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Polymerization of 5-Substituted Cyclooctenes with Tungsten and Molybdenum Catalysts

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ABSTRACT

Polymerizations of cyclooctene, 5-methyl, 5-chloro-, and 5-methoxycyclooctenes were studied. Cyclooctene (CO) and 5-methylcyclooctene (MCO) provided high polymers in 80% yield with the use of $WCl_6/AlEt_{1.5}Cl_{1.5}$ or $WCl_6/AlEtCl_2$ catalyst. 5-Chlorocyclooctene gave oligomer in 50% yield with $WCl_6/AlEt_2Cl$ catalyst. Neither polymer nor oligomer was produced from 5-methoxycyclooctene. These polymers were found to be produced through a ring-opening mechanism. The ratio of cis to trans structure in poly(CO) and poly(MCO) was determined by measurements of the decoupled ^{1}H-NMR spectrum. Poly(CO) containing more than 50% trans structure was a crystalline solid at room temperature, while the polymer containing 30% of trans structure did not crystallize at room temperature. Poly(MCO) was amorphous, regardless of the content of trans structure. Poly(CO) and poly(MCO) obtained with $MoCl_5/AlEt_2Cl$ or $MoCl_5/AlEtCl_2$ catalyst contained no carbon-carbon double bond, and a vinyl polymerization mechanism was expected for this system.

INTRODUCTION

It is well known that cycloolefins yield polymers containing carbon-carbon double bonds in the polymer chain through ring-opening polymerization. Catalyst systems consisting of tungsten or molybdenum compounds and alkylaluminum compounds are known to be very effective for the ring-opening polymerization. Polymerization of various kinds of cycloolefins, such as cyclobutene, cyclopentene, cyclooctene, and norbornene, has been reported by several workers [1-6]. Polymerization of cyclopentene has been especially extensively studied with a view to obtaining new types of synthetic rubber [7-10].

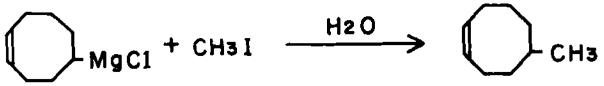
Ring-opening polymerization of cycloolefins is interesting not only for acquiring new polymer materials but also for synthesizing a model of alternating copolymer. For example, ring-opening polymers of 5-substituted cyclooctenes correspond to alternating terpolymers consisting of butadiene-ethylene-vinyl monomers. Polymerization of cyclooctenes and 3-substituted cyclooctenes was investigated in detail by Calderon et al. [11], who used tungsten catalysts. However, little is known about the polymerization of 5-substituted cyclooctenes. Very few investigations have dealt with the characterization of polycyclooctenes. In the present work, polymerization of cyclooctene, 5-methyl, 5-chloro-, and 5-methoxycyclooctenes by use of tungsten and molybdenum catalysts is investigated. The microstructure and thermal properties of the polymers are analyzed.

EXPERIMENTAL

Monomers

Commercially obtained cyclooctene was used after being purified by distillation over sodium. 5-Chlorocyclooctene was synthesized by the reaction of 1,5-cyclooctadiene with hydrogen chloride in the presence of stannic chloride as a catalyst at 0°C. The resulting 5-chlorocyclooctene was purified by steam distillation, followed by distillation under reduced pressure (bp 56-58°C/5 Torr). The purity of the product was found to be 98% by gas chromatography. Standard Grignard procedure was used to prepare 5-methylcyclooctene from 5-chlorocyclooctene according to the reaction sequence shown in Eqs. (1) and (2). The purity of the product obtained by distillation (bp 57°C/30 Torr) was found to be 78% by gas chromatography. The major by-product was identified as 3-methyl-[3,3,0]-bicyclooctane

(1)



(2)

produced through transannular reaction. This compound was proved to have a negligible influence on the polymerization by $WCl_6/AlEtCl_2$ catalyst. 5-Methoxycyclooctene was prepared by the reaction of 1,5-cyclooctadiene with methanol in $HClO_4$ according to the method of Franz et al [12]. The resulting 5-methoxycyclooctene was purified by repeated distillation under reduced pressure (bp 85°C/20 Torr). The purity of the distillate was found to be 92%.

Polymerization

Polymerization was carried out in glass ampules under nitrogen with monomer concentration of 20% by volume in toluene and was terminated by pouring the reaction mixture into a large amount of methanol containing about 5% of HCl. The polymer was purified by repeated reprecipitation from benzene solution into methanol and dried under vacuum at room temperature.

Measurements

^{1}H-NMR spectra were measured for deuterochloroform solution of polymer (ca. 7% w/v) with JEOL JNM-MH 100 and JEOL C-60 HL spectrometers (100 and 60 MHz, respectively) at room temperature. Chemical shifts were measured from tetramethylsilane added as an internal standard. For decoupled olefinic proton signals chemical shifts were measured from methylene chloride and were converted to tetramethylsilane scale.

The IR spectra were obtained with a JASCO IR-S spectrometer using a film cast from benzene solution on a KBr plate.

DSC curves were recorded with a Rigaku 8001 CS differential scanning calorimeter.

TABLE 1. Polymerization of cyclooctene (CO) and 5-Methylcyclooctene (MCO) by $WCl_6/AlEt_xCl_{3-x}$[a]

Monomer	Aluminum compound	$\frac{\text{Al}}{\text{W}}$[b]	$\frac{\text{Monomer}}{\text{W}}$[b]	Temp (°C)	Yield (%)	trans (%)	[η] (dl/g)[c]
CO	$AlEt_3$	8	1000	25	trace	-	-
	$AlEt_2Cl$	8	1000	25	35	32	-
	$AlEt_{1.5}Cl_{1.5}$	8	1000	25	80	71	2.6
	$AlEtCl_2$	8	1000	25	81	73	2.5
	$AlEt_{1.5}Cl_{1.5}$	8	2500	20	80	50	2.8
	$AlEt_{1.5}Cl_{1.5}$	5	2500	20	72	51	2.8
	$AlEt_{1.5}Cl_{1.5}$	2.5	2500	20	11	29	3.0
	$AlEt_{1.5}Cl_{1.5}$	5	2500	-10	23	23	4.1
	$AlEt_{1.5}Cl_{1.5}$	2.5	2500	-10	43	26	3.9
	$AlEt_{1.5}Cl_{1.5}$	1.5	2500	-10	0	-	-
MCO	$AlEt_3$	8	1000	25	trace	-	-
	$AlEtCl_2$	8	1000	25	70	66	1.2
	$AlEt_{1.5}Cl_{1.5}$	8	1000	25	81	71	1.4
	$AlEt_{1.5}Cl_{1.5}$	5	1000	25	80	70	1.3
	$AlEt_{1.5}Cl_{1.5}$	2.5	1000	-10	45	32	2.5

[a] Polymerization was carried out in toluene with monomer concentration of 20% by volume.

[b] Mole ratio.

[c] Measured in toluene at 30°C.

RESULTS AND DISCUSSION

Polymerization of cyclooctene (CO) and 5-methylcyclooctene (MCO) was carried out in the presence of tungsten catalysts. Table 1 shows polymerization conditions and polymer yields. Catalysts consisting of tungsten hexachloride and alkylaluminum chlorides such as $AlEt_2Cl$, $AlEt_{1.5}Cl_{1.5}$, and $AlEtCl_2$ yielded polymers in high yields from both CO and MCO, while $AlEt_3/WCl_6$ catalyst provided only

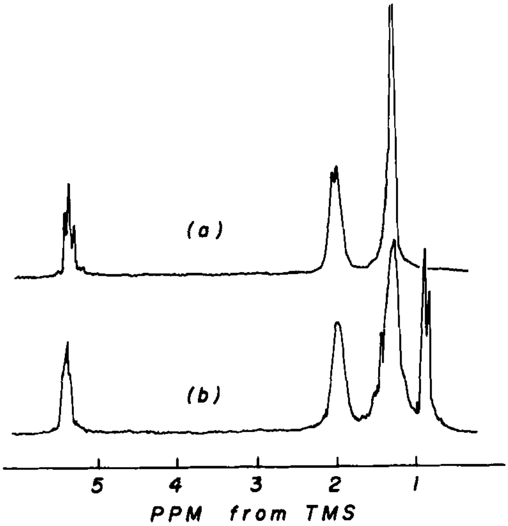


FIG. 1. ^{1}H-NMR spectra of (a) poly(CO) and (b) poly(MCO) prepared with tungsten catalyst.

negligible amounts of polymers from these monomers. With $AlEt_{1.5}Cl_{1.5}/WCl_6$ catalyst the yield of poly(CO) increased as the Al/W ratio increased at 20° C, while at -10° C the yield reached a maximum at an Al/W ratio of 2.5. Poly(CO) and poly(MCO) were almost equal in yield when the same reaction conditions were adopted. This indicates that the methyl group on 5-carbon atom did not influence the yield of polymer.

Figure 1 shows ^{1}H-NMR spectra of poly(CO) and poly(MCO) prepared with a tungsten catalyst. In the spectrum of poly(CO), signals at 5.4, 2.0, and 1.3 ppm were assigned to olefinic, allyl methylene, and other methylene protons, respectively. In the spectrum of poly(MCO), an additional signal was observed at 0.9 ppm as a doublet which was assigned to methyl proton of the substituent on the 5-carbon. The signal due to methine proton attached to the 5-carbon was not observed as an isolated signal, owing to overlapping with the methylene signal. The intensity ratios of these signals were in good agreement with the predicted values for the ring-opening polymers, indicating that the ring-opening mechanism was expected for these polymerizations (Table 2). The structures of these polymers were also confirmed by their IR spectra;

TABLE 2. Intensity Ratio of ^{1}H-NMR Signals[a]

Polymer	$-CH=$ 5.4 ppm	$=C-CH_2-$ 2.0 ppm	$-CH_3$ 0.9 ppm	Others 1.3 ppm
Poly(CO)	13.2	28.0	0	58.8
	(14.3)	(28.6)	(0)	(57.1)
Poly(MCO)	11.1	22.8	19.1	47.0
	(12.5)	(25.0)	(18.7)	(43.8)

[a] Values in parentheses are calculated values for the ring-opening polymer.

out-of-plane deformation bands due to cis and trans units were observed at 730 and 970 cm^{-1}, respectively (Fig. 2).

Tosi et al. [13] determined the ratio of cis to trans units in poly(CO) by IR measurement using two bands at 1404 and 970 cm^{-1} arising respectively from in-plane bending of the cis unit and out-of-plane deformation of the trans unit. However, the absorptivity of the 1404 cm^{-1} band is relatively low. Furthermore, a strong

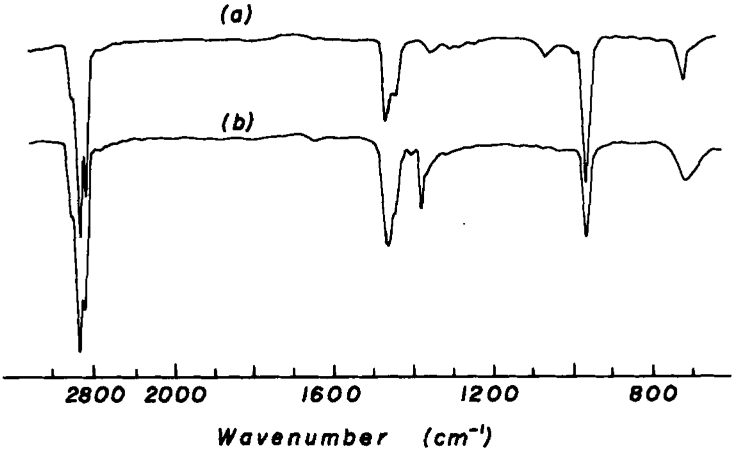


FIG. 2. IR spectra of (a) poly(CO) and (b) poly(MCO) prepared with tungsten catalyst.

methylene scissoring band at 1470 cm^{-1} makes it difficult to separate the band properly. On the other hand, Hatada et al. [14, 15] reported that the olefinic proton signal of 1,4-polybutadiene split into two groups of peaks due to cis and trans units by spin-decoupling from methylene proton. Similar decoupling measurement was applied to the olefinic protons in poly(CO) and poly(MCO). The olefinic proton signals of these polymers also split into two peaks by decoupling from methylene proton as shown in Fig. 3. The two peaks were assigned to signals due to olefinic protons of cis and trans units in order of decreasing magnetic field by considering the relative intensity of 970 cm^{-1} band in IR spectra. In these polymers the olefinic signals of the trans unit resonated at lower field than that of cis unit, which is the same as in the case of 1,4-polybutadiene [14, 15].

The fraction of trans to cis unit was determined from the relative intensities of these two peaks. The results are presented in the seventh column of Table 1. With $AlEt_{1.5}Cl_{1.5}/WCl_6$ catalyst the amount of trans unit in poly(CO) increased as the Al/W ratio and/or

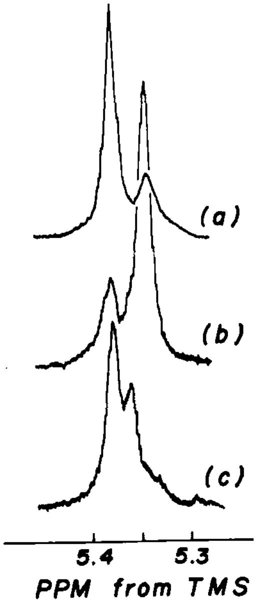


FIG. 3. ^{1}H-NMR spectra of olefinic proton decoupled from allyl methylene proton: (a), (b) poly(CO), (c) poly(MCO).

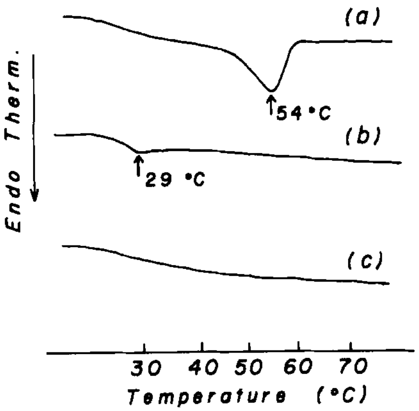


FIG. 4. DSC curves of polymers of CO: (a) 70% trans; (b) 50% trans; (c) 30% trans.

polymerization temperature increased. A similar dependence of the microstructure on the polymerization conditions was observed for poly(MCO) (Table 1). Therefore, it is concluded that the presence of a methyl substituent on the 5-carbon of cyclooctene influences neither the yield of polymer nor the microstructure of the obtained polymer.

Figure 4 shows DSC curves of the polymers of CO. A specimen containing 70% of trans unit (polymer a) exhibited an endothermal peak around 54°C which was estimated to arise from the melting of crystalline portion due to long trans sequences. The melting transition of a polymer containing 50% of trans unit (polymer b) was found to be 29°C, and the peak area was only one ninth of that of polymer a. Polymer c (30% trans units) showed no crystallinity at room temperature. On the other hand, poly(MCO) was amorphous at room temperature, regardless of the amount of trans units, which indicates that the substituent methyl group hindered the crystallization of the polymer.

Polymerization of CO and MCO was also conducted with the use of molybdenum catalysts as shown in Table 3. The yield of polymer decreased in the order, $AlEtCl_2 > AlEt_2Cl > AlEt_3 \simeq 0$. As shown in Fig. 5, poly(CO) and poly(MCO) prepared with molybdenum catalysts displayed no signals due to olefinic protons around 5 ppm. This indicates that these polymers were produced through vinyl polymerization mechanism instead of ring-opening polymerization. The vinyl polymerization mechanism for these polymers was also confirmed by IR spectroscopy; characteristic bands of out-of-plane

TABLE 3. Polymerization of CO and MCO by $MoCl_5/AlEt_xCl_{3-x}$[a]

Monomer	Aluminum compound	Yield (%)	$[\eta]$ (dl/g)[b]
CO	$AlEt_3$	6.4	-
	$AlEt_2Cl$	19.3	0.07
	$AlEtCl_2$	53.6	0.05
MCO	$AlEt_3$	13.6	-
	$AlEt_2Cl$	18.4	0.09
	$AlEtCl_2$	52.2	0.12

[a] Polymerization was carried out in toluene at room temperature with monomer concentration of 20% by volume. Molybdenum catalyst used was 2 mole % for monomer and Al/Mo ratio was 5.

[b] Measured in toluene at 30° C.

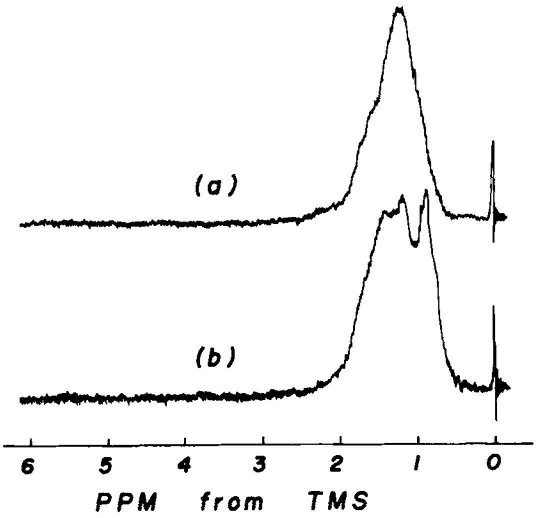


FIG. 5. ^1H-NMR spectra of (a) poly(CO) and (b) poly(MCO) prepared with molybdenum catalyst.

TABLE 4. Polymerization of 5-Chlorocyclooctene by $WCl_6/AlEt_xCl_{3-x}$[a]

Aluminum compound	Temperature (°C)	Yield (%)	Molecular weight[b]	Appearance
$AlEt_3$	50	20	430	Viscous liquid
$AlEt_2Cl$	50	51	670	Viscous liquid
$AlEt_2Cl$	20	53	800	Viscous liquid
$AlEtCl_2$	50	11	-	White powder
$AlEtCl_2$	25	27	-	White powder

[a] Polymerization was carried out in toluene with monomer concentration of 20% by volume. Tungsten catalyst used was 2 mole % based on monomer with Al/W ratio of 4.

[b] Measured by cryoscopic method in benzene.

deformation vibration of –CH=CH– group were not observed around 970 and 730 cm^{-1} in the IR spectra of these polymers.

Polymerization of 5-chlorocyclooctene was carried out by using tungsten catalyst as shown in Table 4. The use of $AlEt_3/WCl_6$ or $AlEt_2Cl/WCl_6$ as catalyst system yielded pale yellow viscous liquids, which were found to be oligomers of molecular weights of 400-800. The yield of oligomer was about 50% under the polymerization conditions examined. As shown in Fig. 6a, the oligomer showed an olefinic proton signal at 5.3 ppm and a signal due to methine proton on the chlorinated carbon around 4 ppm. This indicates that the oligomer was produced by ring-opening mechanism and that the elimination of chlorine atom was negligible with these catalysts. With the aid of $AlEtCl_2/WCl_6$ catalyst, white powder was obtained. This compound showed neither olefinic proton signal nor the signal due to methine proton on the chlorinated carbon but displayed new signals around 7.0 and 2.2 ppm, which were assigned to aromatic proton and methyl proton on the benzene ring, respectively (Fig. 6b). This indicates that $AlEtCl_2/WCl_6$ catalyst brought about vinyl polymerization coupled with Friedel-Craft type substitution of chlorine atom with toluene. It is clear from Table 4 that the presence of the substituent chlorine atom has direct effect on the molecular weight of the product as well as the yield.

Polymerization of 5-methoxycyclooctene was attempted by using tungsten catalyst at -20 to 70°C. Neither polymer nor oligomer was

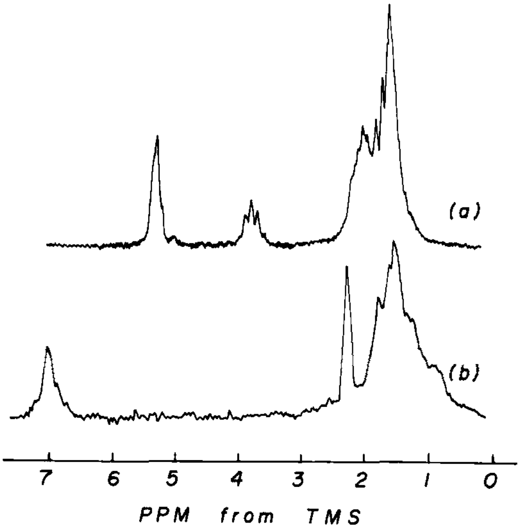


FIG. 6. ^{1}H-NMR spectra of poly(5-chlorocyclooctene)s prepared with (a) $AlEt_2Cl/WCl_6$ and (b) $AlEtCl_2/WCl_6$ catalysts.

obtained from this monomer, which indicates that the oxygen of substituent methoxy group interacted so strongly that the carbon-carbon double bond could not coordinate the catalyst.

REFERENCES

[1] G. Natta, G. Dall'Asta, I. W. Bassi, and G. Carella, Makromol. Chem., 91, 87 (1966).
[2] P. R. Marshall, Eur. Polym. J., 5, 29 (1969).
[3] G. Dall'Asta, Makromol. Chem., 154, 1 (1972).
[4] E. A. Ofstead and N. Calderon, Makromol. Chem., 154, 21 (1972).
[5] C. P. Pianazzi, J. Cattiauz, and J. C. Brosse, Makromol. Chem., 169, 45 (1973).
[6] W. L. Truett, P. R. Johnson, I. M. Robinson, and B. A. Montague, J. Amer. Chem. Soc., 82, 2337 (1960).
[7] G. Natta, G. Dall'Asta, and G. Mazzanti, Angew. Chem., 76, 163 (1963).

[8] G. Dall'Asta and P. Scoglione, Rubber Chem. Technol., 42, 1235 (1969).

[9] N. Calderon and R. L. Hinrichs, Chemtech, 627 (1975).

[10] G. Pampus and G. Lehnert, Makromol. Chem., 175, 2605 (1975).

[11] N. Calderon, E. A. Ofstead, and W. A. Judy, J. Polym. Sci. A-1, 5, 2209 (1967).

[12] H. J. Franz, W. Höbold, R. Höhn, G. Müller-Hagen, R. Müller, W. Pritzkow, and H. Schmidt, J. Prakt. Chem., 312, 622 (1970).

[13] C. Tosi, T. Ciampelli, and G. Dall'Asta, J. Polym. Sci. Polym. Chem. Ed., 11, 529 (1973).

[14] K. Hatada, Y. Tanaka, Y. Terawaki, and H. Okuda, Polym. J., 5, 327 (1973).

[15] K. Hatada, Y. Terawaki, H. Okuda, Y. Tanaka, and H. Sato, J. Polym. Sci. Polym. Letters Ed., 12, 305 (1974).

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