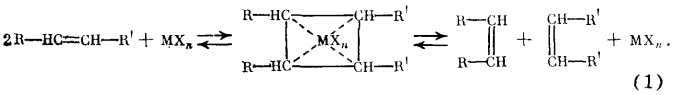
$$CH_3HC{=}CHCH_3 + CD_3DC{=}CDCD_3 \rightleftarrows 2CH_3HC{=}CDCD_3 \quad .$$

On the basis of a study of the composition of the decomposition products of ozonised copolymers of ^{14}C-labelled cyclopentene with cyclo-octene, Dall'Asta and Montroni[27] showed that the polymerisation of cyclo-olefins with ring opening also proceeds with the rupture of the double bonds and that its character is analogous to that of the reaction of olefins under the influence of the same catalytic systems. Subsequently the term "metathesis reactions" was proposed for the reactions of the given type proceeding via a stage involving the dissociation of multiple carbon–carbon bonds.

Reviews have been devoted to various aspects of the metathesis reactions[28-37]. Table 1 presents the compositions of the catalytic system used for the polymerisation of cyclo-olefins.

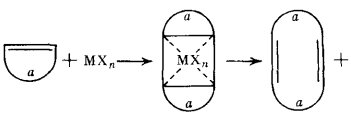
1. Development of Ideas about the Process Mechanism

In order to account for the mechanism of the metathesis reactions of olefins, Bradshaw et al.[38] introduced the concept of an intermediate consisting of a quasi-cyclobutane ring made up of two olefin molecules in which all the carbon atoms are linked by equivalent bonds to the transition metal:



(1)

Scott[39] applied these ideas to ring opening in cyclo-olefins:



(2)

Eqns.(1) and (2) presuppose a stepwise process with formation of oligomeric cyclo-olefin polymerisation products in the initial stages in the latter case. It has been noted[40] that these ideas conflict with the formation of high-molecular-weight products in polymerisation processes, which enabled the authors[40] to put forward certain considerations concerning the chain nature of the process involving carbene complexes.

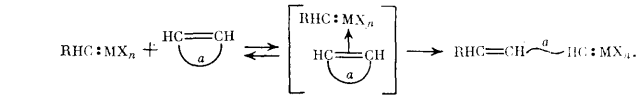
Systematic investigations[41–44] have shown that, even for a low degree of conversion of cyclo-olefins (cyclopentene, norbornene, cyclo-octene, and cyclo-octadiene), high-molecular-weight products are formed. In certain systems the intrinsic viscosity of the polymers formed in the initial stages of the process reached 7–9. These results yielded the unambiguous conclusion that the process has a chain mechanism[40–42,45,100]. As will be shown below, the formation of a small amount of oligomers in certain cases is due to the development of the reverse cyclodegradation process.

Table 1. Catalytic metathesis systems active in the cyclo-olefin ring opening reaction.

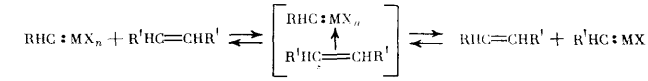
Transition metal compound (A)	Alkylating agent (B)	[A]/[B], mol mol^{-1}	Cyclo-olefin	Refs.
		Heterogeneous systems		
$MoO_3\|Al_2O_3$	$LiAlH_4$	—	Cyclopentene	[11]
$CoO—MoO_3\|Al_2O_3$	—	—	Cyclo-octene	[12, 13]
$Re_2O_7\|Al_2O_3$	—	—	Cyclo-octene, cyclopentene	[14]
		Homogeneous systems		
$TiCl_4$	C_2H_5MgBr	2/1	Norbornene	[1]
$TiCl_4$	$LiAl(C_3H_7)_4$	3/1÷5/1	Norbornene	[3]
$(NH_4)_2IrCl_6$; $RuCl_3$	$SnCl_2$; Zn+CH_3COOH	—	Norbornene derivatives	[17]
$MoCl_5$	$Al(C_2H_5)_3$	2 5/1	Cyclobutene, cyclopentene	[4, 5]
WCl_6	$Al(C_2H_5)_3$	2.5/1	Cyclopentene	[5]
WCl_6	$Al(C_2H_5)Cl_2$	5/1	Cycloheptene,	[6]
WF_6	$Al_2(C_2H_5)_3Cl_3$	7/1÷1/2	Cyclo-octene	[18]
$MoCl_2\cdot 2P(C_6H_5)_3(NO)_2$	$Al(CH_3)Cl_2$	10/1	Cyclopentene	
$WCl_2\cdot 2P(C_6H_5)_3(NO)_2$	$Al_2(CH_3)_3Cl_3$	10/1	Cyclopentene	[19, 20]
$(CO)_5W=C(C_6H_5)_2$	—	—	Cyclo-octene	[21]
$TaCl_5$	$LiCH_2Si(CH_3)_3$	1/1	Cyclo-octene	[16]

The possibility of the initiation of the cyclo-olefin polymerisation reaction by the decomposition products of diazo-compounds arising when the latter interacts with WCl_6 and $MoCl_5$ constitutes direct experimental proof of the carbene nature of the active centres[46,47]. Phenyldiazomethane, diazoacetate, and trimethylsilyldiazomethane, which are decomposed catalytically under the influence of tungsten and molybdenum halides with the liberation of nitrogen and the formation of carbene complexes, were used as the initial diazo-compounds.

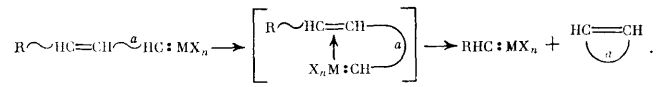
The results obtained served as a basis for the consideration of the reaction mechanism[40,45]. The scheme presented below presupposes the coordination of the monomer to the transition metal attached to a carbene species and its incorporation into the chain with regeneration of the carbene complex:



An analogous mechanism has been proposed for the metathesis of olefins:



Since the polymer chain formed in the polymerisation of cyclo-olefins retains the double bonds, the latter can participate in metathesis reactions. When the growing carbene active centre interacts with a double bond in its own chain, a cyclodegradation reaction, which leads to the formation of cyclic oligomeric molecules, takes place:



The contribution of these reactions in the polymerisation of cyclo-olefins increases as the monomer concentration diminishes, which leads to the formation of oligomers and to the broadening of the molecular weight distribution (MWD) of the polymer. Fig. 1 presents data illustrating the variation of the MWD with the degree of reaction[48].

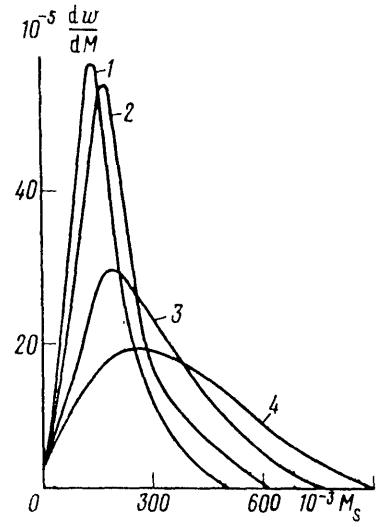


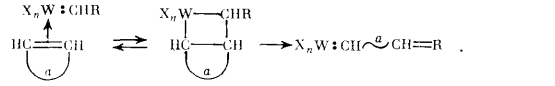
Figure 1. The molecular weight distribution of cyclo-octa-1,5-diene (COD) polymers obtained for different degrees of conversion; [COD] = 0.9 M; [Al]/[W] = 5/1; [COD]/[W] = 800/1; 20 °C in toluene. Degree of conversion (%): 1) 19; 2) 25; 3) 31; 4) 44.[48]

If there is no monomer in the system, then, as will be shown below, the same catalysts induce the cyclodegradation of unsaturated polymers in solution. The idea that the process has a chain mechanism (via stages involving the formation of carbene complexes) was subsequently confirmed by a number of other investigators[49–51] and is at present generally accepted.

On the grounds that metallocyclobutane compounds of the type



initiate the ring opening in cyclo-olefins, the authors of a number of studies suggested that the chain propagation stage can proceed via similar intermediates[49,51,53–56]:

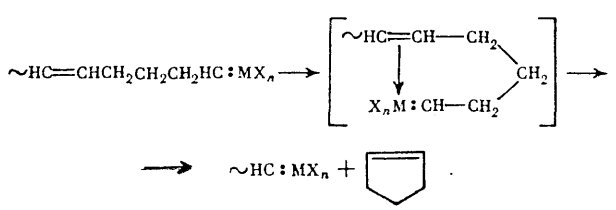


This hypothesis appears to us unlikely, since the rate of chain propagation exceeds by several orders of magnitude the rate of initiation by such organometallic compounds. Furthermore, one should note that the decomposition of compounds of this kind at low temperatures proceeds via carbene formation stages[57].

In a number of studies devoted to the reactions of stable carbene complexes of tantalum and niobium incorporating olefins, the formation of intermediate unstable metallocyclobutane species has been postulated[58,59]. However, the decomposition of these intermediate compounds proceeds via the usual β-elimination pathway and leads to various isomers of linear olefins containing the initial carbene fragment. An extremely striking feature is that the products of the metathetical reaction were not detected in the instances considered[22,58], but in a number of reactions it was possible to isolate a metallocyclopentane complex formed as a result of the cycloaddition of two molecules of the initial olefin to the transition metal compound[60]. Similar metallocyclopentane complexes had been considered earlier as intermediates in the metathesis reaction[61], but in subsequent studies by Grubbs and co-workers[62] and Schrock and co-workers[63,64] it was shown that the cyclopentane derivatives of tantalum and niobium are effective catalysts of the selective dimerisation of various olefins and show no activity in the metathesis reaction.

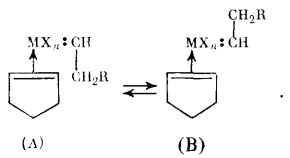
The polymerisation of cyclo-olefins under the influence of metathesis catalysts is a reverisble process which in the case of cyclopentene leads to a polymer–monomer equilibrium, while in the case of other cyclo-olefins a polymer–oligomers equilibrium obtains. The position of equilibrium in a polymerisation reaction for *trans*- and *cis*-polypentenamers is characterised by the data in Fig. 2.[65,66]

For the *cis*-conformation of the units of the polypentenamer, the equilibrium content of the monomer in solution is significantly higher than for the *trans*-polypentenamer, which is apparently due to the greater steric mobility of the coordination of the active centre to the double bond of the neighbouring unit:



The ratio of the *cis*- and *trans*-units in the cyclo-olefin polymers depends significantly on the nature of the catalytic system and the polymerisation temperature. Table 2 presents data characterising the microstructure of the chain in polypentenamers obtained in the presence of various catalytic systems and at various temperatures.

The initial cyclo-olefins are characterised in most cases by the *cis*-conformation of the units (cyclobutene, cyclopentene, norbornene, cyclo-octadiene, and cyclo-octene); the formation of *trans*-units in the polymer must therefore be associated with isomerisation steps. It has been suggested[69] that the isomerisation may be due to the rotation of the carbene active centre. The energy of rotation about the C : M bond for various carbenes bound in complexes with tantalum compounds is 12–22 kcal mole^{-1}.[70] For systems active in metathesis reactions, these values may be significantly lower. It is most likely that the rotations about the C : M carbene bond are executed at the instant of the coordination of the monomer to the transition metal:



The state (A) leads to the *cis*-unit and the state (B) to the *trans*-unit. The very marked temperature dependence of the ratio of the *cis*- and *trans*-units in the polypentenamer (Table 2) indicates a low activation energy for the *cis*–*trans* rotations of the carbene active centre. A similar temperature dependence, albeit less marked, has been observed also for other cyclo-olefins.

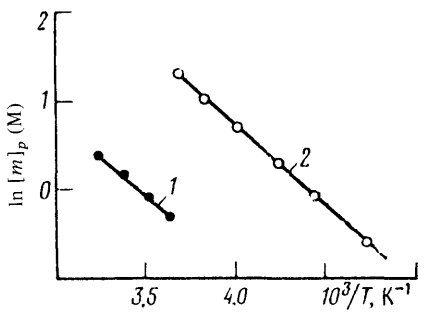


Figure 2. Temperature variation of the equilibrium monomer concentration $[m]_p$ in the cyclopentene–polypentenamer system: 1) *trans*-polypentenamer[65]; 2) *cis*-polypentenamer[66].

Table 2. The influence of temperature and catalyst on the structure of cyclopentene polymers.

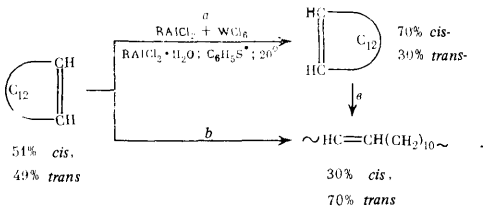
Catalytic system	*t*, °C	Content of units, %		Refs.
		cis-	*trans*-	
WCl_6–C_2H_5OH–$Al(C_2H_5)Cl_2$	+20	20	80	[65]
WCl_6–$(C_2H_5)_2O$–$Sn(C_2H_5)_4$	−30	80	20	[67]
Ditto	0	30	70	[67]
»	+30	18	82	[67]
WCl_6-tetra-allylsilane	−40	100	0	[66]
Ditto	0	76	24	[66]
»	+20	40	60	[66]
$MoCl_5$–$Al(C_2H_5)_3$	+20	100	0	[5]
$MoCl_5$–$(C_4H_9Cl)_2O$–$Sn(C_2H_5)_4$	+20	18	82	[68]
WF_6–$Al(C_2H_5)Cl_2$: Al/W = 1/2	−30	85	15	[18]
Al/W = 7/1	+30	10	90	[18]

In the catalysis of metathesis by systems incorporating tungsten compounds, tungsten atoms in a valence state ranging from zero to 4–5 are apparently involved. An example of the participation of zero-valent tungsten is the initiation of polymerisation under the influence of $(CO)_5W : C(C_6H_5)_2$.[21]

In the usual systems containing $RAlCl_2$ and WCl_6 tungsten is in the (4–5)-valence state[71]. An example of the initiation of metathesis under the influence of Mo^{2+} is provided by the

$MoCl_2.2NO.(C_6H_5)_3P-RAlCl_2$ system[20]. Catalytic systems containing Mo^{4+} are also effective[72]. In the stable Fischer carbenes the valence of the metal is always zero or 1, and the carbene species contain as a rule one or two heteroatoms (O, N, or S) at the carbene carbon atom. These factors and also the presence of stabilising ligands (CO, phosphine groups, etc.) at the metal atoms are responsible for the stability of the carbene complexes. It has been shown[73] in relation to chromium complexes that some of them can be used in metathesis reactions.

Since the rate of chain propagation depends greatly on the nature of the metal and the ligands surrounding it, this is reflected correspondingly also in the chain microstructure; the higher the rate of propagation the smaller the contribution of the *cis–trans* isomerisation of the active centre. The *cis–trans* isomerisation can occur also in the polymer chain under the influence of the components of catalytic systems. Thus it has been shown for cyclododecane containing a non-equilibrium proportion of molecules in the *cis*- and *trans*-conformations that it isomerises under the influence of metathesis catalysts, cationic systems, and C_6H_5S radicals[74]:



Reaction *a*, leading to a state of equilibrium of cyclododecene, is much faster than reaction *b*. The equilibrium content of the *cis*- and *trans*-units, characteristic of linear olefins, is therefore found in the polymer chain obtained at room temperature.

As in all other chain polymerisation processes, in the reactions considered very small amounts of compounds leading to the formation of carbene species more stable than the growing chain species partially or completely inhibit the polymerisation. Thus, in the polymerisation of cyclopentene in the presence of metathesis catalysts, very small amounts of alkyl vinyl ethers, alkyl vinyl sulphides, and trimethylvinylsilane fully inhibit the polymerisation reaction[75–77]:

$$\sim HC{=}CH(CH_2)_3HC:MX_n + H_2C{=}CHXR \rightarrow RXHC:MX_n + \sim HC{=}CH(CH_2)_3HC{=}CH_2\,;$$
$$X = O, S, Si\ .$$

The presence of a heteroatom at the carbene active centre is known to entail the stabilisation of the carbene, which renders energetically unfavourable its participation in the opening of the cyclopentene ring, since it leads to the formation of a more active carbene species. The above considerations are correlated with the finding that the efficiency of the initiation by diazo-compounds decreases in the sequence

$$C_6H_5CHN_2 > RO{-}CO{-}CHN_2 > (CH_3)_3SiCHN_2\ .$$

The compound $\begin{matrix}C_6H_5\\C_6H_5CO\end{matrix}\!\!>\!CN_2$, leading to the formation of the stable carbene $\begin{matrix}C_6H_5\\C_6H_5CO\end{matrix}\!\!>\!C:MX_n$, does not initiate polymerisation[78].

The chain character of the process and the decisive role of the reactivity of the carbene species in its kinetics can be illustrated also in relation to the metathesis of olefins. It has been shown[79–81] that a degenerate metathesis reaction of α-olefins [reaction (3)] is 10^2–10^3 faster than reaction (4):

$$RHC{=}CH_2 + R'HC{=}CD_2 \begin{cases}\rightarrow RHC{=}CD_2 + R'HC{=}CH_2\ , & (3)\\ \rightarrow RHC{=}CHR' + H_2C{=}CD_2\ . & (4)\end{cases}$$

The cause of this phenomenon has been explained[58,82]. Pathway (3) occurs as a result of the alternate exchange of the secondary carbene complexes with similar reactivities:

$$R'HC:MX_n \rightarrow RHC:MX_n \rightarrow R'HC:MX_n \text{ etc.}$$

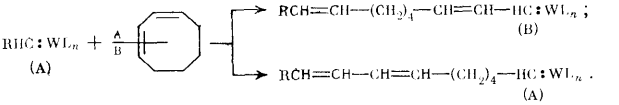
Reaction (4) can proceed only via consecutive stages involving the formation of secondary and primary carbene complexes:

$$\underline{R'HC:MX_n} \uparrow\downarrow \underline{RHC:MX_n} \uparrow\downarrow \underline{R'HC:MX_n} \text{ etc.}$$
($H_2C:MX_n$ above the first junction; $D_2C:MX_n$ above the second junction)

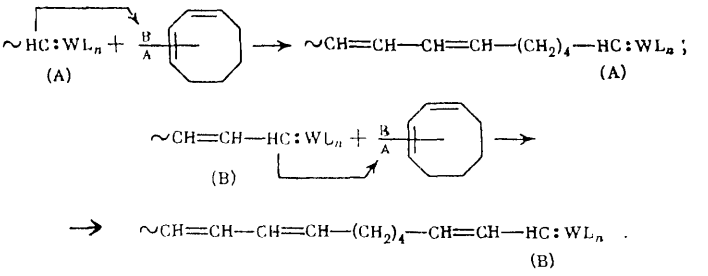
Under the conditions of the chain process, in which the length of the kinetic chain reaches 10^5–10^7, even small differences between the reactivities of the primary and secondary carbene complexes lead to a marked retardation of the reaction. These features are fully analogous to those of the free radical reactions of olefins.

An interesting case of the involvement of conjugated dienes in a metathesis reaction has been investigated[83]. It was shown that cyclo-octa-1,3-diene polymerises in the presence of the $Cl_4W[OCH(CH_2Cl)_2]_2-Al(C_2H_5)_2Cl$–dibutyl ether systems; up to a degree of conversion of the monomer of 30%, the process occurred with formation of a high-molecular-weight soluble polymer. The fairly high effectiveness of cyclo-octa-1,3-diene in the polymerisation reaction is apparently due to the displacement of the double bonds in its molecule from coplanarity[84]. The polymer obtained contained conjugated diene groups, which, in contrast to the initial monomer, readily underwent the Diels–Alder reaction, forming reactive adducts.

In contrast to cyclo-olefins and non-conjugated cyclodienes, in the polymerisation of cyclo-octa-1,3-diene there is a possibility of the formation of two different types of carbene centres differing in their reactivities[83]:

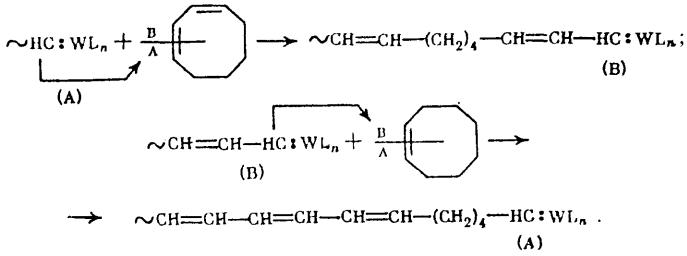


The "head-to-tail" chain propagation should involve the formation of a polymer containing regularly alternating diene sequences. In this case, after each addition of an alternate cyclo-octa-1,3-diene molecule, an active centre of the same type is regenerated (A or B):



However, the presence of triene and isolated –C=C– bonds in the cyclo-octa-1,3-diene polymers together with diene bonds indicates the occurrence of interconversions of the non-conjugated carbene centre (A) and the carbene centre

(B) conjugated with a double bond:



The conversion of the non-conjugated carbene centre into the more stable conjugated centre, (A) → (B), is energetically more favourable, which leads to the preferential formation of diene sequences in the polymer.

The molecular weight characteristics and the MWD of cyclo-octa-1,3-diene polymers have been investigated[48] and it has been shown that, up to a degree of polymerisation of 35%, the molecular weight of the polyoctadienamer increases linearly with the degree of conversion, which is consistent with the mechanism of the propagation of "live" chains. Fig.1 shows that the polymers obtained initially have a narrow molecular weight distribution with a polydispersity coefficient of 1.25 to 1.30. The equality of the polydispersity coefficients found ($\bar{M}_W/\bar{M}_n \cong \bar{M}_Z/\bar{M}_W$) as well as the form of the MWD curves confirm the fact that the cyclo-octa-1,5-diene polymers investigated (polyoctadienamers) have a molecular weight distribution close to the Poisson distribution.

Analogous results have been obtained for polypentenamer specimens obtained in the presence of the $Cl_3Mo(stearate)_2$–$Al(C_2H_5)_2Cl$ system, as shown by Pakuro et al.[86] This demonstrates the occurrence of a polymerisation process without termination in the presence of the systems indicated. It is noteworthy that a very small number of the active centres, in which the carbene species are stabilised by coordination to the transition metal atom, participate in the polymerisation reaction. For a number of other catalytic systems, a broad MWD is observed in the initial stage of the process, which may be associated both with the low rate of the initiation stage[87,88] and with chain termination.

As in the case of typical Ziegler catalysts, chain termination in the metathesis reaction can occur as a consequence of the presence of various admixtures (water, alcohols, etc.) in the reaction systems. However, complete termination of the chain metathesis process is also possible as a result of side reactions leading to the destruction of the carbene species. This applies particularly to reactions involving insertion into the C–H, C–C, and C=C (the formation of cyclopropane groups) bonds, as well as other reactions characteristic of free carbenes.

The unstable carbene complex $(CO)_5W:C(H)(C_6H_5)$ has been obtained[89]; by reacting at the instant of formation with various α- and β-olefins, it gave rise to cyclopropane derivatives in a yield up to 98%. An analogous reaction involving conversion into cyclopropane derivatives has been described for the stable carbene complexes of chromium and iron[90,91]. This reaction is undoubtedly one of the possible variants of chain termination in metathesis, which was first noted by Dolgoplosk et al.[40] On the basis of quantum-chemical calculations for various intermediate states of the carbene complexes of tungsten, molybdenum and chromium, Rappe and Goddard[92] concluded that in the case of chromium this termination pathway is dominant and that this explains the low activity of chromium in metathesis reactions.

2. Generation of Carbene Active Centres in the Decomposition of Organometallic Compounds of Transition Metals

The question of the pathways leading to the formation of carbene active centres initiating the metathesis reaction remained least clear. Since the primary step in metathesis systems always leads to the formation of an organometallic compound, only the decomposition of such a compound can serve as a source of carbenes. Schrock and co-workers[93–95] showed that stable carbene species are formed on decomposition of pentabenzyltantalum and pentaneopentyltantalum:

$$(C_6H_5CH_2)_5Ta \rightarrow (C_6H_5CH_2)_3Ta:CHC_6H_5 ,$$
$$[(CH_3)_3CH_2]_5Ta \rightarrow [(CH_3)_3CH_2]_3Ta:CHC(CH_3)_3 .$$

The ways in which carbene species arise on decomposition at the instant of the formation of various organometallic compounds of transition metals have been investigated in greatest detail by Dolgoplosk and co-workers[97–99,101]. The $(CH_3)_3.SiCH_3Li$–WCl_6 system proved to be effective for the polymerisation of cyclopentene at temperatures down to −78 °C. The reaction of $(CH_3)_3SiCH_2Li$ with tungsten and other transitional metal halides in the absence of a monomer can proceed via the following main pathways:

$$(CH_3)_3SiCH_2MCl_n \rightarrow (CH_3)_3SiCl + H_2C:MCl_{n-1} ; \quad (5)$$

$$[(CH_3)_3SiCH_2]_2MCl_{n-1} \rightarrow (CH_3)_4Si + (CH_3)_3SiHC:MCl_{n-1} ; \quad (6)$$

$$[(CH_3)_3SiCH_2]_2MCl_{n-1} \rightarrow (CH_3)_3Si{-}CH_2CH_2Si{-}(CH_3)_3 + MCl_{n-1} . \quad (7)$$

Reaction (5) leads to the formation of methylene carbene; its contribution can be estimated from the yield of $(CH_3)_3SiCl$. The contribution of reaction (6) can be estimated from the yield of $(CH_3)_4Si$, since it has been shown that the formation of $(CH_3)_3SiCH_2D$ is not observed in the products of the reaction when the latter is carried out in a perdeuteriated solvent. The experimental data are listed in Table 3. These questions have been examined in greatest detail by Dolgoplosk[15].

Table 3. Composition of the products of the interaction of $(CH_3)_3SiCH_2Li$ with MCl_n.

MCl_n	RLi/MCl_n, mol mole^{-1}	Yield, % of theoretical			Overall group balance, %	Refs.
		$(CH_3)_4Si$	$(CH_3)_3SiCl$	R–R*		
WCl_6	1.0	17	31	—	90	[98]
WCl_6	2.0	23	23	—	95	[16]
$MoCl_5$	2.0	31	10	14	86	
$TaCl_5$	0.5	43	10	traces	96	[16]
$TaCl_5$	1.0	35	12	traces	93	[16]
$ReCl_5$	0.5	7	9	81	105	[102]
$ReCl_5$	1.0	20	5	55	100	[102]

*Recombination product.

When metal (W, Mo, Ta, Re, or Nb) halides are used, a considerable number of methylene species, which are the most active in the initiation of metathesis reactions, are formed. The formation of a considerable amount of tetramethylsilane in all cases proves that carbenes of the type $(CH_3)_3SiCH$: play a role; as shown in the decomposition of $(CH_3)_3SiCHN_2$, these carbenes are also involved in the initiation of the metathesis reaction but with a lower efficiency. Twice the amount of the $(CH_3)_4Si$ found, $(CH_3)_3SiCl$, and the groups forming part of the composition of the R–R products enter into the overall group balance.

In the case of the $(CH_3)_3GeCH_2Li$–WCl_6 system, the reaction involving the formation of methylene carbene predominates (up to 50% of the total amount of the groups which have reacted[98]). The decomposition of trideuteromethyl derivatives of tungsten and molybdenum in dibutyl ether proceeds analogously[101]. The main decomposition products are CD_3CD_3, $CD_2{=}CD_2$, and CD_4. The yield of CD_4 is 60 to 70% mole in the case of $MoCl_5$, which shows that the reaction leads to the formation of carbynes:

$$(CD_3)_2MoCl_3 \rightarrow CD_4 + D_2C{:}MoCl_3 \ ;$$
$$(CD_3)_3MoCl_2 \rightarrow 2CD_4 + DC{\vdots}MoCl_2 \ .$$

Carbene, carbyne, and carbide species bound to the metal have been found in the reaction products. For all the metal halides quoted above, the reaction with benzylmagnesium chloride takes place analogously in diethyl ether at 20 °C.[104] The fraction of carbene species can be estimated from the yield of toluene, because, when the reaction was carried out in perdeuterodiethyl ether, the formation of appreciable amounts of $C_6H_5CH_2D$ was not observed:

$$(C_6H_5CH_2)_2MX_n \rightarrow C_6H_5CH_3 + C_6H_5HC{:}MX_n \ ;$$
$$(C_6H_5CH_2)_3MX_{n-1} \rightarrow 2C_6H_5CH_3 + C_6H_5C{\vdots}MX_{n-1} \ .$$

Table 4 presents the compositions of the reaction products.

Table 4. Composition of the products of the interaction of benzylmagnesium chloride with metal halides in ethyl ether at 20 °C.

MCl_n	$RMgCl/MCl_n$, mol mole^{-1}	Yield, % of theoretical				Refs.
		toluene	stilbene	tolane	bibenzyl	
$MoCl_5$	3	14—16	0.8—1.5	0.3—0.7	25—27	[104]
WCl_6	4	17.7	0.5	0	19.1	[103]
$ReCl_5$	3	22—27	1.7—2.0	0	18—20	[103]

Thus the carbene pathway to the decomposition is characteristic not only if the compounds of the metals used in metathesis reactions but also of many other transition metals widely employed in heterogeneous and homogeneous catalysis. In the tetra-allylsilane–WCl_6 system[105,106], recommended for the synthesis of *cis*-polypentenamer by the polymerisation of cyclopentene at −30 °C, the reaction leads to the generation of considerable amounts of propene:

$$(H_2C{=}CHCH_2)_2WCl_4 \rightarrow CH_3HC{=}CH_2 + H_2C{=}CHHC{:}WCl_4 \ .$$

The polymerisation of cyclopentene is apparently initiated by the vinylcarbene complex. The catalytic systems usually consist of alkyl derivatives of aluminium or tin and tungsten and molybdenum halides. It is well known that the alkyl derivatives of transition metals decompose via the β-elimination pathway:

$$(CH_3CH_2)_2MX_n \rightarrow H_2C{=}CH_2 + H_3C{-}CH_3 \ .$$

So far there are no direct ways of investigating the contribution of α-decomposition in the systems indicated, which leads to a formation of carbene active centres. However, experimental studies have shown that α-decomposition also takes place in the systems considered:

$$(CH_3CH_2)_2MX_n \rightarrow H_3C{-}CH_3 + CH_3HC{:}MX_n \ .$$

When the reaction was carried out with WCl_6 and $MoCl_5$ in the presence of trimethylvinylsilane, the formation of appreciable amounts of propene was observed[107,108]. Since the presence of the silicon atom at the carbene active centre greatly stabilises the latter, the chain transfer reaction

$$CH_3HC{:}MX_n + H_2C{=}CHSi(CH_3)_3 \rightarrow (CH_3)_3SiHC{:}MX_n + CH_3HC{=}CH_2$$

becomes energetically favourable.

The data obtained illustrate only qualitatively the α-decomposition reactions, since the carbenes formed in this process largely disappear as a result of side reactions with the solvent and only a small fraction of the carbenes, stabilised as a result of coordination to the transition metal, are involved in polymerisation.

In the analysis of the nature of the transition metal–carbene bond, Rappe and Goddard[92] concluded that it depends significantly on the valence state of the metal. Quantum-chemical calculation has shown that this bond is covalent for transition metal complexes in higher oxidation states and is mainly of the coordinate type (with a low barrier to rotation) for the more reduced forms of the metal, for example in the complex $(C_5H_5)_2TaCH_2(CH)_3$.[22,70]

II. THE DEGRADATION OF POLYMERS UNDER THE INFLUENCE OF METATHESIS CATALYSTS

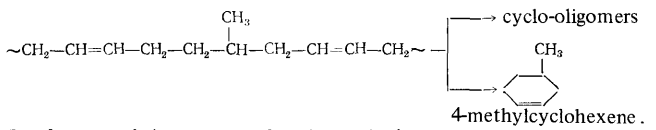
1. Cyclodegradation of Polyalkenamers

It has been shown for the first time in a number of studies[109–111] that *cis*-polybutadiene undergoes rapid degradation in solution under the influence of metathesis catalysts at room temperature. The chain character of this process has been demonstrated[112] by carrying out the reaction in dilute (1%) solution of *cis*-polybutadiene in the presence of minimal amounts of the catalyst. In this case the carbene active centres arise only on individual polymeric molecules and intramolecular chain transfer reactions mainly develop as a consequence of the low polymer concentration. The study of the reaction products demonstrated the constancy of the MWD of the high-molecular-weight polybutadiene in the simultaneous presence in the system of oligomeric products formed on decomposition of the individual polybutadiene molecules. Thus this process, which occurs at room temperature, is of the same chain character as the radical depolymerisation reactions of polystyrene and poly(methylacrylates) at high temperature. In the last two processes the initial monomer is formed preferentially, while the products of metathesis reactions are cyclic oligomers arising as a result of chain transfer with rupture.

In certain cases the degradative cyclisation reaction of polyalkenamers leads to the formation of cyclo-olefins, which has been demonstated for polypentamer[65] and an alternating propene–butadiene copolymer[113]. The degradative cyclisation of polypentamer and the character of the variation of the MWD under the influence of the WCl_6–tetramethyldisilacyclobutane system, active in the metathesis reactions in linear olefins, have been investigated[87,88]. The degradation of polypentamer (72–83% of *trans*-units) was carried out at 20 °C at a polymer concentration below the equilibrium monomer concentration at the given temperature (equal to 0.88 M for the formation of *trans*-polypentamer). Under these conditions, the degradation proceeds with 100% conversion of polypentenamer into cyclopentene:

$$-[-CH_2-CH{=}CH-CH_2-CH_2-]_n- \rightarrow n\square \ .$$

The degradation of the alternating butadiene–propene copolymer under the influence of the $Cl_4W[OCH(CH_2Cl)_2]_2$–$AlC_2H_5Cl_2$ system takes place with formation of cyclo-oligomers, which are subsequently converted into 4-methylcyclohexene (yield above 90%):[113,160]



4-methylcyclohexene.

In the remaining cases the degradation of unsaturated polymers leads to cyclic oligomeric products. The degradative cyclisation of linear *cis*-polybutadiene and *cis*-polyoctadienamer in the presence of tungsten-containing catalysts is accompanied by an appreciable *cis-trans* isomerisation of the double bonds (Table 5).

Table 5. Degradative cyclisation of *cis*-polyalkenamers in solutions at 20 °C.

Catalyst	*c*, wt.%	τ, min	Initial polymer		Oligomers		α, %		Refs.
			$\bar{M}_n$	$[\eta]$, dl g^{-1}	$\bar{M}_n$	$[\eta]$, dl g^{-1}	α^P, %	α^O, %	
Polybutadiene									
WCl_6–$C_2H_5AlCl_2$	4	20	127 000	—	3 400	—	92	—	[109]
Ditto	8	25	220 000	—	9 000	—	92	—	[109]
»	8	30	220 000	—	10 000	—	92	—	[109]
$MoCl_3$(stearate)$_2$–$(C_2H_5)_2AlCl$	10	15	200 000	—	3 680	—	92	92	[108]
Ditto	10	75	200 000	—	1 400	—	92	91	[108]
$WCl_4(OR)_2$–$C_2H_5AlCl_2$	8	20	—	2.5	—	0.24	95	82	[114]
Ditto + Δ	8	40	—	2.5	—	0.17	95	47	[114]
Polyoctadienamer									
$WCl_4(OR)_2$–$C_2H_5AlCl_2$	8	3	—	2.0	—	0.30	85	60	[114]
Ditto	8	30	—	2.0	—	0.24	85	55	[114]
Ditto + Δ	8	68	—	2.0	—	0.20	85	30	[114]
Polyisoprene*									
$WCl_4(OR)_2$–$(C_2H_5)_2AlCl$–anisole	6	12	—	5.9	—	0.95	97	97	[115]
Ditto	6	24	—	5.9	—	0.75	97	97	[115]
»	6	120	—	5.9	—	0.39	97	97	[115]

Notation: *c* is the polymer concentration, α^P and α^O are the contents of *cis*-units in the polymer and oligomer respectively, and Δ is a fresh portion of the catalyst.

*For the polyisoprene degradation processes, the time is given in hours.

The use of the $MoCl_3(stearate)_2$–$(C_2H_5)_2AlCl$ molybdenum-containing systems makes it possible to achieve a far-reaching degradation of *cis*-polybutadiene with retention of the *cis*-configuration of the double bonds in the cyclo-oligomers. After 15–20 min have elapsed from the start of the reaction, the molecular weight of polybutadiene diminishes by a factor of approximately 100 and the system rapidly attains a state close to equilibrium, as shown by the constant molecular weight, i.e. the intrinsic viscosity $[\eta]$, after the addition of a fresh portion of the catalyst. The study of the polydispersity of the cyclo-oligomers obtained indicates a broad MWD of the final product ($\bar{M}_w/\bar{M}_n > 4$).

The degradation of *cis*-polyisoprene in dilute solutions in hydrocarbons proceeds at a considerably lower rate[115]. In view of the high sensitivity of the polymer to cationic reactions, due to the presence of tungsten and alkylaluminium halides, the process is carried out in the presence of an electron donor (anisole, etc.). The $W[OCH(CH_2Cl)_2]_2Cl_4$–$Al(C_2H_5)_2Cl$–anisole metathesis system (with the ratios Al : W : AH=5 : 1 : 5) is extremely stable and remains active for several days. The degradative cyclisation of polyisoprene makes it possible to obtain oligomers with more than 97% of *cis*-units and the theoretical degree of bond unsaturation; $[\eta] = 0.3$, while the initial intrinsic viscosity is $[\eta] = 5.9$ ($\bar{M}_v = 1.07 \times 10^6$).

As already mentioned previously, the degradative cyclisation of polyalkenamers takes place in the polymerisation of cyclo-olefins simultaneously with the chain propagation reaction. It has been shown[113,114] that the decrease of the molecular weight of the polymer during the polymerisation of cyclo-octa-1,5-diene at an initial monomer concentration of 8 wt.% is particularly rapid after the consumption of the monomer. The cyclo-oligomers formed, with $[\eta] = 0.22$, are characterised by a broad MWD ($\bar{M}_w/\bar{M}_n = 4$–5).

It has been established that the concentration of cyclo-oligomers increases with time[116] and that the state of equilibrium depends on the initial concentration of double bonds in the system[114]. The equilibrium concentrations of the cyclo-oligomers of cyclo-octa-1,5-diene and cyclo-octene have been found and their entropies of formation have been determined[117].

Thus the application of metathesis catalysts made it possible to achieve intramolecular cyclisation reactions, which had been previously believed to be characteristic solely of polycondensation processes. Jacobson and Stockmayer[118] were the first to examine theoretically the ring–linear chain equilibrium and pointed out the possibility of obtaining macrocyclic polymers under conditions close to the critical concentration of the solution. Studies of the hydrodynamic properties of solutions of polyoctadienamer relative to linear 1,4-polybutadiene permitted the conclusion that macrorings are present in cyclo-octa-1,5-diene polymers[48]. Scott[154] arrived at an analogous conclusion on the basis of the gel-chromatographic analysis of high-molecular-weight polypentenamer specimens.

2. Degradation of Polyalkenamers in the Presence of Linear Olefins

The cometathesis of polyalkenamers with linear olefins made it possible to achieve a more far reaching degradation process in order to obtain low-molecular-weight linear oligomers.

Low-molecular-weight *cis*-oligomers of isoprene[115] were first obtained by the degradation of high-molecular-weight *cis*-polyisoprene in the presence of the $Cl_4W[OCH(CH_2Cl)_2]_2$–$Al(C_2H_5)_2Cl$–anisole system and linear olefins (Table 6). The formation of oligomers with the most probable molecular weight distribution and a slight loss of unsaturation, due to the presence in the oligomers of residues of C_9–C_{19} olefins in the form of end groups, are characteristic features in this instance.

The products of the degradation of 1,4-polybutadiene in the presence of oct-4-ene and dodec-6-ene under the influence of the WCl_6–$Al(C_2H_5)Cl_2$ catalyst have been investigated chromatographically in a series of studies[119–121] and oligomers having the general formula $R{=}[{=}CH{-}(CH_2)_2{-}CH{=}]_n{=}R$, where R is the residue of a symmetrical olefin and n = 1–4, were obtained. A function for the final molecular weight distribution of the linear products of the cometathesis of

polyalkenamers with olefins was obtained[122] and is one of the variants of the statistical Schultz–Flory distribution.

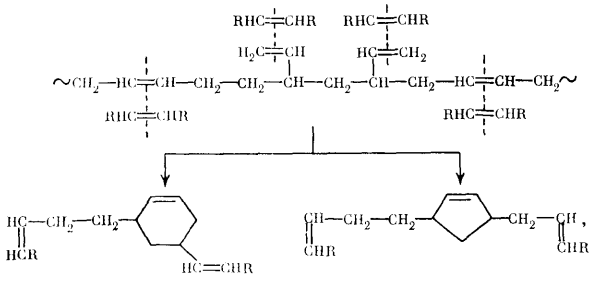
The degradation of modified rubbers[126–128] does not proceed quite so smoothly and the yield of oligomeric products is as a rule low. The cometathesis of partially hydrogenated 1,4-*cis*-polybutadiene (which is a successful model of the ethylene–butadiene copolymer) with oct-4-ene has been carried out in the presence of the WCl_6–$Sn(CH_3)_4$ system[123,124]. Analysis of the composition of the low-molecular-weight products permitted the conclusion that the homogeneous hydrogenation is statistical in character, while in heterogeneous catalytic hydrogenation the formation of block structures was observed.

Table 6. Certain properties of the oligomers obtained by the cometathesis of *cis*-polyisoprene with C_9–C_{12} α-olefins in the presence of the $Cl_4W(OR)_2$–$Al(C_2H_5)_2Cl$–anisole system (Al : W : AH = 5 : 1 : 5, 20 °C).

$[\eta]$*, dl g^{-1}	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Loss of unsaturation *a*, %	Content of units, %		
					cis-	3,4-	*trans*-
0.15	8390	4160	2.01	6	95	3	2
0.16	11 150	5000	2.23	8	96	3	1
0.12	6 200	3100	2.00	7	94	3	3

*Initial viscosity $[\eta]$ = 5.9.

The degradation of cross-linked rubbers in order to elucidate their structure was investigated by Ast and co-workers[123,125] and Hümmel and co-workers[129,130]. Studies of the degradation of a weakly cross-linked 1,4-*cis*-polybutadiene in the prsence of hex-3-ene have been carried out[130] over a wide range of temperatures and component ratios of the WCl_6–$Al(C_2H_5)Cl_2$ catalytic system in order to discover the optimum process conditions. An interesting result has been obtained in a study[131] where the possibility of obtaining mono- and di-substituted cyclopentenes and cyclohexenes by the cometathesis of polybutadienes having a high content of 1,2-units with various olefins has been demonstrated. The reaction takes place in the presence of the catalytic system WCl_6–$Sn(C_2H_5)_4$–$(C_2H_5)_2O$ via the mechanism



and when hex-3-ene is used, but-1-ene, which is a product of the cometathesis of the vinyl groups with the initial olefin, is also formed[132].

III. THE SYNTHESIS OF POLYMERS AND OLIGOMERS BY THE METATHESIS OF CYCLO-OLEFINS

1. Thermodynamics of Ring Opening in Cyclo-olefins

A characteristic features of the polymerisation reactions of the majority of cyclo-olefins under the influence of metathesis catalysts is low enthalpy changes, which makes it possible to carry out the reaction in solutions at high concentrations and in bulk in the monomer. The heat of reaction depends on the strain energy of the initial cyclo-olefin, which is determined by the distortion of the main valence angles of the carbon–carbon bonds and the deformation resulting from the interaction of the atoms non-bonded by valence forces.

Data allowing inferences about the strain energies of the rings in cyclo-olefins have not yet been obtained for all cyclo-olefins. To a certain extent, the heats of hydrogenation of cyclo-olefins reflect the ring strain. It has been shown, for example, that the heats of hydrogenation of *trans*- and *cis*-cyclo-octenes are 134.8 and 98.1 kJ mol^{-1} respectively[133], which indicates a greater ring strain in the *trans*-isomer. The heat of hydrogenation of bicyclo-[2.2.1]hept-2-ene (norbornene) is extremely high and amounts to 138.4 kJ mol^{-1}.[133]

The ring strain energy of C_5 and C_6 cyclo-olefins should be minimal. As a consequence of the low enthalpies of ring opening, the equilibrium for these monomers is markedly displaced towards the monomer. The ΔH_n, ΔS_n^0, and G_n^0 for the polymerisation processes cyclopentene (liq.) → *trans*-polypentenamer (h.e.†)[134] and cyclopentene (liq.) → *cis*-polypentenamer (h.e.)[135] have been determined in a number of studies and the limiting temperatures of these transitions have been estimated (305 and 350 K respectively[135]).

Table 7. Thermodynamic parameters of the polymerisation of cyclo-olefins in bulk (298.15 K; 101.325 kPa).

Monomer	Physical state of monomer and polymer*	$-\Delta H_n$, kJ mole^{-1}	$-\Delta S_n^0$, J mole^{-1}K^{-1}	$-\Delta G_n^0$, J mole^{-1}	Refs.
Cyclopentene**	—	18.4	62.3	—	[65]
Cyclopentene***	—	15.5	67.7	—	[66]
Cyclopentene	liq.; *cis*-h.e.	15.4	51.8	0.27	[134,135]
Cyclopentene	liq.; *trans*-h.e.	18.1	51.8	2.56	[134,135]
Cyclohexene	liq.; *cis*-h.e.		31.0	—6.2	[136]
Cyclohexene	liq.; *trans*-h.e.	—(1—3)	28.0	—7.2	[136]
4-Methylcyclohexene	liq.; liq.	—1.2	49.0	—15.8	[136]
Cyclo-octene	liq.; cryst.	29.8	51.4	14.5	[137]
Cyclo-octene	liq.; h.e.	13.1	—2.9	14.0	[137]
Cyclo-octa-1,5-diene	liq.; h.e.	36.6	29.4	27.8	[137]

*Abbreviations: liq. = liquid, cryst. = crystalline, and h.e. = highly elastic.

**The value for the cyclopentene → *trans*-polypentenamer transition in polymerisation in solution is quoted.

***The value for the cyclopentene → *cis*-polypentenamer transition in polymerisation in solution is quoted.

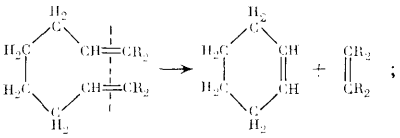
Kulagina[136] and Lebedev[137] determined the thermodynamic parameters of the cyclo-olefin → polyalkenamer transitions for certain other cyclo-olefins: cyclohexene, cyclo-octene,

† Highly elastic (Ed of Translation).

and cyclo-octa-1,5-diene. The enthalpy of polymerisation of the latter monomer has also been determined by Kozina and Cherednichenko[138].

Table 7 presents published standard enthalpies, entropies, and Gibbs free energies for the polymerisation reactions of certain cyclo-olefins. It is seen that the cyclohexene (liq.) → polyhexenamer (h.e.) transition is thermodynamically impossible at room temperature; however, the positive Gibbs free energy $\Delta G_n^0 = +6.2$ kJ mol^{-1} is low and does not rule out in principle the possibility of the opening of the cyclohexene ring by metathesis with formation of a crystalline polymer. The available reports in the literature concerning the attempt at the polymerisation of cyclohexene in the presence of metathesis catalysts show that a polyhexenamer has not yet been obtained.

Treatment of non-conjugated octa-1,7-dienes with metathesis catalysts induces the intramolecular ring closure reaction and leads to the formation of cyclohexene[139-141]:



R = H, D.

It has been shown[142] that this reaction proceeds quantitatively and with a selectivity close to 100%. A non-conjugated cyclic diene, namely cyclohexa-1,4-diene, has been obtained analogously by the metathesis of linoleic and linolenic esters isolated from natural oils[143].

The thermodynamic parameters of the polymerisation of 4-methylcyclohexene with ring opening have been determined[136] and it has been shown that the polymerisation is thermodynamically prohibited in all phase states down to 0 K. Indeed it has been established[160] that the alternating butadiene–propene copolymer is fully degraded to 4-methylcyclohexene under the influence of metathesis catalysts.

The ring strain in cyclo-olefins such as *cis*-cyclo-octene and *cis,cis*-cyclo-octa-1,5-diene (Table 7) is fairly high and the equilibrium monomer concentration is low at the usual temperatures.

2. Synthesis of Cyclo-olefin Polymers and Oligomers

The metathesis reactions of cyclo-olefins make it possible to obtain polymers which could not be synthesised by the methods of polymer chemistry known previously. Among all the cyclo-olefin polymers known at the present time, those of cyclopentene, norbornene, and cyclo-octene have acquired the greatest technical importance.

Polypentenamer, in which the double bonds have predominantly the *trans*-configuration, is obtained by the polymerisation of cyclopentene under the influence of metathesis catalysts based on tungsten compounds, for example WCl_6–$Al(C_2H_5)_3$ [5] and WCl_6–C_2H_5OH–$Al(C_2H_5)Cl_2$ [65] at room temperature. A polymer with a high content of *trans*-units has also been obtained using tungsten hexafluoride in combination with $Al(C_2H_5)Cl_2$.[18] In the polymerisation of cyclopentene in the presence of the WCl_6–$Al(C_2H_5)_3$ system modified by the introduction of benzoyl peroxide, the content of *trans*-units reaches 90%.[144] The melting point of *trans*-polypentenamer (80% of *trans*-units) is close to room temperature; this polymer is capable of undergoing forced crystallisation on extension, which leads to the spontaneous strengthening of rubbers[145,146].

The *cis*-polypentenamer described by Natta et al.[5] was obtained in the presence of the $MoCl_5$–$AlEt_3$ molybdenum-containing catalyst. Later Haas et al.[18] reported the synthesis of a polypentenamer containing up to 85% of *cis*-units, for which tungsten hexafluoride and a polymerisation temperature of −30 °C were employed. An effective system for the catalysis of the *cis*-polymerisation of cyclopentene, proposed by Makovetskii and Red'kina[66], consists of a combination of WCl_6 with tetra-allylsilane and ensures the formation at −30 °C of a polypentenamer containing 98% of *cis*-units. The *cis*-polypentenamer obtained has the lowest glass point $T_g = -114$ °C among polyhydrocarbons and exhibits an extremely low rate of crystallisation at low temperatures (−78 °C).[35,144] This elastomer is one of the most frost-resistant rubbers.

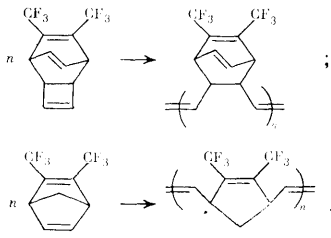
Polynorbornene, the polymer of norbornene, which is the first representative of the group of bicyclo-olefin polymers, has also found a practical application. Oil-filled rubbers (up to 400 wt.%) based on it are manufactured and are used as vibration eliminating materials[85,96]. The polymerisation of this most reactive cyclo-olefin with ring opening can be achieved in the presence of virtually any metathesis catalyst[17,147], including titanium-containing catalytic systems[3]. The polymers obtained, having a mixed *cis*/*trans* configuration (43/57), have an amorphous structure and $T_g = 54$ °C.[148] A *trans*-polyoctenamer, a crystalline polymer with a melting point of 62 °C and containing 90% of *trans*-units[6], has been obtained by the polymerisation of cyclo-octene in the presence of the WCl_6–$Al(C_2H_5)Cl_2$ system. A polyoctenamer with a melting point of 58 °C and containing 65% of *trans*-units has been obtained in the presence of the WCl_6–$Al(iso\text{-}Bu)_2Cl$ system[150]. This polymer can be of interest for the preparation of biodegradable films. Its *cis*-isomer is also promising as regards practical applications[151]. As a consequence of the relatively low content of α-methylene groups at the double bonds, this elastomer is much more resistant to oxidation than rubbers based on butadiene and isoprene. A disadvantage of *cis*-polyoctenamer is a high rate of crystallisation. However, its capacity for crystallisation can be appreciably reduced by the introduction of *trans*-units. Thus polyoctenamers containing approximately 30% of *trans*-units do not crystallise down to −100 °C.[152]

The polymerisation of cyclo-octa-1,5-diene leads to the possibility of obtaining polymers (analogues of 1,4-polybutadiene) without vinyl side groups; however, the formation of oligomeric products in the course of polymerisation[100,149] renders this process unpromising from the practical standpoint.

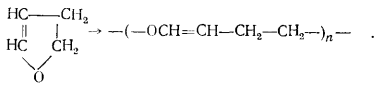
Various rubbers, including non-crystallisable rubbers, can be obtained from cyclo-octa-1,5-diene–cyclo-octene copolymers. These have not undergone a technical development because the above cyclo-olefins are not manufactured in sufficient amounts. The copolymerisation reactions of various cyclo-olefins have been investigated in detail[148,150,153].

The modification of finished rubbers can be achieved by their cometathesis with cyclo-olefins containing functional groups or by the copolymerisation of the usual cyclo-olefins and cyclo-olefins with functional group substituents. Thus the copolymerisation of the *exo*-adduct of cyclopentadiene and maleic anhydride with cyclopentene has been achieved[155] and a polymer containing anhydride groups has been obtained. It is of interest that the *endo*-adduct does not exhibit a catalytic activity in the metathesis reaction.

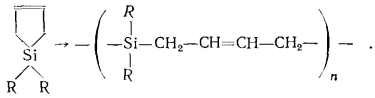
Polymers of fluorine-containing cyclo-olefins have been obtained[156,157]:



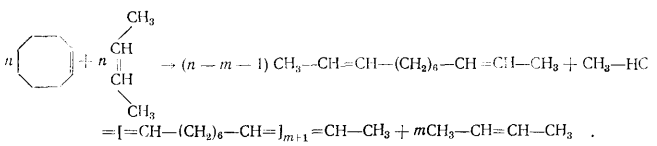
It has been shown[73] that 2,3-dihydrofuran can be polymerised with ring opening in the presence of the stable Fischer carbenechromium complexes $(CO)_5Cr{=}CPh_2$ and $(CO)_5Cr{=}C(OCH_3)Ph$:



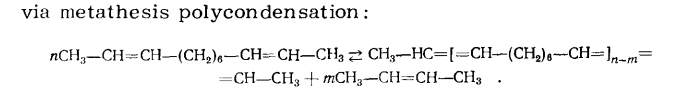
The polymerisation of dialkylsilacyclopentene with ring opening in the presence of metathesis catalysts had been reported even earlier[158]:



The cometathesis of cyclic and linear olefins as well as the degradation reactions of saturated polymers in the presence of linear olefins are reactions of the same type and can be used to synthesise linear unsaturated oligomers. In this case linear olefins are effective chain transferring agents comparable in their reactivity with cyclo-olefins. The cometathesis of cyclopentene and cyclo-octene with *cis*- and *trans*-but-2-enes and *trans*-oct-4-ene under the influence of the WCl_6–tetramethyldisilacyclobutane system in stoichiometric proportions of the olefins has been studied[159]. The cometathesis reaction was completed by the formation of linear oligomers in a quantitative yield. The ratios of the rate constants for reactions involving chain transfer to a linear olefin and the propagation rate constants were 0.16 (cyclo-octene–*trans*-octene), 0.48 (cyclo-octene–*trans*-but-2-ene), and 0.82 (cyclo-octene–*cis*-but-2-ene), which indicates virtually identical reactivities for *cis*-but-2-ene and cyclo-octene. In the latter case mainly the linear dodeca-2,10-diene and a small amount of oligomers are formed for equimolar amounts of cyclo-octene and *cis*-but-2-ene:[115]



The removal of the equilibrium amount of but-2-ene leads to an increase of the molecular weight of linear oligomers via metathesis polycondensation:



This reaction proceeds via stages with a chain mechanism and at the same time has the main features of equilibrium polycondensation. The determination of the equilibrium constant yielded a very low value (1.3×10^{-3}), which indicates an almost complete shift of the equilibrium to the left. Nevertheless, if the low-molecular product (but-2-ene) is carefully removed from the reaction mass, it is possible to obtain oligomers with $\bar{M}_n = 20\,000$.

The synthesis of oligomers of cyclo-octa-1,5-diene and cyclo-octene by their cometathesis with oct-1-ene, propene, pent-1-ene, hex-1-ene, and hept-1-ene has been described[152]. The use of higher C_9–C_{12} α-olefins makes it possible to regulate simultaneously the degree of unsaturation of the oligomers obtained. Thus products whose degree of unsaturation was close to that of plant oils have been obtained in this way from cyclopentene[160].

The cometathesis reactions of polybutadiene and polyisoprene with olefins are undoubtedly of interest as a new method for the synthesis of oligomeric products. The process takes place at room temperature and leads to the formation of low-molecular-weight isoprene *cis*-oligomers and butadiene oligomers with a mixed structure. In contrast to the degradative cyclisation process, in the latter case oligomeric products are characterised by an exponential equilibrium distribution ($\bar{M}_w/\bar{M}_n \cong 2$).[115] The use of metathesis catalysts also leads to the possibility of carrying out the degradation of polybutadiene and polyisoprene gels with transfer of the degradation products to the solution.

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Thus it was shown above that the metathesis reaction proceeds via a chain mechanism under the influence of carbene complexes of transition metals. The carbene species are formed on decomposition of organometallic compounds of transition metals at the instant of their generation. In the presence of metathesis catalysts degradative chain cyclisation of unsaturated polymers takes place at room temperature with formation of a set of cyclic oligomeric molecules having a broad molecular weight distribution. In the presence of olefins the same reactions lead to linear oligomers with the most probable molecular weight distribution. The metathesis reaction is promising from the standpoint of the synthesis of polymeric materials.

REFERENCES

1. A.W.Anderson and N.G.Merklin, US P.2 721 189, 1955; Chem.Abs., 1956, **50**, 3008.
2. W.L.Truett, D.R.Johnson, and J.M.Robinson, "Abstr.of 130th National Meeting Amer.Chem.Soc.", New York, 1956, Vol.19, p.15.
3. W.L.Truett, D.R.Johnson, J.M.Robinson, and G.Montague, J.Amer.Chem.Soc., 1960, **82**, 2337.
4. G.Natta, G.Dall'Asta, G.Mazzanti, and G.Montroni, Makromol.Chem., 1963, **69**, 163.
5. G.Natta, G.Dall'Asta, and G.Mazzanti, Angew.Chem., 1964, **76**, 765.
6. G.Natta, G.Dall'Asta, J.W.Bassi, and G.Carella, Makromol.Chem., 1966, **91**, 87.
7. N.Calderon, E.A.Ofstead, and W.A.Judy, J.Polymer Sci., 1971, A-1, **5**, 2209.
8. T.Saegusa, T.Tsujino, and J.Furukawa, Makromol. Chem., 1964, **78**, 231.
9. G.Natta, G.Dall'Asta, and J.Furukawa, Makromol. Chem., 1965, **81**, 253.
10. R.L.Banks and G.C.Bailey, Ind.Eng.Chem., Prod. Res.Develop., 1964, **3**, 170.
11. H.S.Eleuterio, US P.3 074 918, 1957; Chem.Abs., 1961, **55**, 16 005.

12. D.L.Crain, US P.3 575 947, 1966; Chem.Abs., 1971, **75**, 6607.
13. H.J.Alkema and R.Van Helden, B.P.1 118 517, 1967; Chem.Abs., 1968, **69**, 96 066.
14. L.Turner and C.P.C.Bradshaw, B.P.1 105 565, 1965; Chem.Abs., 1968, **68**, 87 758.
15. B.A.Dolgoplosk, Uspekhi Khim., 1983, **52**, 1086 [Russ. Chem.Rev., 1983(6)].
16. I.L.Kershenbaum, L.N.Grebenyak, I.A.Oreshkin, B.A.Dolgoplosk, and E.I.Tinyakova, Dokl.Akad.Nauk SSSR, 1978, **238**, 359.
17. K.E.Rinehart and N.B.Smith, J.Polymer Sci., 1965, **B3**, 1049.
18. F.Haas, K.Nutzel, G.Pampus, and D.Theisen, Rubber Chem.Technol., 1970, **43**, 1116.
19. E.A.Zuech, US P.3 635 700, 1967.
20. E.A.Zuech, Chem.Comm., 1968, 1182.
21. T.J.Katz, S.J.Lee, and N.Acton, Tetrahedron Letters, 1976, 4247.
22. R.R.Schrock, Acc.Chem.Res., 1978, **12**, 98.
23. N.Calderon, H.Y.Chen, and K.W.Scott, Tetrahedron Letters, 1967, 3327.
24. N.Calderon, E.A.Ofstead, J.P.Ward, W.A.Judy, and K.W.Scott, J.Amer.Chem.Soc., 1968, **90**, 4133.
25. A.Clark and C.Cook, J.Catal., 1969, **15**, 420.
26. J.C.Mol, J.A.Moulijn, and C.Boelhouwer, Chem.Comm., 1968, 633.
27. G.Dall'Asta and G.Montroni, Europ.Polymer J., 1971, **7**, 707.
28. G.C.Bailey, Catal.Rev., 1969, **3**, 67.
29. M.L.Khidekel', A.D.Shebaldova, and I.V.Kalechits, Uspekhi Khim., 1971, **40**, 1416 [Russ.Chem.Rev., 1971(8)].
30. N.Calderon, Acc.Chem.Res., 1972, **5**, 127.
31. R.L.Banks, Top.Curr.Chem., 1972, **25**, 39.
32. W.B.Hughes, Organomet.Chem.Synth., 1972, **1**, 341.
33. J.C.Mol and J.A.Moulijn, Adv.Catal., 1975, **24**, 131.
34. R.J.Haines and G.J.Leigh, Chem.Soc.Rev., 1975, **4**, 155.
35. G.Dall'Asta, Rubber.Chem.Technol., 1974, **47**, 511.
36. T.J.Katz, Adv.Organomet.Chem., 1977, **16**, 283.
37. R.H.Grubbs, "Progress in Inorganic Chemistry, John Wiley, New York, Vol.24, 1978, p.1.
38. C.P.C.Bradshaw, E.J.Howman, and L.Turner, J.Catal., 1967, **7**, 269.
39. R.Scott, Chem.Eng.News, 1968, **46**(17), 54.
40. B.A.Dolgoplosk, K.L.Makovetskii, and E.I.Tinyakova, Dokl.Akad.Nauk SSSR, 1972, **202**, 871.
41. Yu.V.Korshak, L.M.Vardanyan, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1973, **208**, 1138.
42. B.A.Dolgoplosk, K.L.Makovetsky, T.G.Golenko, Yu.V.Korshak, and E.I.Tinyakova, Europ.Polymer J., 1974, **10**, 901.
43. V.M.Kuteinikov, Abstract of Candidate's Thesis in Chemical Sciences, Mendeleev Moscow Institute of Chemical Engineering, Moscow, 1976.
44. Yu.V.Korshak, V.M.Kuteinikov, and B.A.Dolgoplosk, Trudy Moskov.Khim.-Tekhnol.Inst.im.Mendeleeva, 1975, **86**, 117.
45. B.A.Dolgoplosk, K.L.Makovetskii, Yu.V.Korshak, I.A.Oreshkin, E.I.Tinyakova, and V.A.Yakovlev, Vysokomol.Soed., 1977, **19A**, 2464.
46. B.A.Dolgoplosk, T.G.Golenko, K.L.Makovetskii, I.A.Oreshkin, and E.I.Tinyakova, Dokl.Akad.Nauk SSSR, 1974, **216**, 807.
47. T.G.Golenko, B.A.Dolgoplosk, K.L.Makovetskii, and I.Ya.Ostrovskaya, Dokl.Akad.Nauk SSSR, 1975, **220**, 863.
48. L.M.Vardanyan, Yu.V.Korshak, S.A.Pavlova, G.I.Timofeeva, and B.A.Dolgoplosk, Dokl.Akad. Nauk SSSR, 1973, **208**, 1349.
49. J.-L.Herisson and Y.Chauvin, Makromol.Chem., 1971, **141**, 161.
50. R.H.Grubbs, P.L.Burk, and D.D.Carr, J.Amer.Chem. Soc., 1975, **97**, 3265.
51. T.J.Katz and R.Rotchild, J.Amer.Chem.Soc., 1976, **98**, 2519.
52. B.A.Dolgoplosk, Kinetika i Kataliz, 1981, **22**, 807.
53. D.J.Cardin, M.J.Doyle, and M.F.J.Lappert, Chem. Comm., 1972, 927.
54. R.H.Grubbs, D.D.Carr, C.Hoppin, and P.L.Burk, J.Amer.Chem.Soc., 1976, **98**, 3478.
55. T.Y.Katz and J.McGinnis, J.Amer.Chem.Soc., 1975, **97**, 1592.
56. M.T.Mocella, M.A.Busch, and E.L.Muetterties, J.Amer.Chem.Soc., 1976, **98**, 1283.
57. G.J.A.Adam, S.G.Davies, A.F.Keith, M.Ephritikhine, P.F.Todd, and M.L.H.Green, J.Mol.Catal., 1980, **8**, 15.
58. S.J.McLain, C.D.Wood, and R.R.Schrock, J.Amer. Chem.Soc., 1977, **99**, 3519.
59. S.M.Rocklage, J.D.Fellmann, G.A.Rupprecht, L.W.Messerle, and R.R.Schrock, J.Amer.Chem.Soc., 1981, **103**, 1440.
60. S.J.McLain, C.D.Wood, and R.R.Schrock, J.Amer. Chem.Soc., 1979, **101**, 4558.
61. R.H.Grubbs and T.K.Brunk, J.Amer.Chem.Soc., 1972, **94**, 2538.
62. R.H.Grubbs and A.Miyashita, J.Amer.Chem.Soc., 1978, **100**, 7416.
63. S.J.McLain, J.Sancho, and R.R.Schrock, J.Amer. Chem.Soc., 1980, **102**, 5610.
64. J.Holmes and R.R.Schrock, J.Amer.Chem.Soc., 1981, **103**, 4599.
65. E.A.Ofstead and N.Calderon, Makromol.Chem., 1972, **154**, 21.
66. K.L.Makovetskii and L.I.Red'kina, Dokl.Akad.Nauk SSSR, 1976, **231**, 143.
67. G.Pampus and G.Lehenert, Makromol.Chem., 1974, **175**, 2605.
68. G.Lehenert, D.Maetens, and G.Pampus, 1974, **175**, 2617.
69. K.J.Ivin, Pure Appl.Chem., 1980, **52**, 1907.
70. L.J.Guggenberger and R.R.Schrock, J.Amer.Chem. Soc., 1975, **97**, 6578.
71. J.Wang and H.R.Menapace, J.Org.Chem., 1968, **33**, 3794.
72. N.I.Pakuro, A.R.Gantmakher, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1975, **223**, 868.
73. C.T.Thu, T.Bastelberger, and H.Hocker, Makromol. Chem., Rapid Comm., 1981, **2**, 383.
74. L.M.Vardanyan, Yu.V.Korshak, M.P.Teterina, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1972, **207**, 345.
75. I.A.Kop'eva, I.A.Oreshkin, E.I.Tinyakova, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1979, **249**, 374.
76. B.A.Dolgoplosk, I.A.Oreshkin, S.A.Smirnov, I.A.Kop'eva, and E.I.Tinyakova, Europ.Polymer J., 1979, **15**, 237.
77. S.A.Smirnov, I.A.Kop'eva, I.A.Oreshkin, E.I.Tinyakova, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1978, **239**, 392
78. B.A.Dolgoplosk, K.A.Makovetskii, E.I.Tinyakova, T.G.Golenko, and I.A.Oreshkin, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 1084.

79. J.McGinnis, T.J.Katz, and S.Hurwitz, J.Amer.Chem. Soc., 1976, **98**, 605.
80. M.T.Mocella, M.A.Bush, and E.L.Muetterties, J.Amer. Chem.Soc., 1976, **98**, 1283.
81. W.J.Kelly and N.Calderon, J.Macromol.Sci., Chem., 1975, **9**, 911.
82. B.A.Dolgoplosk, E.I.Tinyakova, and V.A.Yakovlev, Dokl.Akad.Nauk SSSR, 1977, **232**, 1075.
83. M.A.Tlenkopachev, E.T.Avdeikina, Yu.V.Korshak, G.N.Bondarenko, B.A.Dolgoplosk, and D.F.Kutepov, Dokl.Akad.Nauk SSSR, 1982, **268**, 133.
84. K.Ziegler and H.Wilms, Annalen, 1950, **567**, 1.
85. Polymer News, 1976, **3**, 90.
86. N.I.Pakuro, E.I.Agapova, A.L.Izyumnikov, A.R.Gantmakher, and B.A.Dolgoplosk, Dokl.Akad. Nauk SSSR, 1976, **230**, 897.
87. Yu.V.Korshak, Al.Al.Berlin, E.R.Badamshina, G.I.Timofeeva, and S.A.Pavlova, Dokl.Akad.Nauk SSSR, 1979, **248**, 372.
88. E.R.Badamshina, G.I.Timofeeva, Yu.V.Korshak, Al.Al.Berlin, V.M.Vdovin, D.F.Kutepov, and S.-S.A.Palova, Vysokomol.Soed., 1982, **24A**, 143.
89. P.Casey and S.W.Polichnowski, J.Amer.Chem.Soc., 1977, **99**, 6097.
90. E.O.Fischer and K.H.Dotz, Chem.Ber., 1970, **103**, 1273.
91. M.Brookhart, M.B.Humphrey, H.J.Kratzer, and G.O.Nelson, J.Amer.Chem.Soc., 1980, **102**, 7802.
92. A.R.Rappe and W.A.Goddard, J.Amer.Chem.Soc., 1982, **104**, 448.
93. R.R.Schrock and G.M.Parshall, Chem.Rev., 1976, **76**, 243.
94. R.R.Schrock, J.Amer.Chem.Soc., 1974, **96**, 6796.
95. R.R.Schrock and J.D.Fellmann, J.Amer.Chem.Soc., 1978, **100**, 3359.
96. C.Stein and A.Marbach, Rev.gen.caoutch.et plast., 1975, **52**, 71.
97. B.A.Dolgoplosk, K.L.Makovetskii, I.A.Oreshkin, E.I.Tinyakova, and V.I.Svergun, Dokl.Akad.Nauk SSSR, 1975, **223**, 1369.
98. I.A.Oreshkin, B.A.Dolgoplosk, E.I.Tinyakova, and K.L.Makovetskii, Dokl.Akad.Nauk SSSR, 1976, **228**, 1351.
99. B.A.Dolgoplosk, I.A.Oreshkin, and K.L.Makovetsky, Organomet.Chem., 1977, **128**, 339.
100. L.M.Vardanyan, Candidate's Thesis in Chemical Sciences, Institute of Petrochemical Synthesis, USSR Academy of Sciences, Moscow, 1973.
101. S.A.Smirnov, I.A.Oreshkin, V.G.Daikin, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1979, **245**, 1400.
102. I.L.Kershenbaum, I.A.Oreshkin, B.A.Dolgoplosk, E.I.Tinyakova, and L.M.Grebenyak, Dokl.Akad.Nauk SSSR, 1981, **256**, 1400.
103. L.S.Cherezova, V.A.Yakovlev, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1981, **258**, 1380.
104. L.S.Cherezova, V.A.Yakovlev, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1980, **254**, 1410.
105. I.A.Oreshkin, L.I.Red'kina, I.L.Kershenbaum, G.M.Chernenko, K.L.Makovetskii, and B.A.Dolgoplosk, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2566.
106. I.A.Oreskin, L.I.Redkina, J.L.Kershenbaum, G.M.Chernenko, K.L.Makovetsky, E.I.Tinyakova, and B.A.Dolgoplosk, Europ.Polymer J., 1977, **13**, 447.
107. S.A.Smirnov, I.A.Kop'eva, I.A.Oreshkin, E.I.Tinyakova, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1978, **239**, 392.
108. N.I.Pakuro, A.G.Gantmakher, and B.A.Dolgoplosk, Vysokomol.Soed., 1978, **20B**, 805.
109. E.N.Kropacheva, B.A.Dolgoplosk, D.E.Sterenzat, and Yu.A.Patrushin, Dokl.Akad.Nauk SSSR, 1970, **195**, 1388.
110. G.Pampus, J.Witte, and M.Hoffmann, Rev.gen.caoutch. et plast., 1970, **47**, 1343.
111. E.N.Kropacheva, D.E.Sterenzat, Yu.A.Patrushin, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1972, **206**, 878.
112. Yu.V.Korshak, M.A.Tlenkopachev, T.I.Timofeeva, S.A.Pavlova, and Yu.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1976, **226**, 1344.
113. Yu.V.Korshak, B.A.Dolgoplosk, and M.A.Tlenkopachev, Rec.Trav.chim., 1977, **96**, M64.
114. M.A.Tlenkopachev, I.A.Kop'eva, N.A.Bychkova Yu.V.Korshak, G.I.Timofeeva, E.I.Tinyakova, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, 1976, **227**, 889.
115. Yu.V.Korshak, M.A.Tlenkopachev, B.A.Dolgoplosk, E.G.Avdeikina, and D.F.Kutepov, J.Mol.Catal., 1982, **15**, 207.
116. J.Witte and M.Hoffmann, Makromol.Chem., 1978, **179**, 641.
117. H.Hocker, L.Reif, W.Reimann, and K.Riebel, Rec. Trav.chim., 1977, **96**, M47.
118. H.Jacobson and W.H.Stockmayer, J.Chem.Phys., 1950, **18**, 1600.
119. K.Hümmel and W.Ast, Makromol.Chem., 1973, **166**, 39.
120. W.Ast and K.Hümmel, Naturwiss., 1970, **57**, 545.
121. D.Wewerka and K.Hümmel, Kolloid.-Z.Z.Polymer, 1976, **254**, 116.
122. K.Hümmel, F.Stelzer, P.Heiling, O.Wedam, and A.Griesser, J.Mol.Catal., 1980, **8**, 253.
123. W.Ast, C.Zott, H.Bosch, and R.Kerber, Rec.Trav. chim., 1977, **96**, M81.
124. W.Ast, C.Zott, and R.Kerber, Makromol.Chem., 1979, **180**, 315.
125. W.Ast, H.Bosch, and R.Kerber, Angew.Makromol. Chem., 1979, **76–77**, 67.
126. K.Hümmel, W.Kathan, I.Kovar, and O.A.Wedam, Kautsch.Gummi, Kunstst., 1977, **30**, 7.
127. K.Hümmel, H.Demel, and D.Wewerka, Makromol. Chem., 1977, **178**, 19.
128. H.Demel and K.Hümmel, Makromol.Chem., 1977, **178**, 1699.
129. K.Hümmel and G.Kaiser, Kolloid.-Z.Z.Polymer, 1964, **197**, 90.
130. V.A.Dürr and K.Hümmel, Kolloid.-Z.Z.Polymer, 1971, **243**, 155.
131. E.Canji and H.Perner, Makromol.Chem., 1979, **180**, 919.
132. E.Canji and H.Perner, Makromol.Chem., 1978, **179**, 567.
133. R.B.Turner and W.R.Meadow, J.Amer.Chem.Soc., 1957, **79**, 4133.
134. B.V.Lebedev, I.B.Rabinovich, V.Ya.Lityagov, Yu.K.Korshak, and V.M.Kuteinikov, Vysokomol.Soed., 1976, **28A**, 2444.
135. B.V.Lebedev, I.B.Rabinovich, and V.Ya.Lityagov, Dokl.Akad.Nauk SSSR, 1977, **237**, 877.
136. T.G.Kulagina, Abstract of Candidate's Thesis in Chemical Sciences, Lobachevskii Gorky State University, Gorky, 1983.
137. B.V.Lebedev, Abstract of Doctoral Thesis in Chemical Sciences, Lomonosov Moscow State University, Moscow, 1978.
138. M.P.Kozina and V.M.Cherednichenko, Termodinam. Org.Soed., Gor'kii, 1978(7), 48.

139. E.A.Zuech, W.B.Hughes, D.Kubicek, and E.T.Kittleman, J.Amer.Chem.Soc., 1970, **92**, 528.
140. W.R.Kroll and G.Doyle, Chem.Comm., 1971, 839.
141. R.H.Grubbs, D.D.Carr, C.Hoppin, and P.L.Burk, J.Amer.Chem.Soc., 1976, **98**, 3478.
142. M.F.Farona and W.S.Greenlee, Chem.Comm., 1975, 759.
143. E.Verkuijlen and C.Boelhouwer, Chem.Comm., 1974, **19**, 793.
144. R.J.Minchak and H.Tucker, Amer.Chem.Soc.Polymer Prepr., 1972, **13**, 885.
145. F.Haas, K.Nützel, G.Pampus, and D.Theisen, Rubber Chem.Technol., 1970, **43**, 1116.
146. G.Kraus and J.T.Gruver, Amer.Chem.Soc.Polymer Prepr., 1972, **13**, 891.
147. T.Oshika and H.Tabuchi, Bull.Chem.Soc.Japan, 1968, **41**, 211.
148. L.M.Vardanyan, Yu.V.Korshak, and B.A.Dolgoplosk, Vysokomol.Soed., 1973, **15B**, 268.
149. V.M.Kuteinikov, Candidate's Thesis in Chemical Sciences, Mendeleev Moscow Institute of Chemical Engineering, Moscow, 1976.
150. L.M.Vardanyan, Yu.V.Korshak, M.A.Markevich, N.A.Nechitailo, M.P.Teterina, and B.A.Dolgoplosk, Vysokomol.Soed., 1974, **16B**, 24.
151. G.Dall'Asta and R.Manetti, Italian P.932 461, 1971.
152. Yu.V.Korshak, B.S.Turov, L.M.Vardanyan, V.A.Efimov, M.A.Tlenkopachev, A.Yu.Koshevnik, and B.A.Dolgoplosk, Vysokomol.Soed., 1980, **22A**, 781.
153. V.M.Kuteinikov, Yu.V.Korshak, and B.A.Dolgoplosk, Vysokomol.Soed., 1976, **18B**, 363.
154. K.W.Scott, Amer.Chem.Soc.Polymer Prepr., 1972, **13**, 874.
155. K.F.Castner and N.Calderon, "Abstr.IV Int.Symp.on Olefin Metathesis, Belfast, 1981".
156. A.B.Alimuniar, J.H.Edwards, K.Harper, and W.I.Feast, "Abstr.IV Int.Symp.on Olefin Metathesis, Belfast, 1981".
157. F.Stelzer, Ch.Grainmann, and K.Hümmel, "Abstr.IV Int.Symp.on Olefin Metathesis, Belfast, 1981".
158. H.Lammens, G.Sartori, J.Siffert, and N.Sprecher, J.Polymer Sci., 1971, **9B**, 341.
159. E.R.Badamshina, M.A.Tlenkopachev, Yu.V.Korshak, and B.A.Dolgoplosk, Vysokomol.Soed., 1981, **23B**, 828.
160. E.R.Badamshina, Abstract of Candidate's Thesis in Chemical Sciences, Mendeleev Moscow Institute of Chemical Engineering, Moscow, 1979.

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