Copolymerization of 3,3-Bis(chloromethyl)oxacyclobutane and β-Propiolactone by Boron Trifluoride Etherate and Stannic Chloride. Nuclear Magnetic Resonance Studies of Sequence Distribution

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ABSTRACT: All four kinds of the diad sequences were directly determined by nmr for the copolymers of 3,3-bis(chloromethyl)oxacyclobutane (M_1) and β-propiolactone (M_2) initiated with BF_3OEt_2 and $SnCl_4$ catalysts. The apparent monomer reactivities are as expected for the normal cationic copolymerization; *i.e.*, the more basic M_1 monomer is far more reactive than the less basic M_2 monomer with both catalysts. However, the observed diad concentrations for M_2M_2 sequence were found too high to be expected from the over-all copolymer compositions. In addition to the normal cationic copolymerization process, a particular different mechanism is suggested to operate to account for a preferential polymerization of M_2 at M_2 chain end.

Previously we discussed the cationic copolymerization of cyclic ethers, formals, and lactones in terms of the monomer reactivity parameters by relating to monomer basicity and free energy considerations.[1] While most copolymerizaton systems have long been analyzed and interpreted by the usual Mayo–Lewis equation, there remain some uncertainties as to the question whether the derived monomer reactivity ratios exactly have the meanings as defined, *i.e.*, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. We have assumed the different propagating species might have significant effects upon the copolymerization statistics, resulting in deviation from those expected for the Mayo–Lewis equation (simple Markov process).

Determination of monomer sequence distribution along a copolymer chain permits a most convenient check for a copolymerization statistics.[2] Several free-radical systems have thus been proved to obey the Mayo–Lewis equation from the nmr examination.[3] However, there has been little experimental evidence for the application of the Mayo–Lewis equation to ionic copolymerizations. Tada, Saegusa, and Furukawa[4] examined the hydrolyses products of cationic copolymers from β-propiolactone (PL) and 3,3-bis(chloromethyl)oxacyclobutane (BCMO) and found the PL sequences to be considerably longer than those calculated with the copolymerization parameters. They later ascribed this result to the formation of different active species during polymerization leading to a PL-rich copolymer.[5] In the present paper, we report the direct determination of all four kinds of diad sequences for the same copolymer system by use of nmr, and show that the copolymerization process is too complicated to allow a simple mechanism. Copolymerization of BCMO and γ-butyrolactone is also included to prove the nmr interpretation.

Experimental Section

Materials. All reagents were commercially supplied. Monomers were distilled, dried by calcium hydride, and redistilled under reduced pressure before use. Toluene as a polymerization solvent was treated with concentrated sulfuric acid and then with aqueous sodium carbonate, washed with water, and distilled over sodium. Boron trifluoride etherate (BF_3OEt_2) was once distilled and stannic chloride ($SnCl_4$) was used as supplied.

Polymerization. Monomers and toluene were charged to a total volume of 4 ml in a glass tube under nitrogen. Initiator (0.5 mol % to monomer) was added at Dry Ice temperature and the tube was sealed. Polymerization was conducted at 20° for a desired time, and stopped by pouring into methanol containing a small amount of sodium methoxide. Precipitated polymers were collected, washed with HCl–methanol and then repeatedly with methanol, and dried under vacuum to constant weights. Copolymerization of γ-butyrolactone (BL) and BCMO was also similarly conducted.

Polymerization results are summarized in Tables I, II, and III. Polymer appearances range from white tacky solid to white powders with increasing BCMO content. All copolymer samples were soluble in chloroform at the condition of nmr measurement but the sample from run no. 310 was incompletely soluble giving a turbid solution. The

TABLE I

COPOLYMERIZATION OF BCMO (M_1) AND PL (M_2) BY BF_3OEt_2

	Feed					
Run no.	M_1, g	M_2, g	$[M_1]/[M_2]$ mole ratio	Polymzn time, min	Convn, wt %	M_1, mole %, in polymer
293	0.620	2.880	1/10	19	19.0	58
294	0.930	2.880	3/20	6	8.6	62
295	0.775	1.800	1/5	12	3.1	73
296	0.600	1.260	1/4	8	2.9	79
297	1.550	1.080	2/3	8	1.7	89

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(1) Y. Yamashita, T. Tsuda, M. Okada, and S. Iwatsuki, *J. Polym. Sci., Part A-1*, **4**, 2121 (1966).

(2) K. Ito and Y. Yamashita, *ibid., Part A*, **3**, 2165 (1965).

(3) For example, Y. Yamashita, K. Ito, H. Ishii, S. Hoshino, and M. Kai, *Macromolecules*, **1**, 529 (1968).

(4) K. Tada, T. Saegusa, and J. Furukawa, *Makromol. Chem.*, **71**, 71 (1964).

(5) K. Tada, T. Saegusa, and J. Furukawa, *ibid.*, **102**, 47 (1966).

TABLE II
COPOLYMERIZATION OF BCMO (M_1) AND PL (M_2) BY $SnCl_4$

Run no.	Feed: M_1, g	Feed: M_2, g	Feed: $[M_1]/[M_2]$ mole ratio	Polymzn time, min	Convn, wt %	M_1, mole %, in polymer
302	0.310	2.880	1/20	16	3.1	9
303	0.620	2.880	1/10	11	5	55
304	0.930	2.880	3/20	2	2.3	64
305	0.775	1.800	1/5	4	3.3	69
308	1.550	1.080	2/3	20	19.0	85
310	1.450	0.500	3/2	225	1.8	95

TABLE III
COPOLYMERIZATION OF BCMO (M_1) AND BL (M_2) BY BF_3OEt_2

Run no.	Feed: M_1, g	Feed: M_2, g	Feed: $[M_1]/[M_2]$ mole ratio	Polymzn time, hr	Convn, wt %	M_1, mole %, in polymer
318	0.482	2.324	1/9	20	9.9	50
319	0.926	2.066	1/4	20	17.4	50
320	1.364	1.785	3/7	17	25.0	54
322	2.290	1.281	1/1	7	2.1	64
323	3.215	0.788	3/2	6	1.8	80

copolymer compositions listed were determined from nmr by the procedure described below.

Nmr Measurement. Nmr spectra were measured at 60° in chloroform (about 50 mg of polymer in 0.5 ml of chloroform). Japan Electron Optics Spectrometer (C-60) working at 60 Mc was used. Tetramethylsilane was used as an internal standard.

Interpretation of Nmr Spectra and Determination of Diad Sequences

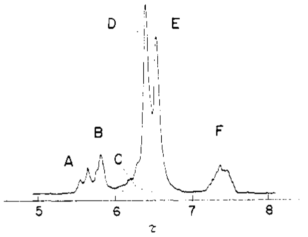


Figure 1. Nmr spectrum of BCMO–PL copolymer from run no. 304.

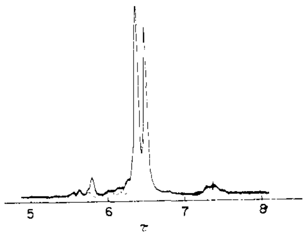


Figure 2. Nmr spectrum of BCMO–PL copolymer from run no. 308.

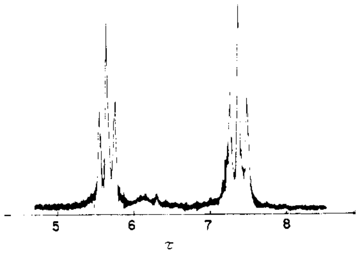
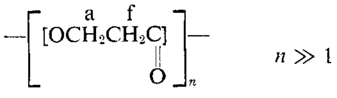


Figure 3. Nmr spectrum of PL homopolymer.

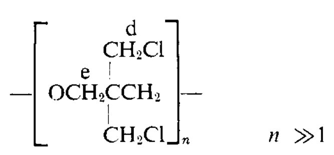
Typical nmr spectra of copolymers are given in Figures 1 and 2. PL homopolymer shows two triplets due to α-CH_2 and β-CH_2 protons at τ 7.3 and 5.6, respectively, as shown in Figure 3.



$$-\!\left[\overset{a}{\text{OCH}_2}\overset{f}{\text{CH}_2}\underset{\underset{\text{O}}{\|}}{\text{C}}\right]_n\!-\qquad n \gg 1$$

a, τ 5.6 (triplet); f, τ 7.3 (triplet)

BCMO homopolymer should show two singlet peaks of equal strength at τ 6.3 and 6.42, which can be assigned to the CH_2 groups of the side and main chains, respectively.

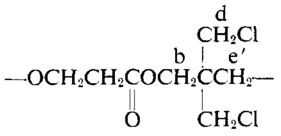


$$-\!\left[\text{O}\overset{e}{\text{CH}_2}\overset{\overset{d}{\text{CH}_2\text{Cl}}}{\underset{\text{CH}_2\text{Cl}}{\text{C}}}\text{CH}_2\right]_n\!-\qquad n \gg 1$$

d, τ 6.3; e, τ 6.42

However, the observed spectra of copolymers have several additional features depending upon the copolymer composition. The OCH_2 peak of BCMO unit at τ 6.42 decreases in peak strength as compared with the CH_2Cl peak at τ 6.3 with increasing amount of PL unit. Instead, a new singlet peak appears at τ. 5.7. Similarly, for the PL unit, the peak area of the triplet at τ 5.6 due to the β-CH_2 group is smaller than that of the α-CH_2 group at τ 7.3 which now appears as an ill-defined multiplet. These observations can be accounted for by dividing the copolymer spectra into six peaks, A, B, . . . , F, as in Figure 1, and by considering the following monomer sequences, where M_1 and M_2 represent BCMO and PL units, respectively.

For the M_2M_1 sequence

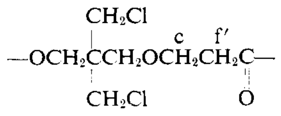


$$-\text{OCH}_2\text{CH}_2\underset{\underset{\text{O}}{\|}}{\text{C}}\text{O}\overset{b}{\text{CH}_2}\overset{\overset{d}{\text{CH}_2\text{Cl}}}{\underset{\text{CH}_2\text{Cl}}{\text{C}}}\overset{e'}{\text{CH}_2}-$$

b, τ 5.7; d, τ 6.3; e′, τ 6.42

The protons b should appear at a lower magnetic field than the protons e or e′ because of a deshielding effect of a carbonyl group in a preceding PL unit. Thus the protons b in the M_2M_1 sequences can be assigned to a B peak of Figure 1.

For the M_1M_2 sequence



$$-\text{OCH}_2\overset{\text{CH}_2\text{Cl}}{\underset{\text{CH}_2\text{Cl}}{\text{C}}}\text{CH}_2\text{O}\overset{c}{\text{CH}_2}\overset{f'}{\text{CH}_2}\underset{\underset{\text{O}}{\|}}{\text{C}}-$$

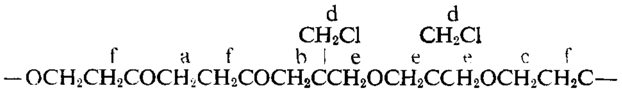
c, τ ~6.2; f′, τ ~7.3

The protons c are distinguished from the protons a by the absence of a carbonyl group in a preceding unit, so that they should give rise to a triplet at a higher field, thus probably assigned to a C peak in Figure 1.

It may be reasonable to assume that the protons e′ and f′ are not very different in magnetic environment from the protons e and f, respectively, because all of these protons are far separated from the PL carbonyl groups which might be present in the preceding and following monomer units. These protons are thus assumed in the following to give the peaks E and F independently of the monomer sequences. The observed multiplet pattern of the peak F, however, suggests a slight difference in the chemical shifts of the protons f and f′. For the peak D due to the CH_2Cl group in the side chain it is also reasonable to assume no dependence upon the monomer sequence.

The M_1M_1 and M_2M_2 sequences can be characterized by e and a protons giving E and A peaks, respectively, as in the case of the corresponding homopolymers.

From the above, all protons in a copolymer chain can be assigned the appropriate one of the peaks A to F, depending upon whether the preceding monomer unit is M_1 or M_2. As an example, the assignments for the protons in the $-M_2M_2M_1M_1M_2-$ sequence follow.



$$-\overset{f}{O}CH_2\overset{a}{C}H_2\underset{\|\atop O}{C}O\overset{f}{C}H_2CH_2\underset{\|\atop O}{C}O\overset{b}{C}H_2\overset{CH_2Cl}{\underset{CH_2Cl}{C}}\overset{e}{C}H_2O\overset{e}{C}H_2\overset{CH_2Cl}{\underset{CH_2Cl}{C}}\overset{e}{C}H_2O\overset{c}{C}H_2\overset{f}{C}H_2\underset{\|\atop O}{C}-$$

Consequently the mole fractions, $p\{i\text{-}j\}$, of the respective diad sequences M_iM_j, where i, j is 1 or 2, can be determined using the following relations

$$p\{1\text{-}1\} = k(E - B)/2 = k(D - 2B)/2 \qquad (1)$$

$$p\{2\text{-}1\} = kB \qquad (2)$$

$$p\{1\text{-}2\} = kC = k(F - A) \qquad (3)$$

$$p\{2\text{-}2\} = kA \qquad (4)$$

where A to F denote the corresponding peak areas, and it is clear that $F = A + C$ and that $D = B + E$. k is a normalization factor so that

$$p\{1\text{-}1\} + p\{2\text{-}1\} + p\{1\text{-}2\} + p\{2\text{-}2\} = 1 \qquad (5)$$

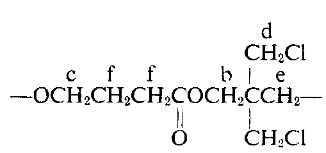
Also the copolymer compositions $p\{1\}$ and $p\{2\}$ can be given by

$$p\{1\} = k(B + E)/2 = kD/2 = p\{1\text{-}1\} + p\{2\text{-}1\} \qquad (6)$$

$$p\{2\} = kF = p\{1\text{-}2\} + p\{2\text{-}2\} \qquad (7)$$

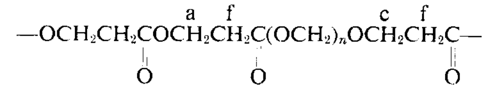
Apparently from these relations, it is sufficient for the present purpose to measure only the peak areas of A, B, E (or D in the case of the BCMO–BL system below), and F, which are easy to determine without any ambiguity for peak separation.

The assignment for the protons b of the M_2M_1 sequence can be supported by examining the spectra of BCMO–BL copolymers. Because BL monomer cannot homopolymerize,[6] a BL unit (M_2) must always be followed by a BCMO unit (M_1) so that the appearance of the peak B at τ 5.7 is convincingly attributed to the M_2M_1 sequence (see Figure 4). The copolymer composition and the diad fractions for this system can also be determined using eq 1–7, with the peak designations as given in Figure 4, except that half of the peak areas due to the α- and β-CH_2 groups should be used as F for calculation and that $p\{2\text{-}2\} = kA = 0$ in this case.



$$-\overset{c}{O}CH_2\overset{f}{C}H_2\overset{f}{C}H_2\underset{\|\atop O}{C}O\overset{b}{C}H_2\overset{\overset{d}{CH_2Cl}}{\underset{CH_2Cl}{C}}\overset{e}{C}H_2-$$

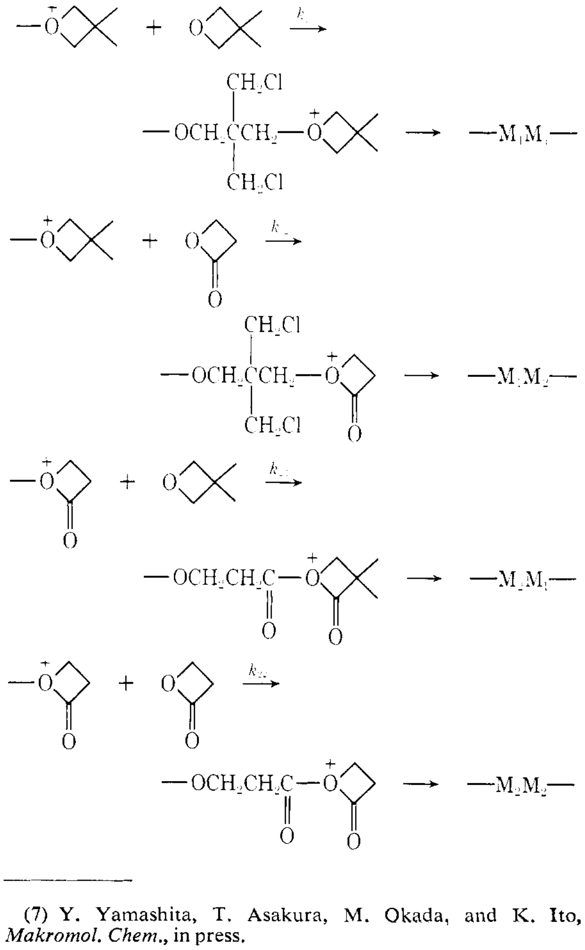
Similarly, the assignment for the protons c at about τ 6.2 as compared with the protons a at τ 5.6 was also confirmed by the appearance of two triplets at the same positions in the spectra of PL–trioxane copolymers, as shown in Figure 5. The sum of the peak areas of these two triplets was equal to the area of the multiplet due to the α-CH_2 groups, *i.e.*, $A + C = F$. As to the formal protons, $-(OCH_2)_n-$, the peak position appears to depend on the monomer sequence and also on its length, n, as also found in the case with the trioxane-dioxolane copolymers.[7]



$$-OCH_2\overset{a}{C}H_2\underset{\|\atop O}{C}OCH_2\overset{f}{C}H_2\underset{\|\atop O}{C}(OCH_2)_nO\overset{c}{C}H_2\overset{f}{C}H_2\underset{\|\atop O}{C}-$$

Results and Discussion

Nmr spectra of copolymers were so far interpreted according to the following propagation mechanism (Scheme I). Ring opening of PL monomer by the



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[6] T. Tsuda, T. Shimizu, and Y. Yamashita, *Kogyo Kagaku Zasshi*, **67**, 2150 (1964).

[7] Y. Yamashita, T. Asakura, M. Okada, and K. Ito, *Makromol. Chem.*, in press.

TABLE IV
COPOLYMER COMPOSITION AND DIAD COMPOSITIONS OF BCMO(M_1)–PL(M_2) COPOLYMERS INITIATED BY BF_3OEt_2

Run no.	Observed					Calculated[a]		
	$p\{2\}$	$p\{2\text{-}2\}$	$p\{2\text{-}1\}$	$p\{1\text{-}2\}$	$p\{1\text{-}1\}$	$p\{2\text{-}2\}$	$p\{2\text{-}1\} = p\{1\text{-}2\}$	$p\{1\text{-}1\}$
293	0.42	0.24	0.25	0.18	0.32	0.10	0.31	0.28
294	0.38	0.17	0.23	0.21	0.39	0.06	0.27	0.40
295	0.27	0.17	0.19	0.10	0.54	0.03	0.23	0.51
296	0.21	0.07	0.15	0.14	0.64	0.02	0.21	0.56
297	0.11	0.00	0.09	0.11	0.80	0.00	0.12	0.76

[a] Calculated by eq 10–14 with the apparent monomer reactivity ratios; $r_1 = 10$, $r_2 = 0.03$.

TABLE V
COPOLYMER COMPOSITION AND DIAD COMPOSITIONS OF BCNO(M_1)–PL(M_2) COPOLYMERS INITIATED BY $SnCl_4$

Run no.	Observed					Calculated[a]		
	$p\{2\}$	$p\{2\text{-}2\}$	$p\{2\text{-}1\}$	$p\{1\text{-}2\}$	$p\{1\text{-}1\}$	$p\{2\text{-}2\}$	$p\{2\text{-}1\} = p\{1\text{-}2\}$	$p\{1\text{-}1\}$
302	0.91	0.85	0.07	0.06	0.01	0.21	0.34	0.11
303	0.45	0.28	0.24	0.17	0.31	0.13	0.33	0.21
304	0.36	0.24	0.22	0.12	0.42	0.08	0.29	0.34
305	0.31	0.16	0.20	0.15	0.49	0.05	0.26	0.43
308	0.15	0.05	0.14	0.10	0.81	0.01	0.14	0.71
310	0.05	0.02	0.07	0.03	0.87	0.00	0.06	0.88

[a] Calculated by eq 10–14 with the apparent monomer reactivity ratios; $r_1 = 8$, $r_2 = 0.04$.

TABLE VI
COPOLYMER COMPOSITION AND DIAD COMPOSITIONS OF BCMO(M_1)–BL(M_2) COPOLYMERS INITIATED BY BF_3OEt_2

Run no.	Observed				
	$p\{2\}$	$p\{2\text{-}2\}$	$p\{2\text{-}1\}$	$p\{1\text{-}2\}$	$p\{1\text{-}1\}$
318	0.50	0	0.50	0.50	0
319	0.50	0	0.50	0.50	0
320	0.46	0	0.46	0.46	0.08
322	0.36	0	0.36	0.36	0.28
323	0.20	0	0.20	0.19	0.61

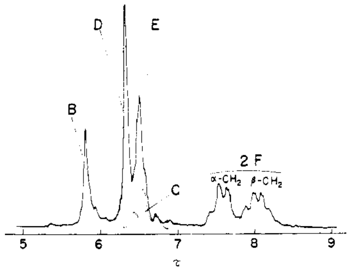

Figure 4. Nmr spectrum of BCMO–BL copolymer from run no. 319.

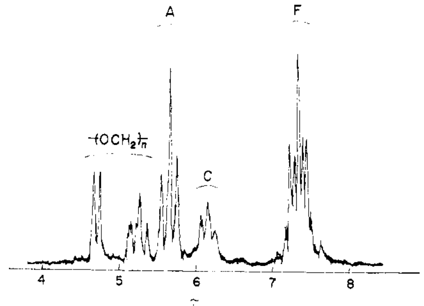

Figure 5. Nmr spectrum of trioxane–PL copolymer; feed ratio of trioxane/PL = $^1/_4$.

acyl oxygen fission through the oxonium ion mechanism has been already discussed.[8–10]

The copolymer composition and the diad compositions determined from nmr are summarized in Tables IV, V, and VI for both BCMO–PL and BCMO–BL systems. It is important to note first that all diad concentrations were obtained directly and independently from the separation of the respective nmr peaks. The given nmr assignments are again supported by the experimental findings for BCMO (M_1)–BL (M_2) system in Table VI that

$$p\{1\text{-}2\} = p\{2\text{-}1\} \tag{8}$$

which must strictly hold for the present case of an M_2 unit not adding to an M_2 unit so that any M_2 unit must always be preceded and followed by M_1 units. In contrast, usual vinyl copolymers do not permit a separate determination of $p\{1\text{-}2\}$ and $p\{2\text{-}1\}$ because there is no way for distinguishing between any sequence and its reversed sequence.

According to the usual copolymerization theory,[2] the copolymer composition and the diad concentrations should be given by the following probability relations

$$p\{1\} = P_{21}/(P_{12} + P_{21}) = 1 - p\{2\} \tag{9}$$

$$p\{1\text{-}1\} = p\{1\}P_{11} = p\{1\}(1 - P_{12}) \tag{10}$$

$$p\{1\text{-}2\} = p\{2\text{-}1\} = p\{1\}P_{12} = p\{2\}P_{21} \tag{11}$$

$$p\{2\text{-}2\} = p\{2\}P_{22} = p\{2\}(1 - P_{21}) \tag{12}$$

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(8) T. Tsuda, T. Shimizu, and Y. Yamashita, *Kogyo Kagaku Zasshi*, **67**, 1661, 2145 (1964); *Makromol. Chem.*, **86**, 304 (1965).

(9) K. Ito, T. Inoue, and Y. Yamashita, *ibid.*, **117**, 279 (1968).

(10) Y. Yamashita, K. Umehara, K. Ito, and T. Thuda, *J. Polym. Sci., Part B*, **4**, 241 (1966).

where P_{ij} is the conditional probability of an M_i unit being followed by an M_j unit, with i or j denoting 1 or 2. $[M_1]$ and $[M_2]$ are monomer concentrations in

$$P_{12} = 1 - P_{11} = \frac{k_{12}[M_2]}{k_{12}[M_2] + k_{11}[M_1]} = \frac{1}{1 + r_1[M_1]/[M_2]} \qquad (13)$$

$$P_{21} = 1 - P_{22} = \frac{k_{21}[M_1]}{k_{21}[M_1] + k_{22}[M_2]} = \frac{1}{1 + r_2[M_2]/[M_1]} \qquad (14)$$

feed. The parameters r_1 and r_2 are the respective monomer reactivity ratios which are usually determined from the composition data based on the Mayo–Lewis equation.

Figures 6 and 7 show the polymer–monomer composition data for the BCMO–PL system with the theoretical curves from eq 9 and 13, eq 14 using the apparent reactivity ratios as follows: $r_1 = 10$, $r_2 = 0.03$ for BF_3OEt_2 catalyst; $r_1 = 8$, $r_2 = 0.04$ for $SnCl_4$ catalyst. These apparent monomer reactivities are in accordance with the basicity difference of BCMO and PL,[1] indicating that the attack of the basic oxygen in monomer toward a cationic center in a propagating chain end is a rate-controlling step. Furthermore, the similar copolymerization results were obtained with both BF_3OEt_2 and $SnCl_4$ catalysts in spite of their very different catalytic behaviors for homopolymerizations; BF_3OEt_2 is much more effective for BCMO, while $SnCl_4$ is so for PL homopolymerizations. Therefore, the propagation reactions must occur mainly through the normal cationic copolymerization mechanism, where a more basic BCMO monomer (M_1) is far more reactive than a less basic PL monomer (M_2).

However, we must also note the abnormal nature of the present copolymerization system. Although there appears to be good agreement between the experimental and theoretical copolymer compositions, Tables IV and V clearly show that the usual copolymerization theory cannot be applied to the present system, because the observed diad compositions deviate seriously from the calculated ones using eq 10–14 with the above monomer reactivity ratios. Particularly, the observed diad concentration, $p\{2\text{–}2\}$, as compared to the calculated one, is abnormally high in spite of the apparent much lower reactivity of M_2. Therefore there appears to coexist a particular mechanism which should account for a much higher probability for M_2 homopropagation step than otherwise expected from the over-all composition data. However, we cannot say more about the detailed mechanism from the present data alone. Tada, Saegusa, and Furukawa[5] suggested for BF_3OEt_2 system the coexistence of a different active species favorable for PL propagation. Similar complicated mechanism proceeding through the different catalytic sites has also recently been suggested by Schaefer, *et al.*, for the propylene oxide–maleic anhydride and –SO_2 copolymerizations using Lewis acids.[11]

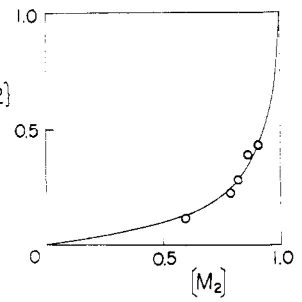

Figure 6. Polymer–monomer composition data for BCMO–PL copolymerization by BF_3OEt_2 with the theoretical line based on the apparent reactivity ratios; $r_1 = 10$, $r_2 = 0.03$.

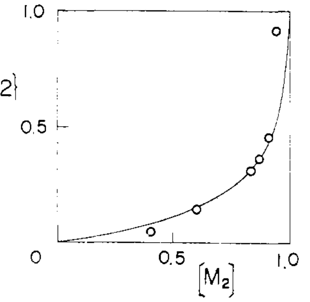

Figure 7. Polymer–monomer composition data for BCMO–PL copolymerization by $SnCl_4$ with the theoretical line based on the apparent reactivity ratios; $r_1 = 8$, $r_2 = 0.04$.

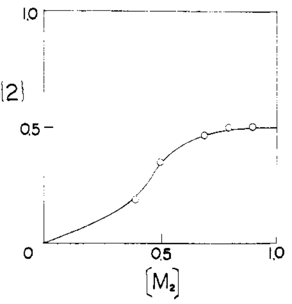

Figure 8. Polymer–monomer composition data for BCMO–BL copolymerization by BF_3OEt_2.

The failure of eq 8 to fit to some copolymer samples is also a reason of inapplicability of the usual copolymerization theory. The trend in Tables IV and V that $p\{2\text{–}1\}$ is often larger than $p\{1\text{–}2\}$ may probably be the result of relatively low degree of polymerization coupled with the apparent higher reactivity of M_1. However, this trend cannot explain the observed abnormally high $p\{2\text{–}2\}$, for which we must again assume a particular different mechanism favorable for M_2 homopropagation step. As the future problems, we feel the importance of fractionations of polymers coupled with the microstructure and molecular weight determinations of each fraction to specify the more detailed copolymerization mechanisms.

The result for BCMO–BL system in Table VI and Figure 8 supports the formation of alternating copolymers at higher BL feed, as reported previously.[6] This alternating tendency, although it might appear to be somewhat peculiar in view of the much higher basicity of BCMO than that of BL, may also be accounted for by assuming a particular active species which would preferentially activate or solvate the lactone monomers. Then, the formation of the alternating copolymers is explained merely as the result of inability of BL monomer to homopolymerize.

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(11) J. Schaefer, R. J. Katnik, and R. J. Kern, *Macromolecules*, **1**, 101 (1968); J. Schaefer, R. J. Kern, and R. J. Katnik, *ibid.*, **1**, 107 (1968); J. Schaefer, *ibid.*, **1**, 111 (1968).