Anionic Copolymerization of *p*-Anisaldehyde with Dimethylketene Initiated by Benzophenone-Dialkali Metal Complexes

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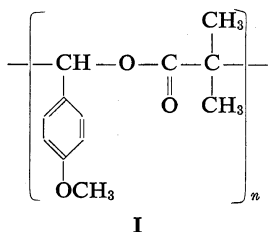
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ABSTRACT: The influence of alkali metal counter cations of initiators on the anionic copolymerization of *p*-anisaldehyde (ANA) with dimethylketene (DMK) in tetrahydrofuran at −78°C was investigated. The copolymerization using benzophenone-disodium and -dipotassium complexes resulted in the formation of an ANA—DMK copolymer rich in DMK units, while the lithium complex gave the ANA—DMK alternating copolymer as previously reported. An obvious difference in the sequence distribution of the copolymers was detected by the NMR analysis.

KEY WORDS: Anionic Copolymerization / *p*-Anisaldehyde / Dimethylketene / Counter Cation / Ion Pair / Structural Analysis /

In the preceding study,[1] the anionic copolymerization of *p*-anisaldehyde (*p*-CH$_3$O—C$_6$H$_4$—CHO, ANA) with dimethylketene ((CH$_3$)$_2$C=C=O, DMK) initiated by benzophenone-dilithium complex (Li$_2$-BzPh) was found to give an alternating copolymer (**I**) in such a polar solvent as tetrahydrofuran (THF).

$$\left[-CH-O-C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}- \right]_n$$

with the benzene ring bearing OCH$_3$ and the C=O group.

I

The present investigation is concerned with the influence of alkali-metal counter cations of initiators on the anionic copolymerization of ANA with DMK.

EXPERIMENTAL

All procedures, including purification of materials, preparation of initiators, and polymerization, were carried out in a high-vacuum system as previously described.[1-3] The average molecular weight of the copolymer, $\bar{M}_n$, was determined by the vapor-pressure osmometry (Hewlett Packard Model 302) in benzene at 37°C. NMR spectra of the solution in deuterat-ed chloroform were taken with JNM-4H-100 and JNM-MH-100 spectrometers, using tetramethyl-silane as a reference.

RESULTS AND DISCUSSION

Tables I and II summarize the results of the anionic copolymerization of ANA with DMK initiated by benzophenone-disodium (Na$_2$-BzPh) and -dipotassium (K$_2$-BzPh) complexes, respectively. The rate of copolymerization in the present systems was higher than that with Li$_2$-BzPh.[1] Because of the high rates of copolymerization especially in the range of higher mole fractions of DMK in the feed, an extremely small amount of the initiator had to be used in order to make the isolation of the copolymer at low conversions easier, at the sacrifice of the accuracy of the initiator concentration (about 10^{-5} mol/*l*).

As shown in Figure 1, the compositions of Na-copolymer and K-copolymer (the ANA—DMK copolymers prepared by use of Na$_2$-BzPh and K$_2$-BzPh, respectively) depend upon the monomer compositions, particularly in the lower range of mole fraction of ANA in the feed. Such a tendency was also observed in the copolymerization using sodium-naphthalene complex and sodium benzylate as initiators.
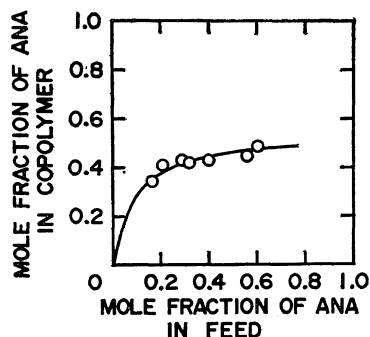
Table III gives the apparent values of mono-

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Table I. Anionic copolymerization of p-anisaldehyde with dimethylketene initiated by benzophenone-disodium complex[a]

Exptl no.	Monomer			Na_2-BzPh, mol% to monomer	Time, sec	Polymer yield,[b] %	Mole fraction of ANA in copolymer[c]
	ANA, g	DMK, g	Mole fraction of ANA				
40	6.56	2.03	0.62_5	0.03	50	14.3	0.46_6
30	5.26	2.56	0.51_4	0.02	45	8.7	0.44_9
57[d]	6.79	3.45	0.50_3	0.06	60	76.0	0.45_6
39	1.78	1.43	0.39_1	—	30	5.1	0.42_4
63[d,e]	1.46	1.41	0.34_7	ca. 0.01	20	1.8	0.40_8
38	2.19	3.40	0.24_9	<0.01	30	1.2	0.36_6
29	1.35	2.87	0.19_6	0.02	30	38.9	0.27_1
58[d]	1.41	3.46	0.17_3	ca. 0.01	30	75.7	—
54	0.96	2.59	0.16_1	ca. 0.01	ca. 10	65.5	—

[a] Temp, $-78°C$; solvent, THF, 50 ml.
[b] Referred to the total weight of the monomers.
[c] Estimated from the peak intensity in the NMR spectrum.
[d] 100 parts of $NaBPh_4$ were added to 1 part of the initiator.
[e] Initiator, Li_2-BzPh.

Table II. Anionic copolymerization of p-anisaldehyde with dimethylketene initiated by benzophenone-dipotassium complex[a]

Exptl no.	Monomer			K_2-BzPh, mol% to monomer	Time, sec	Polymer yield,[b] %	Mole fraction of ANA in copolymer[c]
	ANA, g	DMK, g	Mole fraction of ANA				
47	3.37	1.17	0.59_6	0.04	30	9.5	0.48_9
59	6.88	3.19	0.52_9	0.02	20	45.9	0.44_9
46	4.55	3.58	0.39_6	ca. 0.01	30	5.7	0.43_2
60	2.88	2.96	0.33_4	ca. 0.01	20	29.9	0.41_9
49	2.75	3.58	0.28_4	<0.01	30	2.1	0.43_2
53	1.76	3.45	0.20_7	<0.01	40	2.4	0.41_2
61	1.47	3.49	0.17_8	<0.01	20	19.3	0.34_3

[a] Temp, $-78°C$; solvent, THF, 50 ml.
[b] Referred to the total weight of the monomers.
[c] Estimated from the peak intensity in the NMR spectrum.
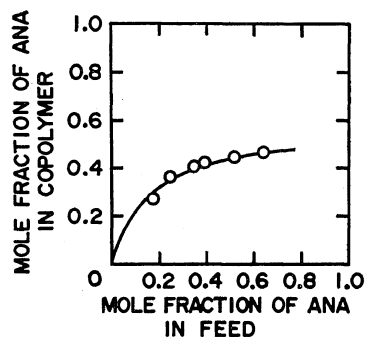
(A) Initiator, Na_2-BzPh   (B) Initiator, K_2-BzPh

Figure 1. Copolymer composition curves of ANA—DMK copolymers: Condition, THF, $-78°C$. Curves were calculated from the values of (A) $r_1=0$ and $r_2=0.29$ and (B) $r_1=0$ and $r_2=0.16$ (ANA= monomer 1).

Table III. Monomer reactivity ratios in copolymerization of ANA (M_1) with DMK (M_2)[a]

Initiator	r_1	r_2
Li_2-BzPh	0	0
Na_2-BzPh	0 ± 0.04	0.29 ± 0.06
K_2-BzPh	0 ± 0.05	0.16 ± 0.05

[a] Solvent, THF; polymerization temperature, $-78°C$.

mer reactivity ratios calculated by using the Mayo—Lewis integral scheme. These values reflect that the DMK—DMK diad in the copolymers increases with the change of counter cations of initiators from Li^+ to Na^+ or K^+. As described later, this corresponds to the appearance of many methyl peaks from DMK units in NMR spectra of Na-copolymer and K-copolymer.

In the copolymerization initiated by Na_2-BzPh, an addition of a considerable amount of sodium tetraphenylboron ($NaBPh_4$) has no influence on the copolymer composition (Exptl no. 57 in Table I), which suggests little contribution of the free anion to the propagating species.

On the other hand the addition of $NaBPh_4$ in the copolymerization initiated by Li_2-BzPh (Exptl no. 63 in Table I) brought on the DMK-rich copolymer just like the Na-copolymer, although the lithium complex without the addition of $NaBPh_4$ gave the alternating copolymer (Licopolymer) as previously described.[1] This fact shows as exchange of the counter cation in the growing ion pair from Li^+ to Na^+.

Table IV gives the results of elution fractionation of the copolymers obtained in the present systems, together with the softening points and molecular weights. The softening point of the copolymers was not high, and increased with the mole fraction of ANA in the copolymer.

The infrared spectra of Na-copolymer and K-copolymer show characteristic absorption bands attributed to the ester group at 1735, 1250, and $1120\ cm^{-1}$ as well as that of the ANA—DMK alternating copolymer (Li-copolymer), which shows that the main structure of Na-copolymer and K-copolymer also consists of the same polyester type. However the variation with the copolymer composition was not clearly
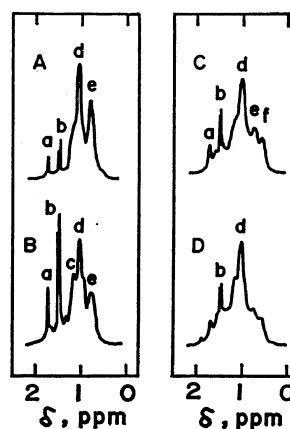
Figure 2. NMR spectra of ANA—DMK copolymers: (A), Na_2-BzPh, $x=0.42_4$; (B), Na_2-BzPh, $x=0.36_6$; (C), K_2-BzPh, $x=0.41_2$; (D), K_2-BzPh, $x=0.34_3$. Deuterated chloroform solution, 70°C; x, mole fraction of ANA in copolymer.

Table IV. Results of elution fractionation of ANA—DMK copolymers

Sample no.[a]	Mole fraction of ANA in feed	Initiator	Mole fraction of ANA in copolymer	Benzene-soluble			Benzene-insoluble	
				Weight, %	Softening point,[b] °C	$\bar{M}_n$[c]	Weight, %	Softening point,[b] °C
57	0.50_3	Na_2-BzPh	0.45_6	78.1	144—167	4800	21.9	145—199
29	0.19_6	Na_2-BzPh	0.27_1	100	109—122	7800	0	—
59	0.52_9	K_2-BzPh	0.44_9	63.4	145—178	4400	36.6	153—206
61	0.17_8	K_2-BzPh	0.34_3	98.6	113—124	7900	1.4	119—143

[a] Sample numbers refer to products of experiments listed in Tables I and II.
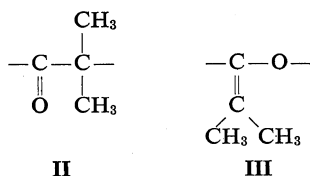[b] Observed through Yanagimoto microscopic melting point measuring apparatus.
[c] Vapor pressure osmometry in benzene at 37°C.
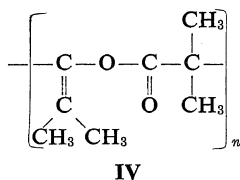
detected in their spectra.

On the other hand the NMR spectra of Na-copolymer and K-copolymer shown in Figure 2 represent clearly the variation of the copolymer structure with copolymer composition, where x is the mole fraction of ANA in the copolymer, and with the counter metal cation.

In the NMR spectrum of the alternating Li-copolymer (**I**), methyl protons give two peaks having the same intensity as each other at the δ values corresponding to peaks d and e in Figure 2[1] which is due to the magnetic anisotropy of the polar groups surrounding the methyl protons. The many other methyl peaks due to the DMK unit appear in the spectra of Na-copolymer and K-copolpmer as given in Figure 2. The relative intensity of the peaks varies with the mole fraction of DMK in the copolymer.

As described by Natta, *et al.*,[4-6] and Yamashita, *et al.*,[7] DMK can polymerize through the opening of both C=C and C=O groups.

$$\underset{\textbf{II}}{\overset{\displaystyle \begin{array}{c} CH_3 \\ | \\ -C-C- \\ \| \ \ | \\ O \ \ CH_3 \end{array}}{}} \qquad \underset{\textbf{III}}{\overset{\displaystyle \begin{array}{c} -C-O- \\ \| \\ C \\ \diagup \diagdown \\ CH_3 \ CH_3 \end{array}}{}}$$

The many methyl peaks ascribed to the DMK unit in Figure 2 show that there are two different DMK units, DMK_{C-C} (**II**) and DMK_{C-O} (**III**), also in the DMK-rich copolymers produced by Na_2-BzPh and K_2-BzPh. The highly polyester-type homopolymer (**IV**) gives two peaks having a peak ratio of about $1:3$ at the δ values corresponding to the peaks a and b in Figure 2.[3]

$$-\left[\begin{array}{c} \qquad \quad CH_3 \\ \quad \ \ | \\ -C-O-C-C- \\ \| \qquad \ \ | \\ C \qquad \ O \ \ CH_3 \\ \diagup \diagdown \\ CH_3 \ CH_3 \end{array}\right]_n$$

IV

From the viewpoint of the relative intensity of the peaks a, b, d, and e in the spectra, the Na-copolymer should contain considerably longer blocks of the $ANA-DMK_{C-C}$ alternating unit and the $DMK_{C-O}-DMK_{C-C}$ alternating unit.

On the other hand, the NMR spectra of the K-copolymer have broad peaks assignable to the presence of many methyl protons in various circumstances. Thus the copolymerization initiated by the potassium complex might give a more random copolymer also containing the other dyads, for example, $ANA-DMK_{C-O}$. This is supported by the fact that the exchange of counter cations of initiators from Li^+ to Na^+ or K^+ in the anionic homopolymerization of DMK brings on an increase of the C=O opening of DMK.[6,7]

The electronegativity and the ionization potential suggest that the lithium ion-pair is more covalent than the sodium or potassium ion-pair. Stokes' radii determined by the study of electric conductivity[8-10] show that Li^+ is solvated more strongly than Na^+ or K^+, while anions are known to be scarcely solvated except in such polar protic solvents as water and alcohol.[10,11] The solvation of the counter cations by monomers more polar than THF may be responsible for the selective addition of the monomers to the growing species and then structure of DMK sequence.

Aggregation of the propagating species, especially in the case of lithium, plays an important role on the anionic polymerization of nonpolar monomers such as styrene or conjugated dienes in nonpolar solvents.[12-16] However in the present system consisting of polar monomers and solvent, such aggregation may be considered to be of little importance.

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