Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Guay, C. and Léonard, J.(1991) 'Bulk Metathesis Polymerization of Cyclooctene', Journal of Macromolecular Science, Part A, 28: 3, 359 — 372

To link to this Article: DOI: 10.1080/00222339108052148

URL: http://dx.doi.org/10.1080/00222339108052148

J. MACROMOL. SCI.—CHEM., A28(3 & 4), pp. 359–372 (1991)

BULK METATHESIS POLYMERIZATION OF CYCLOOCTENE

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ABSTRACT

The bulk ring-opening metathesis polymerization (ROMP) of cyclooctene initiated with the $WCl_6/Sn(CH_3)_4$ catalytic system was investigated at 40, 100, and 160°C using high vacuum techniques. The polymerizations were followed over a period of several days. Detailed analyses of the polymerization products by gel permeation chromatography (GPC) and ^1H and ^{13}C NMR were carried out. Along with unsaturated high molecular weight (HMW) polymer (polyoctenamer), low molecular weight (LMW) polymer was found, the proportion of the latter increasing with time. The LMW fraction contains saturated LMW polymer together with ring polymer. The results are explained in terms of kinetic and thermodynamic arguments.

INTRODUCTION

Polyoctenamer can be obtained from the ring-opening metathesis polymerization (ROMP) of cyclooctene through the cleavage of the cycloalkene double bond to form a linear carbon chain. In the same manner, the active center at the end of a propagating chain of polyoctenamer can, through a back-biting mechanism, undergo a metathesis reaction with any of the double bonds of the growing polymer chain. The resulting species are a shorter linear chain, that can still propagate through a metathesis reaction, and a ring-molecule of variable size. Moreover, the possibility of *cis/trans* isomerization of the double bonds found in the polymer adds to the complexity of the reaction.

The polymerization of cyclooctene has been investigated in many solvents [1], and it has been found [2] that the solvent can interfere with the polymerization first through a reaction with the initiator and then with the monomer, leading to the formation of saturated oligomers.

In an attempt to limit the number of species involved and facilitate our study, the polymerization of cyclooctene was undertaken in bulk. The catalytic system consisted of tungsten hexachloride as the catalyst and tetramethyl tin as the cocatalyst; this system is known for its high metathesis activity [3].

EXPERIMENTAL

Materials

Cyclooctene (Eastman Kodak) was prepurified by distillation over calcium hydride. Additional purification was performed by distilling the prepurified cyclooctene under vacuum over a sodium mirror. Cyclooctene was repeatedly distilled over a new sodium mirror until the mirror remained intact. Tungsten hexachloride (Aldrich) was stored under highly purified argon in a special air-tight ampule which makes transfer easy. Tetramethyl tin (Aldrich) was also stored under dry argon over 5 Å molecular sieves in order to prevent its contamination by water.

Polymerizations

All polymerizations were carried out by using high vacuum techniques. Since the activity of tungsten hexachloride (WCL_6) toward the metathesis reaction is affected by the presence of oxygen and/or water, it is always handled in an air-tight system under a constant flow of dry argon. A small amount (usually 10 mg, 2.5×10^{-5} mol) of WCl_6 was transferred from the main supply to the polymerization ampule under a flow of argon. The ampule was then evacuated ($\approx 10^{-5}$ mmHg). The walls of the glass ampule were degased with an acetylene torch several times before and after the addition of WCl_6. The tetramethyl tin ($Sn(CH_3)_4$) was distilled under static vacuum into the polymerization ampule containing WCl_6. A molar ratio of 2:1 for Sn/W was used since it seems to give the best results as observed by Höcker and Reif [4]. All the glassware used in our experiments was thoroughly cleaned several times with a diluted fluorhydric acid solution and then dried under vacuum before use. Sulfochromic acid is to be avoided since chromium-based compounds may be active in the metathesis reaction and interfere with the main reaction. The monomer was first distilled and measured in a graduated flask (about 5 mL, 0.04 mol) and then distilled into the polymerization ampule. The ampule was frozen in liquid nitrogen, sealed off under vacuum, and immersed in a bath at a controlled temperature. At a given time, the ampule was broken, and the polymer was precipitated in methanol, dried under vacuum, and weighed. The oligomers were extracted from the reaction mixture according to the method proposed by Höcker and Musch [5, 6]. Isopropanol was added to the reaction mixture at 0°C. After some time, the polymer stiffened, separated from the liquid, and was dried under vacuum. The isopropanol was evaporated to obtain the oligomers. The kinetics of the polymerization was followed by preparing a series of ampules under the same conditions, followed by stopping the polymerizations at different times, and analyzing the reaction products.

Analysis

The compositions of the samples, both oligomers and high polymer, were determined by gel permeation chromatography (GPC or SEC, size exclusion chromatography) using tetrahydrofuran as the solvent and a combined UV-refractive index detector. UV measurements were carried out at 254 nm. In order to obtain high resolution, a sequence of five columns was used: 1 Ultrastyragel Linear, 1 μ-Styragel 500 Å, and 3 μ-Styragel 100 Å. Refractive index increments, *dn/dc*, were measured with a Brice-Phoenix differential refractometer. *dn/dc* in tetrahydrofuran was found to vary slightly from sample to sample, and an average value of 0.09 ± 0.01 mL/g was found over 10 samples.

The nuclear magnetic resonance (NMR) studies for ^{1}H (200 MHz) and ^{13}C (50 MHz) were performed with a multinucleus Varian 200XL-NMR. All the samples were analyzed in *d*-chloroform at room temperature.

RESULTS

In order to understand the bulk ROMP of cyclooctene initiated with the $WCl_6/Sn(CH_3)_4$ catalytic system, and eventually to determine the parameters controlling the equilibrium position with respect to the mi-

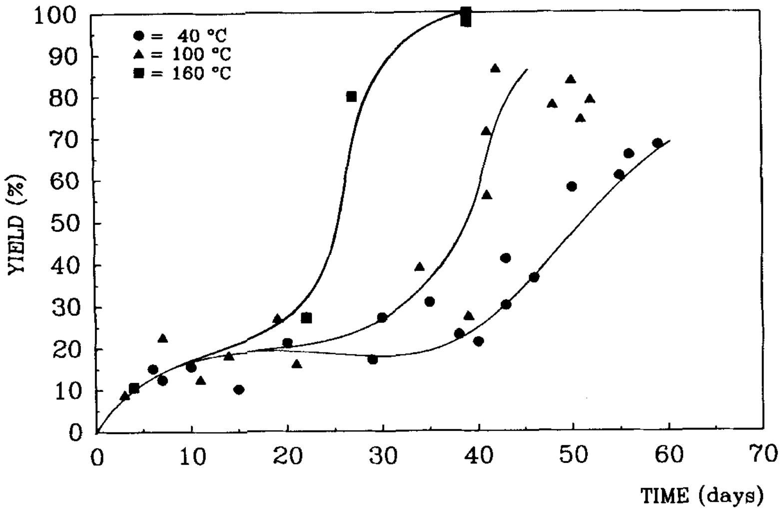


FIG. 1. Variation of the total yield with time for the bulk ROMP of cyclooctene at various temperatures.

crostructure of the polymer and the ring-chain equilibrium, a detailed investigation of the polymerization was attempted. This was accomplished through GPC and NMR analyses of the polymerization products obtained for various degrees of advancement of the reaction at 40, 100, and 160°C.

Figure 1 shows the variation of the yield in polymer with time for the bulk ROMP of cyclooctene at 40, 100, and 160°C. The yield includes low molecular weight (LMW) as well as linear high molecular weight (HMW) polymer. The S-shaped kinetic curves are similar to the kinetic curves observed in the case of the gas-phase ROMP of cyclopentene [7, 8]. This type of curve is characteristic of two consecutive first-order reactions or autocatalytic reactions [9–11]. The concentration of WCl_6 has no effect on the rate of polymerization. Bulk polymerization is much slower than polymerization in solution. It has been found that, with the same catalytic system, the ROMP of cyclooctene in chlorobenzene is completed within an hour [12]. GPC analyses of polymer samples taken at various degrees of advancement clearly show that every sample contains a LMW and a HMW polymer fraction. A typical example of GPC analysis, using a refractive index and a UV detector, is shown in Fig. 2.

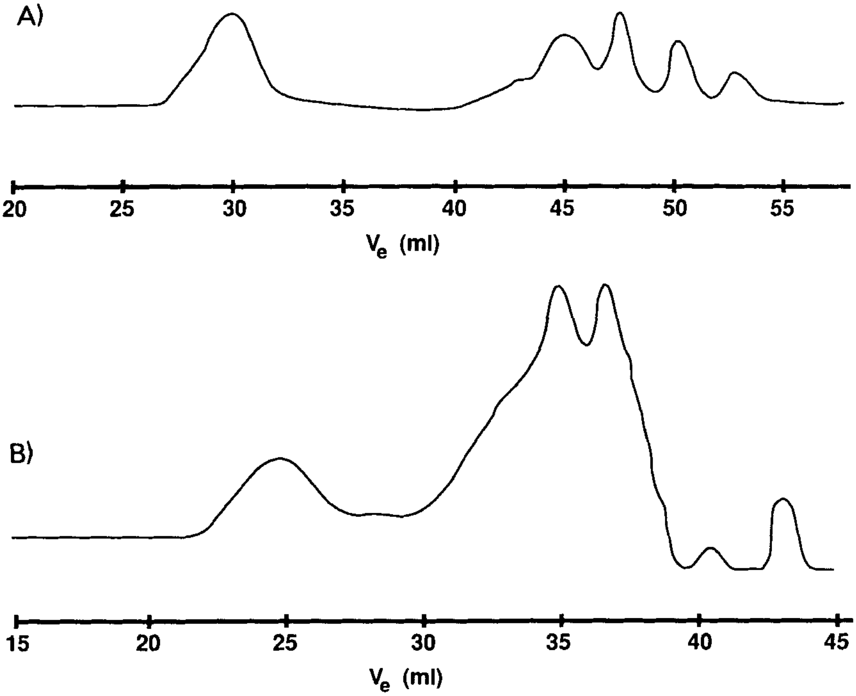


FIG. 2. GPC of two samples using A) a refractive index detector and B) a UV detector.

The refractive index detector is used in order to evaluate the overall proportions of LMW and HMW polymer in the samples. That result cannot be obtained with a UV detector if the samples contain saturated species since these species cannot be detected by UV. Figure 3 shows the variation of the LMW fraction (in weight percent) with increasing yield at 40, 100, and 160°C. Since the yield is obtained as a function of time (Fig. 1), the yield can also be considered as a measure of the degree of advancement of the reaction. In all cases the LMW fraction is quite high (even at 160°C), especially at high yield.

Samples obtained at 40, 100, and 160°C were investigated through ^{1}H- and ^{13}C-NMR analyses. ^{13}C-NMR spectra provide information about the geometrical structure of the polymers. Whereas many signals are observed between 14 and 35 ppm (see Fig. 4), the chemical shift for the carbons of the double bonds is singled out at 130 ppm. The proportion

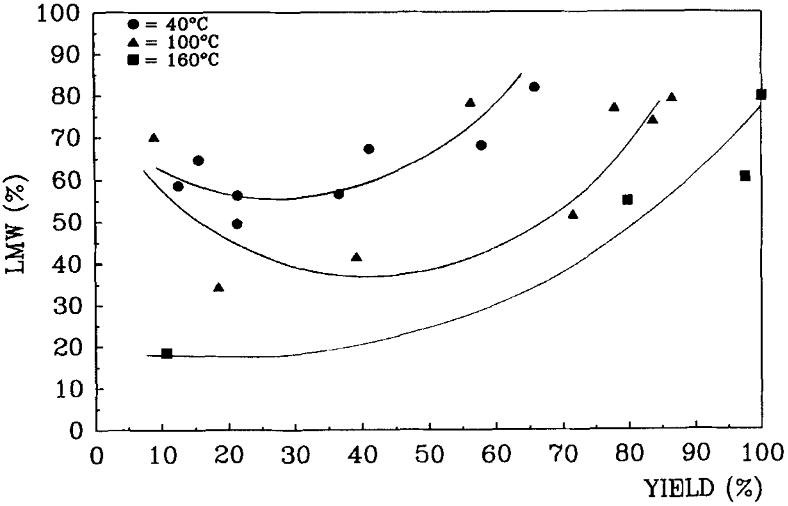


FIG. 3. Variation of the LMW fraction with yield at 40, 100, and 160°C.

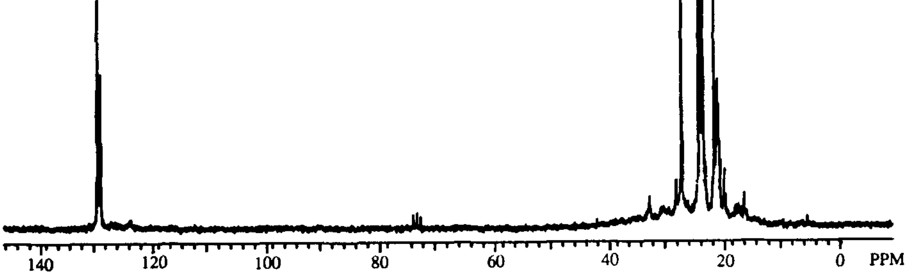


FIG. 4. ^{13}C-NMR spectrum for a sample obtained at 160°C.

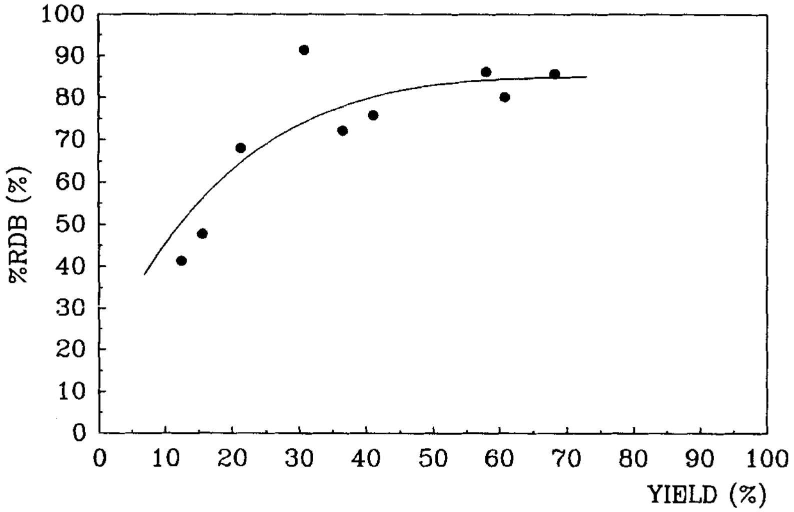


FIG. 5. Variation of the remaining double bonds (% RDB) with the yield for polymerizations at 40°C.

of *cis* and *trans* double bonds is evaluated from the split signal at 129.79 (*cis*) and 130.26 (*trans*). These observations compare well with the reported values of 129.98 (*cis*) and 130.46 (*trans*) [13]. The *cis* content of the polymer is found to decrease from 75% for the polymer obtained at 40°C to 40% for that at 160°C, with a middle value of 65% for that at 100°C. At 40°C, the value remains constant at ±5% for an advancement of the reaction ranging from 10 to 70%. ^{1}H NMR can be used in order to evaluate the fraction of remaining double bonds (% RDB). If all the double bonds are retained in the course of metathesis polymerization, the ratio of double bond protons over the total number of protons is 2/14. Then using ^{1}H-NMR data, the fraction is evaluated from

$$\% \text{ RDB} = 700 I_{4\text{-}6}/I_{0\text{-}6} \qquad (1)$$

where $I_{4\text{-}6}$ and $I_{0\text{-}6}$ represent the integration of the ^{1}H-NMR peaks between 4 and 6 ppm and between 0 and 6 ppm, respectively. Figure 5 shows the evolution of the double bonds content with the advancement of the polymerization at 40°C. An important loss of double bonds (up to 60%) can be noted early in the reaction. That loss seems to be associated with the LMW fraction of the polymer. This is illustrated with Fig.

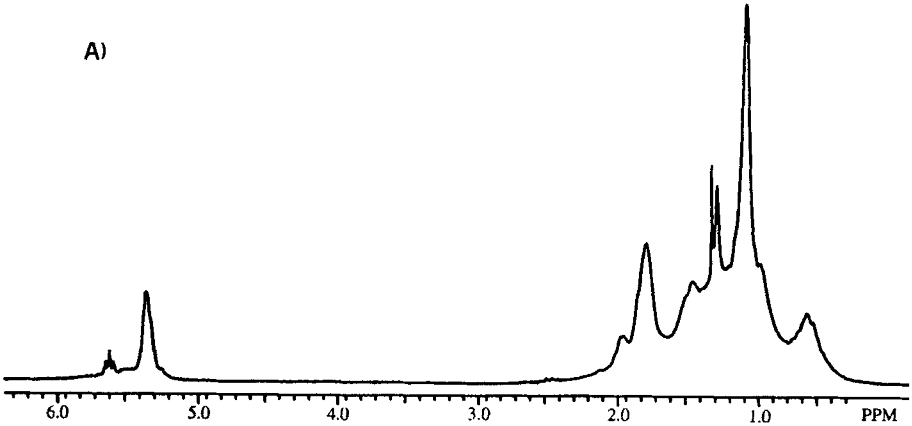


FIG. 6(A). ^{1}H-NMR spectrum of the polymer prepared at 160°C before extraction of the oligomers.

6(A) which shows the ^{1}H-NMR spectrum of a sample prepared at 160°C before extraction of the oligomers. Peaks of the $=CH-$ protons for polymers (5.35 ppm) and monomer (5.65 ppm) are apparent. The spectrum of the oligomers extracted from the sample is shown in Fig. 6(B). It was found that the double bond content is much smaller in the LMW fraction than it is in the original sample containing HMW polymer. The ^{13}C-NMR spectrum of the same oligomeric fraction (Fig. 6C) shows the same result with the disappearance of the 130 ppm signal.

The change in the double bond content with temperatures for the LMW fractions is not significant. The proportion of double bonds decreases slightly from 23 to 15% when the temperature is raised from 40 to 160°C. No trend is observed for the HMW fractions, and the proportion of double bonds is always above 70%.

DISCUSSION

From the results, it is quite obvious that two concurrent reactions take place in the course of the bulk ROMP of cyclooctene initiated with WCl_6 and $Sn(CH_3)_4$. In the metathesis reaction, the carbene $Cl_4W{=}CH_2$ is formed [14] which then reacts with the monomer to yield the propagating species according to

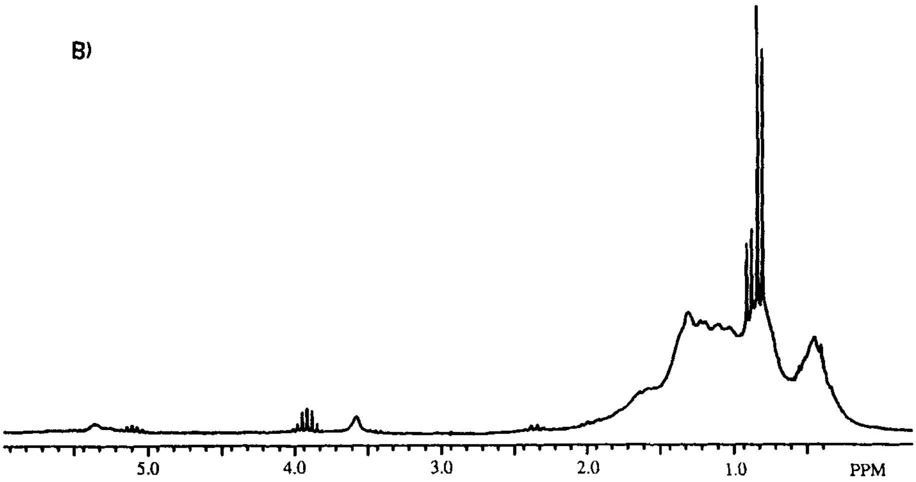


FIG. 6(B). ^{1}H-NMR spectrum of the extracted oligomers.

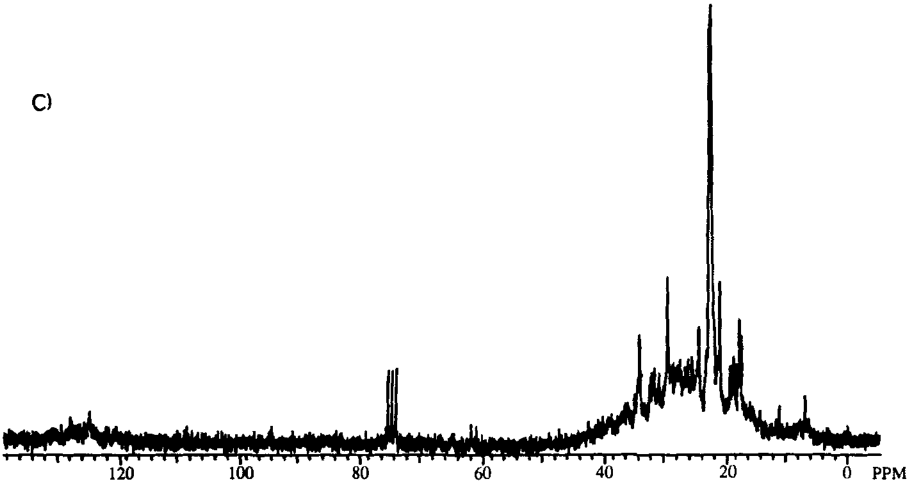
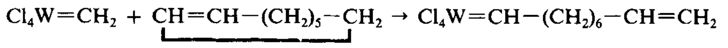


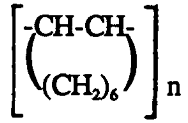
FIG. 6(C). ^{13}C-NMR spectrum of the oligomers.



$$Cl_4W{=}CH_2 + CH{=}CH{-}(CH_2)_5{-}CH_2 \rightarrow Cl_4W{=}CH{-}(CH_2)_6{-}CH{=}CH_2 \qquad (2)$$

The product of the reaction is a linear unsaturated polymer (polyoctenamer) with the formula $(-CH{=}CH-(CH_2)_6-)_n$. In the course of polymerization, a growing chain may undergo a back-biting reaction, leading to a ring-chain equilibrium (see page 369).

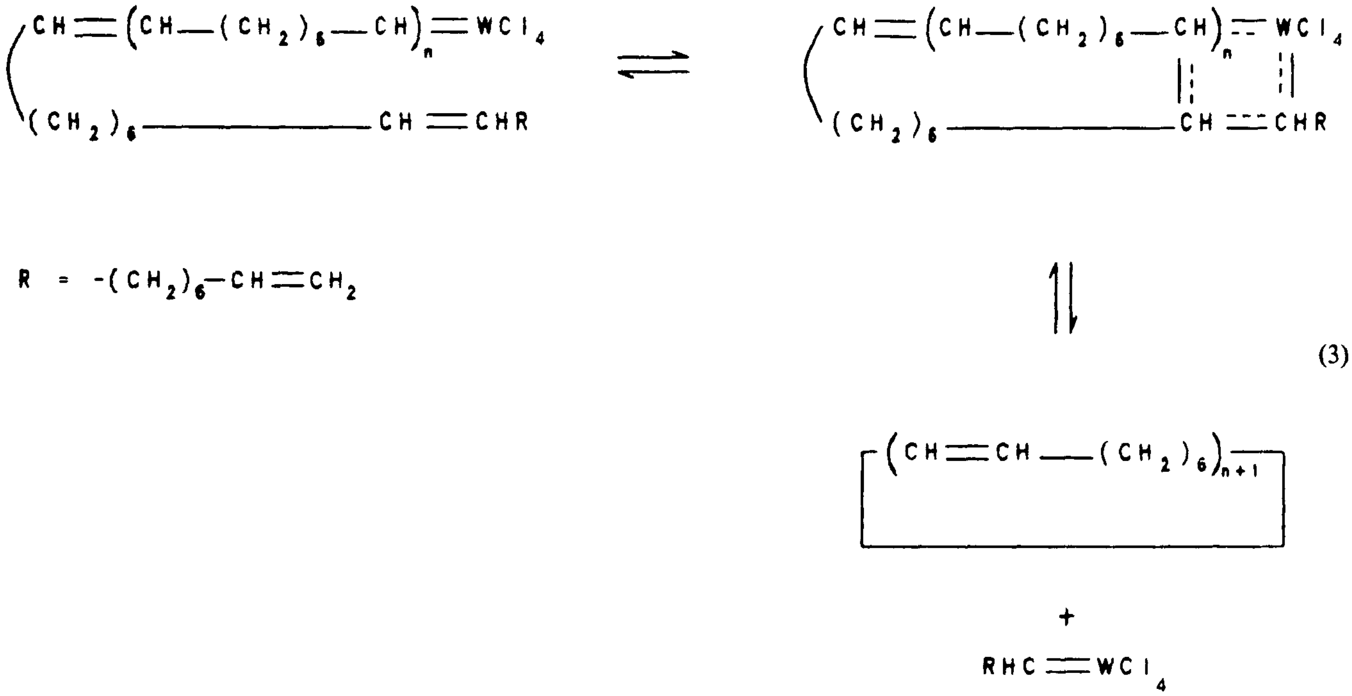
Neither the linear propagation nor the back-biting can account for the loss of double bonds with respect to the original amount of cyclooctene as observed through NMR analysis. The loss of double bonds can be explained through the formation of LMW polymers having the structure



(4)

This polymer has been found for the polymerization of cyclooctene in benzene [2], and the same type of reaction has been reported very recently for the polymerization of norbornene in toluene [15]. It was also reported [16] that the attempted polymerization of cyclohexene in chlorobenzene using $Re(CO)_5Cl\text{-}EtAlCl_2$ as the catalyst leads to the formation of oligomers. The ^{13}C NMR of this polymer shows about 30 signals in the 14 to 36 ppm range, but no signal for the double bond carbons, a result similar to the spectrum shown in Fig. 6(C).

From the present set of results it is concluded that the reaction can take place in the absence of solvent. The propagation is believed to take place through a cationic mechanism simultaneously with the metathesis mechanism. This has been suggested for the polymerization of tetrahydroindane initiated with the $WCl_6/EtAlCl_2$ system [17, 18]. In addition to the formation of the carbene, WCl_6 may act as a Lewis acid which can initiate a cationic propagation. In the present case, because of the steric hindrance due to a 1,2 substitution arising from the cyclic nature of the monomer, the average degree of polymerization of this polymer is low. The proportion of saturated polymer remains quite high throughout the polymerization. This result means that chain transfer reactions take place or that new chains are initiated from the initial unreacted WCl_6. Moreover, from the combined results of Figs. 1, 3, and 5, this reaction is found to be initiated more rapidly than the metathesis reaction, since the most abundant species at the beginning of the polymerization is the saturated LMW polymer.



$R = -(CH_2)_6-CH=CH_2$

(3)

In the LMW fraction of polymer samples, unsaturated cyclic oligomers resulting from the back-biting reaction are found along with the saturated oligomers. Most of these molecules are found once the polymerization has reached a high degree of advancement. This is in agreement with the findings of Höcker and coworkers [6, 19] who observed that ring polymers are formed after the formation of the linear polymer chains. As can be seen from Fig. 3, the LMW fraction becomes very important. One must bear in mind that, in addition to the above reactions that lead to oligomeric species, short chains may originate from the cross-metathesis reaction with the double bonds of unsaturated polymer chains. Although it is difficult to account in detail for the S-shaped curves of Fig. 1 in terms of two consecutive first-order reactions, an explanation may be attempted in the light of the above results. The propagation is a second-order reaction. However, if the active centers of the propagating species are stable and their concentration remains constant, this reaction can be treated as a first-order reaction. The metathesis propagation is followed by a back-biting reaction which is zero order in monomer. This reaction cannot account "*per se*" for the increase in yield observed in Fig. 1 since there is no consumption of monomer in a back-biting reaction. Assuming the concentrations of active centers remain constant once initiation is over, both cationic and metathesis propagations may be considered as first-order reactions. From the results gathered from Figs. 1 and 5, initiation of cationic propagation is faster than its metathesis counterpart. However, the propagation rate constant of the latter is higher than it is for the cationic propagation. The result of the metathesis propagation is a steep increase in the curves of Fig. 1, along with an increase in the double bond content (Fig. 5) and a lowering in the LMW polymer fraction (Fig. 3). The last stage of the polymerizations coincides with an increase in LMW polymers (Fig. 3). This may be the result of the formation of unsaturated cyclic or linear oligomers and saturated oligomers. In the latter case, the increase in the saturated LMW polymer should originate from a transfer reaction to the monomer. Results such as those illustrated in Fig. 2 show that the final number of molecules far exceeds the number that can be formed solely from the initiation step. The overall results also coincide with thermodynamic arguments. Basically, metathesis reactions are reversible and the polymerization system should tend toward equilibrium. This can also be the case for the cationic propagation where a monomer-active polymer equilibrium is possible. It is worth noting that the system remains active for a very long period of time (see Fig. 1). Since it has been shown that short chain polymers increase the concentration of polymer for an equilibrium polymerization in solution [20] and in bulk [21], and that small ring polymer may have a similar effect [22], the increase in LMW polymer due to the formation of saturated oligomers and ring polymers may explain, at least in part, the increase in yield.

CONCLUSION

The bulk metathesis polymerization of cyclooctene initiated with the $WCl_6/Sn(CH_3)_4$ catalytic system is slow compared with polymerizations carried out in solvent and with other types of catalyst. The metathesis propagation leads to the formation of an unsaturated polymer (polyoctenamer) followed by the formation of unsaturated ring oligomers. Variations in the composition of the polymerization system were followed by means of GPC and NMR, and it was found that large amounts of LMW polymer are formed along with unsaturated chain and ring polymer. However, because of the formation of a large amount of saturated oligomers, the system is not appropriate for investigating ring-chain equilibrium. It was also found that the *cis* content of the polymer varies to a great extent with temperature.

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Received May 22, 1990
Revision received October 6, 1990