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# Polymerization *via* Betaine. II.[1] Alternating Copolymerization of 2-Oxazoline with β-Lactones

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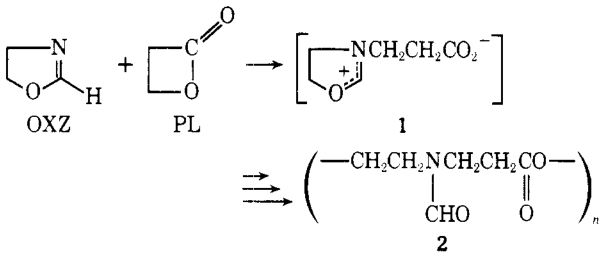
ABSTRACT: The present paper describes the alternating copolymerization of 2-oxazoline (OXZ) with α-methyl-β-propiolactone (MePL) and with α,α-dimethyl-β-propiolactone ($Me_2PL$). Copolymerization took place without any added initiator at room temperature in acetonitrile or dimethylformamide. The structure and composition of copolymer were determined by nmr, ir, and elemental analyses as well as by the alkaline hydrolysis experiments. The copolymerizations are reasonably explained by a mechanism of propagation *via* betaine intermediates. Further support for the propagation *via* betaines was obtained by the two-stage copolymerization of OXZ with β-propiolactone (PL) and by the comparison of relative copolymerization reactivities of PL, MePL, and $Me_2PL$ with OXZ at lower temperatures.

Recently we have reported an alternating copolymerization of 2-oxazoline (OXZ) with β-propiolactone (PL) to give a copolymer of amino ester type structure 2.[1] The copolymerization took place at 40° without any added initiator in dimethylformamide. For this type of alternating copolymerization, a new concept has been proposed, in which the betaine (1) from OXZ and PL adds to the end of the so-called a macrozwitterion of the propagating species.


OXZ PL 1 2 (1)

This result prompted us to explore further possibilities of alternating copolymerization *via* betaine. In the present paper we report the alternating copolymerizations of OXZ with α-methyl-β-propiolactone (MePL) and with α,α-dimethyl-β-propiolactone ($Me_2PL$). The copolymerizations of the present study may also be explained by the betaine mechanism. In the copolymerization of OXZ the relative reactivities of PL, MePL, and $Me_2PL$ were examined qualitatively, which were quite compatible with the mechanism of the propagation *via* betaine.

## Experimental Section

**Reagents.** OXZ monomer was prepared and purified as previously reported.[2] PL is a commercial reagent and was distilled before use. MePL and $Me_2PL$ were synthesized according to Yamashita *et al.*[3,4] and purified by repeated distillation. Solvents (acetonitrile and dimethylformamide) were purified by distillation. All distillations were carried out under nitrogen. Authentic compounds of *N*-(2-hydroxyethyl)-2-methyl-β-alanine and *N*-(2-hydroxyethyl)-2,2-dimethyl-β-alanine were prepared by the equimolar reactions of monoethanolamine with MePL and with $Me_2PL$, respectively, according to the reported procedures.[1,5] *N*-(2-Hydroxyethyl)-2-methyl-β-alanine: mp 163–164°; nmr ($D_2O$) δ 3.77 (t, 2 H, $—OCH_2$), 3.10 (t, 2 H, $—NCH_2CH_2$), 3.05 (d, 2 H, $—NCH_2CH—$), 2.64 (m, 1 H, $—CHCO_2$), 1.13 (d, 3 H, $—CH_3$). *Anal.* Calcd for $C_6H_{13}NO_3$: C, 48.96; H, 8.90; N, 9.52. Found: C, 48.74; H, 9.16; N, 9.37. *N*-(2-Hydroxyethyl)-2,2-dimethyl-β-alanine: mp 165–167°; nmr ($D_2O$) δ 3.90 (t, 2, H, $—OCH_2$), 3.23 (t, 2 H, $—NCH_2CH_2$), 3.08 (s, 2 H, $—NCH_2$), 1.22 (s, 6 H, $—C(CH_3)_2$). *Anal.* Calcd for $C_7H_{15}NO_3$: C, 52.15; H, 9.38; N, 8.69. Found: C, 52.14; H, 9.51; N, 8.52.

**Polymerization Procedure.** To 2 ml of solvent, 7.5 mmol each of OXZ and β-lactone were added at room temperature and the reaction mixture was kept at a desired temperature. After the reaction, the mixture was poured into 50 ml of diethyl ether to precipitate the polymeric product. The precipitated copolymer was dried *in vacuo* and analyzed by ir, nmr (Figures 1 and 2), and elemental analyses (Table II) and by alkaline hydrolysis.

**Hydrolysis of Copolymer.** To 0.05 g of copolymer was added 0.5 ml of 10% $D_2O$ solution of NaOH and the reaction mixture was refluxed for 3 hr. Then, the reaction mixture was subjected to nmr measurement. Its nmr spectra was compared with that of the authentic compound in alkaline $D_2O$ solution.

**Molecular Weight Determination.** The molecular weight of the copolymer was measured by a vapor pressure osmometer (Hitachi Perkin-Elmer Model 115) in dimethylformamide at 55°. The precision of the method was within ±50.

## Results and Discussion

**Copolymerization and Characterization of Copolymer.** OXZ and β-lactones were successfully copolymerized

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[1] Part I of this series, see T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **5**, 354 (1972).

[2] T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, **3**, 35 (1972).

[3] Y. Yamashita, Y. Ishikawa, T. Tsuda, and S. Miura, *Kogyo Kagaku Zasshi*, **66**, 104 (1963).

[4] Y. Yamashita, Y. Ishikawa, and T. Tsuda, *Kogyo Kagaku Zasshi*, **67**, 252 (1964).

[5] T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert, and F. T. Fiedorek, *J. Amer. Chem. Soc.*, **73**, 3168 (1951).

**Table I**
**Copolymerization of OXZ with MePL and $Me_2PL$[a]**

| Run No. | β-Lactone | Solvent | Temp (°C) | Time (hr) | Yield (%) | Copolymer Composition (%) (OXZ–β-Lactone) | Mol Wt |
|---|---|---|---|---|---|---|---|
| 1 | MePL | $CH_3CN$ | 40 | 6 | 68 | 50–50[b] | 3980[d] |
| 2 | MePL | $CH_3CN$ | 10–20 | 27 | 42 | 50–50[b] | 4000[d] |
| 3 | $Me_2PL$ | DMF | 40 | 10 | | 23–77[c] | *e* |
| 4 | $Me_2PL$ | $CH_3CN$ | 40 | 10 | | 22–78[c] | *e* |
| 5 | $Me_2PL$ | $CH_3CN$ | 30 | 72 | 67 | 44–56[b] | *d* |
| 6 | $Me_2PL$ | $CH_3CN$ | 10–20 | 45 | 21 | 44–56[b] | 3610[d] |

[a] 7.5 mmol for each monomer in 2.0 ml of solvent. [b] The mean value of those determined by nmr and elemental analyses. [c] Determined by elemental analyses. [d] White powder soluble in organic solvents and in water. [e] White powder insoluble in most organic solvents and in water.

**Table II**
**Elemental Analyses of Copolymers**

| | *Anal.* | | | | | | |
|---|---|---|---|---|---|---|---|
| | Found (%) | | | Calcd for the 50–50 Composition (%) | | | |
| Run No. | C | H | N | C | H | N | Copolymer Composition (%) OXZ–β-Lactone |
| 1 | 53.56 | 7.00 | 8.66 | 53.49 | 7.05 | 8.91 | 50–50 |
| 3 | 54.43 | 8.00 | 3.42 | | | | 23–77 |
| 4 | 54.79 | 7.96 | 3.37 | 52.81 | 8.23 | 8.80 | 22–78 |
| 6 | 55.82 | 7.72 | 6.85 | | | | 44–56 |

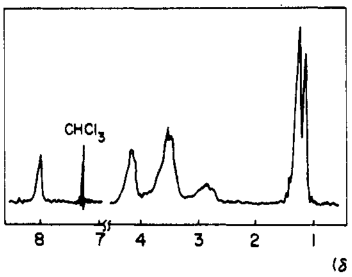


Figure 1. Nmr spectrum of the OXZ-MePL copolymer (in $CDCl_3$).

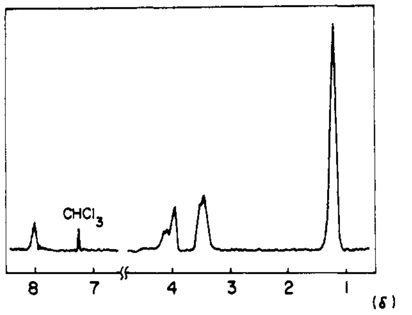
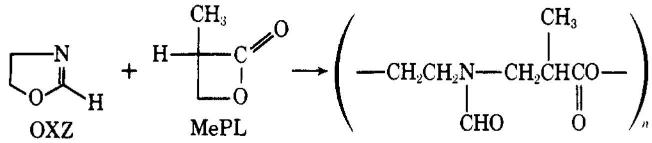


Figure 2. Nmr spectrum of the OXZ-$Me_2PL$ copolymer (in $CDCl_3$).

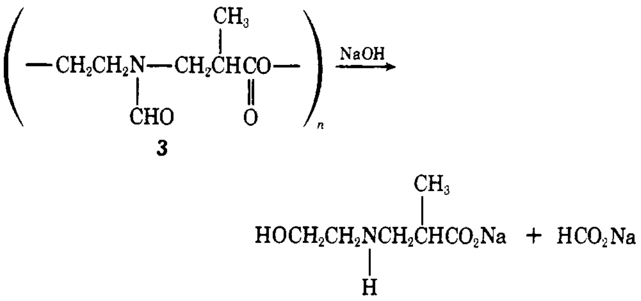
in aprotic dipolar solvents without added initiator. Table I shows the results of copolymerization with an equimolar monomer feed of OXZ and β-lactone. As seen in Table I the copolymer from OXZ and MePL is a 1:1 alternating one in two experiments (runs 1 and 2). The nmr spectrum (Figure 1) of the copolymer has five signals at $\delta$ 8.02 (1 H), 4.20 (2 H), 3.50 (4 H), 2.83 (1 H), and 1.13 (3 H) in $CDCl_3$. They are reasonably assigned respectively to the protons of N—CHO ($\delta$ 8.02), $CO_2CH_2$ ($\delta$ 4.20), $CH_2NCH_2$ ($\delta$ 3.50), CH(Me) ($\delta$ 2.83), and $CH_3$ ($\delta$ 1.13) of 1:1 alternating copolymer **3**. These assignments are well compatible with those of OXZ-PL copolymer.[1] Thus, the determination of copolymer composition was possible and this was made on the integration values of the peaks at $\delta$ 8.02 of >NCHO and at $\delta$ 1.13 of $CH_3$.



**3**

The ir of the copolymer shows characteristic bands at 1740 cm$^{-1}$ due to —$CO_2$— group and at 1670 cm$^{-1}$ due to >NCHO group. The elemental analysis of the copolymer was in good agreement with the calculated value of 1:1 monomer composition as shown in Table II.

In addition, the copolymer structure of **3** was further confirmed by an alkaline hydrolysis experiment in $D_2O$.

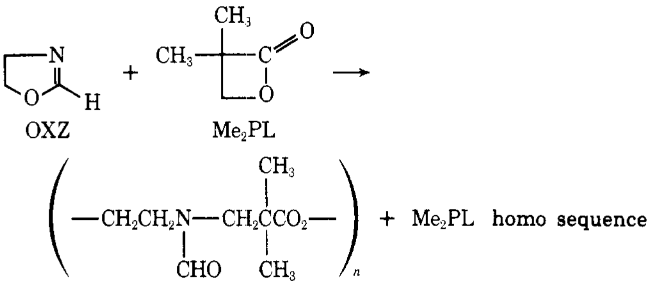


$$\left(-CH_2CH_2\underset{CHO}{N}-CH_2\overset{CH_3}{CH}\underset{O}{\overset{}{C}}O-\right)_n \xrightarrow{NaOH} HOCH_2CH_2\underset{H}{N}CH_2\overset{CH_3}{CH}CO_2Na + HCO_2Na$$

**3** **4**

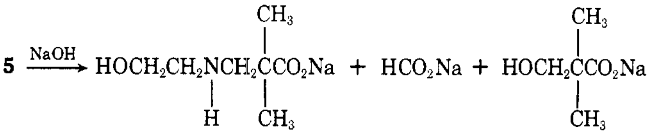
The hydrolysis of **3** gave exclusively two products, β-alanine derivative **4** (Na salt) and $HCO_2Na$, whose nmr spectrum was identical with that of 1:1 mixture of the authentic samples **4** and $HCO_2H$ in NaOH solution of $D_2O$.

Similarly, the copolymer structure of OXZ and $Me_2PL$ was determined. In Figure 2 is shown the nmr spectrum of the copolymer of run 6. It exhibits four signals at $\delta$ 8.02 (1 H), 4.02 (2.6 H), 3.56 (4 H), and 1.19 (7.8 H), which are assigned to N—CHO, $CO_2CH_2$, $CH_2NCH_2$, and —C-$(CH_3)_2$—, respectively. In addition a small peak is seen at $\delta$ 4.15 as a shoulder of large peak of $\delta$ 4.02. This peak is reasonably assigned to the protons of $CO_2CH_2$ of $Me_2PL$ unit in the sequences consisting of more than two units of $Me_2PL$ since the same kind of situation has already been observed in the case of OXZ-PL copolymer.[1] From the integration values of peaks δ 8.02 and 1.19 the copolymer composition was calculated.



5

Alkaline hydrolysis of the OXZ–$Me_2PL$ copolymer was carried out in a similar way above. As the main products of hydrolysis, β-alanine derivative **6** (Na salt) and $HCO_2Na$ were detected by nmr analysis. In addition, a small amount of hydroxypivalic acid (Na salt) was detected which was indicative of the presence of the sequences of $Me_2PL$ homo units in the copolymer. Furthermore, the results of ir and elemental analyses support the copolymer structure of **5**.



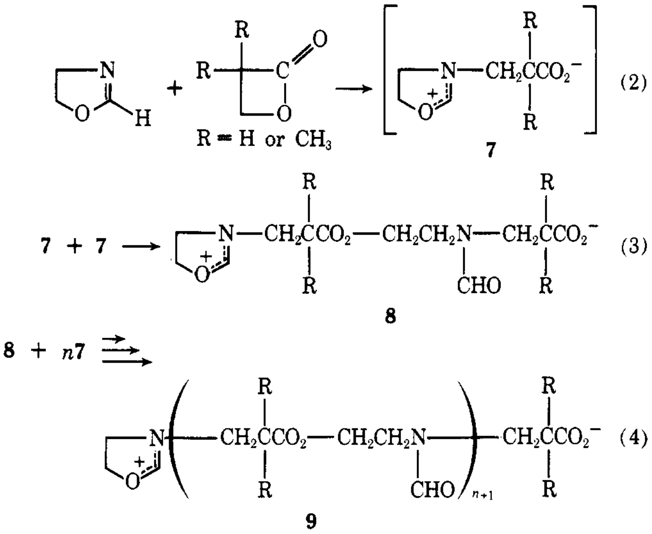
$$5 \xrightarrow{NaOH} HOCH_2CH_2\underset{H}{N}CH_2\overset{CH_3}{\underset{CH_3}{C}}CO_2Na + HCO_2Na + HOCH_2\overset{CH_3}{\underset{CH_3}{C}}CO_2Na$$

6

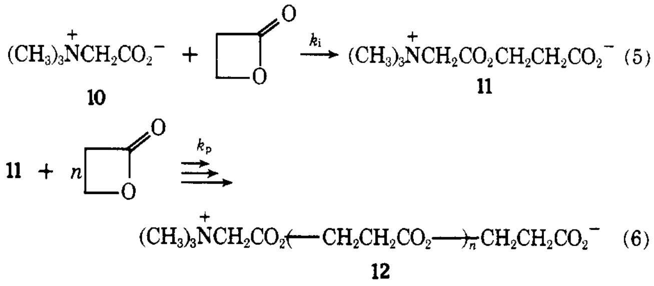
With the raise of the reaction temperature, *i.e.*, 40°, in the copolymerization of OXZ with $Me_2PL$, the content of the $Me_2PL$ unit in the product copolymer increased. In the cases of runs 3 and 4, the formation of real copolymers was established by the solubility characters of the copolymers; *i.e.*, the copolymer was insoluble in most organic solvents and in water. If it contained a homopolymer of OXZ, a portion of poly(OXZ) should be soluble in water.[2] At lower reaction temperatures, *i.e.*, 10–30°, the copolymer composition becomes closer to the 1:1 alternating one. The copolymers of runs 5 and 6 are soluble in acetonitrile, chloroform, dimethylformamide, and water. Thus, the solubilities of these copolymers are quite different from those of poly(OXZ) and poly($Me_2PL$). Poly(OXZ) is soluble only in water, whereas poly($Me_2PL$) is insoluble in most organic solvents and in water.[4]

**Mechanism of Alternating Copolymerization.** In the previous paper[1] a new concept of alternating copolymerization has been proposed, in which the propagation proceeds *via* a betaine intermediate. The copolymerization proceeded without any added catalyst at room temperature in dipolar aprotic solvents.

The same consideration may be applied to the present case. The copolymerization of OXZ and β-lactones can be formulated *via* betaine **7** as seen in eq 2–4. Betaine **7** is first formed from two neutral species, OXZ and β-lactone, in which the cleavage of the alkyl—oxygen bond of β-lactone is involved. It has been already observed that the copolymerization rate of OXZ with PL increased in aprotic polar solvents such as dimethylformamide and $CH_3CN$.[1] This was explained by the reasonable assumption that eq 2 was the rate-determining step, since the formation of such ionic species **7** by a dipole–dipole reaction (eq 2) should be favored in polar solvents.[1] The carboxylate anion of **7** then attacks the oxazolinium ion of another betaine to give **8** which involves the isomerization ring opening of oxazolinium. A zwitterion **8** reacts successively with betaine **7** going into propagation stage (eq 4). Once betaine **7** is formed **7** should react faster with **8** or **9** than with another betaine **7** because the reaction of two betaines to give **8** should need more energy for charge separation than does the reaction of **7** with **8** or with **9**.



As to the nucleophilic reactivities of **7**, **8**, and **9**, the above consideration may be rationalized by the recent results of Mathes and Jaacks.[6] They determined the reactivities of betaine **10**, zwitterion **11**, and macrozwitterion **12** in the polymerization of PL by a betaine (**10**) initiator (eq 5 and 6). The rate constants were obtained to be $k_i = 1.4 \times 10^{-2}$ and $k_p = 6.2 \times 10^{-2}$ l./(mol min) at 20° in ethanol, respectively, *i.e.*, the nucleophilic reactivity of **10** was 4.5 times less than that of **11** or **12**.[6] Consequently, it is reasonably assumed that the propagation of the present copolymerization takes place almost exclusively between macrozwitterion **9** and betaine **7**. This situation is quite compatible with experimental observations of two-stage copolymerization of OXZ with PL (*vide infra*).



In the propagation stage of OXZ and $Me_2PL$ copolymerization the carboxylate anion of **9** attacks not only betaine **7** but also free $Me_2PL$ to produce $Me_2PL$ homo sequences. This becomes more noticeable at higher temperatures probably due to the low concentration of **7**. It should be noted that free OXZ does not attack the oxazolinium of **7**, **8**, and **9** under the copolymerization conditions. This agrees with the experimental fact that the OXZ homo sequence does not exist in the copolymer.

Equation 2 is further rationalized by the recent report[6,7] on the betaine formation from tertiary amine and PL. OXZ is a strong nucleophile like tertiary amine, and hence, can form betaine with β-lactone.

**Two-Stage Polymerization.** According to the scheme of eq 2–4, the oxazolinium and carboxylate ends of the propagating species may remain active after all the monomers have been completely consumed. This problem was examined by a two-stage polymerization. The results are taken to support the living character of the polymerization system.

A mixture of 7.5 mmol each of OXZ and PL in 2 ml of

(6) N. Mathes and V. Jaacks, *Makromol. Chem.*, **142**, 209 (1971).

(7) V. Jaacks and N. Mathes, *Makromol. Chem.*, **131**, 295 (1970).

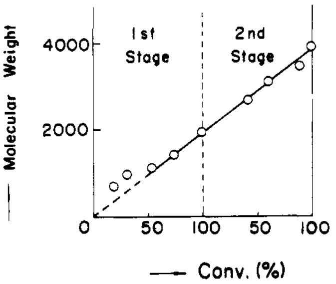


**Figure 3.** Plots of the conversion *vs.* molecular weight in the two-stage copolymerization of OXZ with PL.

dimethylformamide was subjected to the alternating copolymerization at 40°. After 10 hr when the conversions of both monomers were about 100%, the second feed of an equimolar mixture of the two monomers (each 7.5 mmol) in dimethylformamide (2 ml) was added to the system of the first polymerization mixture, and then, the system of the second-stage polymerization was kept at 40° for 10 hr. A plot of the conversion *vs.* molecular weight is shown in Figure 3. A linear relationship is observed. The straight line passes through the origin. In the first stage, however, the beginning in comparison with that at the latter stage This implies that the concentration of the macrozwitterion, *i.e.*, the molar concentration of copolymer, is lower at the beginning in comparison with that at the later stage where the concentration of macrozwitterion remains almost constant. After the concentration of **8** and/or **9** becomes greater betaine **7** reacts preferably with **8** or **9**, and the concentration of macrozwitterion does not increase. In the second stage, the macrozwitterion, whose concentration remains constant, continues to grow. The molecular weight at the end of the second stage is almost twice as high as that at the end of the first stage. The intermolecular and intramolecular reactions between the oxazolinium ring and carboxylate group at the macrozwitterions might take place during the polymerization. But the relationship of Figure 3 does not indicate the occurrence of the above reactions of the macrozwitterions under these conditions.

Table III
Copolymerization of OXZ with PL, MePL, and Me$_2$PL[a]

| Comonomer | Time (hr) | Yield (%) | Mol Wt | Copolymer Composition (%) (OXZ–$\beta$-Lactone) |
|---|---|---|---|---|
| PL | 25 | 61 | 3500 | 50–50[b] |
| MePL | 27 | 42 | 4000 | 50–50[b] |
| Me$_2$PL | 45 | 21 | 3610 | 44–56 |

[a] 7.5 mmol of each monomer in 2.0 ml of acetonitrile at 10–20°. [b] 1:1 alternating copolymer.

**Copolymerization Reactivities of PL, MePL, and Me$_2$PL.** The reactivities of PL, MePL, and Me$_2$PL were examined in the copolymerization with OXZ at lower temperatures. Table III shows the copolymerization results in acetonitrile at 10–20°. In all cases white powdery polymers were obtained. They are hygroscopic and soluble in acetonitrile, chloroform, dimethylformamide, methanol, and water.

The copolymerization reactivities are in a qualitative order of PL > MePL > Me$_2$PL. Introduction of methyl group to the $\alpha$ position of carbonyl group resulted in a decrease of copolymerization reactivities. This order agrees with that observed in the anionic homopolymerization of $\beta$-lactones,[3,4] in which the rate-determining step of the polymerization is the attack of the propagating carboxylate anion on the monomer accompanying the ring opening of $\beta$-lactone. The situation is quite similar to the copolymerization *via* betaine propagation, *e.g.*, the rate-determining step of the copolymerization in the present study is probably the formation of betaine **7** involving the ring opening of $\beta$-lactone by the nucleophic attack of OXZ as shown by eq 2.

Further studies on the betaine propagation are currently undertaken in our laboratory especially from the mechanistic point of view.

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# Mechanism of Charge-Transfer Polymerization. VI. Alternating Radical Copolymerization of *N*-Vinylcarbazole with Electron-Accepting Monomers[1]

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ABSTRACT: *N*-Vinylcarbazole was successfully copolymerized with such electron-accepting monomers as fumaronitrile or diethyl fumarate to give the 1:1 alternating copolymer regardless of the monomer feed composition under conditions of free radical initiation. Characterizations of the copolymers and comparable polymerization features between these two systems are described. A generalized mechanism involving participation of both the monomer charge-transfer complex and the free monomers is proposed for the alternating radical copolymerization.

There have been a number of studies on the alternating radical copolymerization in view of both synthetic and mechanistic interest. Especially, the propagation mechanism for the alternating radical copolymerization has long been the subject of controversy and is still left to be clarified. Numerous alternating radical copolymerization systems, either spontaneously initiated or initiated by a free-radical initiator, have been reported to date in the combinations of various olefins with maleic anhydride or sulfur dioxide in particular.[2-4] With respect to the *N*-vinylcarbazole (VCZ) monomer, which has recently received much

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(1) Part V of this series: K. Tada, Y. Shirota, and H. Mikawa, *J. Polym. Sci., Part A-1*, in press.

(2) For examples, see (a) M. C. deWilde and G. Smets, *J. Polym. Sci.*, **5**, 253 (1950); (b) D. Booth, F. S. Dainton, and K. J. Ivin, *Trans. Faraday Soc.*, **55**, 1293 (1959); (c) M. M. Martin and N. P. Jensen, *J. Org. Chem.*, **27**, 1201 (1962); (d) S. Iwatsuki and Y. Yamashita, *Macromol. Chem.*, **89**, 205 (1965); (e) N. L. Zutty, C. W. Wilson, G. H. Potter, D. C. Priest, and C. J. Whitworth, *J. Polym. Sci., Part A*, **3**, 2781 (1965).