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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

New Aspects of the Ring-Opening Polymerization of Cycloolefins

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To cite this Article Ceașescu, E. , Dimonie, M. , Cornilescu, A. , Chipară, M. , Gheorghiu, M. , Drăguțan, V. , Nicolescu, E. , Popescu, M. , Coca, S. , Bellon, C. , Oprescu, C. and Hubc, G.(1985) 'New Aspects of the Ring-Opening Polymerization of Cycloolefins', *Journal of Macromolecular Science, Part A*, 22: 5, 849 – 876

To link to this Article: DOI: 10.1080/00222338508056640

URL: <http://dx.doi.org/10.1080/00222338508056640>

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New Aspects of the Ring-Opening Polymerization of Cycloolefins

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ABSTRACT

The reaction of cycloolefins with the components of the catalytic system WCl_6 /epichlorohydrin/ $Al(iBu)_3$, active in the ring-opening polymerization of cycloolefins, was investigated in order to get additional information on the mechanism of polymerization. The study led to the following conclusions. 1) Olefin complexation with the transition metal has a decisive influence on active center formation. 2) Trivalent tungsten species resulting from fast reduction of the cycloolefin/transition metal complex by aluminum alkyl or from a slow reduction process of W(VI) in the presence of cycloolefin alone, show a particularly high activity in ring-opening polymerization. 3) In the case of tricomponent systems (e.g., WCl_6 / $Al(iBu)_3$ /epichlorohydrin or WCl_6 / $Al(iBu)_3$ /chloranil), the nature of the third component has a decisive effect on both polymerization kinetics and the molecular weight and structure of the resulting polymer. The data are discussed in the context of a reaction mechanism based on carbene complexes as active centers.

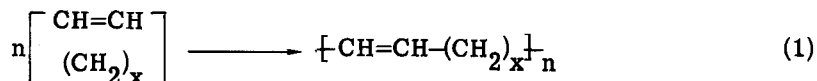
INTRODUCTION

Ring-opening polymerization of cycloolefins was discovered by Eleuterio in 1957 [1], and the field has since had rapid development [2]. Beginning in 1962, Natta and co-workers [3, 4] undertook extensive studies which led to the discovery of a wide range of catalytic systems. The binary catalysts Natta and other investigators developed were based on compounds of several transition metals (usually halides) such as W, Mo, Ta, Nb, Re, Os, Ir, and Ru with an organometallic derivative of Al, Sn, Zn, Li, or Si as the cocatalyst.

Nowadays, the most widely used catalytic systems for the ring-opening polymerization of cycloolefins are the ternary ones subse-

quently discovered [5-10]. Besides the transition metal compound and the organometallic compound, these catalysts contain a third component, including at least one heteroatom such as oxygen, halogen, nitrogen, or phosphorus. The third component essentially increases the polymer yield by controlling catalyst activity and selectivity. Hydroperoxides, alcohols, chlorohydrins, phenols, chlorophenols, epoxides, nitro derivatives, chloroaldehydes, amines, amides, quinones, chloroquinones, etc. have been used.

Ring-opening polymerization of cycloolefins may be formulated according to the following general scheme:



The reaction presents some unusual features which differ from other known polymerization processes: a) the double bond is preserved during ring opening and b) the reaction proceeds under mild conditions.

Until now, ring-opening polymerization has been carried out with a great number of mono- and bicyclic olefins. Except for a few cases (e.g., cyclohexene) the reaction leads to polyalkenamers, some of which (e.g., polypentenamer or polyoctenamer) are elastomers with remarkable properties, while others (e.g., polynorbornene derivatives) behave as plastics.

From known data concerning the ring-opening polymerization of cycloolefins, some general characteristics of the reaction may be inferred. Thus, the nature of the cycloolefin has a drastic influence on the polymerization process. The particular behavior of cycloolefins in this process, according to their structure, requires the use of a rather large range of catalysts. No catalytic system is of general use; even in the case of a specific cycloolefin it is necessary to employ different catalysts in order to obtain the desired molecular weight, structure, and polymer distribution.

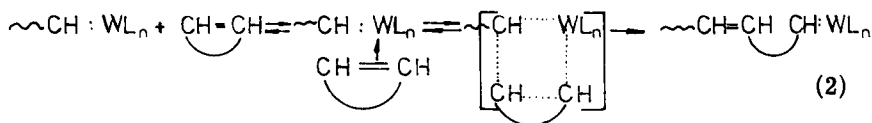
Introduction of substituents in the cycloolefin gives rise to a decrease of its reactivity in ring-opening polymerization. In most cases a severe decrease of the polymerization yield as compared to the unsubstituted analogs is observed. This effect is more pronounced when the cycle is less strained and the substituent is closer to the double bond.

The polyalkenamer structure is affected not only by the catalyst and the nature of the cycloolefin, but also by the temperature and the ratio between the catalytic components. Usually, with increasing reaction temperature a decrease in "cis" structure is obtained [7, 10].

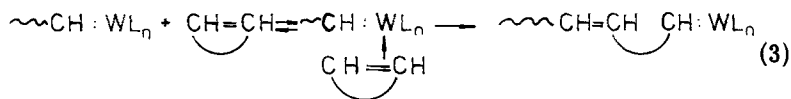
A characteristic feature of ring-opening polymerization is the formation of cyclic oligomers accompanying the high molecular weight polymer. This phenomenon, first studied by Calderon and

Scott [11, 12] and then by Höcker [13-16], was an important contribution to understanding the reaction mechanism. Although it suggested a stepwise metathetic mechanism for ring-opening polymerization, in agreement with the early "quasi-cyclobutane" intermediate postulated for olefin metathesis [17] and with Dall'Asta's ^{13}C -labeled experiments concerning the site of ring scission [18-20], subsequent results on oligomer structure indicated an alternate pathway for this reaction. Furthermore, the formation of high molecular weight polymers from the very beginning of the process could not be explained by a stepwise mechanism.

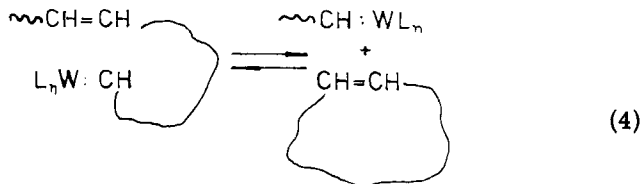
The presently accepted chain "carbene mechanism" proposed by Hérisson and Chauvin [21] and Dolgoplosk [22, 23] seems to explain many aspects of the ring-opening polymerization of cycloolefins. This mechanism assumes that initiation and growth of the process occur via "metallacarbene" species with formation of "metallacyclobutane" intermediates in the transition state:



Dolgoplosk considers that the formation of a metallacyclobutane intermediate is not necessary, the olefin insertion taking place directly into the polymer chain after a previous complexation at the metallacarbene center:



According to this scheme, the active center can react not only with the double bond of the monomer but also with any double bond in the system. Consequently, the cyclic oligomers which accompany the high molecular weight polymer may induce intramolecular reactions of the active center with double bonds in the polymer chain; these processes occur at equilibrium:



Formally, cyclic oligomers are formed in a way similar to that usually encountered in some polycondensation processes.

The wide molecular weight distribution can be described by the following relation based on Stockmayer's law [24]:

$$[M_x] \approx \bar{X}^{-2.5} \quad (5)$$

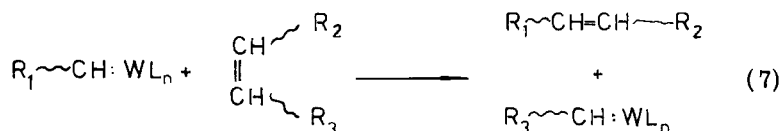
Where $[M_x]$ represents the equilibrium concentration of the species with degree of polymerization x . This behavior is encountered in a large number of examples [15, 16, 18].

In polyalkenamers obtained from lower cycloolefins (e.g., poly-pentenamer), the active center probably attacks the closest neighboring double bond. In these cases polymer growth is accompanied by depropagation, the monomer concentration in the system being unable to decrease below the limit of equilibrium monomer concentration $[M_e]$ given by the thermodynamic parameters of the process:

$$\ln [M_e] = \frac{\Delta H_p}{RT} - \frac{\Delta S_p}{R} \quad (6)$$

The monomer-polymer equilibrium in cyclopentene polymerization depends on the catalyst and polymer structure, and it is strongly shifted toward the monomer when catalytic systems yielding polymers with a "cis" structure are employed. This fact is convincingly shown by the equilibrium values of monomer concentration given in Table 1. The preferential cleavage of monomer units in the "cis" conformation may also be favored by steric factors.

The intermolecular reactions of active centers with the double bonds of the polymer lead to a redistribution of molecular weights whose values are determined by the respective intensities of these processes:



The main arguments supporting the carbene mechanism are:

Metallacarbene compounds of the type $R_1R_2C:M(CO)_5$ (where $R_1 = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$; $R_2 = \text{CH}_3\text{O}, \text{C}_2\text{H}_5\text{O}$; $M = \text{W}, \text{Mo}, \text{Ta}$), alone or in

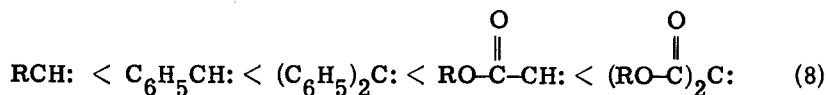
TABLE 1

Catalytic system	$[M_0]$	Reaction temperature, °C	Trans content, %	$[M_e]$	Ref.
$C_2H_5AlCl_2/WCl_6/C_2H_5OH$	2.2	30	70-90	1.199	12
		20		0.88	
		10		0.70	
		0		0.51	
$(CD_3=CH-CH_2)_4Si/WCl_6$	2.3	-20	1-6	2.2	26
		-30		1.61	
		-40		1.16	
		-50		0.83	
		-60		0.55	

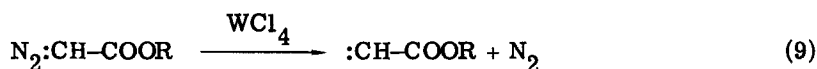
the presence of a Lewis acid, are active in the ring-opening polymerization of cycloolefins [27].

After long contact time between ethylene and metathesis catalysts, cyclopropane or methylcyclopropane are formed. These products are characteristic of the addition of carbenes to a double bond [28].

The conventional carbene generating systems are efficient initiators in the ring-opening polymerization of cycloolefins. Such systems consist, e.g., of a W halide and a diazocompound [27, 28]. The initiating effect decreases with increasing carbene stabilities:



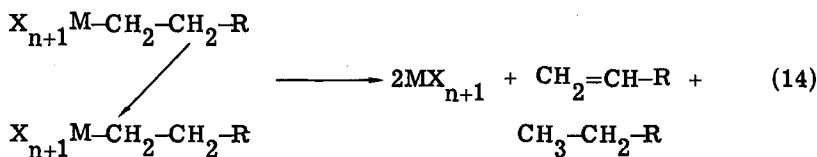
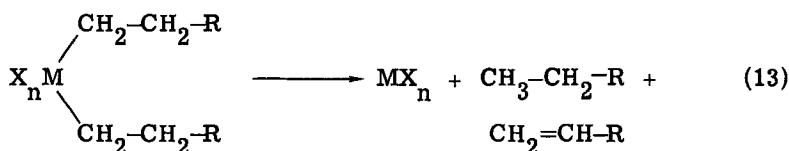
The generation of metallocarbene species is conceived to proceed by a sequence of reactions. For example, in the reaction between WCl_6 and diazoacetic ester (DAE), the reduction of WCl_6 to WCl_4 occurs first, then WCl_4 induces the catalytic decomposition of DAE with the formation of carbene which subsequently complexes to the transition metal.



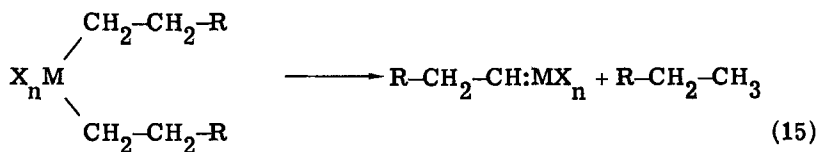
It is known that the most efficient systems for the ring-opening polymerization of cycloolefins are based on transition metal compounds and organometallic compounds [2, 7, 10]. These compounds may easily generate alkyl derivatives of the transition metals. Detailed studies of the decomposition of transition metal alkyl derivatives proved that the reaction does not take place via free radicals as was generally believed earlier [29-31]:

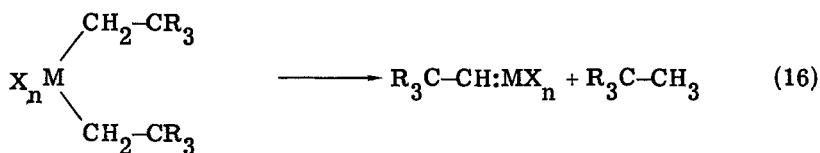


Although the actual mechanism of decomposition is not completely elucidated, the process certainly occurs at the site of the transition metal and probably involves β -elimination reactions [32].



When the transition metals are able to form carbene or carbyne compounds as W, Mo, and Ta do, besides the above-mentioned β -elimination reactions, α -elimination can also take place, leading to complexes assumed to be the active centers in cycloolefin ring-opening polymerization [33-35].





RESULTS AND DISCUSSION

The studies reported in the present work show that formation of active centers in ring-opening polymerization is a complex process, and they indicate that a) the presence of cycloolefin is absolutely necessary in the formation of the active centers, b) the transition metal undergoes a gradual reduction to lower oxidation states under the influence of cycloolefin, c) well-defined bicyclic hydrocarbons form during the interaction of WCl_6 and cycloolefin, and d) the kinetics of cyclopentene polymerization is strongly dependent on the nature of the catalyst components.

On the Order of Reactant Addition

In our experiments on cyclopentene polymerization catalyzed by the $\text{WCl}_6/\text{iBu}_3\text{Al}/\text{ECH}$ (ECH = epichlorohydrin) system in toluene [36], it was unequivocally established that a certain sequence of reactant addition is necessary. This fact assumes previous contact between WCl_6 and cyclopentene followed by the introduction of the organoaluminum compound (Fig. 1). If otherwise, polymerization does not take place. When cyclohexene is used as the reaction medium instead of toluene (under the reaction conditions cyclohexene does not polymerize but can form complexes with WCl_6), the order of reactant addition is not significant; however, the polymerization rate is lower.

The order of reactant addition has a drastic influence in the case of other catalytic systems. Thus, the time evolution of cyclopentene polymerization initiated by WCl_6 and diazoacetic ester usually shows a sigmoidal characteristic curve and exhibits an induction period (Fig. 2). The induction period decreases with an increase of the contact time between cyclopentene and WCl_6 . If the monomer is added to the system after only 5 min of contact between WCl_6 and diazoacetic ester, the reaction does not take place.

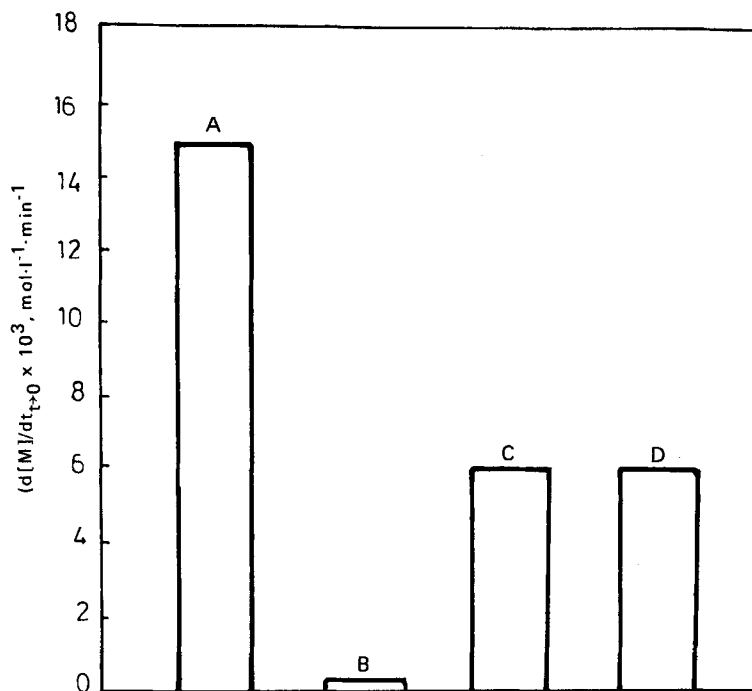


FIG. 1. Influence of sequence of reactant addition upon reaction rate for cyclopentene polymerization. (A) Toluene as solvent; sequence of addition: 1) solvent; 2) WCl_6 ; 3) ECH; 4) CP; 5) iBu_3Al . (B) Toluene as solvent; sequence of addition: 1) solvent; 2) WCl_6 ; 3) ECH; 4) iBu_3Al ; 5) CP. (C) Cyclohexene as solvent; sequence of addition: 1) solvent; 2) WCl_6 ; 3) ECH; 4) CP; 5) iBu_3Al . (D) Cyclohexene as solvent; sequence of addition: 1) solvent; 2) WCl_6 ; 3) ECH; 4) iBu_3Al ; 5) CP (Reaction conditions: CP = 3.43 mol/L; WCl_6 = 1.2×10^{-3} mol/L; temperature = 0°C ; Al/W = 1.3; ECH/ WCl_6 = 2) (CP = cyclopentene; ECH = epichlorohydrin).

ESR and Mass Spectroscopic Measurements on Cycloolefin/ WCl_6 -Based Systems

The interaction between WCl_6 and cycloolefins (cyclopentene, cyclohexene, cyclooctene, cyclododecene) in the presence or ab-

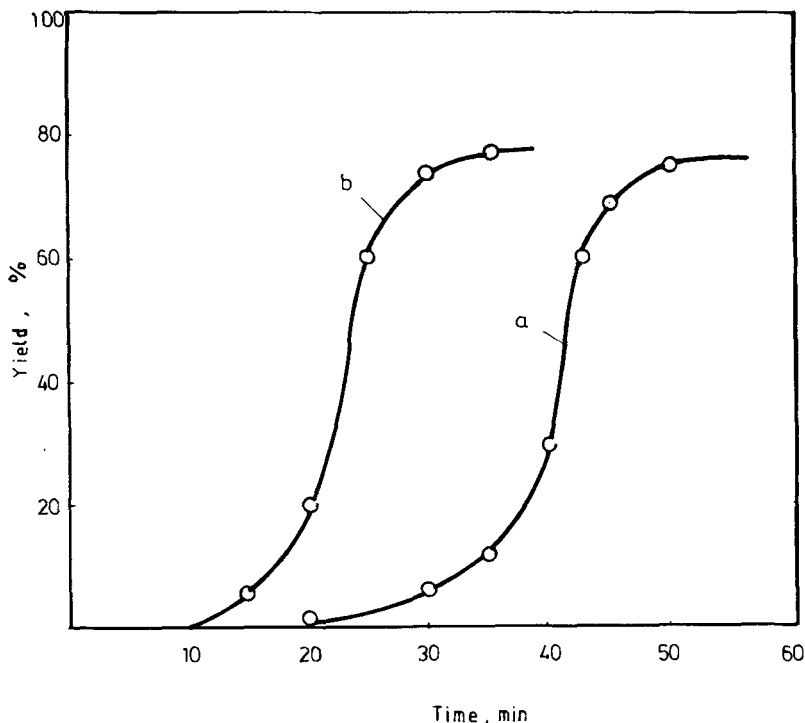


FIG. 2. Effect of premixing time between cycloolefin and WCl_6 on the polymerization reaction (catalyst WCl_6/EDA ; $EDA = N_2CHCOOEt$). (A) Sequence of addition: 1) solvent; 2) WCl_6 ; 3) CP; 4) EDA; (a) premixing time WCl_6 -CP $\tau = 0$; (b) premixing time WCl_6 -CP $\tau = 12$ min. (B) Sequence of addition: 1) solvent; 2) WCl_6 ; 3) EDA; 4) CP; does not polymerize ($\tau = 5$ min). Reaction conditions: Toluene as solvent; CP = 3.43 mol/L; $WCl_6 = 2 \times 10^{-3}$ mol/L; $EDA/WCl_6 = 1$; temperature = $0^\circ C$.

sence of other components of the catalytic system was followed by ESR and mass spectrometry.

Paramagnetic species assigned to W(V) and W(III) were detected by ESR measurements in the liquid phase during interaction of cyclopentene with WCl_6 or WCl_6 -based catalytic system [37]. A strong dependence of ESR signals on the contact time between cyclopentene and WCl_6 was observed (Fig. 3). At contact times between 20 and 200

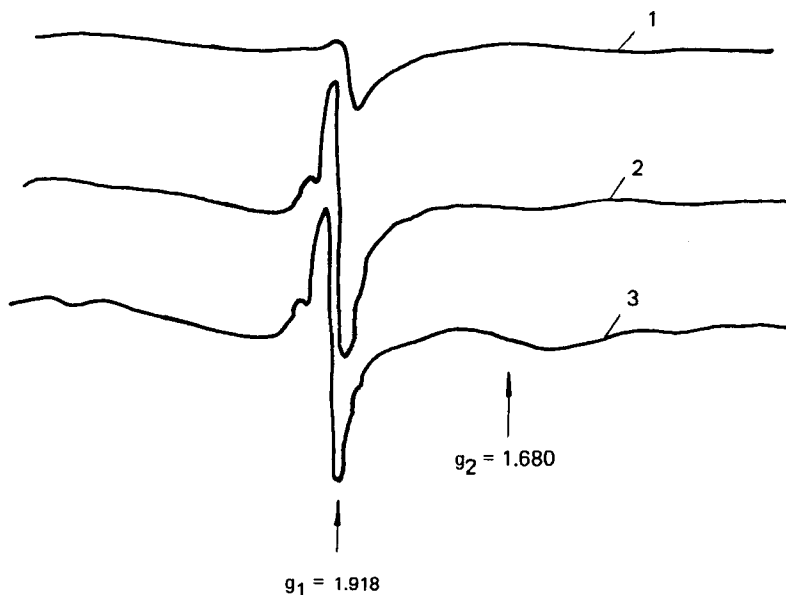


FIG. 3. Time evolution of ESR signals appearing from the interaction between WCl_6 and cyclopentene: (1) $40 \text{ min} < \tau < 100 \text{ min}$; (2) $100 \text{ min} < \tau < 1000 \text{ min}$; (3) $\tau > 4 \times 10^3 \text{ min}$ ($\nu = 9.450 \text{ MHz}$; $3400 \pm 500 \text{ Gs}$).

min, only one resonance line appeared, with a gyromagnetic factor $g_1 = 1.918 \pm 0.004$. This signal is assigned to the W(V) species [38]. (Due to the ^{183}W isotope ($I = 1/2$) having a natural abundance of 14.3%, two weak signals can be observed on both sides of the main line.) The signal intensity varies with the concentration of W(V) according to a sigmoidal curve, the maximum amplitude being reached after 200 min of contact between the reactants (Fig. 4).

After 72 h of interaction between cyclopentene and WCl_6 , a second signal ($g_2 = 1.68 \pm 0.04$) appears whose amplitude increases slowly with time. This signal was assigned to the W(III) species by comparison with the ESR spectrum recorded on a standard aqueous solution containing W^{3+} ions (as determined by ceriometric titration) obtained by deeply reducing Na_2WO_4 with $Zn + HCl$ in argon.

During the interaction between cyclohexene and WCl_6 , the occurrence of paramagnetic species both in the liquid phase and in the precipitate were observed. In the liquid phase a signal at $g_1 = 1.910$ was

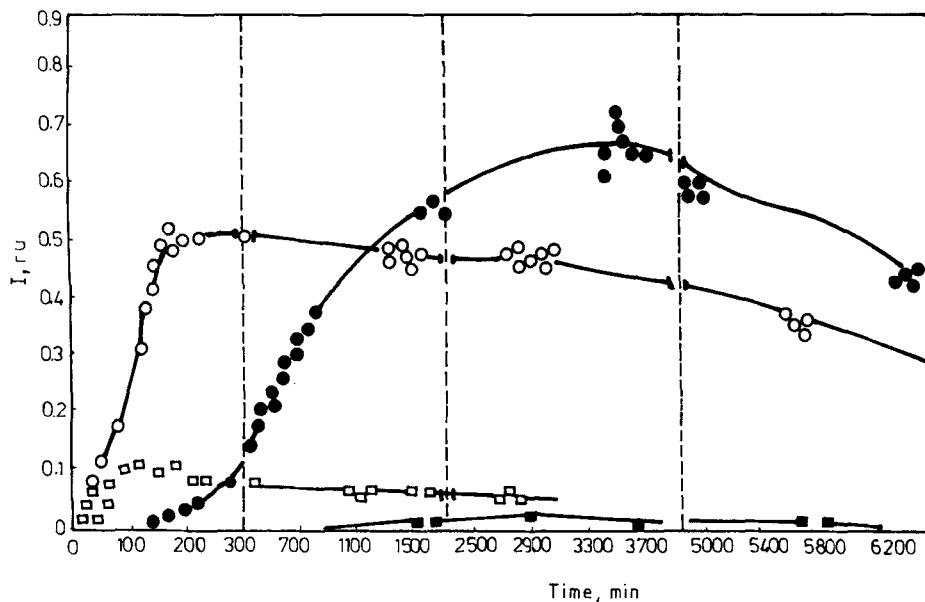
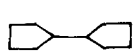


FIG. 4. Time evolution of the amplitude of the ESR signal assigned to the W(V) species appearing during the interaction of cycloolefins with WCl_6 : (○) cyclopentene, (●) cyclohexene, (□) cyclooctene, (■) cyclo-dodecene.

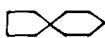
found, whereas in the precipitate this signal and an additional one with $g_2 = 2.102$ were recorded (Fig. 5).

Analysis by mass spectrometry of low molecular weight compounds resulting from the interaction of cycloolefins with WCl_6 showed that well-defined products are formed. The structure of these products substantially varies with the cycloolefin and reaction time [39].

When cyclopentene was contacted with WCl_6 , it was found that at short contact time (under 2 h) 3-chlorocyclopentene (1) was the only reaction product. However, at longer reaction times (more than 24 h), cyclic hydrocarbons were formed in variable amounts: dicyclopentane (2), spiro[4,5]decane (3), decalin (4), and pentylidenecyclopentane (5).



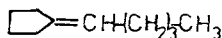
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4



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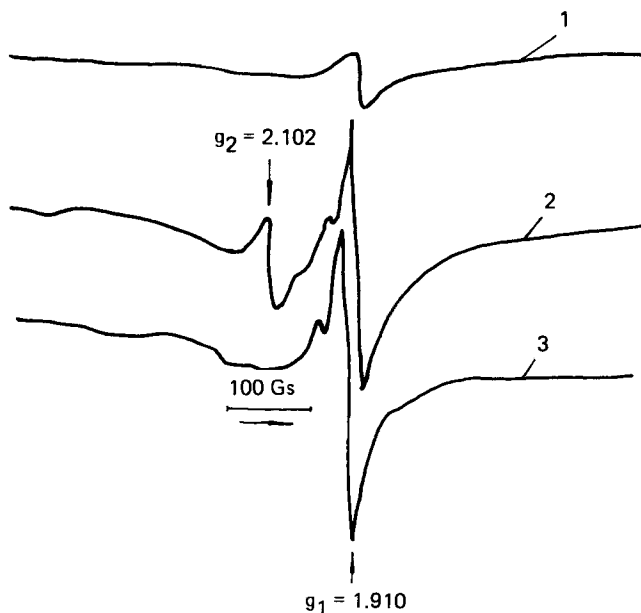
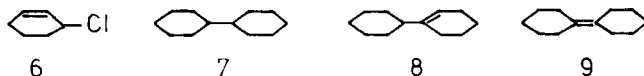


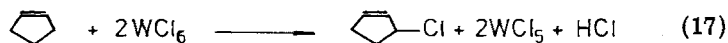
FIG. 5. Time evolution of ESR signals appearing during the interaction between cyclohexene and WCl_6 : 1) $\tau < 200$ min; 2) $\tau > 5 \times 10^3$ min (precipitate); 3) $\tau > 5 \times 10^3$ min (solution); (reaction conditions: cyclohexene = 15 mL; WCl_6 = 0.05 g).

Analogously, in the reaction of cyclohexene with WCl_6 , at a short reaction time (about 1/2 h), 3-chlorocyclohexene (6) was identified. At a longer reaction time (about 10 h), dicyclohexane (7), cyclohexenylcyclohexane (8) and bicyclohexylidene (9) were found along with other unidentified compounds.



In contrast to cyclopentene and cyclohexene, higher cycloolefins behave slightly differently. Thus, after 2 h of interaction between cyclooctene and WCl_6 , 20% of low molecular weight polyoctenamer, as determined by IR spectrum, was obtained. Cyclododecene exhibited an even lower activity toward WCl_6 ; in this case the low molecular weight products could not be identified.

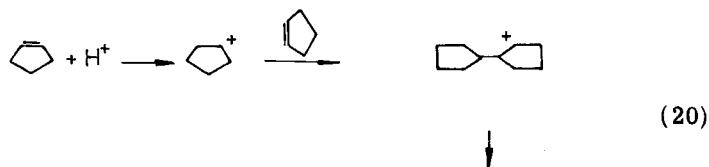
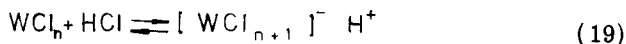
The formation of the above-mentioned products during the interaction of cycloolefins with WCl_6 suggests a rather complex mechanistic scheme. Detection by ESR spectroscopy of the W(V) and W(III) species with parallel identification by mass spectrometry of 3-chlorocycloalkene in an early reaction stage may be rationalized by the following reactions:

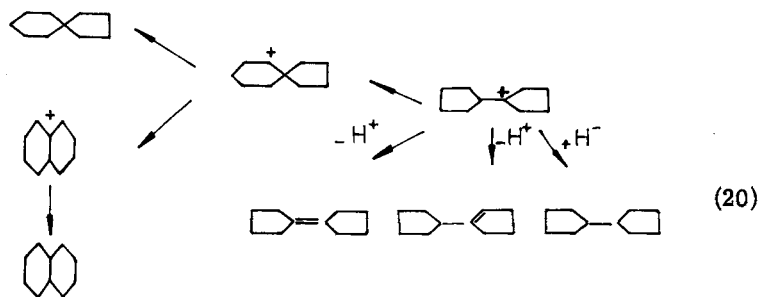


The mechanism is probably homolytic, although an alternate ionic pathway [40] cannot be ruled out. The process progresses through the reduction of the W species to lower valence states. Presumably, the cycloolefin precoordinates to WCl_6 by forming complexes of type (I). Our attempts to characterize such compounds by UV-VIS spectroscopy have failed so far.



On the other hand, formation of various bicyclic structures at longer interaction times between cycloolefins and WCl_6 indicates several cationic sequences including alkylation, isomerizations, Wagner-Meerwein rearrangements, hydrogen abstractions, and proton eliminations. The occurrence of these phenomena seems very likely, taking into account that W halides in their lower valence states may generate a strong Lewis acid in the reaction medium. A mechanism explaining the reaction products is illustrated in the following reaction sequence:





Ring-opening polymerization of cyclopentene in the presence of $WCl_6/iBu_3Al/epichlorohydrin$ was followed by ESR at room temperature in high vacuum (10^{-3} torr). Three distinct signals of different intensities were found (Fig. 6). A first signal with $g_1 = 1.955 \pm 0.005$ and a second one with $g_2 = 1.730 \pm 0.03$ were assigned to the W(V) and W(III) species, respectively. A third signal ($g_3 = 2.018$), having a low amplitude, was associated with a hydrocarbon radical; a similar signal was also reported in the literature [41].

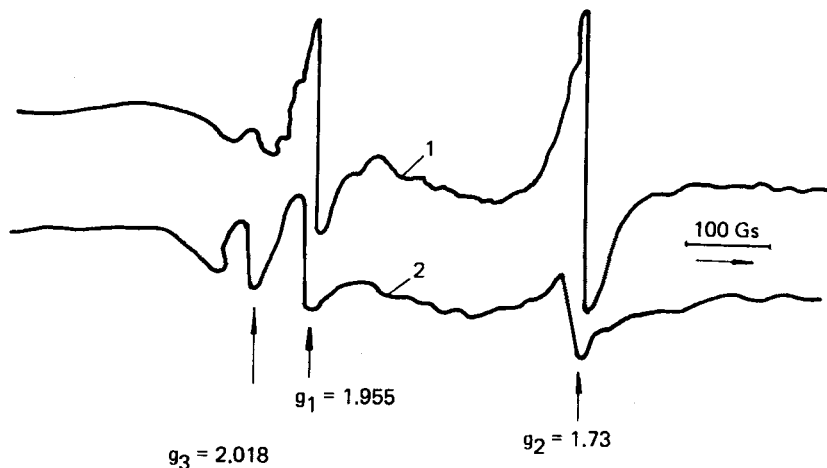


FIG. 6. ESR spectra recorded during cyclopentene polymerization initiated by the $WCl_6/ECH/iBu_3Al$ system: 1) $\tau = 10$ min; 2) $\tau = 40$ min; (reaction conditions: cyclopentene = 15 mL; $WCl_6 = 0.08$ g; $ECH/W = 1/1$; $Al/W = 1.3/1$).

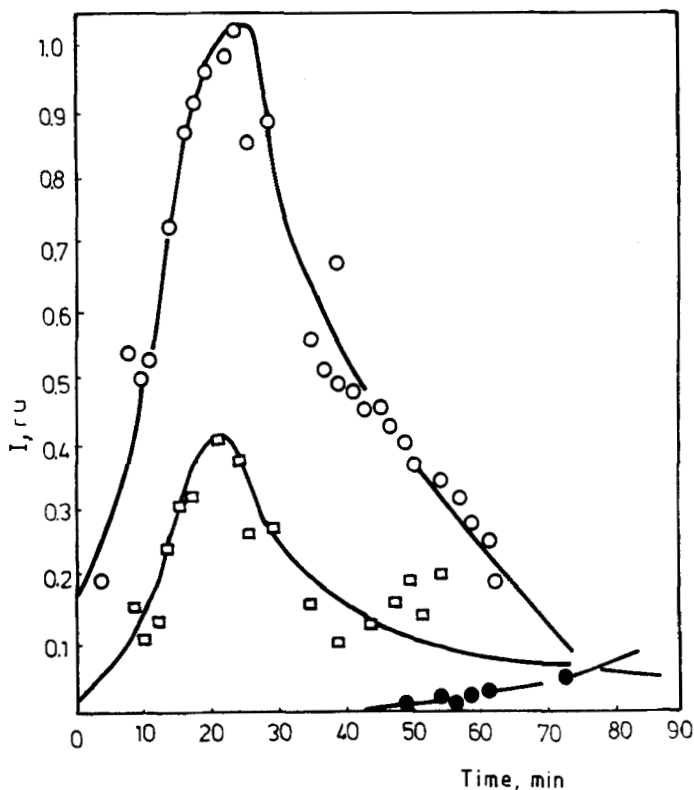


FIG. 7. Time evolution of ESR signals recorded during cyclopentene polymerization initiated by the $WCl_6/ECH/iBu_3Al$ system: cyclopentene = 15 mL; WCl_6 = 0.08 g; ECH/W = 1; iBu_3Al/WCl_6 = 1.3: (○) signal of $g = 1.730$, (□) signal of $g = 1.955$, (●) signal of $g = 2.018$.

Interestingly, the amplitude of the above three signals exhibits a characteristic evolution during the reaction (Fig. 7). The most intense signal, assigned to the $W(III)$ species, decreased substantially during polymer formation, suggesting that this species may be the actual precursor of the active centers. On the other hand, the increase in amplitude of the signal associated with a hydrocarbon radical during regression of the process indicates that this radical is involved in deactivation.

Mass spectroscopic analyses of low molecular weight products resulting from cyclopentene polymerization under the above conditions showed the formation of dicyclopentylidene and benzylidene-tripentenamer along with some unidentified compounds. The absence

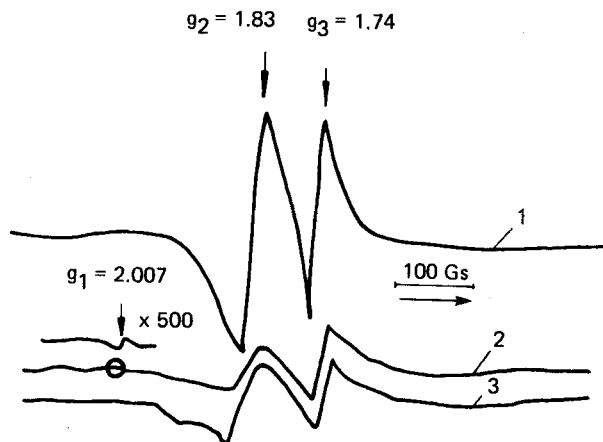
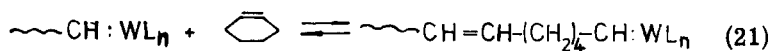


FIG. 8. ESR spectra recorded during the interaction between cyclohexene and the $\text{WCl}_6/\text{ECH}/i\text{Bu}_3\text{Al}$ system: 1) $\tau = 1$ min; 2) $\tau = 15$ min; 3) $\tau = 60$ min; (cyclohexene = 15 mL; $\text{WCl}_6 = 0.08$ g; $\text{ECH}/\text{WCl}_6 = 1$; $i\text{Bu}_3\text{Al}/\text{WCl}_6 = 1.3$).

of 3-chlorocyclopentene demonstrates that the reduction of W halide was brought about by the organoaluminum derivative and not by the cycloolefin.

In contrast to cyclopentene, cyclohexene has a particular behavior in the presence of the catalytic system $\text{WCl}_6/i\text{Bu}_3\text{Al}/\text{epi-chlorohydrin}$. Under these conditions cyclohexene did not polymerize but its ESR spectrum exhibited three characteristic signals with $g_1 = 2.007 \pm 0.001$, $g_2 = 1.830 \pm 0.02$, and $g_3 = 1.740 \pm 0.02$, respectively (Fig. 8). Remarkably, the signal of the g_1 factor, assigned to the W(V) species, was substantially shifted toward higher fields. In addition, the amplitude of all three signals decreases drastically during the first minutes of interaction.

These data suggest another interpretation for the nonpolymerizability of cyclohexene under the above conditions than the presently accepted thermodynamic concept [15]. Thus, if the monomer-polymer equilibrium described by Eq. (21) (shifted to the left) were the actual reason for cyclohexene behavior, then the significant difference between ESR signals for cyclopentene and cyclohexene could not be easily explained.



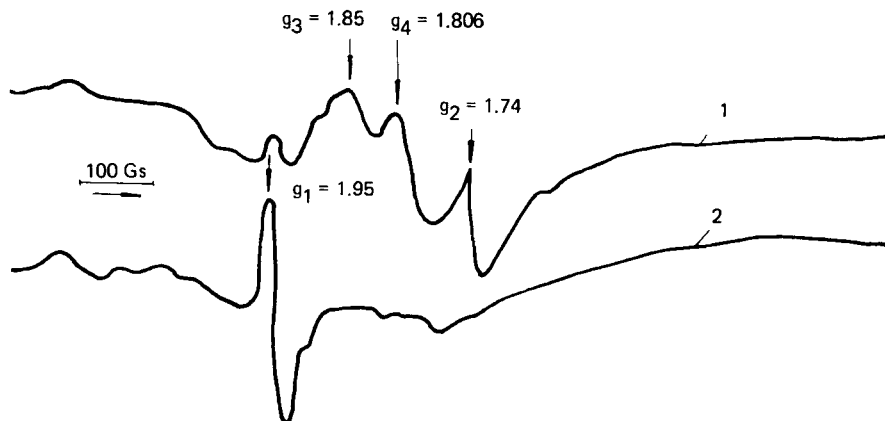


FIG. 9. ESR spectra recorded during the interaction of WCl_6 with iBu_3Al in toluene as solvent in the absence of cycloolefin: 1) $\tau = 5$ min; 2) $\tau = 24$ h ($WCl_6 = 0.08$ g; toluene = 15 mL; Al/W = 1.3; 3400 ± 1000 Gs).

However, these results seem to indicate that in the early stages of interaction with the catalyst, cyclohexene tends to form more stable intermediates that are responsible for the nonpolymerizability of this monomer.

The interaction between WCl_6 and iBu_3Al in toluene but in the absence of cycloolefin was also followed by ESR at room temperature and high vacuum; a multitude of ESR signals was found whose amplitudes varied drastically with time (Fig. 9). The signals with $g_1 = 1.950$ and $g_2 = 1.740$, previously assigned to the W(V) and W(III) species, respectively, were easily identified along with new signals ($g_3 = 1.850$ and $g_4 = 1.806$). Significantly, after 24 h only the signal with $g_1 = 1.950$, whose intensity grows substantially with time, was detectable.

On the Role of Activators in Ring-Opening Polymerization

The important role that activators play on the activity of ring-opening polymerization catalysts has been known for a long time. However, the specific influence of oxygen, water, or UV irradiation, as well as other catalytic components, is not completely understood. We now report some of our results concerning the activating effect

of oxygen, UV irradiation, water, and catalytic components such as epichlorohydrin or chloranil on the ring-opening polymerization of cyclopentene.

Several authors [42, 43] have pointed out the part oxygen plays in the initiation and propagation of cycloolefin ring-opening polymerization. Furthermore, Amass et al. [42] showed that WCl_6 does not initiate the ring-opening polymerization of cyclopentene in the absence of oxygen. However, we observed that cyclopentene can polymerize slowly in the total absence of oxygen (under high vacuum conditions) if the storage time of cycloolefin on WCl_6 is long enough to allow the formation of a high concentration of low valence W species; the induction period was between 7 and 8 days, after which polymerization proceeded gradually. The reaction is considerably accelerated either by admission of air or UV irradiation. Quantitative investigations on these aspects are in progress.

On the other hand, the introduction of small quantities of water in the reaction medium, after contact time between WCl_6 and cyclopentene long enough to yield the W(III) species, leads to rapid polymerization of cycloolefin (Fig. 10). The yield, however, slows down with an increase of the $H_2O:WCl_6$ molar ratio (Fig. 11). Consequently,

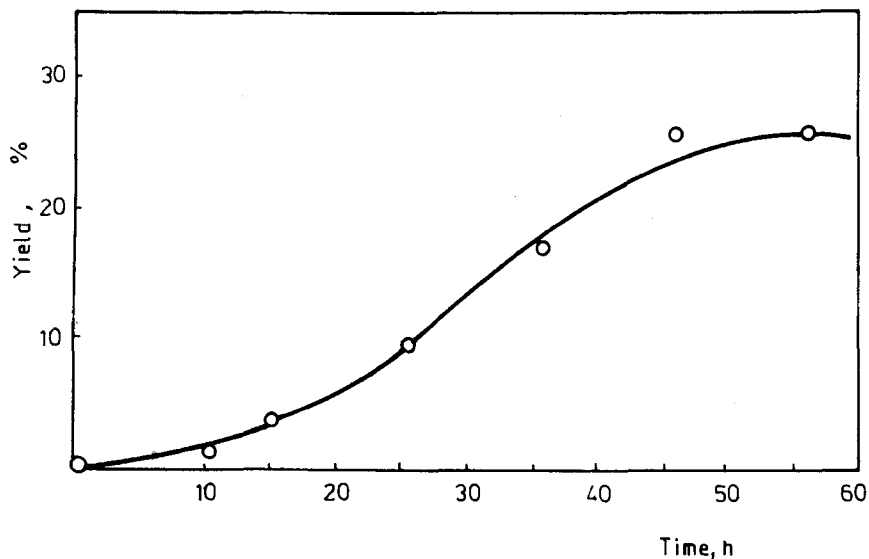


FIG. 10. Dependence of conversion on the premixing time of cyclopentene with WCl_6 in ring-opening polymerization initiated by water.

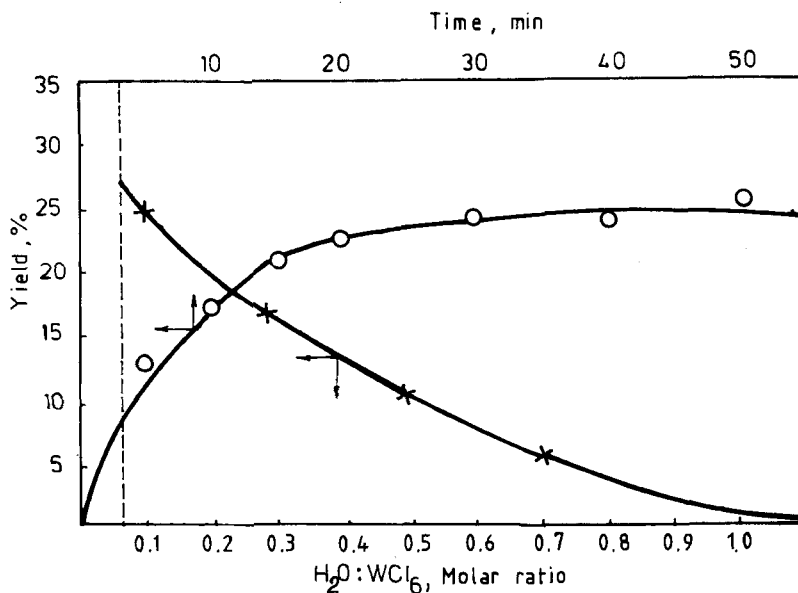
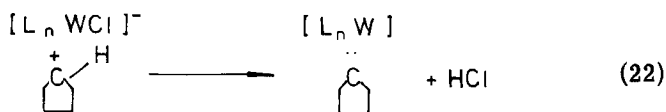


FIG. 11. Influence of $H_2O:W$ ratio on conversion (\times) and the dependence of conversion upon reaction time (\circ). (\times): $WCl_6 = 0.08$ g; cyclopentene = 15 mL; contact time WCl_6 -CP = 52 h. (\circ): $WCl_6 = 0.08$ g; cyclopentene = 15 mL; contact time WCl_6 -CP = 52 h; $H_2O:WCl_6 = 0.1$.

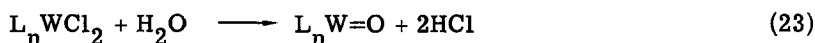
water seems to have a double effect on the WCl_6 /cyclopentene system, i.e., the formation and then the deactivation of the active centers. Assuming that water, if present in certain proportions, acts as a co-catalyst of polymerization reactions, and that in excess it deactivates the active centers, the yield variation with the $H_2O:WCl_6$ molar ratio would follow a Gaussian curve. It is very likely that the region of water concentration studied was situated on the descending branch of the curve. This hypothesis seems to be supported by the fact that only a small fraction of the precursor of the active centers participates in the polymerization reaction, i.e., those existing in the liquid phase as the $W(III)$ species.

It is difficult to establish the real course of initiation under the above-mentioned conditions. However, polyalkenamers formation in the absence of organoaluminum compound indicates that metallacarbene species may arise directly from cyclopentene and a reduced state of W. A possible route may be the generation of a cyclo-

pentylidene tungsten complex from an ion pair via hydrochloride elimination:

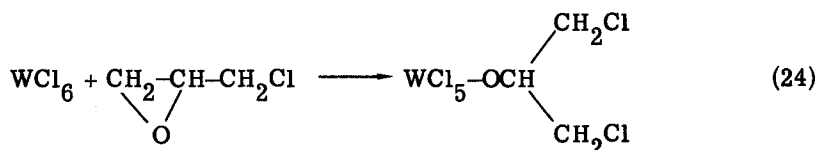


The formation of a cyclopentyl carbocation seems to be favored by the strongly acidic character of the reaction medium containing lower valence states of W while hydrochloride elimination is favored by the presence of water. At the same time, another alternative may be taken into account, i.e., the role of water could be to provide oxygen as a ligand of the reduced W atom able to initiate polymerization:



The kinetic study of cyclopentene polymerization induced by various catalytic systems revealed the drastic influence of the third component on the catalytic activity and molecular weight. Thus, cyclopentene polymerization with WCl_6/iBu_3Al containing a third component is characterized by intense deactivation reactions; the kinetics of the process is complex and consequently the reaction order cannot easily be ascertained (Figs. 12 and 13).

This behavior may be explained by assuming that distinct intermediates arise from the interaction of the third component with the tungsten species during polymerization. Thus, it is known that epichlorohydrin reacts with WCl_6 to give alkoxy tungsten compounds of the following type [7]:



The product resulting from replacing a chlorine in WCl_6 by an alkoxy group is stable in the absence of air and moisture. Epichlorohydrin as a catalytic component leads to a marked decrease of the deactivation reactions, the decay of active centers obeying a second-order process with respect to their concentration [44]. The kinetics of the process is described by the simple laws:

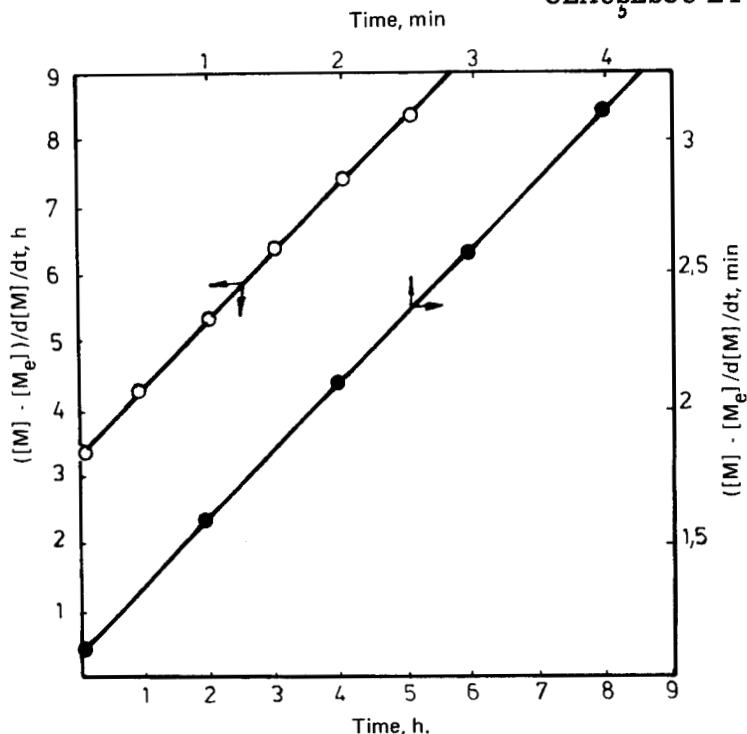


FIG. 12. Plot of $([M] - [M_e]) / d[M] / dt$ against time for cyclopentene polymerization. (\circ) Activator = epichlorohydrin (cyclopentene = 3.43 mol/L; $WC1_6 = 1.2 \times 10^{-3}$ mol/L; $Al/W = 1.3$; epichlorohydrin/W = 1). (\bullet) Activator = chloranil (cyclopentene = 2.3 mol/L; $WC1_6 = 1.2 \times 10^{-3}$ mol/L; $Al/W = 1.3$; chloranil/W = 1).

$$\ln \left\{ \frac{[M_0] - [M_e]}{[M] - [M_e]} \right\} = \frac{k_{pr}}{k_t} \ln (1 + k_t [C^*] t) \quad (25)$$

$$\frac{[M] - [M_e]}{d[M] / dt} = \frac{1}{k_{pr} [C_0]} + \frac{k_t}{k_{pr}} t \quad (26)$$

in agreement with experimental data.

It is obvious that the substitution of the $OCH(CH_2Cl)_2$ group for chlorine in $WC1_6$ is accompanied by a very significant change in the W compound activity. At longer contact time between $Cl_5WOCH(CH_2-$

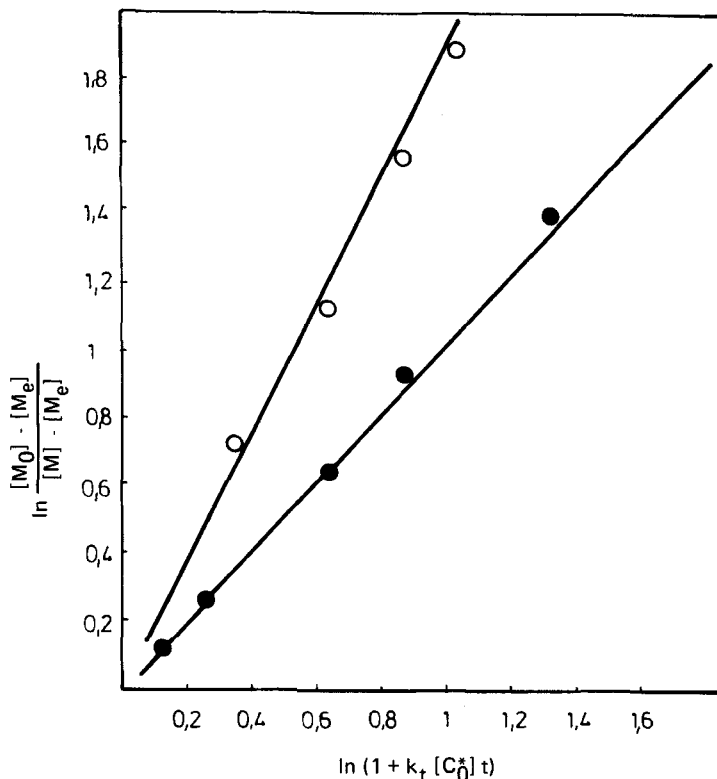
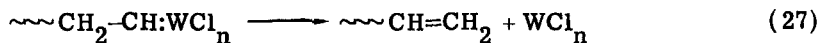
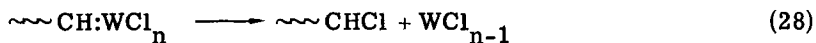


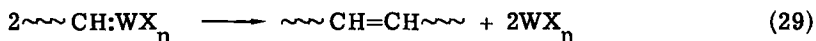
FIG. 13. Plot of $\ln \left\{ \frac{[M_0] - [M_e]}{[M] - [M_e]} \right\}$ against $\ln (1 + k_t [C_0^*] t)$ for cyclopentene polymerization. (○) Activator = epichlorohydrin (cyclopentene = 3.43 mol/L; $WCl_6 = 1.2 \times 10^{-3}$ mol/L; Al/W = 1.3; epichlorohydrin/W = 1). (●) Activator = chloranil (cyclopentene = 2.3 mol/L; $WCl_6 = 1.2 \times 10^{-3}$ mol/L; Al/W = 1.3; chloranil/W = 1).

Cl_2 and cyclopentene, the reduction is suppressed and the lower molecular weight compounds resulting from cationic isomerization cannot be identified in the reaction medium. The termination reaction may proceed by a monomolecular process [45].





This is not the only possible termination route. Our data suggest that in cyclopentene polymerization with $\text{WCl}_6/\text{iBu}_3\text{Al}$ systems, both first- and second-order termination reactions occur, proceeding at the same time. Thus, the introduction of $\text{OCH}(\text{CH}_2\text{Cl})_2$ as a ligand probably has the effect of strongly diminishing the unimolecular reaction (Eq. 27) and favoring the following bimolecular process:



In contrast to epichlorohydrin, the introduction of chloranil as an activator of the system $\text{WCl}_6/\text{iBu}_3\text{Al}$ leads to a sharp increase of the polymerization rate without conferring stability to the active centers; the decay of the active centers is faster in this case and proceeds via a second-order reaction. Within experimental errors, the deactivation of the reaction centers follows second-order kinetics, as in the case of epichlorohydrin as activator (Table 2).

When comparing the initial molecular weight of polypentenamer with the $1/k_{\text{pr}}[\text{C}_o^*]$ and k_{pr}/k_t ratios, it may be concluded that: a)

the drastic increase of the reaction rate when chloranil is used as activator is due to a larger propagation rate constant, and this increase is not related with the concentration of the active centers; and b) the comparable values of the k_{pr}/k_t ratios indicate that the increase in activity of the systems containing chloranil is accompanied by an enhancement of termination processes via bimolecular reactions. Remarkably, in all cases the initial high molecular weight of the polymer rapidly decreases with time (Fig. 14).

From the above results it may be inferred that epichlorohydrin and chloranil are activators operating in different ways in cyclopent-

TABLE 2

Activator	1	k_t	$M_n \times 10^5$
	$k_{\text{pr}}[\text{C}_o^*]$	$\frac{k_{\text{pr}}}{k_t}$	
Epichlorohydrin	198	1	4.5
Chloranil	1.1	0.5	8.4

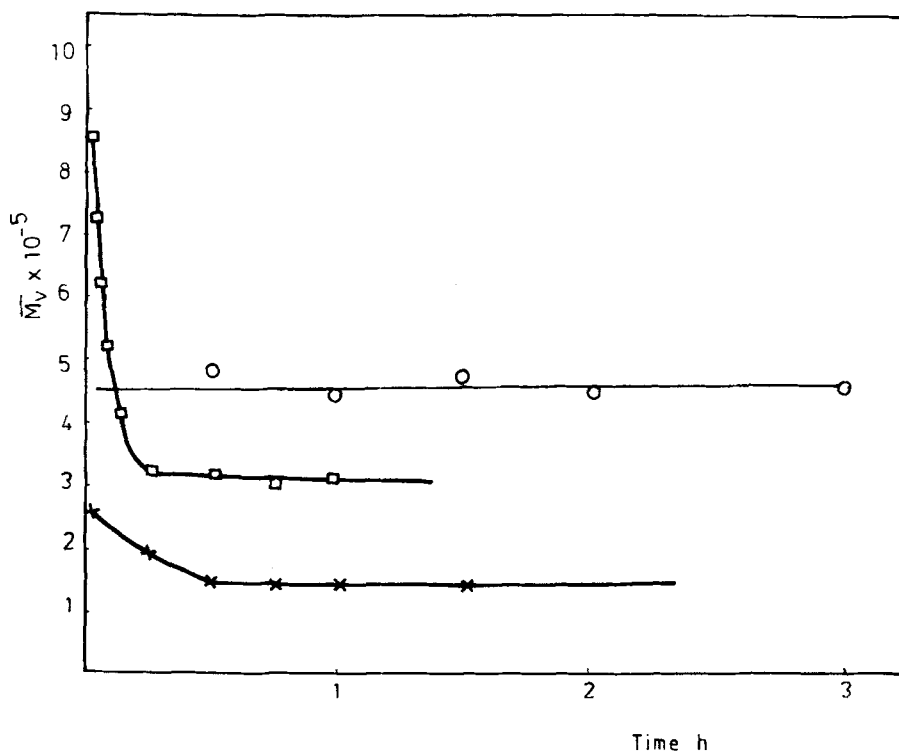


FIG. 14. Effect of the nature of the activator on the time course of poly(pentenamer) molecular mass (catalyst: WCl_6/iBu_3Al): (x) without activator; (o) activator epichlorohydrin; (•) activator chloranil (reaction conditions as in Fig. 13).

tene ring-opening polymerization; while the former conveys stability to the active centers, the latter enhances their activity. The reaction between WCl_6 and chloranil has not yet been studied in detail, but it is known that transition metal compounds give π -complexes with such quinones. The stability of these complexes depends both on the metal and its ligands and the quinone. We observed that the interaction product between WCl_6 and chloranil using cyclohexene as the solvent is totally inactive in polymerization (even after 24 h storage). Presumably, chloranil, due to its acceptor propensity, leads to a pronounced decrease of electron density at the transition metal, thus favoring complexation of the cycloolefin. At the same time, for catalytic systems containing chloranil, the increase of complexing

between the active centers and the double bond of the polymeric chain occurs simultaneously with the increase of the intra- and intermolecular scission processes. Consequently, a drop in molecular weight is to be expected as observed experimentally.

CONCLUSIONS

Our results for the ring-opening polymerization of cycloolefins with WCl_6 -based systems strongly suggest that the cycloolefins play an important role in controlling the reduction of WCl_6 to lower valence states. From ESR measurements it is inferred that the $W(III)$ paramagnetic species are the actual precursors of active centers.

Mass spectroscopic data reveal the formation of well-defined cyclic hydrocarbons during the interaction of cycloolefins with WCl_6 , evidencing the presence of a strong Lewis acid in the reaction medium.

Initiation of ring-opening polymerization in the absence of organo-aluminum compound demonstrates that metallocarbene species may arise directly from cycloolefin and a W reduced species; in this case the role of water in initiating ring-opening polymerization is rationalized either by the intervention of an oxy-ligand of the W species or in providing assistance for hydrochloride elimination from an ion pair.

Finally, the sharp differences in polymerization kinetics and molecular weight distribution when various additives for WCl_6/iBu_3Al catalysts are employed indicate the formation of distinct structures for the intermediates as a function of the electronic nature of the additive. In these intermediates, olefin complexation at the transition metal plays an important part.

REFERENCES

- [1] H. S. Eleuterio, U.S. Patent 3,074,118 (June 20, 1957).
- [2] For recent reviews see V. Dragutan, A. T. Balaban, and M. Dimonie, Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins, Editura Academiei, Bucharest; Wiley, Chichester, 1985, 544 pp.; K. J. Ivin, Olefin Metathesis, Academic, New York, 1983, 416 pp.
- [3] G. Dall'Asta, G. Mazzanti, G. Natta, and L. Porri, Makromol. Chem., **56**, 224 (1962).
- [4] G. Natta, G. Dall'Asta, G. Mazzanti, and G. Motroni, Ibid., **69**, 163 (1963).
- [5] G. Dall'Asta and G. Carella, British Patent 1,062,367; Chem. Abstr., **66**, 19005g (1967).

- [6] G. Dall'Asta, G. Motroni, and G. Carella, French Patent 1,545,643; Chem. Abstr., **71**, 13733 (1969).
- [7] P. Günther, F. Haas, G. Marwede, K. Nützel, W. Oberkirch, G. Pampus, N. Schön, and J. Witte, Angew. Makromol. Chem., **14**, 87 (1970); **16/17**, 27 (1971).
- [8] G. Pampus and J. Witte, German Offen. 1,770,143 (April 6, 1968).
- [9] G. Pampus, J. Witte, and M. Hoffmann, German Offen. 1,954,092 (December 28, 1969).
- [10] G. Dall'Asta, Rubber Chem. Technol., **47**, 511 (1974).
- [11] N. Calderon, E. A. Ofstead, and W. A. Judy, J. Polym. Sci., Part A1, **5**, 2209 (1967).
- [12] K. W. Scott, N. Calderon, E. A. Ofstead, W. A. Judy, and J. P. Ward, Adv. Chem. Ser., **91**, 399 (1969).
- [13] H. Höcker, W. Rieman, K. Riebel, and Z. Zsentivanyi, Makromol. Chem., **177**, 1707 (1976).
- [14] H. Höcker, L. Reif, W. Rieman, and K. Riebel, Rec. Trav. Chim., **96**, M47 (1976).
- [15] H. Höcker, W. Rieman, L. Reif, and K. Riebel, J. Mol. Catal., **8**, 191 (1980).
- [16] L. Reif and H. Höcker, Makromol. Chem., Rapid Commun., **2**, 183 (1981).
- [17] C. P. C. Bradshaw, E. J. Howman, and L. Turner, J. Catal., **7**, 269 (1967).
- [18] G. Dall'Asta, Makromol. Chem., **154**, 1 (1972).
- [19] G. Dall'Asta and G. Motroni, Eur. Polym. J., **7**, 707 (1971).
- [20] G. Dall'Asta and G. Motroni, Angew. Makromol. Chem., **16/17**, 51 (1971).
- [21] J. L. Hérisson and Y. Chauvin, Makromol. Chem., **141**, 161 (1970).
- [22] B. A. Dolgoplosk, K. L. Makovetsky, T. G. Golenko, Yu. V. Korshak, and E. I. Tinyakova, Eur. Polym. J., **10**, 901 (1974).
- [23] B. A. Dolgoplosk, K. L. Makovetsky, and E. I. Tinyakova, Vysokomol. Soedin., A., **13**, 1287 (1971).
- [24] H. Jakobson and W. H. Stockmayer, J. Chem. Phys., **18**, 1600 (1950).
- [25] E. A. Ofstead and N. Calderon, Makromol. Chem., **154**, 21 (1972).
- [26] K. L. Makovetsky and L. I. Redkina, Dokl. Akad. Nauk SSSR, **231**, 143 (1976).
- [27] B. A. Dolgoplosk, K. L. Makovetsky, and E. I. Tinyakova, Ibid., **202**, 871 (1972).
- [28] T. G. Golenko, B. A. Dolgoplosk, K. L. Makovetsky, and I. A. Ostrovskaya, Ibid., **220**, 863 (1975).
- [29] W. T. Sung, B. A. Dolgoplosk, and B. L. Erusalinsky, Izv. Akad. Nauk SSSR, OKhN, p. 469 (1960).
- [30] V. A. Kropachev, B. A. Dolgoplosk, N. M. Geuer, and M. N. Zelenina, Ibid., p. 1044 (1960).

- [31] V. M. Zgonnik, O. A. Kropachev, N. I. Nikolaev, and B. A. Dolgoplosk, *Ibid.*, p. 2157 (1960).
- [32] I. L. Kershenbaum, K. L. Makovetsky, and B. A. Dolgoplosk, *Ibid.*, p. 1170 (1973).
- [33] I. A. Oreshkin, K. L. Makovetsky, B. A. Dolgoplosk, and E. I. Tinyakova, *Vysokomol. Soedin. B*, **55**, 1911 (1977).
- [34] B. A. Dolgoplosk, K. L. Makovetsky, Yu. V. Korshak, I. A. Oreshkin, E. I. Tinyakova, and V. A. Yakovlev, *Vysokomol. Soedin., A*, p. 2464 (1977).
- [35] I. A. Oreshkin, L. I. Redkina, I. L. Kershenbaum, G. M. Chernenko, K. L. Makovetsky, E. I. Tinyakova, and B. A. Dolgoplosk, *Izv. Akad. Nauk SSSR, Ser. Khim.*, p. 2566 (1977); *Eur. Polym. J.*, **13**, 447 (1977).
- [36] E. Ceausescu, S. Bittman, M. Dimonie, A. Cornilescu, C. Cincu, E. Nicolescu, M. Popescu, S. Coca, C. Boghina, and Gh. Hubca, Paper Presented at the National Congress on Chemistry, Bucharest, September 11-14, 1978.
- [37] E. Ceausescu, M. Dimonie, V. Dragutan, M. Chipara, A. Cornilescu, E. Nicolescu, M. Popescu, S. Coca, C. Belloiu, G. Opreacu, and Gh. Hubca, Paper Presented at the 5th International Symposium on Olefin Metathesis, Graz, August 22-26, 1983.
- [38] *La Resonance Paramagnetique Electronique*, Dunod, Paris, 1967.
- [39] E. Ceausescu, M. Dimonie, V. Dragutan, M. Gheorghiu, M. Chipara, A. Cornilescu, E. Nicolescu, S. Coca, and C. Belloiu, Paper Presented at the 5th International Symposium on Olefin Metathesis, Graz, August 22-26, 1983.
- [40] A. J. Amass, D. Gregory, and M. Lotfipour, Paper Presented at the 5th International Symposium on Olefin Metathesis, Graz, August 22-26, 1983.
- [41] A. M. Shapiro, Yu. V. Korshak, M. A. Tlenkopachev, and B. A. Dolgoplosk, *Dokl. Akad. Nauk SSSR*, **248**, 1173 (1979).
- [42] A. J. Amass and T. A. McGourtey, *Eur. Polym. J.*, **16**, 235 (1979).
- [43] K. J. Ivin, B. S. R. Reddy, and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, p. 1062 (1981).
- [44] E. Ceausescu, *Noi Cercetari in Domeniul Compusilor Macromoleculari*, Editura Academiei RSR, Bucharest, 1981, p. 100.
- [45] A. N. Nesmeyanov and K. A. Kotschekova, *Metod Elemento-Organicheskoi Khimii*, Nauka, Moscow, 1975.