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 Drapeau, A. and Leonard, J.(1983) 'Polymerization of Cyclooctene in Benzene Initiated with a Metathesis Catalyst', Journal of Macromolecular Science, Part A, 20: 9, 989 — 1005
To link to this Article: DOI: 10.1080/00222338308060807
URL: http://dx.doi.org/10.1080/00222338308060807

J. MACROMOL. SCI.-CHEM., A20(9), pp. 989-1005 (1983)

Polymerization of Cyclooctene in Benzene Initiated with a Metathesis Catalyst

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ABSTRACT

Cyclooctene was polymerized in benzene at temperatures ranging from 10 to 80°C. The polymerization was initiated with the metathesis catalyst $WCl_6/C_2H_5)AlCl_2/C_2H_5OH$ for initial monomer concentrations varying from 0.11 to 4.0 mol/L. Polymerization products obtained from the metathesis reaction and the alkylation of benzene were found. The metathesis products consisted of a high molecular weight polymer and cyclic oligomers of cyclooctene. The double bond content was the same as in the monomer. The alkylation products were characterized by the presence of an aromatic nucleus and a low double bond content. Benzene was found to react with the double bond of cyclooctene and the cyclic dimer. It may also lead to the formation of saturated oligomer consisting of short chains of cyclooctyl units. Their presence is not temperature dependent and increases with decreasing initial monomer concentrations. For initial monomer concentrations above 1.0 mol/L, the alkylation reaction cannot be detected.

0022-233X/84/2009-0989$3.50/0

INTRODUCTION

Metathesis reactions of alkenes are initiated with Calderon's catalyst ($WCl_6/(C_2H_5)AlCl_2/C_2H_5OH$) [1, 2]. When this catalyst is used in benzene, alkylation of the benzene ring with normal alkenes is reported to take place [3-7]. The alkylation reactions seem to be enhanced by a low alkene/tungsten hexachloride ratio and a low alkene concentration. With cycloalkenes, Calderon's catalyst leads to the formation of polyalkenamers and macrocyclic molecules [8-13] but, except for one case [11], no mention of side reactions is made. However, alkylation of benzene with various cycloalkenes without the formation of polyalkenamer is reported with this catalyst [14]. In the present paper the analysis of various species obtained when cyclooctene is polymerized in benzene with Calderon's catalyst is reported. Experimental conditions which enhanced the formation of polymer through metathesis are also determined.

EXPERIMENTAL

Materials

Tungsten hexachloride (Ventron Alfa Division) was purified by subliming impurities under a nitrogen stream at 200°C. Ethanol (99%) was dried over anhydrous silica gel and distilled under an argon atmosphere. Tungsten hexachloride/ethanol solutions in benzene were prepared in a 1/1 molar ratio. These solutions were allowed to react for a period of 30 min before being used. Dichloroethyl-aluminum (Aldrich Chemical) in solution in toluene (25% by weight) was used without further purification. This solution was diluted in benzene immediately before use. Benzene (99.8%) (BDH Chemical) was dried over sodium and distilled under argon. Cyclooctene (Aldrich Chemical) was distilled three times under argon and dried over molecular sieves. Its purity was then better than 99.8%.

Polymerizations

All the glassware used was cleaned with a sulfochromic acid mixture. It was dried at 150°C for 12 h and cooled under a nitrogen stream immediately before use. The reacting mixtures were prepared under a nitrogen atmosphere in a glove box. The mixtures were prepared in the following way: the tungsten hexachloride/ethanol solution was added to benzene, followed by the dichloroethylaluminum, and finally by cyclooctene. The ampules containing the mixtures were sealed and immersed in an isothermal bath for 24 h. Polymerizations were terminated through the addition of a few drops of methanol. The volatile materials were evaporated under vacuum until constant weight was attained.

A first series of polymerizations was carried out for initial concentrations of cyclooctene varying from 0.6 to 4.0 mol/L at temperatures ranging from 10 to 80°C (± 0.05). The cyclooctene/tungsten molar ratios were allowed to vary between 275 and 2080 while the aluminum/tungsten molar ratio was equal to 4. A second series of polymerizations was carried out for initial concentrations of cyclooctene of 0.11, 0.22, 0.33, and 0.45 mol/L. Temperatures were set at 10, 25, 35, and 45°C. The cyclooctene/tungsten molar ratio was 125 in the case of the 0.11 mol/L concentration and 250 for all the other concentrations. The aluminum/tungsten ratio was kept equal to 4.

In a certain number of polymerizations low molecular weight products were extracted. The extractions were performed by adding a 10-mL isopropanol/hexane (1/1 vol) solution to 0.8 g of polymer [11]. The supernatant liquid was removed after 24 h. The procedure was repeated twice. The supernatant solutions were collected and the volatile components were evaporated under vacuum. The residue obtained after extraction consisted of high molecular weight products while the extract yielded low molecular weight products.

Analyses

NMR spectra were obtained using a 60-MHz Varian spectrometer, model EM 360A. Polymerization products were dissolved in carbon tetrachloride, and tetramethylsilane was used as a reference.

IR measurements were carried out with an IR Perkin-Elmer spectrophotometer, model 457. The samples were prepared by evaporating carbon tetrachloride solutions containing polymerization products on sodium chloride windows.

Gel permeation chromatograms were obtained with a Waters Associates liquid-liquid chromatograph, model ALG/GPC 501, using four Styragel columns of 100, 500, 10^3, and 10^4 Å. Tetrahydrofuran was used as solvent. The calibration curve was obtained with cyclooctene and seven polystyrene standards. The molecular weight of polystyrene standards was multiplied by 1.22 in order to take into account differences between polystyrene and polyoctenamer [15].

Mass spectra were obtained with a Hewlett-Packard GCMS, model 5980. The chromatograph was equipped with a 2-m SP 2330 column loaded with 10% HP-W Chromosat, 100 to 120 mesh. The oven temperature was programmed to be maintained at 100°C for 2 min after injection and then to increase the temperature up to 240°C at a rate of 16°/min. Low molecular weight materials dissolved in pentane were analyzed in this manner.

UV spectra of polymerization products in solution in heptane were recorded with a Hewlett-Packard spectrophotometer, model 8450 A.

RESULTS AND DISCUSSION

Results for polymerization may be divided in two types: polymerizations with an initial monomer concentration larger or smaller than 0.6 mol/L. In the former case, all polymerizations lead to the formation of a gel. The degree of conversion associated with these polymerizations varies from 20 to 95%. These variations may be explained in part by the very high viscosity of the medium. Unreacted monomer may be trapped during the formation of the gel. Polymers obtained after evaporation of the solvent are rubbery and are poorly soluble, probably due to cross-linking. For this reason their molecular weight cannot be measured. The proportion of double bonds in these polymers is identical to that in the monomer.

For initial concentrations of cyclooctene varying from 0.11 to 0.45 mol/L, the proportion of double bonds in the polymerization products is smaller to that in the monomer. Figure 1 shows NMR spectra of low molecular weight samples where 50% (Fig. 1a) and near 100% (Fig. 1b) of all the double bonds have disappeared. It is observed that, while peaks at 5.3 and 2.0 ppm decrease, peaks at 7.0 and 1.6 ppm increase. The 5.3 and 2.0 positions are associated with the protons on the double bond and the protons in the α position of the double bond, respectively. With the opening of the double bond, the olefinic protons are transformed into methine protons at 1.6 ppm. The peak at 7 ppm indicates the presence of benzene protons either as residual benzene in the sample or as aromatic nuclei being part of the oligomer molecules.

The proportion of remaining double bonds, DB, expressed in terms of polymerized cyclooctene, is obtained from the integration over the peaks in the 0 to 6 ppm, I_{0-6}, and the 4 to 6 ppm, I_{4-6}, regions. DB, expressed in percent, is readily obtained from

$$DB = (700 I_{4-6})/I_{0-6} \tag{1}$$

This proportion varies between 15 and 80% from one polymerization to another. This cannot be related to the polymerization temperature or to the initial monomer concentration. However, when the initial concentration of cyclooctene is 0.11 mol/L and the cyclooctene/tungsten hexachloride molar ratio is 125, the remaining proportion of double bonds is always nil.

Integrations of peaks in the 6 to 8 ppm, I_{6-8}, and in the 0 to 6 ppm, I_{0-6}, regions are used to evaluate the average degree of oligomerization, $\overline{DO}$. $\overline{DO}$ is defined as the average number of cyclooctene units per aromatic nucleus. $\overline{DO}$ may be estimated through the relationship

$$\overline{DO} = 0.357 I_{0-6}(1 - DB/100)/I_{6-8} \tag{2}$$

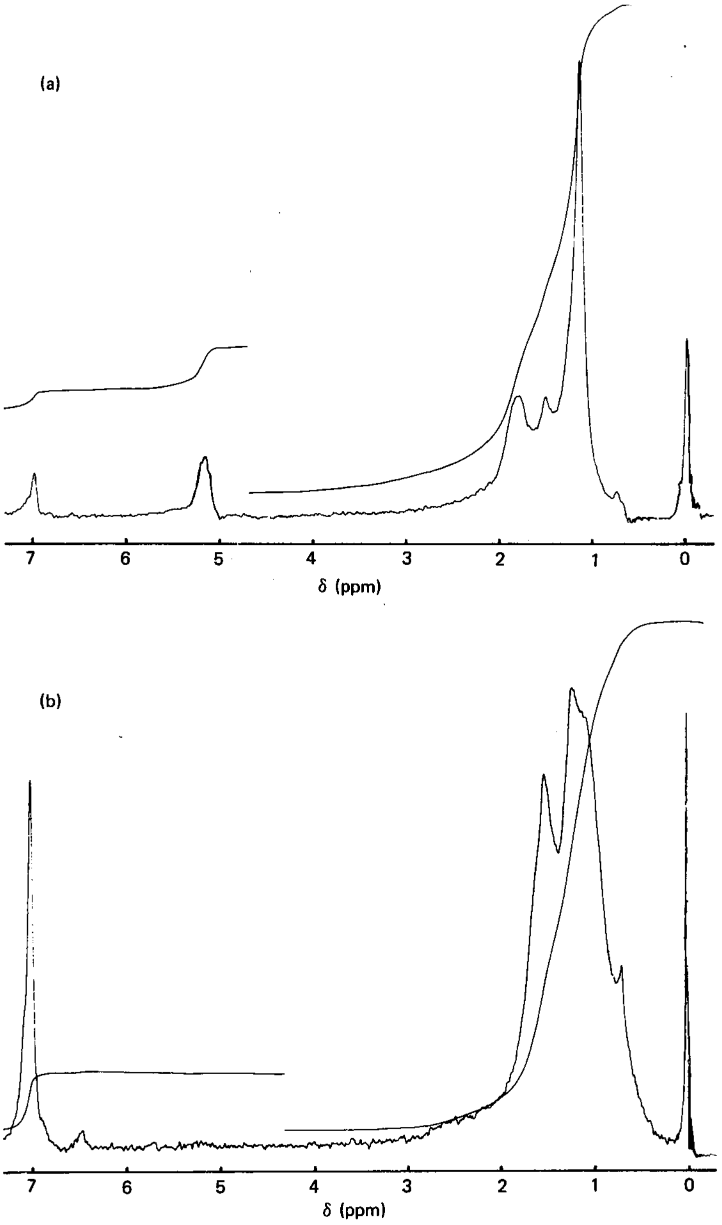


FIG. 1. NMR spectra of polymerization products: (a) with 50% of the double bonds remaining, $\overline{DO} = 4$; (b) with all the double bonds saturated, $\overline{DO} = 3$.

TABLE 1. Average Degree of Oligomerization, $\overline{DO}$, Obtained for Various Initial Monomer Concentrations, $[CO]_0$

$[CO]_0$ (mol/L ± 0.01)	Number of runs	$\overline{DO}$	Standard Deviation
0.45	20	7.7	2.0
0.33	20	5.8	1.7
0.22	21	5.4	1.8
0.11	8	3.1	0.2

As can be seen from Table 1, $\overline{DO}$ is found to vary with the initial monomer concentration, $[CO]_0$, for concentrations lower than 0.6 mol/L.

In order to evaluate the percent degree of conversion of cyclooctene, % CON, from the initial weight of monomer, m^0, and the weight of polymerization product, m_p, one ought to take into account the amount of benzene which reacted with cyclooctene (see below). With the NMR data available, the % CON may be calculated from:

$$\% \text{CON} = \frac{m_p}{m^0} \left(\frac{I_{0-6}}{I_{0-6} + 1.96\, I_{6-8}} \right) 100 \qquad (3)$$

As can be seen from Table 2, the average degree of conversion, $\overline{\% \text{CON}}$, does not vary for initial monomer concentrations above 0.11 mol/L. $\overline{\% \text{CON}}$ also remains constant with temperature in the 10 to 45°C range.

Through the examination of IR spectra (Fig. 2) it is found that the decrease of the double bond bands (trans, 965 cm^{-1}; cis, 742 cm^{-1}) is proportional to the intensity of a new band (750 cm^{-1}), showing the presence of monosubstituted benzene ring. This leads to the conclusion that benzene reacts with cyclooctene. This is confirmed by UV

TABLE 2. Average Percent Conversion, $\overline{\% \text{CON}}$, for various $[CO]_0$

$[CO]_0$ (mol/L ± 0.01)	Number of runs	$\overline{\% \text{CON}}$[a]
0.45	20	93 ± 2
0.33	19	94 ● 2
0.22	21	94 ± 3
0.11	10	84 ± 3

[a] Values of % CON smaller than 50% were discarded.

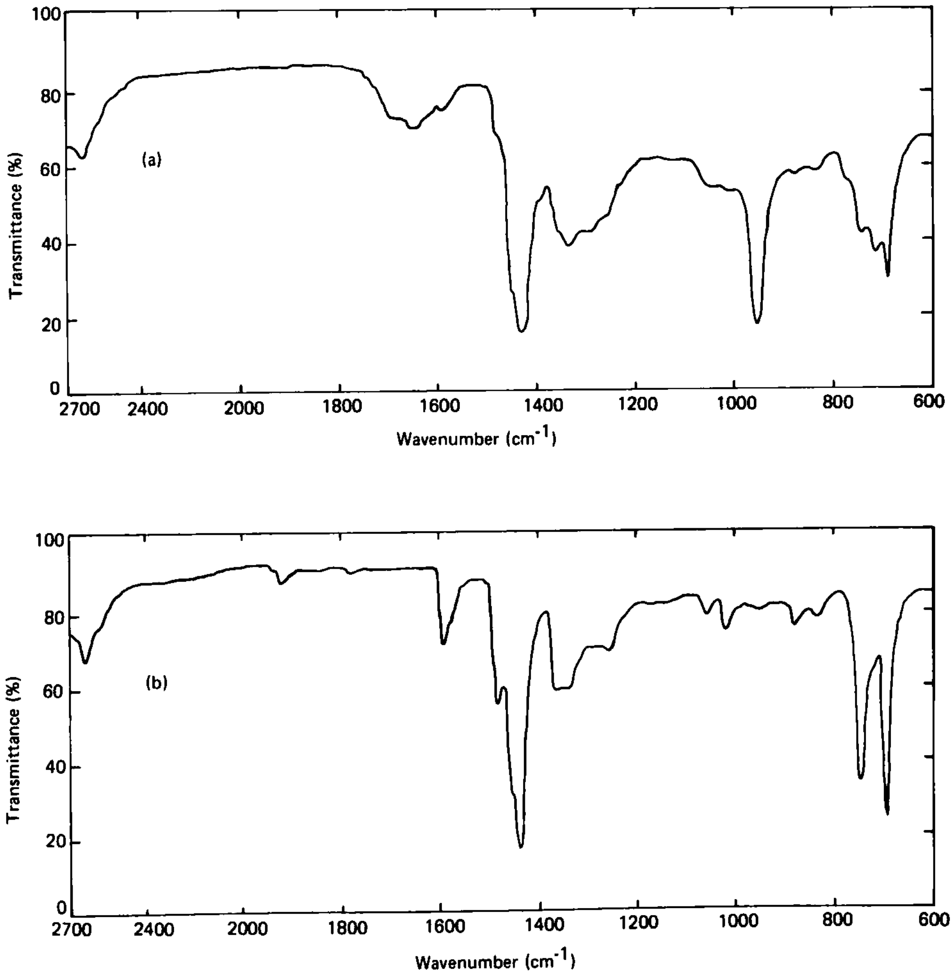


FIG. 2. IR spectra of polymerization products: (a) with all the double bonds saturated, (b) with 70% of the double bonds remaining.

spectrophotometry. Figure 3 shows that UV spectra of polymerization products which are double-bond free are very similar to the ones of tert-butylbenzene and isopropylbenzene [16]. This shows that in the polymerization products, the benzene ring is attached to a cyclooctyl unit in a way similar to that existing in tert-butylbenzene or isopropylbenzene. Moreover, it is found that the intensity of the UV bands decreases when the double bond content increases.

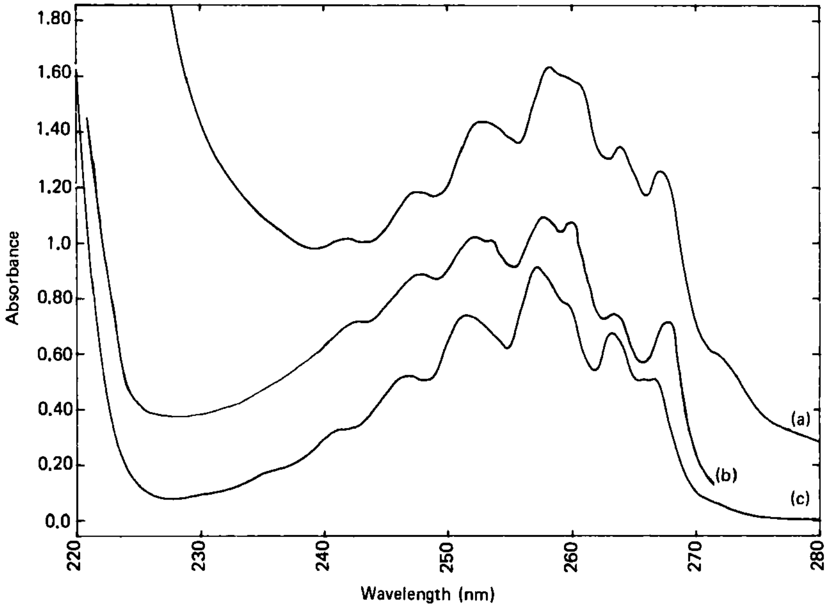


FIG. 3. UV spectra of (a) polymerization products with all the double bonds saturated, (b) isopropylbenzene, (c) tert-butylbenzene.

GPC analyses show broad molecular weight distributions with molecular weights ranging from about 160 to 200,000 g/mol. The relative amount of high molecular weight polymer with respect to low molecular weight products (oligomers) decreases together with the initial monomer concentration. Figure 4 shows that for an initial monomer concentration of 0.11 mol/L, the molecular weight does not exceed 1000 g/mol.

The mass spectrometry (GCMS) analysis shows two types of oligomers: oligomers with and without aromatic nucleus. Compounds containing a benzene ring are characterized by a fragmentation peak at a mass of 91. Four compounds of this type were identified, and they are listed in Table 3. The first one, phenylcyclooctane, is found at a mass of 188 with the main fragmentation peaks at 91, 104, and 117 (Fig. 5a). At a mass of 298, two kinds of spectra are obtained which might indicate that isomers are present. In the first case (Fig. 5b), the main peaks are found at 55, 91, 104, and 117. In the second case (Fig. 5c), the main peaks are at 41, 55, 83, and 97 with the 91 peak always present. For the mass of 408 (Fig. 5d), only one type of spectra is found. Since the main fragmentation peaks show up at 41, 55, 91, and 97, it seems that the 408 compound has a structure similar to the one observed in Fig. 5c. Because NMR analysis shows that the double

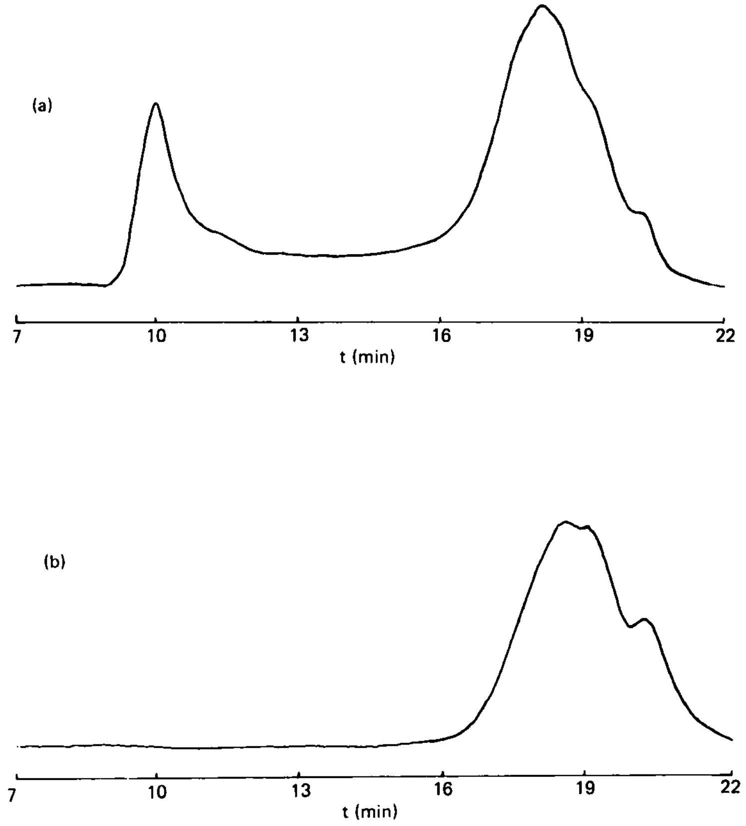


FIG. 4. GPC chromatograms of polymerization products (a) with 20% of the double bonds remaining, (b) with all the double bonds saturated.

bonds tend to disappear with the presence of a benzene ring, the 408 compound would be phenyl-tri-cyclooctane and the 298 parent compound would be phenyl-bi-cyclooctane (or 1-phenyl-2-cyclooctanylcyclooctane). The isomer shown in Fig. 5b would be 1-phenyl-8-cyclohexadecene.

Compounds which do not contain an aromatic nucleus are found to have moelcular weights of 220, 222, and 330 and are listed in Tables 3 and 4. The 220 and 330 compounds are obviously the dimer and the trimer of cyclooctene, and their spectra are shown in Figs. 6a and 6c. The 222 compound could be bi-cyclooctane or 1-cyclohexadecene, and the spectrum of this compound (Fig. 6b) is found to be slightly different from Fig. 6a.

When the polymerization products are separated by extraction, NMR

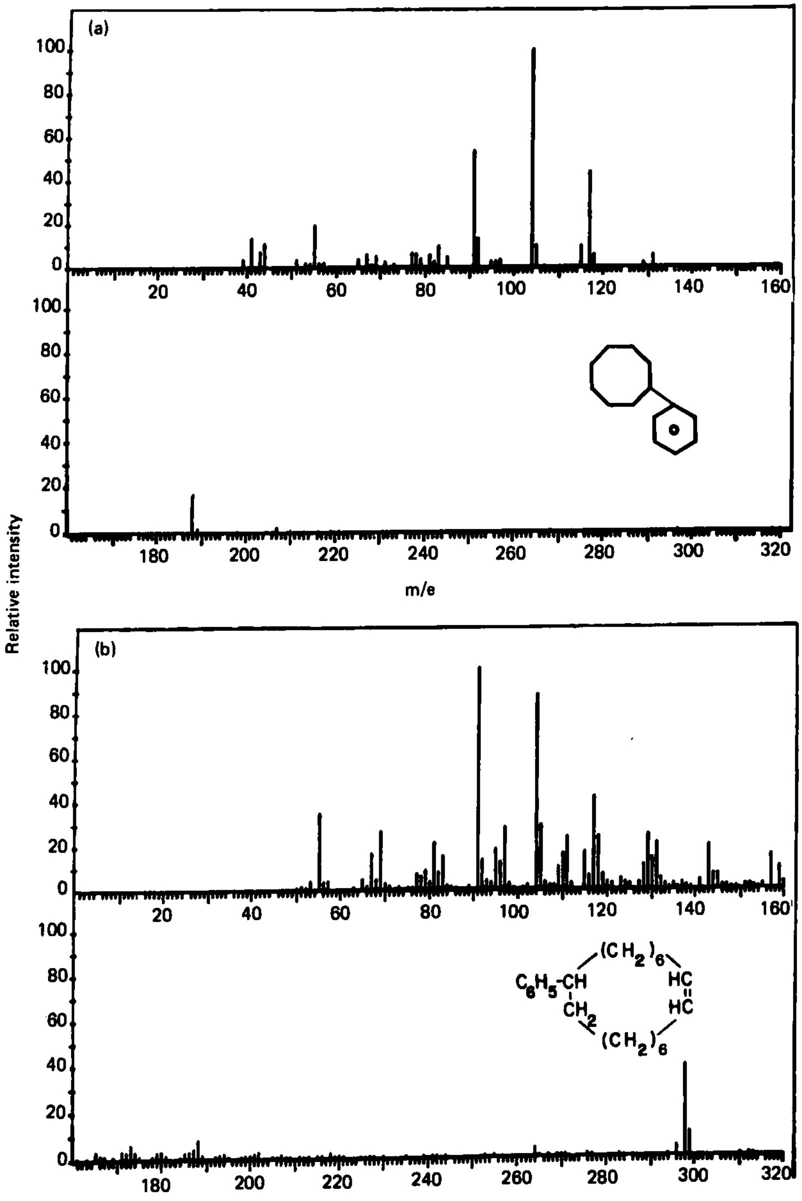


FIG. 5. GCMS spectra of aromatic compounds with a molecular weight of (a) 188, (b) 298 (1-phenyl-8-cyclohexadecene), (c) 298 (phenyl-bi-cyclooctane), (d) 408.

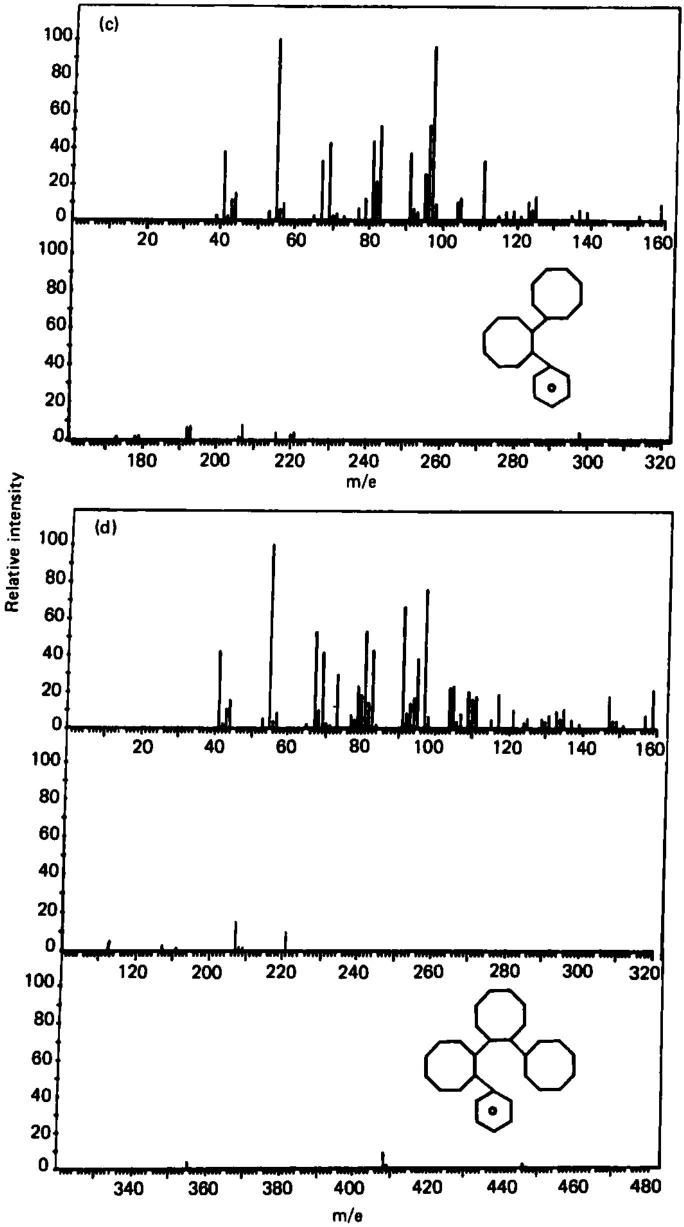


FIGURE 5 (continued)

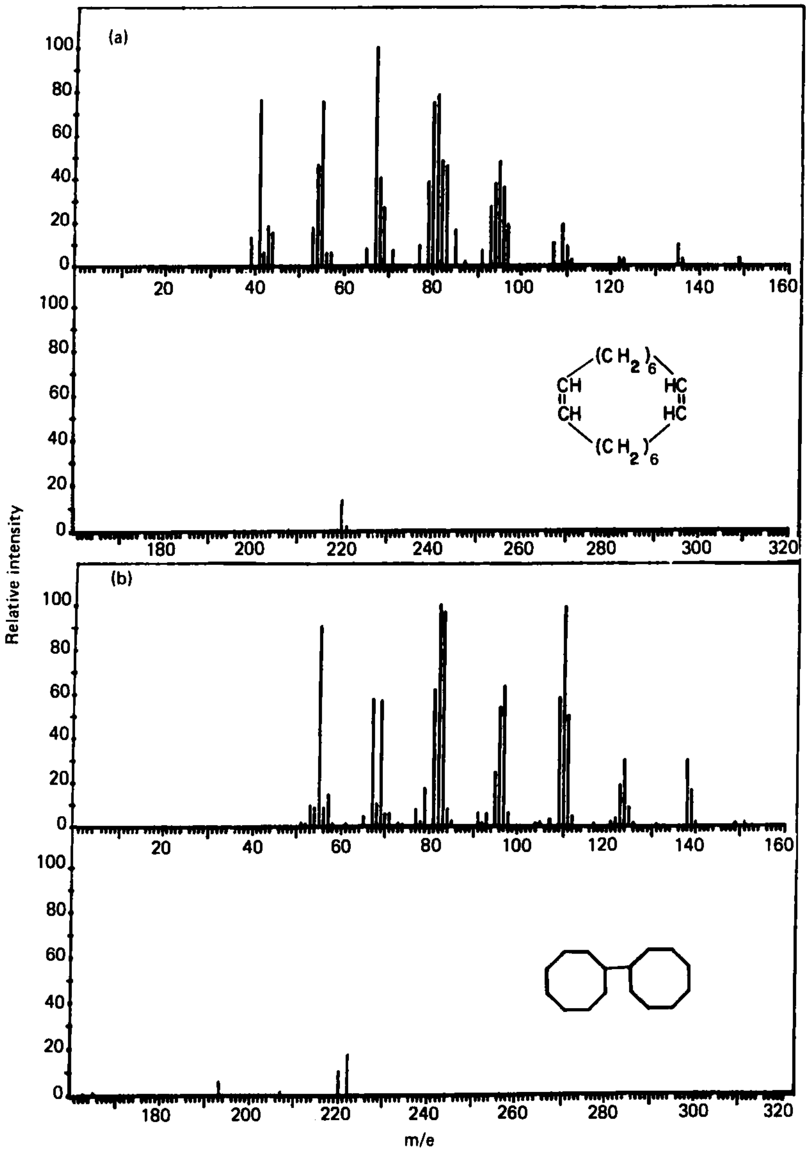


FIG. 6. GCMS spectra of nonaromatic compounds with a molecular weight of (a) 220, (b) 222, (c) 330.

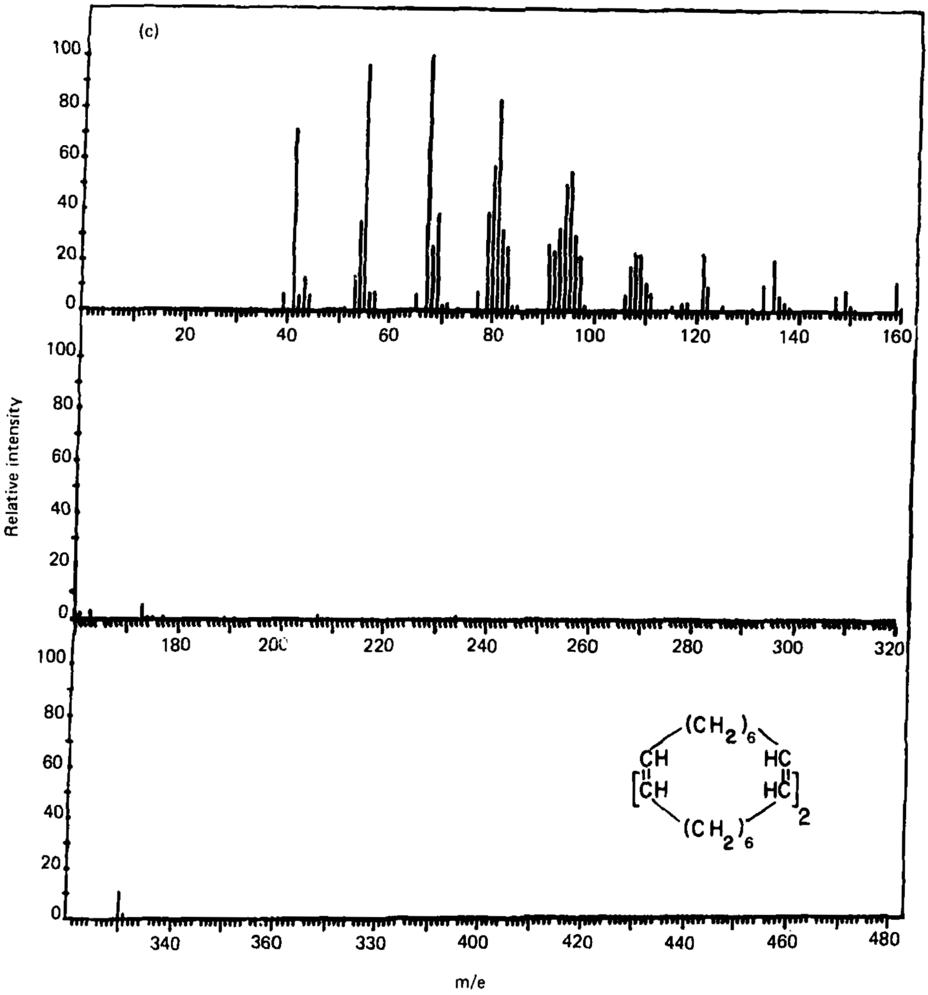


FIGURE 6 (continued)

TABLE 3. Polymerization Products Obtained through Secondary Reactions

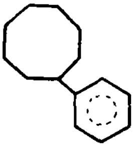
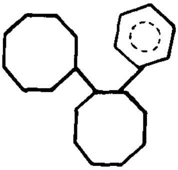
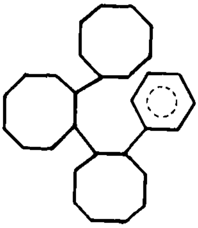
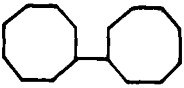
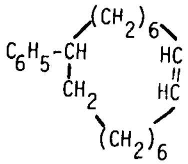
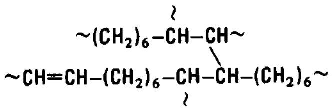
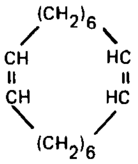
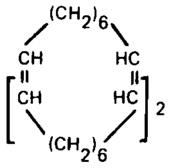
Structure	Techniques of analysis	Molecular weight (g/mol)
	NMR/IR/GCMS/UV	188
	NMR/IR/GCMS/UV	298
	NMR/IR/GCMS/UV	408
	GCMS	222
	NMR/IR/GCMS/UV	298
 $\sim(CH_2)_6-CH-CH\sim$ $\sim CH{=}CH-(CH_2)_6-CH-CH-(CH_2)_6\sim$	NMR/solubility	

TABLE 4. Polymerization Products Obtained through Metathesis Reactions

Structure	Techniques of analysis	Molecular weight (g/mol)
$\left[CH=CH-(CH_2)_6 \right]_n$	NMR/IR/GPC	10,000 to 200,000
	GCMS	220
	GCMS	220

and IR analyses show that the double-bond content is much higher for high molecular weight products than for low molecular weight ones. Moreover, the benzene ring is found in low molecular weight products.

CONCLUSION

From the above results it may be concluded that, in the case of the polymerization of cyclooctene in benzene initiated with Calderon's catalyst, the products of metathesis listed in Table 4 are obtained together with products originating from the alkylation of benzene. The latter result is in agreement with previous reports regarding the alkylation of benzene with various type of olefins [3-7, 11, 14]. Under present conditions, alkylation occurs through the opening of the double bond of cyclooctene. Activation of the double bond may lead to the subsequent addition of molecules of cyclooctene through the opening of the double bond to form saturated oligomers. Oligomers containing up to three monomer units have been detected. Because the average degree of oligomerization is higher than three (see Table 1), higher oligomers might be formed. However, due to steric hindrance, the number of monomer units in this type of oligomers should remain small. Benzene is also found to react with the cyclic dimer, 1,8-cyclohexadecadiene, to form 1-phenyl-8-cyclohexadecene. Since aromatic nuclei are not detected with the trimer, it is suggested that benzene reacts mainly with the monomer and the dimer. Small amounts of bi-cyclooctane are also detected. The formation of these oligomers is not a function of temperature.

The relative amount of oligomers varies with the initial monomer concentration. With an initial monomer concentration of 0.11 mol/L, the molecular weights do not exceed 1000, the aromatic content is high, and the double bond content is low. The proportion of high molecular weight products increases with increasing initial monomer concentration. In that case the presence of benzene ring cannot be detected and the double bond content is equal to that of the monomer. Alkylation can be reduced to a minimum if polymerizations are carried out with an initial concentration of cyclooctene larger than 1.0 mol/L. However, cross-linking of the polymer is likely to occur under these conditions.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Conseil de recherches en sciences naturelles et en génie of Canada and the Fonds FCAC of Quebec. They also wish to thank Dr R. Massé, INRS-Santé, for the GCMS measurements. This work has been carried out as part of the general research program of the Groupe de recherche sur les macromolécules at this University.

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Accepted by editor April 25, 1983
Received for publication June 1, 1983