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Cationic Polymerization Behavior of Some Vinyl Ketone Cyclodimers

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ABSTRACT

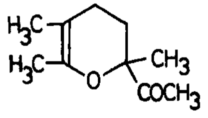
Cationic polymerizations of 2,3-dihydropyran derivatives, methyl isopropenyl ketone cyclodimer (MIPKD), chloromethyl vinyl ketone cyclodimer (CMVKD), and methyl isopropenyl ketone-chloromethyl vinyl ketone cyclocodimer, D(MIPK-CMVK), were investigated in the presence of various Lewis acids at 0°C. These monomers were found to undergo cationic polymerization to give low molecular weight polymer which consisted mainly of a vinylene structure. However, the ring-opening polymerization was found to occur to a minor extent in cationic polymerizations of MIPKD and D(MIPK-CMVK) cyclodimer.

INTRODUCTION

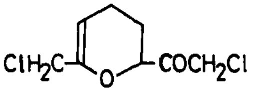
It has been reported that unsaturated cyclic ethers such as 2,3-dihydrofuran [1], coumarone [2], acrolein dimer [3], and

2,3-dihydropyran [4] undergo cationic polymerization. However, most of these ethers polymerize through the opening of their vinylene groups, but in some unsaturated cyclic ethers both vinylene and ring-opening polymerizations occur competitively. An example of the former is 2,3-dihydrofuran [1], and one of the latter is 2,3-dihydropyran [4]. However, 2-acetyl-6-methyl-2,3-dihydropyran, 2-carbomethoxy-2-methyl-2,3-dihydropyran and 2-methyl-2-phenyl-2,3-dihydropyran were subsequently found to follow the pattern of opening of the vinylene groups, indicating that the polymerization modes of 2,3-dihydropyrans changed with their substituents [5].

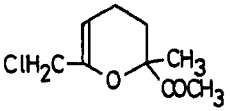
To confirm this point, cationic polymerizations of methyl isopropenyl ketone cyclodimer (MIPKD), chloromethyl vinyl ketone cyclodimer (CMVKD), and methyl isopropenyl ketone chloromethyl vinyl ketone cyclocodimer D(MIPK-CMVK) were undertaken and the structure of the resulting copolymers analyzed. The results obtained are described in this study.



(MIPKD)



(CMVKD)



D(MIPK-CMVK)

EXPERIMENTAL

Materials and Polymerization

The above three dihydropyran derivatives used in this study were prepared by the methods described in a previous paper [6]. After purification by distillation, these monomers were polymerized in a glass ampoule under vacuum in the presence of $BF_3O(C_2H_5)_2$, $FeCl_3$, and $SnCl_4$ catalysts. After polymerization for a given time, the polymerization mixture was poured into methanol containing a small amount of ammonia. The polymer was filtered and isolated by reprecipitation from tetrahydrofuran and water. Solvents, precipitants, and α,α'-azobisisobutyronitrile(AIBN) used were purified by usual methods.

Analysis of Polymers

The molecular weight distribution of the polymers was measured by means of gel-permeation chromatography (GPC) with a Shimazu-Du Pont HLC-830 instrument, based on the universal calibration curve, in which the hydrodynamic volume in the polymer was considered according to the method of Grubisic et al. [7]. A standard polystyrene was used in tetrahydrofuran at room temperature. The IR spectrum was recorded with a Jasco Model IR-G instrument at room temperature.

RESULTS AND DISCUSSION

The cationic polymerizations of the three dihydropyrans, MIPD, CMVD, and D(MIPK-CMVK) are shown in Table 1, in which the results of their radical polymerizations with AIBN are also indicated.

TABLE 1. Polymerizations of MIPKD, CMVKD, and D(MIPK-CMVK)[a]

			Reaction conditions		
Starting dimer	Catalyst	Solvent	Temp (°C)	Time (hr)	Yield (%)
MIPKD	$BF_3O(C_2H_5)_2$	CH_2Cl_2	0	48	52
	$BF_3O(C_2H_5)_2$	CH_2Cl_2	-78	48	43
	$BF_3O(C_2H_5)_2$	$(CH_3)C_6H_5$	0	48	45
	$SnCl_4$	CH_2Cl_2	0	48	40
	$AlCl_3$	CH_2Cl_2	0	48	36
	AIBN	None	60	7	0
CMVKD	$BF_3O(C_2H_5)_2$	CH_2Cl_2	0	19	18
	AIBN	None	60	7	0
D(MIPK-CMVK)	$BF_3O(C_2H_5)_2$	CH_2Cl_2	0	72	31
	AIBN	None	60	7	0

[a] Polymerization conditions: [catalyst] = 5×10^{-2} mole/liter; [solvent] = 50 vol %.

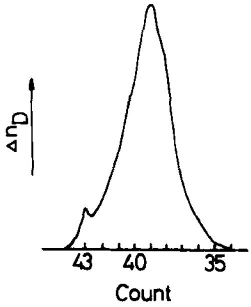


FIG. 1. GPC curve of the polymer of MIPKD obtained by $BF_3O(C_2H_5)_2$ in methylene chloride.

TABLE 2. Standard Polystyrene[a]

Count	MW
27.78	498,000
28.53	200,000
34.72	20,400
36.20	10,000
38.17	4,000
38.78	2,100

[a] Determined in THF at room temperature.

It is clear that all monomers can readily polymerize with $BF_3O(C_2H_5)_2$, but not with AIBN. MIPKD is also polymerized by $SnCl_4$ and $AlCl_3$, and the effect of such Lewis acids on the polymer yield is found to decrease in the order: $BF_3O(C_2H_5)_2 > SnCl_4 > AlCl_3$. This order is consistent with the result obtained the cationic polymerization of 2,3-dihydropyran by such Lewis acids [7].

In general, cationic polymerizations of 2,3-dihydropyran derivatives have been known to give low molecular weight (MW) polymers. The polymers obtained by cationic polymerizations of MIPKD, CMVKD,

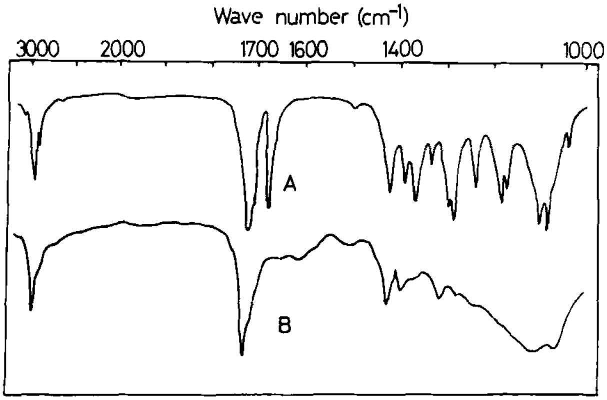
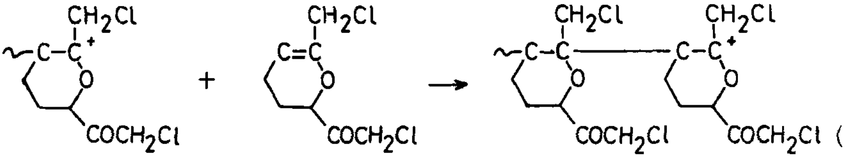


FIG. 2. IR spectra of CMVKD and its polymer obtained by $BF_3O(C_2H_5)_2$.

and D(MIPK-CMVK) were also materials of low molecular weight consisting of a wide range of distribution, i.e., MW = 500-20,000. As an example, the observed GPC curve of the polymer of MIPKD obtained by $BF_3O(C_2H_5)_2$ is shown in Fig. 1. In this case, the number-average molecular weight is calculated to be 1600, from a comparison to the standard polystyrene (Table 2).

Figure 2 shows, for example, the IR spectra of CMVKD and its polymer obtained by $BF_3O(C_2H_5)_2$. The absorption band at 1670 cm^{-1} due to the double bond at 5,6-positions in pyran ring of CMVKD disappears in the polymer obtained, and that due to the tetrahydropyran ring at 1060 and 1085 cm^{-1} remains in both CMVKD and its polymer. Therefore, it may be considered that this polymerization proceeds through the opening of a vinylene group in the dihydropyran ring, i.e., by a vinylene polymerization mechanism, as is shown in Eq. (1).



(1)

On the other hand, the polymers obtained from MIPKD and D(MIPK-CMVK) show the absorption bands at 1620-1630, 1060, and

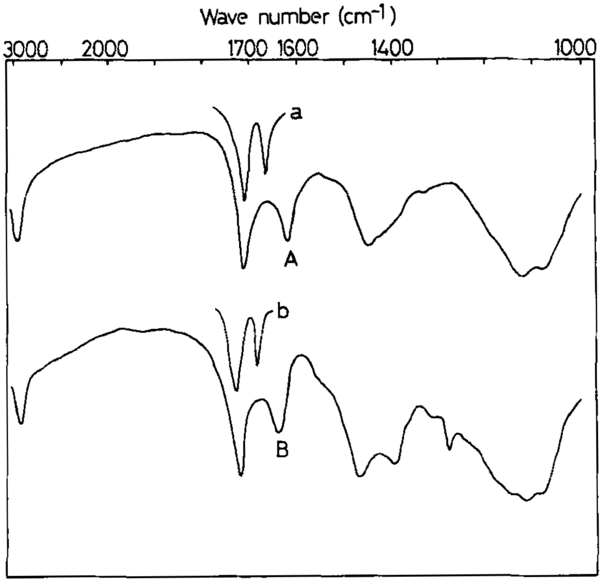
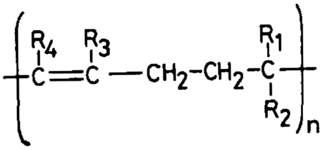


FIG. 3. IR spectra of polymers of (A) MIPKD and (B) D(MIPK-CMVK) and (a, b) their respective monomers.

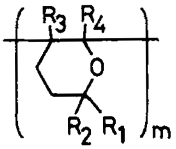
1085 cm^{-1}, as can be seen in Fig. 3, in which IR spectra between 1600 and 1800 cm^{-1} of the starting cyclodimers are also indicated. The presence of these bands seem to suggest the existence of an acyclic double bond and a tetrahydropyran ring in these polymers. Therefore, it may be considered that the polymers of MIPKD and D(MIPK-CMVK) consist of the structure I and II, which originate from both vinylene and ring-opening polymerizations of these cyclodimers.

In this case, the ring-opening polymerization seems to proceed

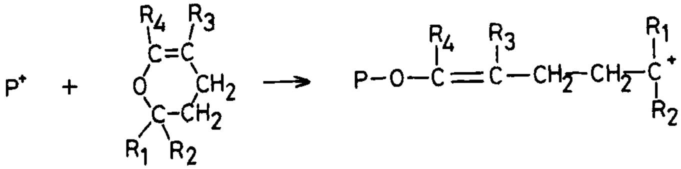


$$\left[\overset{R_4}{\overset{|}{C}}=\overset{R_3}{\overset{|}{C}}-CH_2-CH_2-\underset{\underset{R_2}{|}}{\overset{R_1}{\overset{|}{C}}}\right]_n$$

(I): $R_1 = R_3 = R_4 = CH_3$,
$R_2 = COCH_3$



(II): $R_1 = CH_3$, $R_2 = COCH_3$,
$R_3 = H$, $R_4 = CH_2Cl$



(2)

through the reaction shown in Eq. (2), where P^+ is a growing polymer cation.

Thus, the difference in polymerization modes between CMVKD and MIPKD or D(MIPK-CMVK) cyclodimers may reflect differences in stability of the carbonium ion produced by the ring-opening, i.e., the latter two cyclodimers give more a stable tertiary carbonium ion than the cyclodimer CMVKD, which produces a secondary carbonium ion.

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