# Polymerization of β-Cyanopropionaldehyde

VIII.   Anionic Copolymerization with Dimethylketene

Kazuhiko Hashimoto and Hiroshi Sumitomo

Faculty of Agriculture, Nagoya University, Chikusa-ku, Nagoya, Japan.

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ABSTRACT: Anionic copolymerization of β-cyanopropionaldehyde (CPA, M_1) with dimethylketene (DMK, M_2) initiated by benzophenone-dilithium complex was carried out at 0°C and −78°C. The values of monomer reactivity ratio at −78°C were determined to be $r_1 = 0.6 \pm 0.1$ and $r_2 = 0.04 \pm 0.03$. The structure of the resulting copolymer was investigated by means of IR and NMR analyses. The main structure of the copolymer was found to consist of sequence I formed through the alternating addition of the $C = O$ bond of CPA with the $C = C$ bond of DMK. The copolymer which is rich in the CPA component is believed to contain sequence II in addition to I, but the former must be extremely limited. The DMK-rich copolymer has sequence III in addition to I.
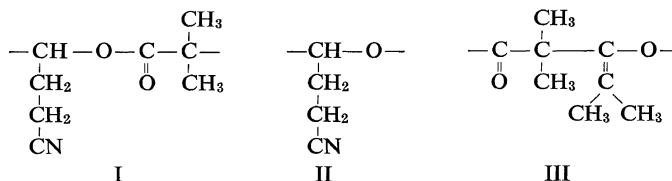
These facts suggest that the selectivity of elementary reactions in the copolymerization process is relatively high but not complete, which might be explained in terms of the different preferable forms of ambient anions.

KEY WORDS   Anionic Copolymerization / β-Cyanopropionaldehyde / Dimethylketene / Structural Analysis / NMR / Ambient Anion / Reactivity/

In the preceding papers, β-cyanopropionaldehyde (NC–CH₂–CH₂–CHO, CPA) was polymerized to give poly(cyanoethyl)oxymethylene with the use of various ionic initiators.[1-8]

Dimethylketene $((CH_3)_2C = C = O$, DMK) is known to polymerize to polyester, polyketone, polyacetal[9-13] and also to copolymerize with or some carbonyl compounds leading to alternating copolymers.[14-17]

The present paper is concerned with the anionic copolymerization of CPA with DMK initiated by benzophenone-dilithium complex (Li₂–BzPh), and the structural analyses of the obtained copolymer.

EXPERIMENTAL

All procedures including purification of materials, preparation of initiator and polymerization were carried out in a high vacuum system.[6]

Materials

CPA, tetrahydrofuran (THF), and benzophenone (BzPh) were purified in the same way as in the previous paper.[6] DMK was obtained by pyrolysis of its solid dimer (tetramethylcyclobutane-1,3-dione) in a stream of nitrogen,[18] and distilled *in vacuo* after drying over Molecular Sieves. Li₂-BzPh was prepared as previously described.[6] The cyclic trimer of CPA, 2,4,6-tris-(β-cyanoethyl)-s-trioxane, was prepared by the addition of one drop of a mineral acid to CPA[1] and the white needle-shaped product was recrystallized from methanol.

Polymerization

A solution of CPA and DMK in THF was added to THF solution of Li₂-BzPh complex while stirring.   Polymerization was terminated by pouring the solution into a large amount of methanol.

The precipitated polymer was washed in methanol and dried under reduced pressure. Average molecular weight of the polymer, M_n, was measured by vapor pressure osmometry (Hewlett-Packard Model 302) in dimethylformamide (DMF) at 37°C.

Structural Analyses of the Copolymers

NMR analysis was carried out with a JNM-4H-100 spectrometer. Infrared spectra of the copolymers were measured by the KBr method, using JASCO Model IR-E and IR-G spectrophotometers.

RESULTS AND DISCUSSION

Copolymerization proceeded in a homogeneous phase in contrast with the case of homopolymerization of CPA.[6,7] The results of the anionic copolymerization of CPA with DMK initiated by Li$_2$-BzPh at -78°C are given in Table I.

The resulting polymer obtained as a white powder was found to be composed of CPA and DMK structural units on the basis of the elementary analysis. It was soluble in DMF, pyridine, and THF, and insoluble in benzene (see Table II). On the other hand, DMK homopolymer (polyester type) is known to be soluble in benzene and insoluble in DMF. The poor solubility of the CPA homopolymer, poly(cyanoethyloxymethylene), confirms that the copolymer obtained here contains neither homopolymer of CPA nor that of DMK.

The average molecular weight, M_n, and melting point of the copolymer were not high, suggesting the frequent occurrence of chain transfer reactions. In addition, both values decrease with the mole fraction of CPA in monomer feed as shown in Figure 1. These factors suggest that the CPA monomer itself acts as a chain transfer agent through its active hydrogens.

It was observed in the thermogravimetric analy-

Table I. Anionic copolymerization of β-cyanopropionaldehyde with dimethylketene at -78°C[a]

| Run No. | Monomer | | | Li$_2$–BzPh, mol % to monomer | Polymer yield (%)[b] | Mole fraction of CPA in copolymer[c] |
	CPA (g)	DMK (g)	Mole fraction of CPA			
43	3.12	0	1.00	0.1[d]	63.6	1.00
59	6.32	1.77	0.75$_1$	//	29.0	0.76$_3$
58	4.37	3.58	0.50$_7$	//	52.6	0.59$_1$
61	2.17	3.64	0.33$_9$	//	53.3	0.53$_7$
62	1.22	3.79	0.21$_3$	//	53.8	0.39
60	0	1.72	0	0.3	36.6	0
57	4.32	3.07	0.54$_2$	0.6	39.3	0.59$_4$

[a] At $<10^{-4}$mm Hg; 1 day; Solvent, THF; Volume ratio of solvent to monomer, 5.
[b] Calcd. for the total weight of the monomers.
[c] Estimated from the elementary analysis.
[d] Na$_2$-BzPh.

Table II. Properties of copolymer obtained at -78°C

| Run No. | Mole fraction of CPA in monomer | M_n[a] | mp (°C) | Solubility[b] | | | |
				DMF	Pyridine	THF	Benzene
43	1.00	3000	—	△	×	×	×
59	0.75$_1$	—	51 ~ 58	○	△	△	×
58	0.50$_7$	3550	67 ~ 74	○	○	○	×
61	0.33$_9$	4410	71 ~ 80	○	○	○	×
62	0.21$_3$	7690	91 ~107	○	○	○	×
60	0	10970[c]	156~162	×	○	○	○

[a] Vapor pressure osmometry in DMF at 37°C.
[b] At room temperature, △: Soluble; ○: Partially soluble; ×: Insoluble.
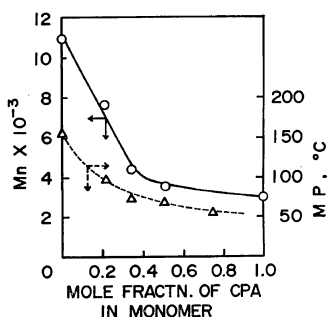[c] In benzene at 37°C.

Figure 1. Influence of monomer composition on properties of CPA—DMK copolymer.

sis that the weight loss of the copolymer was much smaller than that of CPA homopolymer, poly-(cyanoethyloxymethylene). The X-ray diagram of the copolymer (run No. 58) has two peaks at $2\theta = 11.5°$ and $20°$. But the broad peaks indicate that the crystallinity of the copolymer is not high.

From copolymerization data in the system of CPA (M_1) and DMK (M_2) the values of monomer reactivity ratio, $r_1 = 0.6 \pm 0.1$ and $r_2 = 0.04 \pm 0.03$, were determined by using Mayo—Lewis' integral scheme. It is known that highly alternated copolymers are formed in anionic copolymerizations of DMK with some carbonyl compounds in non-polar solvents.[14-17] The values of monomer reactivity ratios obtained here, however, suggest that not only cross-propagation but homo-propagation occurs. And the value of r_1 being higher than that of r_2 indicates that the CPA units in the copolymer continue longer than those of DMK.

A mechanism for alternating copolymerizations of DMK with carbonyl compounds through the formation of the following chelate complex was presented by G. Natta et al.[15]
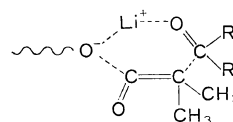
In the copolymerization of DMK with CPA at $-78°C$ in such a poor polar solvent as THF, the copolymer composition is greatly dependent on the monomer composition. This suggests that the interaction between the two monomers and the growing ion pair is not strong in the present system.

The results of the anionic copolymerization at $0°C$ are listed in Table III. It is interesting to note that CPA gives a copolymer with DMK at $0°C$, in spite of the fact that practically no homopolymerization of CPA takes place at that temperature. Since CPA itself has also been known to give no high polymer at $0°C$ even with the use of cationic initiators, the ceiling temperature of the monomer would be below $0°C$. In the anionic polymerization some side reactions, for example an aldol condensation reaction, should occur at this temperature. But the material balance shows that almost all the CPA polymerized in run No. 68. When the ratio of CPA to DMK in the monomer feed is lower than 1, occurrence of side reactions seems to be repressed even at $0°C$.

It is known that the polymerization of aldehydes is generally reversible. Therefore the following elementary reaction should also be reversible.
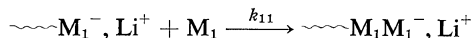
$$\sim\sim\sim M_1^-, Li^+ + M_1 \xrightarrow{k_{11}} \sim\sim\sim M_1 M_1^-, Li^+$$

Table III. Anionic copolymerization of β-cyanopropionaldehyde with dimethylketene at $0°C$[a]

Run No.	Monomer			Li_2-BzPh, mol % to monomer	Polymer yield (%)[b]	Mole fraction of CPA in copolymer[c]
	CPA (g)	DMK (g)	Mole fraction of CPA			
70	4.30	0	1.00	0.1	0	—
66	4.26	0.47	0.86_3	//	Trace	—
67	8.41	2.06	0.77_5	//	//	0.53_5
63	4.20	3.79	0.48_3	//	8.4	0.53_4
68	0.99	2.62	0.24_1	//	53.7	0.39_4
69	0	1.09	0	0.2	40.3	0

[a] At $<10^{-4}$mm Hg; 1 day; Solvent, THF; Volume ratio of solvent to monomer, 5.

[b] Calcd. for the total weight of the monomers.
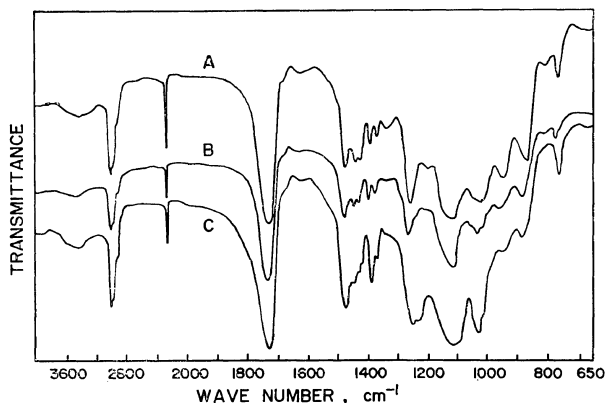
[c] Estimated from the elementary analysis.

Figure 2. Infrared spectra of CPA—DMK copolymers (KBr).
A: Run No. 57, $x = 0.59_4$.
B: Run No. 61, $x = 0.53_7$.
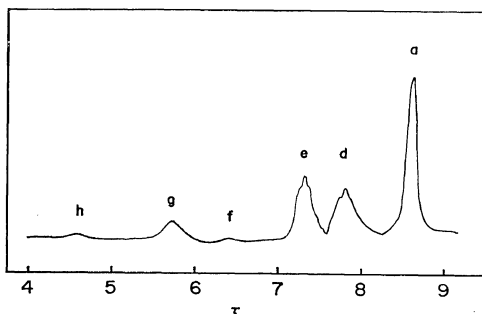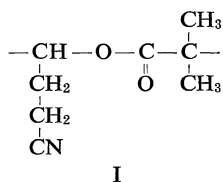C: Run No. 62, $x = 0.39$.

Figure 3. NMR spectrum of CPA—DMK copolymer; Run No. 57, $x = 0.59_4$; 10% Pyridine solution; 100°C.

An increase in polymerization temperature may be accompanied by an increase in the reverse reaction rate of the elementary step resulting in a relative decrease in the apparent value of k_{11}. The copolymerization data at 0°C can be understood if the monomer reactivity ratios are given as $r_1 = 0$ and $r_2 = 0.04$.

Infrared spectra of the copolymers of CPA with DMK (see Figure 2) are quite different from those of their own homopolymers[1-3,9-13] and have characteristic absorption bands at 2250 cm^{-1} based on the nitrile group and 1730, 1260 and 1110 cm^{-1} on the ester group, which may show that the main structure of the CPA—DMK copolymer consists of sequence I.

$$
\begin{array}{c}
\overset{\displaystyle CH_3}{\underset{\displaystyle \underset{\displaystyle \underset{\displaystyle CN}{|}}{\underset{\displaystyle CH_2}{|}}}{\underset{\displaystyle CH_2}{|}}\\
-CH-O-C-\overset{|}{C}-\\
\underset{\displaystyle CH_2}{|}\overset{\displaystyle ||}{O}\overset{\displaystyle CH_3}{}
\end{array}
$$

I

It may be seen from Figure 2 that these absorptions change with the copolymer composition, in which x represents a molar fraction of the CPA unit in the copolymer determined by an elemental analysis. Such variation of the spectra with the copolymer composition suggests that the copolymers contain structural units other than sequence I, with varying contents.

This is distinctly reflected in the NMR spectra of the copolymers measured in 10% pyridine solution (Figures 3 and 4).

The decrease in x is accompanied by an increase in the ratio of peak a to peaks d and e, and new strong peaks b and c appear in the spectrum of the copolymer of $x < 0.5$.

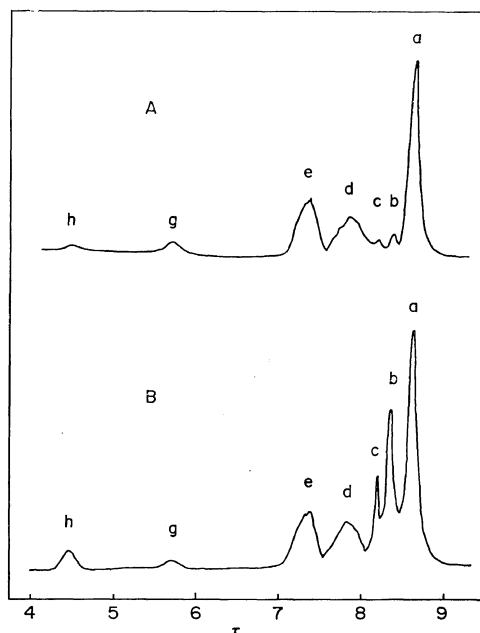Measurements of NMR spectra of the homopolymer of DMK (run No. 60) and of the cyclic

Figure 4. NMR spectra of CPA—DMK copolymers.
A: Run No. 63, $x = 0.53_4$; B: Run 62, $x = 0.39$; 10% Pyridine solution; 20°C.

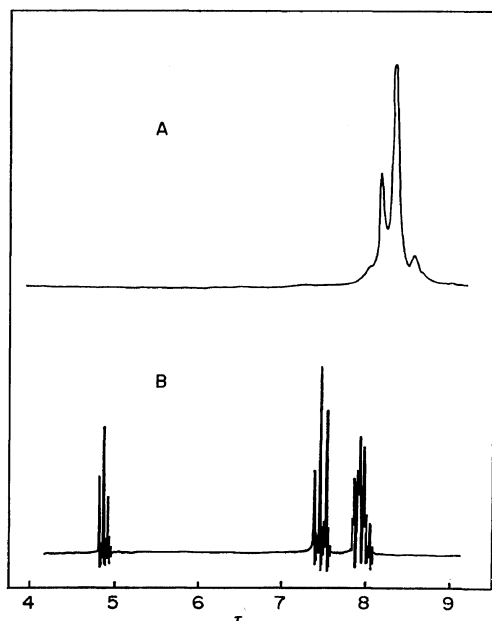trimer of CPA (2,4,6-tris(β-cyanoethyl)-s-trioxane) are shown in Figure 5 below.

Figure 5. NMR spectra of DMK homopolymer and CPA trimer (2,4,6-tris(β-cyanoethyl)-s-trioxane).
A: Run No. 60, 10% pyridine solution; B: CPA trimer, 10% Chloroform solution; 20°C.

The DMK homopolymer of almost all polyester types gives two peaks with the peak ratio of about 3:1 at the τ values of 8.35 and 8.2 (Figure 5-A). The peak at τ 8.35 may be due to methyl protons in the unit of

$$-\overset{\underset{\|}{O}}{C}-\overset{\underset{|}{CH_3}}{C}-\overset{CH_3}{\underset{\overset{|}{C}}{C}}-O-$$

and either protons of the two methyl groups in the unit of $-\overset{\underset{\|}{C}}{C}-O-$ and the other at τ 8.2 might
$$\overset{}{\underset{CH_3 \, CH_3}{}}$$
come from the other methyl protons. The small peak at about 8.6 τ suggests that this DMK homopolymer has a different unit. In the spectrum of the cylic trimer of CPA shown in Figure 5-B, three peaks at the τ values of 7.9, 7.4 and 4.9 are assignable to α-, β-methylene and methine protons, respectively.

Spectrometric data characteristic of both homopolymers of CPA and DMK are listed in Table IV.

The fact that the copolymer obtained here gives the two peaks of b and c with a peak ratio of about 3:1 at the same chemical shifts as the DMK homopolymer does, suggests that the copolymer contains sequence III. But the strongest peak based on methyl protons is peak a, which is confirmed to be due to methyl protons of sequence I taking account of the considerably high chemical shift of the peak a (τ 8.6).

From a comparison of the spectrum of CPA cyclic trimer (Figure 5-B) with those of the copolymers (Figures 3 and 4), peaks d(τ 7.8) and e (τ 7.3) are attributed to α- and β-methylene protons respectively of the CPA unit, which is consistent with the fact that the ratio of peak d to peak e is always approximately 1:1.

Table IV. Spectrometric analytical data of homopolymers of CPA and DMK

Structural unit	$-CH-O-$ $\underset{}{CH_2CH_2CN}$	$-\overset{\underset{\|}{O}}{C}-\overset{\underset{\|}{CH_3}}{C}-\overset{CH_3}{\underset{\overset{\|}{C}}{C}}-O-$ $\underset{CH_3 \, CH_3}{}$	$-\overset{\underset{\|}{O}}{C}-\overset{CH_3}{\underset{\overset{\|}{CH_3}}{C}}-$	$-\overset{}{C}-O-$ $\underset{CH_3 \, CH_3}{\overset{\|}{C}}$
IR (cm^{-1})	2250[a] 950–1130	1740[b] 1230 1100	1670[b]	1710[b]
NMR (τ)	7.9 7.4 4.9	8.35 8.2	8.3–8.4[c]	8.1–8.2[c]

[a] See ref. 1–3.
[b] See ref. 9–13.
[c] Value for a singlet peak anticipated from its structure.

The peak f (τ 6.4) in Figure 3 is believed to be due to the methine proton of the unit $-CH-O-$ by analogy with the chemical shift of the methine proton of isopropyl ether (τ 6.44).

In view of the fact the methine proton of the unit $-CH-O-C-$ generally appears at a lower magnetic field than that of the unit $-CH-O-$, the peak g (τ 5.7) may come from the methine proton of the unit $-CH-O-C-$. The methine proton of CPA cyclic trimer gives a peak at 4.9, which corresponds to that of the unit $-O-CH-O-$. This peak is not observed in the spectra of the copolymer, which shows little or no trace of the corresponding methine. The peak h observed at the lower magnetic field (τ 4.5) may be attributed to the methine proton of the unit $-O-CH-O-C-$.

The composition of the copolymer, calculated from the ratio of the peak a or peaks a + b + c– based on the methyl protons of the DMK unit– to peaks d and e–due to the methylene protons of the CPA unit–agrees satisfactorily with that calculated from the elemental analysis as shown in Table V.

Table V. Peak ratios in NMR spectra of CPA–DMK copolymers

Run No.	Peak ratio of (a+b+c):d:e	Mole fraction of CPA in copolymer	
		Calculated from peak ratio	Calculated from elemental analysis
57	2.12: 1: 1	0.58$_5$	0.59$_4$
61	2.43: 1: 1	0.55$_2$	0.53$_7$
63	2.44: 1: 1	0.55$_1$	0.53$_4$
62	4.10: 1: 1	0.42$_3$	0.39

The copolymer rich in CPA units (run No. 57, $x = 0.59_4$) is thought to contain DMK units of a purely ketone type leading to sequence I, since its methyl protons give only one peak a. In other words, the DMK unit enters the CPA-rich copolymer through the opening of the C=C double bond without homo-propagating.
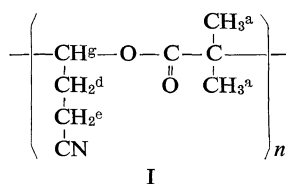
Peaks f and h are attributed, as described above, to the methine protons indicated in the following sequence.
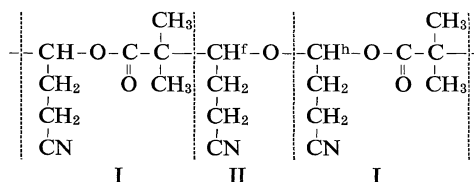
The fact that the peak at τ 4.9 based on the methine proton of $-O-CH-O-$ is not observed here indicates that no more than three CPA units are linked together. In other words sequence II is very short. The CPA-rich copolymer, therefore, may be considered to consist of the alternating sequence I as a main structure, with an extremely short sequence II.

The NMR spectrum of the DMK-rich copolymer (run No. 62, $x = 0.39$) has two more peaks attributed to methyl protons (τ 8.35 and 8.2), suggesting that the copolymer contains sequence III together with sequence I. This is evidenced also by the appearance of the considerably strong peak h as shown in Figure 4.
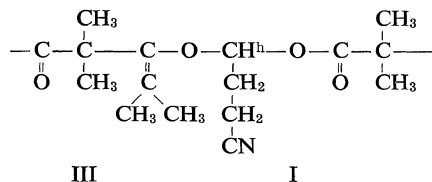
Taking into account the possibility DMK monomer polymerizing through its C=C and C=O groups, the present system can be regarded as a terpolymerization among CPA, C=C and C=O double bonds of DMK. All elementary reactions in the system are listed in Table VI, where DMK_{C-C} and DMK_{C-O} represent

$$-C-C-$$
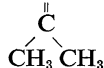
$$O \quad CH_3$$

with CH$_3$ groups, and $-C-O-$ respectively.

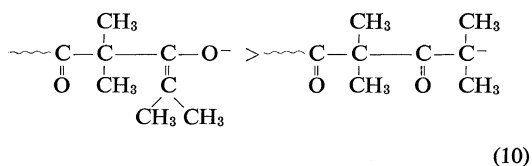Table VI. Elementary reactions in the copolymerization of CPA with DMK

Growing chain	Monomer	Reactivity[a]	
~~(CPA)⁻	CPA	△	(1)
	DMK$_{C-C}$	○	(2)
	DMK$_{C-O}$	×	(3)
~~(DMK$_{C-C}$)⁻	CPA	○	(4)
	DMK$_{C-C}$	×	(5)
	DMK$_{C-O}$	▽	(6)
~~(DMK$_{C-O}$)⁻	CPA	▽	(7)
	DMK$_{C-C}$	▽	(8)
	DMK$_{C-O}$	×	(9)

[a] ○: Frequently occurs; △ and ▽: Occurs at high or low mole fractions of CPA in monomer, respectively; ×: Does not occur.

It is apparent from the results of the structural analysis of resulting copolymers described above that no reactions take place in (3), (5) and (9), but reactions (2) and (4) frequently occur. Reactions (6), (7) and (8) are apt to occur at a lower molar fraction of CPA in monomers, whereas reaction (1) is at a higher molar fraction. The copolymerization of CPA with DMK seems to have a lower selectivity of elementary reactions than that of DMK with acetone or benzaldehyde, in which case considerably highly alternative polyesters are formed.[14-17]

Even in the present system, however, the same extent of selectivity of reactions is considered from comparison of reactivities in the reactions (5), (6), (8) and (9) to be retained as in the case of the homopolymerization of DMK. That is to say it is difficult for the same structure unit of DMK to continue under the present conditions. Reactions (2) and (3) show that the DMK monomer added to the alcoholate anion of CPA always opens its C=C double bond.

These facts suggest that the preferable forms of ambident anions of DMK in the present system might be shown as follows:

$$\begin{array}{c} \quad\quad CH_3 \quad\quad\quad\quad\quad\quad CH_3 \quad CH_3 \\ \sim\sim C - C \underline{\quad\quad} C - O^- \; > \; \sim\sim C - C \underline{\quad\quad} C - C^- \\ \; O \;\; CH_3 \;\; C \quad\quad\quad O \;\; CH_3 \; O \;\; CH_3 \\ \quad\quad\quad\quad CH_3 \; CH_3 \end{array}$$

$$(10)$$

$$\begin{array}{c} \quad\quad\quad CH_3 \\ \sim\sim C - O - C - C^- \quad > \quad \sim\sim C \underline{\quad\quad} O \underline{\quad\quad} C - O^- \\ \; C \quad\quad\; O \;\; CH_3 \quad\quad\quad C \quad\quad\quad C \\ CH_3 \; CH_3 \quad\quad\quad\quad CH_3 \; CH_3 \;\; CH_3 \; CH_3 \end{array}$$

$$(11)$$

$$\begin{array}{c} \quad\quad\quad\quad CH_3 \\ \sim\sim CH - O - C - C^- \; > \; \sim\sim CH - O - C - O^- \\ \; CH_2 \quad\; O \;\; CH_3 \quad\quad\; CH_2 \quad\quad C \\ \; CH_2 \quad\quad\quad\quad\quad\quad CH_2 \quad CH_3 \; CH_3 \\ \; CN \quad\quad\quad\quad\quad\quad\; CN \end{array}$$

$$(12)$$
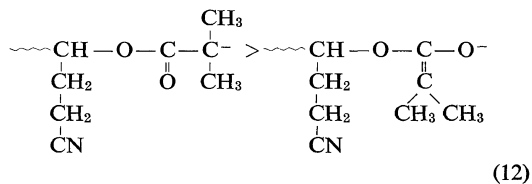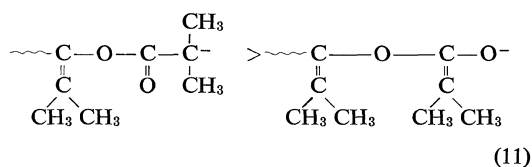
Thus the keto-ambident anion of DMK is liable to lead to the alcoholate anion type (10) and the ester-ambident anion to the carbanion type (11), as was shown by Yamashita et al.[13] In addition, the ester-ambident anion produced from CPA and DMK is also apt to form the carbanion type (12).

The hypothesis, already mentioned, of the formation of a chelate complex presented by Natta et al.[15] might also be applicable to the present case. However CPA has such a polar nitrile group that the formation of the complex may be prevented for this reason.

To some extent at least the selectivities apparent in the present system may be attributed to the existence of the preferable forms in the keto- and ester-ambident anions of DMK.

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