Cationic Copolymerization of β, β-Dimethyl-β-propiolactone with 1,3-Dioxolane, 3,3-Bis(chloromethyl)oxacyclobutane and Styrene. High-Resolution NMR Studies on Sequence Distribution of Copolymers

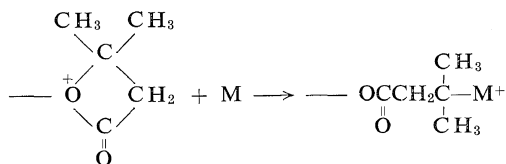Yuya YAMASHITA, Shigeru KONDO, and Koichi ITO

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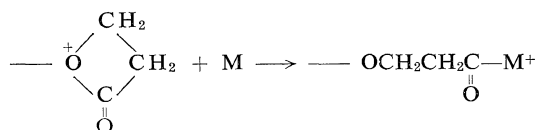*Nagoya University,*
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ABSTRACT: The cationic polymerization mechanism of β,β-dimethyl-β-propiolactone (DMPL) was studied by examining the microstructure of copolymers with 1,3-dioxolane (DOL), 3,3-bis(chloromethyl)oxacyclobutane (BCMO) and styrene (St), using high-resolution NMR. DMPL copolymerizes almost randomly with DOL and BCMO, but hardly copolymerizes with St at all. The relative reactivities of the cyclic monomers are BCMO>DOL>DMPL in accord with the order of monomer basicity. Ring opening polymerization of DMPL occurs through alkyl—oxygen fission, with the oxonium ion more likely to be the propagating species than the carbonium ion.

KEY WORDS Cationic Copolymerization / Sequence Distribution / High-Resolution NMR / β,β-Dimethyl-β-propiolactone / 3,3-Bis(chloromethyl)oxacyclobutane / 1,3-Dioxolane / Styrene /

Previously we reported that β,β-dimethyl-β-propiolactone (DMPL) is much more reactive in cationic polymerization than β-propiolactone (PL),[1] a result which was expected from the higher basicity of the former.[2] Also it appeared that DMPL and PL polymerized by the alkyl—oxygen and acyl—oxygen fissions, respectively, because the IR spectra of the copolymers with styrene (St) showed the absence and presence of the aliphatic ketonic groups.[3]
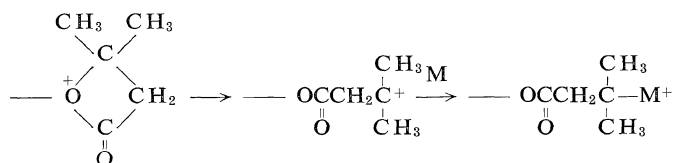
$$-\overset{+}{O}\diagdown\overset{CH_3\ CH_3}{\underset{\underset{O}{\overset{\|}{C}}}{\diagup C \diagdown}}CH_2 + M \longrightarrow - OCCH_2\underset{\underset{CH_3}{\overset{|}{|}}}{\overset{\overset{CH_3}{|}}{\underset{\overset{\|}{O}}{C}}} - M^+$$

(1)

$$-\overset{+}{O}\diagdown\overset{CH_2}{\underset{\underset{O}{\overset{\|}{C}}}{\diagup CH_2}}CH_2 + M \longrightarrow - OCH_2CH_2\underset{\overset{\|}{O}}{C} - M^+$$

(2)

The latter cross-propagation reaction (M = St) was found to occur only with great difficulty, as had been concluded from the determination of the ketonic group content of the copolymers,[4] and also from the examination of the model reaction.[5] It was postulated that vinyl and cyclic monomer pairs with different propagation mechanisms would be difficult to copolymerize randomly. Randomness of the sequence distribution of copolymers may thus be taken as a criterion of the similarity of the growing chain ends.[6]

$$-\overset{+}{O}\diagdown\overset{CH_3\ CH_3}{\underset{\underset{O}{\overset{\|}{C}}}{\diagup C \diagdown}}CH_2 \longrightarrow - OCCH_2\underset{\underset{CH_3}{\overset{|}{|}}}{\overset{\overset{CH_3}{|}}{\underset{\overset{\|}{O}}{C^+}}} \overset{M}{\longrightarrow} - OCCH_2\underset{\underset{CH_3}{\overset{|}{|}}}{\overset{\overset{CH_3}{|}}{\underset{\overset{\|}{O}}{C}}} - M^+$$

(3)

Now it is a question whether the DMPL chain end is an oxonium ion as indicated in Eq. 1 (S_N2 mechanism) or a carbonium ion as in Eq. 3 (S_N1 mechanism).

The purpose of the present paper is to examine the propagation mechanism of DMPL, based on the NMR studies of the copolymers with 1,3-dioxolane (DOL), 3,3-bis(chloromethyl)oxacyclobutane (BCMO) and St. BCMO and St clearly polymerize through the oxonium and the carbonium ions, respectively, and DOL probably through both the oxonium and carbonium ions.[7] Detailed analysis of sequence distribution by high-resolution NMR has recently been given elsewhere with a similar system, PL—BCMO.[8]

EXPERIMENTAL

DMPL was prepared from ketene and acetone as previously described.[1] All the other reagents and solvents were commercially supplied and purified as before.[8]

Monomers and toluene were charged in a glass tube under nitrogen. Catalyst (1.5 mol% to monomer mixture) was added at Dry Ice temperature, and the tube was sealed. Polymerization was carried out at 0°C for the required time, and stopped by adding methanol containing a small amount of hydrochloric acid. After standing at −20°C overnight, polymers precipitated were collected and washed repeatedly with methanol, and dried under vacuum to constant weights.

Results of polymerization are shown in Tables I, II, and III. Polymers obtained were white powders for the DMPL—BCMO and —St systems, and a colorless, tacky solid for the DMPL—DOL system. All samples were soluble in chloroform or carbon tetrachloride, although those with high BCMO contents were partly insoluble in chloroform at room temperature. Molecular weights of some samples were measured by VPO (Hitachi Perkin Elmer 115) in benzene.

NMR spectra were measured at 60°C in chloroform for DMPL—DOL and —BCMO systems, and in carbon tetrachloride for the DMPL—St system, using about 30 mg polymer in 0.5 ml of solvent. A Japan Electron Optics Spectrometer (JNM-C-60) operating at 60 Mc was used.

RESULTS

DMPL—DOL System

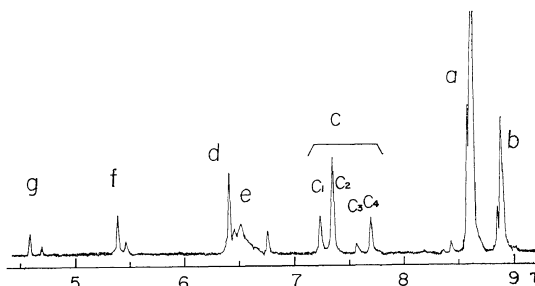A typical NMR spectrum for a copolymer is shown in Figure 1. Judging from the chemical

Figure 1. NMR spectrum of a DMPL—DOL copolymer (sample No. 45).

shifts, the DMPL units should give rise to the peaks a and b, due to the methyl groups, and the peaks c, due to the methylene groups, whereas the DOL units should give the peaks d and e —due to the ethylene oxide units— and the peaks g and f, due to the formal units. DMPL homopolymer gives two singlets at the positions

Table I. Copolymerization of DMPL and DOL[a]

No.	Feed molar ratio DMPL/DOL	Polymerization time (hr)	Conversion (wt %)	DMPL in polymer (mol %)	Polymer molecular weight
44	8.824	16.0	17.3	94.8	2130
45	2.935	6.4	2.5	68.6	—
47	0.807	6.2	0.9	40.6	—
48	0.427	1.4	2.9	22.7	—
49	0.178	0.2	11.4	13.9	4610

[a] Catalyst, SnCl₄; Total monomer, ca. 2 g; Toluene, 1 ml.

Table II. Copolymerization of DMPL and BCMO[a]

No.	Feed molar ratio DMPL/BCMO	Polymerization time (hr)	Conversion (wt %)	DMPL in polymer (mol %)
2	4.016	5.0	1.2	47.6
3	2.349	3.5	4.7	36.2
4	1.235	2.6	9.5	23.9
5	0.681	1.7	12.8	15.0
6	0.347	0.5	6.9	11.2

[a] Catalyst, BF_3OEt_2; Total monomer, ca. 2.5 g; Toluene, 2 ml.

Table III. Copolymerization of DMPL and St[a]

No.	Feed molar ratio DMPL/St	Polymerization time (hr)	Conversion (wt %)	DMPL in polymer (mol %)	Polymer molecular weight
52	2.999	240	8.6	100	2050
75	1.518	37	9.2	100	2130
76	1.015	22	2.8	100	2080
77	0.680	22	0.5	75.4	—
78	0.440	16	1.1	31.3	—
79	0.258	13	2.2	7.2	—
80	0.112	13	34.8	5.3	1820

[a] Catalyst, $SnCl_4$; Total monomer, ca. 2.5 g; Toluene, 2.5 ml.

c_2 and a, and the DOL homopolymer at positions d and f — the peak intensity ratios being 1 to 3, and 1 to 2, respectively, as required.

By assuming alkyl—oxygen fission of DMPL, the assignments for the copolymer sequence, $-M_1M_1M_2M_2M_1-$ for example, are given as follows, where M_1 and M_2 represent DMPL and DOL units, respectively.

magnetic field. Similarly, the formal protons g in the M_2M_1 sequence should appear at a lower magnetic field than the protons f in the M_2M_2 sequence. The protons e in the M_1M_2 sequence would appear at a higher magnetic field because of the absence of the formal unit in the preceding unit, as compared to the protons d.

According to the above peak assigments, the
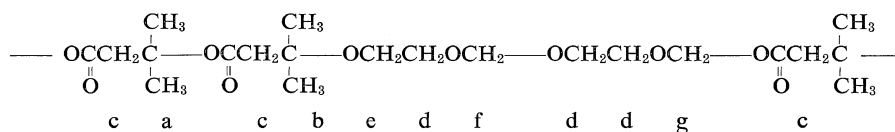
The basis for the assignments is that any group should be deshielded (shifted to a lower magnetic field) by the proximity of the carbonyl group present in a preceding or following monomer unit, as confirmed previously for the PL—BCMO system.[8] Thus the methyl protons b in the M_1M_2 sequence are distinguished from the protons a in the M_1M_1 sequence by the absence of the carbonyl group in the following unit, and therefore should appear at a higher

following relations should hold among the corresponding peak areas.

$$a + b = 3c \qquad (4)$$

$$d + e = 2(f + g) \qquad (5)$$

$$b = 3e = 3g \qquad (6)$$

The last equation means the statistical distribution of monomer units, i.e., the equal probabilities of finding M_1M_2 and M_2M_1 sequences.

These relations were found to hold within experimental errors ($\pm$ 0.03), so that the effects of the end groups can be ignored.

Therefore all the four kinds of diad sequences and the copolymer composition can be determined from measurements of the corresponding peak areas, and be compared with the usual copolymerization theory, using similar procedures as before.[8] The results are given in Figure 2, together with the theoretical curves using the apparent monomer reactivity ratios determined as follows.

$$r_1 = 0.94 \pm 0.05$$
$$r_2 = 1.5 \pm 0.1$$

The agreement between experiment and theory is close to being satisfactory, although some apparent deviation would be probable because of a complication due to the equilibrium phenomenon and the dual nature of the propagating species for the DOL polymerization.[7,9] It is thus reasonable to conclude that the sequence distribution of the DMPL—DOL copolymers is almost completely random.
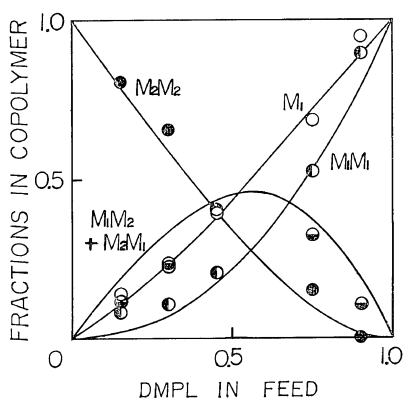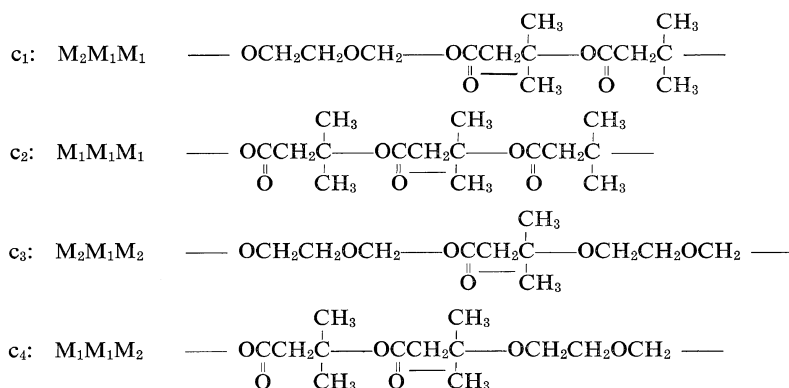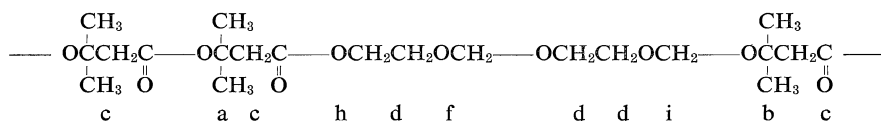
c_1: $M_2M_1M_1$ —— OCH₂CH₂OCH₂——OCCH₂C——OCCH₂C ——
(with CH₃, CH₃ groups, O)

c_2: $M_1M_1M_1$ —— OCCH₂C——OCCH₂C——OCCH₂C ——
(with CH₃ groups, O)

c_3: $M_2M_1M_2$ —— OCH₂CH₂OCH₂——OCCH₂C——OCH₂CH₂OCH₂ ——
(with CH₃, O)

c_4: $M_1M_1M_2$ —— OCCH₂C——OCCH₂C——OCH₂CH₂OCH₂ ——
(with CH₃ groups, O)

Figure 2. Copolymer composition and diad concentrations *vs.* mole fraction of M_1 in feed for DMPL—DOL system: $\bigcirc$, mole fractions of M_1 units; $\mathbb{O}$, M_1M_1 diad; $\ominus$, M_1M_2 and M_2M_1 diads; $\bullet$, M_2M_2 diad. Solid lines show theoretical values.

The splitting of the peak c due to the methylene protons of the DMPL unit appears to be similarly accounted for by considering the above triad sequences.

Thus the methylene group of the central DMPL unit is deshielded by the proximity of the carbonyl group in the following monomer unit, or shielded by the two methyl groups in the preceding monomer unit. The peak area c_1 was found to be equal to c_4, as should be so from the assignments. Qualitative agreement with the copolymerization theory was also found, although precise determinations of such triad sequences were not possible because of the very small peak areas.

In contrast with the above assignments, if we assume the ring opening of DMPL by acyl—oxygen fission, the copolymer sequence ——$M_1M_1M_2M_2M_1$—— should be as follows

—— OCCH₂C—OCCH₂C——OCH₂CH₂OCH₂——OCH₂CH₂OCH₂——OCCH₂C ——
(with CH₃ groups, O)
c   a c   h d f   d d i   b c

It is very difficult to assign the peaks due to the protons h and i, which should appear at lower and higher magnetic fields as compared to the protons d and f, respectively. Therefore the alkyl—oxygen fission of DMPL is also consistent with the present NMR study.

DMPL—BCMO System

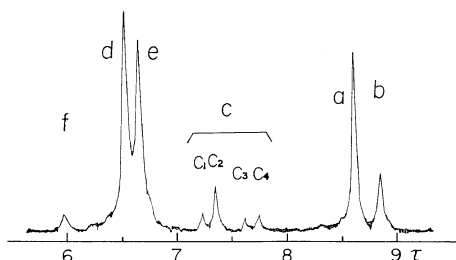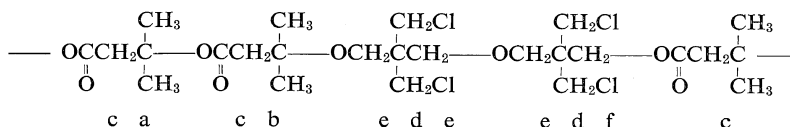Figure 3 shows an example of NMR spectra. BCMO homopolymer shows two singlets of equal

Figure 3. NMR spectrum of a DMPL—BCMO copolymer (sample No. 3).

intensity at the positions d and e due to the CH_2Cl and OCH_2 groups, respectively. The assignments for the copolymer chain are given similarly for the sequence $-M_1M_1M_2M_2M_1-$, also considering the alkyl—oxygen fission of DMPL.

The determined copolymer composition and the diad concentrations are given in Figure 4, to be
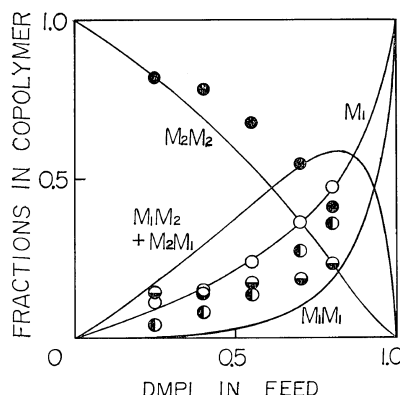

Figure 4. Copolymer composition and diad concentrations *vs.* mole fraction of M_1 in feed for DMPL—BCMO system: $\bigcirc$, mole fractions of M_1 units; $\oplus$, M_1M_1 diad; $\ominus$, M_1M_2 and M_2M_1 diads; $\bullet$, M_2M_2 diad. Solid lines show theoretical values.

compared with the theoretical curves using the apparent monomer reactivity ratios as follows

$$r_1 = 0.15 \pm 0.01$$
$$r_2 = 3.2 \ \pm 0.1$$

$$\begin{array}{ccccc} CH_3 & CH_3 & CH_2Cl & CH_2Cl & CH_3 \\ | & | & | & | & | \\ - OCCH_2C - OCCH_2C - OCH_2CCH_2 - OCH_2CCH_2 - OCCH_2C - \\ \| \quad | & \| \quad | & | & | & \| \quad | \\ O \quad CH_3 & O \quad CH_3 & CH_2Cl & CH_2Cl & O \quad CH_3 \\ \\ \ c \quad a & c \quad b & e \quad d \ e & e \quad d \ f & c \end{array}$$

The assignments for the methyl protons a and b should be the same as before. Now the protons f should appear at a lower magnetic field than the protons e, because of the presence of the carbonyl group in the next monomer unit, as found in the case of the PL—BCMO copolymers.[8] The peak separations, c_1 to c_4, for the protons c would also be accounted for by the same triad assignments as given for the DMPL—DOL copolymers before.

The relations, 7—9, analogous to Eq. 4—6 above, were also found to hold as should be so.

$$a + b = 3c \qquad (7)$$
$$d = e + f \qquad (8)$$
$$b = 3f \qquad (9)$$

M_1 and M_2 are DMPL and BCMO, respectively. The agreement between experiment and theory is, however, less satisfactory than that in the DMPL —DOL system; the observed concentrations for the M_1M_1 and M_2M_2 sequences are higher while those for the M_1M_2 or M_2M_1 sequences are lower than the theoretical. Thus the sequence distribution of the present system can be said to be somewhat less random than that expected for the usual copolymerization theory. Similar but more pronounced deviation was found in the PL—BCMO system.[8,10,11]

DMPL—St System

Figure 5 shows a typical NMR spectrum. Different from the above two systems, the fine structure characteristic of the copolymer is not clear in the spectrum. Indeed, the spectrum
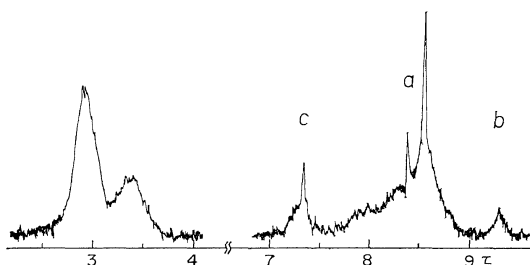
Figure 5. NMR spectrum of a DMPL—St copolymer (sample No. 78).

appears to be merely the superimposition of those of the homopolymers except for the peak b at 9.3 τ. The two separate peaks due to the phenyl protons were observed at 2.9 and 3.4 τ, indicating the presence of long St blocks.[12] Also there appears no splitting of the peak c due to the methylene groups of the DMPL units, and the polymer—monomer composition curve shown in Figure 6 is S-shaped, suggesting very slight oc-
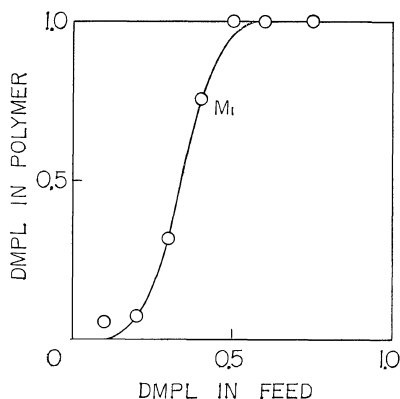

Figure 6. Polymer *vs.* monomer compositions for DMPL—St system.

currence of cross-propagation reactions. All these results indicate that the DMPL—St copolymers are composed of very long block sequences of the respective monomer units.

The appearance of peak b in the NMR spectra of the copolymer, however, suggests some cross-sequences present between DMPL and St units, since this peak appears to come from the methyl groups shielded by the benzene ring current of the neighboring St unit.
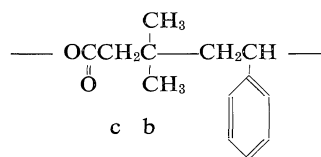
The formation of copolymers was also previously confirmed by the presence of DMPL units in the insoluble fraction of the products in acetic acid, which is a solvent for DMPL homopolymer.[3]

Summarizing the above considerations, the DMPL—St system represents the case where the two monomers grow to polymerize almost independently with very little chance of cross-propagation, as has been similarly concluded for the St—PL system.[4,5] Thus it would be preferable to say that DMPL hardly copolymerizes with St at all.

DISCUSSION

The conclusions drawn from the above results may be summarized as follows

(a) The ring opening of DMPL occurs from alkyl—oxygen fission, as has also been concluded previously.[3]

(b) DMPL copolymerizes almost randomly with DOL and BCMO, but cannot practically copolymerize with St. However, some block character is apparent in the DMPL—BCMO system.

(c) The apparent monomer reactivity ratios for the DMPL—DOL and —BCMO systems show that the relative reactivities decrease in the order BCMO, DOL, and DMPL, in accord with the order of monomer basicities,[6] a result which can be expected for the cationic propagation mechanism.

As to the question whether the growing chain end of DMPL is an oxonium ion or a carbonium ion, the former is preferable because DMPL copolymerizes much more randomly with the cyclic monomers than with St. This conclusion derives from the previous assumption on copolymerization behavior that random copolymerization would be successful for the cyclic monomer pairs which polymerize through the similar oxonium ions as the propagating species, whereas it would be very difficult with the cyclic and vinyl mono-

mer pairs which polymerize through the oxonium and the carbonium ions respectively.[6] Thus we prefer the S_N2 mechanism (1) for the polymerization of DMPL to the S_N1 mechanism (3) given in the introductory section.

The DMPL—BCOM system showed appreciable deviation in sequence distribution from the copolymerization theory. This result appears to be related to the coexistence of different catalytic species which preferentially polymerize the lactone monomers, as also assumed for the PL—BCMO system previously.[8,10,11] This assumption suggests the existence of homopolymer sequences longer than those expected from the overall copolymer compositions, but does not appear to influence the above conclusion regarding the cationic-polymerization mechanism of DMPL. In fact, the results appear to be largely explained by the cationic random copolymerization where the more basic monomer is more reactive, as has been observed. The deviation from the copolymerization theory is less pronounced in the present system than in the PL—BCMO system, which would be also consistent with the higher basicity, and therefore the higher reactivity by cationic mechanism, of DMPL as compared with PL.

At this point it is interesting to compare the above conclusion with the known mechanisms of acid hydrolyses of β-lactones.[13,14] PL and DMPL were reported to be hydrolyzed by the $A_{Ac}1$ and the $A_{Al}1$ mechanisms, respectively. Thus the acyl—oxygen and the alkyl—oxygen fissions of PL and DMPL, respectively, occur commonly in hydrolyses and polymerizations. However, the first-order kinetics for the hydrolyses indicates the rate-determining formation of carbonium ions as the intermediates, which are different from the above conclusion for poly-merization. It is likely to be very difficult for the more stable oxonium ion to be converted to the less stable carbonium ion in such poorly ionizing solvents as are used for polymerization. Alternatively, if any carbonium ion was formed, we feel it would be so unstable that it would immediately add the closest cyclic monomer to become a more stable oxonium ion.

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