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Ring-opening Polymerization of Norbornene and Its Derivatives by $MoCl_5$, WCl_6 and $ReCl_5$ Catalysts

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Norbornene and such of its derivatives as *exo*-5, 6-trimethylene norbornene (*exo*-TMN) and *endo*-dicyclopentadiene (*endo*-DCPD) have been polymerized *via* ring cleavage to high-molecular-weight polymers, soluble in aromatics, by the use of $MoCl_5$, WCl_6, and $ReCl_5$ catalysts in a carbon tetrachloride solvent. The ring-opening polymers obtained by $MoCl_5$ have a trans-structure almost exclusively, on the other hand the polymers obtained by $ReCl_5$ are rich in cis structures and those obtained by WCl_6 are mixtures of the two. The reactivities of the monomers on those catalysts have been found to have the order of decreasing reactivity: *exo*-TMN>NE>*endo*-DCPD. In the ring-opening polymerization of norbornene by $MoCl_5$, carbon disulfide and carbon tetrachloride have been found to be effective solvents. The yield increases with the rise in temperature and also upon the addition of a catalytic amount of tertiary amines in the midst of the polymerization procedure, while the structures of the polymers obtained do not change. The Co-catalyst H_2O is not necessary. Chlorine atoms are found in the polymers. Those results suggest that the ring-opening polymerization of norbornene over $MoCl_5$ occurs through a specific coordinated mechanism.

Three modes of reaction have been established for the polymerization of norbornene: a vinyl polymerization and two types of ring-opening polymerization, giving polymers with trans and cis double bonds. Ring-opening-type polymers have been obtained by Truett,[1] Sartori,[2] and Furukawa[3] using Ziegler-Natta catalysts, and by Michelotti[4] and Rinehart[5] using Ir^{3+}, Ru^{3+} and Os^{3+} in polar media. It has been concluded that the ring-opening polymerization proceeds through the coordinated anionic mechanism.[1,4] On the other hand, the vinyl-type polymer has been obtained using such cationic catalysts as $AlCl_3$, $TiCl_4$, and BF_3.[3] In a previous work in this series[6] it has been shown that the ring-opening polymer of norbornene can be obtained by the use of unicomponent catalyst, $MoCl_5$, in carbon tetrachloride.

In this paper we wish to report on the ring-opening polymerization of norbornene, *exo*-TMN, and *endo*-DCPD by $MoCl_5$, WCl_6 and $ReCl_5$ catalysts and to discuss the polymerization mechanism from the point of view of the effects of the temperature, the solvents, and the co-catalysts.

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Experimental

Materials. The Diels-Alder reaction of ethylene and dicyclopentadiene gave norbornene, bp 96.0—97.0°C (lit.[7] 94—97°C/740 mmHg). *exo*-5, 6-Trimethylene norbornene was prepared from dicyclopentadiene by hydration, hydrogenation, and esterification reactions, followed by pyrolysis; bp 54—56°C/8 mmHg, $n_D^{25}=1.4948$ (lit.[8] $n_{25}^D=1.4943$). An *endo*-dicyclopentadiene received from the Eastman Kodak Company was distilled prior to use; $n_D^{25}=1.5120$ (lit.[9] $n_D^{25}=1.5121$). The solvents were purified by conventional methods.

$NbCl_5$ and $SeCl_4$ were prepared from their respective metals by chlorination.[10] $MnCl_2$[11] was prepared from $MnCl_2 \cdot 2H_2O$; UCl_4[12] was prepared by refluxing UO_3 in disulfo dichloride. $MoCl_4$ was prepared according to the method of Larson.[13] Found: Cl, 55.1; Mo, 40.6%. Calcd for $MoCl_4$: Cl, 59.7; Mo, 40.4%. The other metal chlorides were commercially available in anhydrous pure grades and so were used without further purification.

Polymerization. Polymerization was carried out in a sealed glass tube under an argon atmosphere. The following is a typical example of the procedure employed. Into a 50 m*l* glass tube there was placed 0.682 g of $MoCl_5$; then were added 10 m*l* of CCl_4. After it had thus stood for ten minutes, the tube was immersed and chilled in a dry ice - methanol bath, after which a solution of 4.70 g of norbornene in CCl_4 (10 m*l*) was introduced into the tube; then the tube was sealed off. Polymerization was carried out with agitation in a water bath controlled thermostatically at 50°C. After 4 hr, the contents were poured into a large excess of methanol containing phenyl β-naphthyl amine as a stabilizer. The dark, crude polymer thus obtained was separated and dried at 40°C under vacuum; yield 2.40 g.

In 200 m*l* of hot benzene, 1.0 g of the crude polymer was dissolved and reprecipitated with methanol. There was thus obtained 0.59 g of a white, fibrous polymer, which was soluble in benzene, and 0.01 g of a black, insoluble polymer. Found (for the benzene soluble polymer): C, 88.98; H, 10.63%. Calcd for $(C_7H_{10})_n$: C, 89.29; H, 10.71%. The yields stated in this paper are the totals of the benzene-soluble and -insoluble polymers. The intrinsic viscosity was determined for *p*-xylene solutions at 100°C. The infrared spectrum was recorded using a Japan Spectroscopic Co. apparatus, Model DS 402G.

Results

Polymerization of Norbornene. Polymerization was carried out at 50°C using various metal chlorides in carbon tetrachloride. Table 1 shows that the low-molecular-weight vinyl-type polymers were obtained using such catalysts as $AlCl_3$, $ZrCl_4$, VCl_4, $NbCl_5$, and $TaCl_5$; of these $AlCl_3$ showed the highest activity.

The initially homogeneous system of norbornene polymerized by $MoCl_5$, WCl_6, or $ReCl_5$ becomes heterogeneous as the reaction progresses due to the insolubility of the polymer. The produced polymers are soluble in hot benzene and structurally similar to the products previously reported,[1,2] in which a major portion of the polymer chain consists of cyclopentane rings linked in a *cis*-1, 3 configuration with either trans- or cis double bonds.

In Table 1, $D_{965}/D_{740}/D_{1445}$ are the ratios of the optical densities at 965, 740, and 1445 cm^{-1} in the infrared spectra; these densities are assigned to the deformation of *trans* C=C, *cis* C=C, and CH_2 respectively. Furukawa[3] has found a linear correlation between the D_{965}/D_{1445} ratio and the amounts of trans double bonds in polymers. By the use of this correlation, the trans units can be calculated; then the cis units may be estimated from the difference between the total double bonds as determined by the Wijs method and the trans units as calculated above. By that calculation, it is found that the polynorbornene catalyzed by $MoCl_5$ is of trans units 80—95% and cis units 4—5%; the polymer catalyzed by WCl_6, of trans 50% and cis 39%, and the polymer catalyzed by $ReCl_5$, of trans 23% and cis 75%.

Under the same conditions described in Table 1, no polymer was found when those catalysts were used: $CdCl_2$, BF_3OEt_2, $TiCl_4$, $SnCl_4$, $AsCl_3$, $SbCl_5$, $CrCl_3$, $SeCl_4$, $MoCl_4$, UCl_4, $MnCl_2$, $FeCl_3$, $CoCl_3$, and $RuCl_3$.

Polymerization of *exo*-5, 6-Trimethylene Norbornene (TMN). A number of catalysts like Mo(V), W(VI), and Re(V) which were active in the polymerization of norbornene were found to be also active in the polymerization of TMN, giving benzene-soluble and high-molecular-weight polymers in a maximum total conversion of 75% as shown in Table 2. The polymer obtained by $MoCl_5$ had a strong absorption at 965 cm^{-1}, indicating substantial amounts of trans unsaturation along the polymer chain. On the other hand, the polymer obtained by $ReCl_5$ had strong absorptions at 2980, 1408, and 740 cm^{-1}, absorptions which were attributed to cis double bonds. Since the infrared absorptions of the polymers were similar to those of polynorbornenes obtained by the same catalysts, the structures of poly-TMN must be of a ring-opening trans- or cis-type similar to those of polynorbornenes.

The films or powders of poly-TMN prepared with $MOCl_5$, Ziegler, or $AlCl_3$ catalysts were all found by X-ray diffraction to be amorphous.

Polymerization of *endo*-Dicyclopentadiene (DCPD). Many examples have been known of the

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TABLE 1. POLYMERIZATION OF NORBORNENE

Catalyst	Yield %	Soluble/Insoluble in boiling benzene	Characteristics of the soluble fraction		
			$D_{965}/D_{740}/D_{1445}$	[η]	Softening range, °C
$MoCl_5$	32.6	93/7	3.4/0.5/1.0	0.25	108—128
WCl_6	22.4	100/0	2.1/0.8/1.0	0.70	95—103
$ReCl_5$	83.8	88/12	0.8/1.7/1.0	0.34	94—108
$AlCl_3$	32.0	100/0	0.1/0.0/1.0	0.03	84— 92
$AlBr_3$	11.3	100/0	0.0/0.0/1.0	0.01	45— 60
$ZrCl_4$	1.5	100/0	0.0/0.0/1.0	—	—
VCl_4	3.6	100/0	0.0/0.0/1.0	—	65—120
$NbCl_5$	21.9	100/0	0.1/0.0/1.0	—	vis. liquid
$TaCl_5$	8.1	100/0	0.1/0.0/1.0	—	vis. liquid

Monomer: 4.70 g; concentration: 2 mol/*l*; cat.: 5 mol% of monomer; solvent: CCl_4; polymn. time: 4 hr; temp.: 50°C

TABLE 2. POLYMERIZATION OF *exo*-5, 6-TRIMETHYLENE NORBORNENE

Catalyst	Yield %	Soluble/Insoluble in boiling benzene	Characteristics of the soluble fraction		
			$D_{965}/D_{740}/D_{1445}$	[η]	Softening range, °C
$MoCl_5$	71.7	83/17	2.3/0.2/1.0	1.62	142—145
WCl_6	74.8	85/15	1.3/0.5/1.0	2.47	139—146
$ReCl_5$	71.5	100/0	0.1/0.8/1.0	1.61	106—115
$AlCl_3$	9.8	100/0	0.1/0.0/1.0	0.04	126—142
$AlEt_3$-$TiCl_4$[a]	49.0	10/90	1.7/0.1/1.0	0.83	160—175

Polymerization conditions are the same as in Table 1.

a) $AlEt_3$: 8 mol%; Al/Ti: 4; *n*-heptane solvent

polymerization[14] of DCPD as a third component in the ethylene-propylene-terpolymer. Recently Imoto[15] reported the homopolymerization of DCPD using Ziegler-type catalysts.

Independently, we also obtained the poly *endo*-DCPD by two kinds of catalysts: metal halides and Ziegler-type catalysts. The results of the polymerization are summarized in Table 3. The polymers had absorptions of a double bond on a cyclopentane ring at 1617 and 940 cm^{-1}, but had no absorption of the double bond on a bicyclic ring at 1575 cm^{-1}, as is shown in Fig. 1. These facts suggest that the latter double bond reacted in the polymerization, while the former one did not react. This is in accordance with the results of the addition reaction of H_2O, HX, ROH, and RCOOH to DCPD, in which only the double bond on the bicyclic ring can be attacked.[16] Since the poly-DCPD catalyzed by $MoCl_5$ had a strong absorption at 973 cm^{-1} (*trans* C=C), its structure must be of a ring-opening trans type (II):

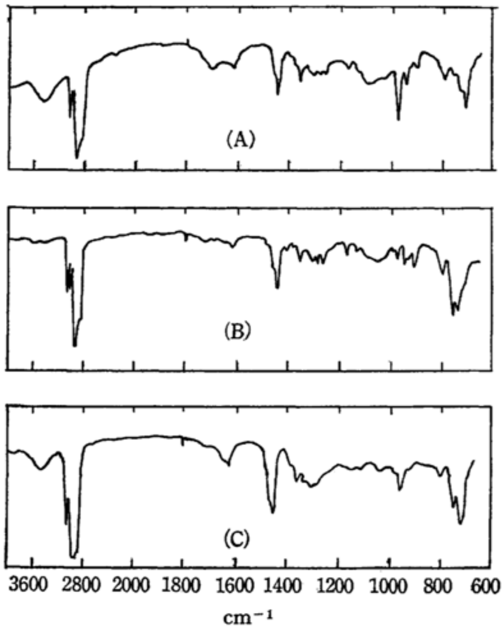

Fig. 1. IR spectra of *endo*-DCPD, (A): $MoCl_5$-catalyzed; (B): $ReCl_5$-catalyzed; (C): $AlCl_3$-catalyzed.

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TABLE 3. POLYMERIZATION OF *endo*-DICYCLOPENTADIENE

Catalyst	Temp. °C	Time hr	Yield %	Soluble/Insoluble in boiling benzene	Characteristics of the soluble fraction $D_{973}/D_{755}/D_{1445}$	$[\eta]$
$MoCl_5$	50	4	23.3	3/97	3.8/0 /1.0[a]	—
WCl_6	50	4	23.6	55/45	0.3/0.5/1.0	0.14
$ReCl_5$	50	4	45.2	86/14	0.4/1.7/1.0	0.45
$AlCl_3$	50	4	25.4	80/20	0.0/0.0/1.0	—
$AlCl_3$	−15	120	19.5	73/27	0.1/0.0/1.0	—
$TiCl_4$	50	10	0.3	—	0.0/0.0/1.0	—
$AlEt_3$-$TiCl_4$[b]	50	10	6.0	0/100	2.6/0.1/1.0[a]	—
$AlEt_3$-$MoCl_5$[b]	−15	10	3.5	0/100	0.3/1.7/1.0[a]	—

Polymerization conditions are the same as in Table 1.

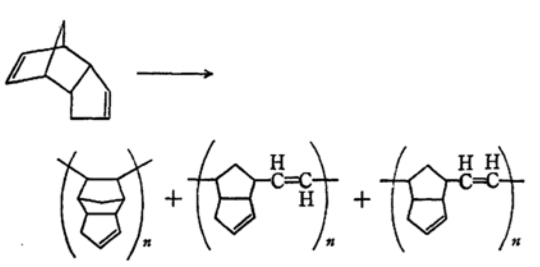
a) Insoluble fraction

b) $AlEt_3$: 8 mol%; Al/Ti (or Al/Mo): 4; *n*-heptane solvent

TABLE 4. POLYMERIZATION OF OLEFINS

Monomer	Temp. °C	Time hr	Yield %	Molecular weight	Micro-structure of polymer	Ref.
Isobutylene	−20	2	37	4990	Polyisobutylene	
Styrene	30	1	90	8240	Amorphous	
α-Methylstyrene	30	4	7	2500		
Trioxane	30	4	50	$[\eta]=0.61$	Polyether	
Isoprene	50	4	95	1820	Bicyclic structure	17
Butadiene	50	4	10	—	Cyclization	
4-Vinylcyclohexene	50	4	4	—	Cyclization	18
Cyclopentene	50	4	3	—	Double bond opening	19

Cat.: $MoCl_5$; 2—5 mol% of monomer; solvent: CCl_4



(I) (II) (III)

On the other hand, the polymer catalyzed by $ReCl_5$ was soluble in boiling benzene, and its IR spectrum showed sharp absorptions at 3000, 1408 and 755 cm^{-1}, absorptions which can be assigned to the cis double bond along the main chain. Thus, the structure is mainly of a ring-opening cis type (III).

The poly-DCPDs produced by Ziegler-type catalysts, $AlEt_3$-$TiCl_4$ or $AlEt_3$-$MoCl_5$, consisted mostly of ring-opening trans- or cis-type structures respectively. It was also possible to get the polymer with a vinyl-type structure (I) by using such Lewis acid catalysts as $AlCl_3$ and $TiCl_4$. Therefore, the effect of catalyst on the micro-structure of poly-DCPD was the same as that on the structures of polynorbornene and poly-TMN.

The polymerization rates of DCPD on various catalysts were smaller than those of norbornene and TMN, and none of the resultant poly-DCPD showed clear softening points, while they decomposed gradually at 150—400°C.

Polymerization of Olefins by $MoCl_5$. The microstructure of polynorbornene obtained by means of $MoCl_5$ was different from those obtained by usual cationic polymerization catalysts, *e.g.*, $AlCl_3$ and $TiCl_4$. To study this point further, it seemed of interest to carry out the polymerization of the other olefins over $MoCl_5$.

As is shown in Table 4, polyisobutylene, mol wt 4990, was obtained at −20°C, and the molecular weight increased with a decrease in the temperature. In the polymerization of isoprene, a low-molecular-weight polymer was obtained in a high yield, and the structure was not linear but of a bicyclic type, as has been reported by Golub.[17] Chloroprene was found poor in polymerizability. Cyclopentene, 4-vinylcyclohexene, and cyclohexadiene were somewhat polymerizable.

For these olefins, it was concluded that $MoCl_5$ catalyzes a normal cationic polymerization as well as typical Lewis acid catalysts.

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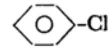
[17] M. A. Golub and J. Heller, *Can. J. Chem.*, **41**, 937 (1963).

TABLE 5. EFFECT OF SOLVENT

Solvent	Yield %	Soluble/Insoluble in boiling benzene	Characteristics of the soluble fraction	
			$D_{965}/D_{740}/D_{1445}$	$[\eta]$
CS_2	69.6	61/39	3.1/0.5/1.0	0.39
CCl_4	32.6	93/7	3.5/0.5/1.0	0.25
$CHCl_3$	31.2	24/76	1.4/0.6/1.0	0.19
CH_2Cl_2	20.8	10/90	1.3/0.3/1.0	—
$C_2H_4Cl_2$	52.8	12/88	1.1/0.3/1.0	0.10
	17.6	76/24	2.5/0.5/1.0	0.42
	38.0	—	2.5/0.5/1.0	—

Monomer: norbornene; cat.: $MoCl_5$, 5 mol% of monomer; 50°C; 4 hr

The copolymerization of norbornene with styrene was attempted in carbon disulfide using a $MoCl_5$ catalyst. The polymer thus obtained was only a mixture of two homopolymers. This suggests that the polymerization mechanism of norbornene is different from that of styrene.

The results of the copolymerization of norbornene with trioxane were complicated. When $MoCl_5$ was added to a carbon disulfide solution of norbornene and trioxane, no polymer was formed. There was the same result when trioxane was added to the brown-colored norbornene-$MoCl_5$ complex. However, when the norbornene was added to the light blue trioxane-$MoCl_5$ complex, only the homopolymer of trioxane was formed. In no case, did we found any evidence of the formation of a copolymer.

Mechanism of Ring-opening Polymerization of Norbornene by $MoCl_5$. *Solvent Effect.* Solvents greatly influenced the yield and the microstructure of the polymer. According to Table 5, the most effective solvents for the polymerization were halogenated hydrocarbons and carbon disulfide. Polymers were not formed in hydrocarbon solvents such as *n*-heptane. When such non-polar solvents as CCl_4 and CS_2 were used, the polymerization rates were large and the structures were predominantly of ring-opening types. In CH_2Cl_2 and $C_2H_4Cl_2$, which are more polar than the solvents mentioned above, the formation of ring-opening polymers decreased. In a very polar solvent such as CH_3NO_2, no polymer was formed.

It has been said that $MoCl_5$ is reduced to $MoCl_4$ in CCl_4 as follows.(20)

$$2\ MoCl_5 \xrightarrow{\text{in } CCl_4} 2\ MoCl_4 + Cl_2$$

Furthermore, it is known that the reaction of $MoCl_5$ with refluxing benzene gives $MoCl_4$ and chlorobenzene.(13) We found that $MoCl_4$ could not polymerize norbornene. From these results, it may be concluded that the true catalyst for polymerization is $MoCl_5$ and not the low valence molybdenum species ($Mo \leqq 4$), although $MoCl_5$ has a tendency to liberate its chlorine atom as an anion in CCl_4 and benzene.

Effect of Cocatalyst. It is well known that cationic polymerization by a Lewis acid generally needs a cocatalyst such as H_2O. If the polymerization over $MoCl_5$ proceeds through a cationic intermediate, therefore, it seems small amounts of water will be necessary, because the solvent, CCl_4, can not work as a cocatalyst.

The effect of the water on the polymerization was examined for dehydrated CCl_4 (water content 18 ppm) and water-saturated CCl_4 (water content 69 ppm). It is clear from Table 6 that the yield decreased with an increase in the water content. A detailed discussion is impossible at the present time, because a completely anhydrous solvent could not be prepared. Roughly, however, water may not be necessary for the polymerization. It is interesting that the structures of the polymers obtained were not influenced by the water content in the polymerization system.

Effect of Temperature. The rate of polymerization increased greatly with an increase in the polymerization temperature. For example, the yield

TABLE 6. EFFECT OF CO-CATALYST

No.	$MoCl_5/H_2O$	Yield %	$D_{965}/D_{740}/D_{1445}$
1	1.0/0.60	2.7	3.9/0.5/1.0
2	1.0/0.26	5.7	3.8/0.5/1.0
3	1.0/0.17	17.5	4.2/0.5/1.0
4	1.0/0.034	19.6	3.2/0.5/1.0
5	1.0/0.013	17.0	3.5/0.5/1.0

Monomer: norbornene; solvent: CCl_4; cat.: $MoCl_5$, 2 mol% of monomer; 50°C; 4 hr for No. 1—3 and 0.5 hr for Nos. 4 and 5.

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18) G. B. Butler and M. L. Miles, *J. Polymer Sci.*, **A3**, 1609 (1965).

19) G. Natta, G. Dall'asta and G. Mazzanti, *Angew. Chem.*, **76**, 765 (1964).

20) I. M. Pearson and C. S. Garner, *J. Phys. Chem.*, **65**, 690 (1961).

TABLE 7. ADDITION OF TERTIARY AMINES

Monomer	Amine	Yield %	Characteristics of the soluble fraction $D_{965}/D_{740}/D_{1445}$	$[\eta]$
Norbornene	none	9.2	3.6/0.6/1.0	0.25
Norbornene	Et_3N	59.5	3.4/0.6/1.0	0.50
Norbornene	n-Bu_3N	26.6	3.8/0.6/1.0	0.76
DCPD	none	4.4	1.2/0.0/1.0a)	—
DCPD	Et_3N	15.1	1.6/0.0/1.0a)	—

Cat.: $MoCl_5$; solvent: CCl_4
Amount of amine: equal mole to cat. was added 30 min after the reaction had started.
For norbornene: 30°C, 4 hr
For DCPD: 50°C, 2 hr
a) $D_{973}/D_{755}/D_{1445}$

of polymers varied with the rise of temperatures in such a manner as: 1.9% (−15°C, 24 hr), 3.6% (0°C, 12 hr), 8.5% (30°C, 2 hr), and 19.6% (50°C, 0.5 hr). The microstructures and intrinsic viscosities of the polymers changed little within the range of polymerization temperature of −15°C—+50°C.

Elementary Analysis of Polymer. The results of carbon and hydrogen analysis of the polynorbornene have been shown in the Experimental section. The polymer produced by $MoCl_5$ in benzene was found to be 0.13% chlorine. Since the molecular weight of this polymer was 20900, one polymer should contain about one chlorine atom. The polymers prepared in carbon tetrachloride or carbon disulfide contained more chlorine atoms than those prepared in benzene.

Addition of t-Amines. The reaction between tertiary amines and $MoCl_5$ in a CCl_4 solution gives an insoluble black complex, R_3N-$MoCl_5$²¹⁾ This complex was inactive in the polymerization of norbornene. However, the tertiary amines were apparently active promoters of the polymerization only when the amines were added to a polymerization system in which an active growing chain of the polymer was present. Thus, norbornene was polymerized by $MoCl_5$ in a glass tube sealed with a stopper. Thirty minutes after the reaction had started, a mole of Et_3N equal to the catalyst was added; the contents then suddenly became viscous. As Table 7 and Fig. 2 show, the yield and the molecular weight increased remarkably upon the addition of Et_3N, but the microstructures remained unchanged. These results suggest that the addition of tertiary amine strongly increases the rate of propagation.

On the other hand, such primary amines as $EtNH_2$ and n-$BuNH_2$, and such secondary amines as n-Bu_2NH, pyridine, and α-picoline were all effective chain stoppers. There was no increase in the yield upon the addition of such electron donors as triphenylphosphine, dioxane, trioxane, and tetrahydrofuran.

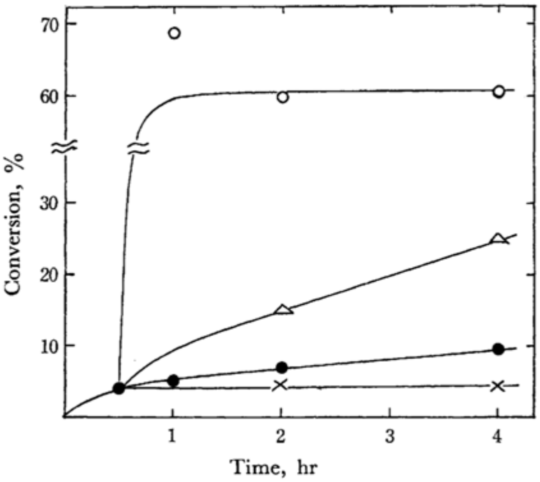

Fig. 2. Addition of amines to norbornene polymerization. Amine was added 30 min after reaction had started.
(○): Et_3N, (△): n-Bu_3N, (×): pyridine, (●): without amine. Polymerization conditions are the same as in Table 7.

Discussion

Ring-opening-type polymers of norbornene, *exo*-TMN, and *endo*-DCPD can be prepared with unicomponent catalysts, $MoCl_5$, WCl_6, and $ReCl_5$. The microstructures of the polymers are influenced by the type of transition metals in the catalysts. The order of increase in the trans units is $MoCl_5 > WCl_6 > ReCl_5$. The reverse order is that of the increase of cis-type polymers. The polymerization activities of the monomers on these catalysts are; *exo*-TMN > norbornene > *endo*-DCPD.

It has been reported that Ziegler-type catalysts modified by the addition of several amines increase

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21) D. A. Edward and G. W. A. Fowles, *J. Chem. Soc.*, **1961**, 24.

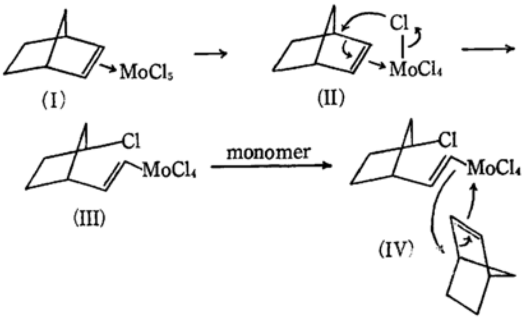
the activity in ring cleavage in the polymerization of norbornene.[3,22] In our study, it was found that the addition of a tertiary amine to the polymerization system remarkably increased the polymerization rate and the molecular weight, without making any change in the microstructures. In addition, several new facts were found in the polymerization of norbornene catalyzed by $\mathrm{MoCl_5}$. Ring-opening polymers were produced by using such nonpolar solvents as $\mathrm{CCl_4}$ and $\mathrm{CS_2}$; on the other hand, vinyl-type polymers were predominant when a more polar solvents, like $\mathrm{CH_2Cl_2}$ and $\mathrm{C_2H_4Cl_2}$, were used. Water was not effective as a cocatalyst. The polymerization rate increased with the rise in the temperature. The polymers contained chlorine atoms which had been liberated from the catalyst. Molybdenum tetrachloride did not work as a catalyst. Copolymers with styrene or trioxane could not be formed.

There are two types of polynorbornene: a vinyl type and a ring-opening type. The former is prepared with typical Lewis acid catalysts, such as $\mathrm{AlCl_3}$, $\mathrm{AlBr_3}$, $\mathrm{BF_3}$, and $\mathrm{TiCl_4}$, through a usual cationic mechanism.[3] The latter is obtained only by those catalysts which act through an anionic coordination mechanism. Included in the latter group are $\mathrm{LiAl\ (C_7H_{15})_4\text{-}TiCl_4}$ (Al/Ti$\geqq$2),[1] $\mathrm{AlEt_3\text{-}TiCl_4}$ (Al/Ti$\geqq$2),[3] Al*iso*$\mathrm{(C_4H_9)_3\text{-}MoCl_5}$ (Al/Mo=2),[2] and $\mathrm{RuCl_3}$ in alcohol.[4]

Judging from the general view that vinyl-type polymers are derived through cationic polymerization, and ring-opening-type polymers, through coordinated anionic polymerization, it may be concluded that the formation of ring-opening polynorbornene with $\mathrm{MoCl_5}$ is through the coordinated anionic mechanism. Experimental findings on the effects of solvents, the temperature, and the addition of amines and water supported this mechanism.

At first sight it seems contradictory that $\mathrm{MoCl_5}$ is an effective catalyst for Friedel-Crafts alkylation and acylation and also a cationic catalyst for α-olefins and dienes, while at the same time it acts as a coordinated catalyst for norbornene and its derivatives. However, this abnormal polymerization of norbornene by $\mathrm{MoCl_5}$ may be due to the specific characteristics of both the monomer and the catalyst. Because of the great ring strain,[4,15] a bicyclic olefin like norbornene is attacked easily at the 1 and 2 carbon atoms by nucleophilic agents. Another important cause is that $\mathrm{MoCl_5}$ is unstable enough to liberate its chlorine as an anion.[13]

The above evidence suggests the following mechanism, which is similar in nature to the ring-opening mechanism by Ziegler-type catalysts.[1]



The monomer is initially activated through π-complex formation (I), followed by a simultaneous, concerted, ring-opening displacement reaction on the bridgehead carbon by the $\mathrm{Cl^-}$ derived from the catalyst (II); this regenerates the active metal center (III) in a reduced oxidation state. The intermediate (III) may further activate another monomer. The repetition of this process leads to the propagation.

The chlorine atom introduced in the initiation step is found in the polymer. As soon as the same moles of norbornene as that of the catalyst are added to the carbon tetrachloride solution of $\mathrm{MoCl_5}$, the red color due to Mo(V) disappears and a pale-colored precipitate is produced. This phenomenon suggests a complex formation between the monomer and the catalyst. Since molybdenum tetrachloride is catalytically inactive, it is considered that molybdenum is not reduced below Mo(IV).

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[22] T. Saegusa, T. Tsujino and J. Furukawa, *Makromol. Chem.*, **78**, 32 (1964); **85**, 71 (1965).