Polymerization via Zwitterion. VIII.[1] Alternating Cooligomerizations of *N*-Benzylideneaniline with Electrophilic Monomers

Takeo Saegusa,* Shiro Kobayashi, and Jun-ichi Furukawa

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. *Received August 11, 1975*

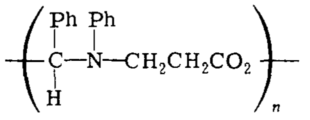
ABSTRACT: Alternating cooligomerizations of a Schiff base, *N*-benzylideneaniline (NBA), with acrylic acid (AA) and with succinic anhydride (SAn) have been studied. Cooligomerizations apparently took place without any added initiator at elevated temperatures. The alternating cooligomerization was observed when the AA/NBA feed ratio was less than 0.80. With the NBA-SAn system the alternating cooligomerization occurred regardless of the feed molar ratio of both monomers examined. The cooligomerizations are explained by a mechanism involving zwitterion intermediates.

Recently we have reported a series of the new alternating copolymerizations which apparently took place without added initiator between a nucleophilic monomer (M_N) and an electrophilic one (M_E) via zwitterion intermediates.[1-9] In these copolymerizations we used cyclic monomers such as cyclic imino ethers[1-6] and 1,3,3-trimethylazetidine[7] as M_N in all cases. It appeared worthwhile, therefore, to employ a Schiff base of *N*-benzylideneaniline (NBA), a noncyclic monomer, as an M_N component. To the best of our knowledge only two papers have so far been reported on the polymerization of Schiff bases.[10,11] This paper describes the results in which NBA underwent alternating cooligomerization with M_E monomers of acrylic acid (AA) and of succinic anhydride (SAn).

Results and Discussion

Cooligomerization of NBA with AA. A typical example (No. 3 of Table I) is as follows. A mixture of 7.5 mmol of NBA and 6.0 mmol of AA containing 0.03 mmol of *p*-methoxyphenol as a radical inhibitor was kept at 100° for 110 hr. The reaction mixture was then poured into a large excess amount of diethyl ether to precipitate the product. The oligomer was isolated by filtration and dried in vacuo to give 1.56 g (87% yield of the total monomer). The nitrogen content was found by elemental analysis to be 5.45%, from which the NBA content in the cooligomer was calculated to be 51%. The NMR spectrum of the cooligomer in CD_3OD shows a broad signal at δ 7.2–6.0 for phenyl protons (10 H), a singlet at δ 5.20 for methine proton (1 H), and two signals centered at δ 3.5 and 2.5, respectively, for the methylene protons (2 H) of $N-CH_2$ and of CH_2CO_2 (Figure 1). From the peak areas of the C_6H_5 and the CH_2CO_2 protons the NBA unit content in the cooligomer was determined to be 51%, which was identical with the value obtained from the nitrogen content. The ir spectrum of the cooligomer indicates the presence of an ester group $\gamma_{C=O}$ at 1730 cm^{-1} (Figure 2).

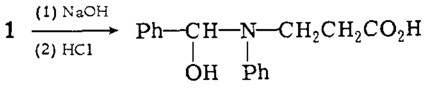
All the above data suggest that the cooligomer structure is best represented as an amine ester, 1, an alternating arrangement of NBA and AA arising by hydrogen transfer from AA.[4-7]



$$\left(\underset{H}{\overset{Ph}{C}}-\overset{Ph}{N}-CH_2CH_2CO_2\right)_n$$

1

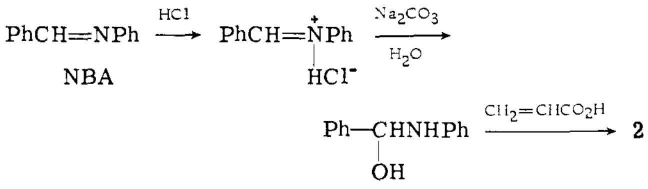
Structure 1 was further confirmed by alkaline hydrolysis of the cooligomer. Complete hydrolysis of the cooligomer was achieved by the reaction of 1 (0.10 g) with 10% aqueous NaOH solution (1.0 ml) at 100° for 20 hr. When the reaction mixture was neutralized with aqueous HCl, a precipitate was obtained. The NMR spectrum of the precipitate (Figure 3a) is compatible with the structure of the hydrolysis product 2, *i.e.*, a signal at δ 7.2–6.4 (C_6H_5, 10 H), a singlet at 5.18 ($\equiv$CH, 1 H), and two signals centered at δ 3.5 and 2.45 (NCH_2, 2 H and CH_2CO_2, 2 H).



$$1 \xrightarrow[(2)\ HCl]{(1)\ NaOH} Ph-\underset{OH}{CH}-\underset{Ph}{N}-CH_2CH_2CO_2H$$

2

N-(α-Oxybenzyl)-*N*-phenyl-β-alanine, 2, has not previously been prepared. To confirm the above assignment an authentic sample of 2 was synthesized.

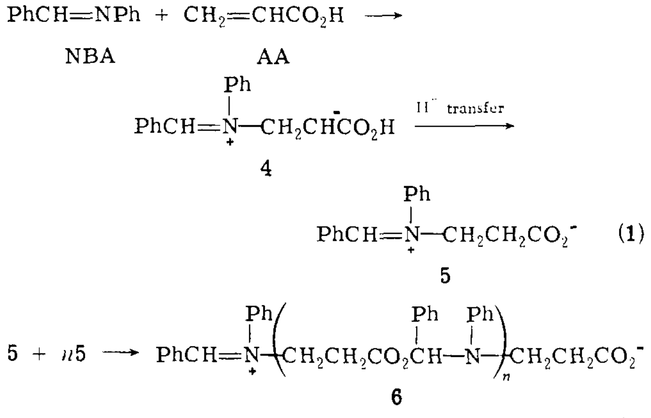


$$\underset{NBA}{PhCH=NPh} \xrightarrow{HCl} \underset{HCl^-}{PhCH=\overset{+}{N}Ph} \xrightarrow[H_2O]{Na_2CO_3} \underset{OH}{Ph-CHNHPh} \xrightarrow{CH_2=CHCO_2H} 2$$

3

To obtain 2, it is important to perform the reaction of 3[12] with AA in an aqueous solution without isolation of 3 (see Experimental Section). Compound 2 thus obtained is a greenish powder (mp 67–68°). Its NMR spectrum is shown in Figure 3b. The similarity of the signal pattern between Figures 3a and 3b supports the structure 2 for the alkaline hydrolysis product of 1.

Similarly, the cooligomerization of NBA with AA was examined under various reaction conditions (Table I). The



$$\underset{NBA}{PhCH=NPh} + \underset{AA}{CH_2=CHCO_2H} \longrightarrow \underset{4}{PhCH=\overset{+}{\overset{Ph}{N}}-CH_2\overset{-}{C}HCO_2H} \xrightarrow{H^+\ transfer} \underset{5}{PhCH=\overset{+}{\overset{Ph}{N}}-CH_2CH_2CO_2^-} \quad (1)$$

$$5 + n5 \longrightarrow \underset{6}{PhCH=\overset{+}{\overset{Ph}{N}}\left(CH_2CH_2CO_2\overset{Ph}{C}H-\overset{Ph}{N}\right)_n CH_2CH_2CO_2^-} \quad (2)$$

Table I
Cooligomerization of NBA with AA Under Various Conditions[a]

No.	Feed AA/NBA molar ratio	Reaction temp, °C	Reaction time, hr	Yield,[b] %	N of cooligomer,[c] %	Cooligomer composition NBA unit, % From N	From NMR	Mol wt[d]	Mp of cooligomer, °C
1	0.50	80	142	44	5.55	50	50	930	
2	0.50	100	118	58	5.57	49	50	705	128–120
3	0.80	100	110	87	5.45	51	51	823	127–128
4	1.00	100	100	67	4.87	42	41	722	114–115
5	1.00	100	53	30	4.74	40	38	623	
6	3.00	100	20	65	2.76	18	17	515	65–66

[a] The charged NBA = 7.5 mmol in 2.0 ml of CH_3CN containing *p*-methoxyphenol (0.5 mol % for AA) as a radical inhibitor. [b] (Cooligomer (g)/total feed monomer (g)) × 100. [c] The calculated N(%) = 5.53 for the 1:1 composition. [d] Vapor pressure osmometry in DMF at 55°.

cooligomer composition was determined by elemental analysis (N% in the cooligomer) and by NMR spectroscopy. Both methods gave very similar values. Alternating cooligomerization took place when the initial amount of NBA was in excess (No. 1–3). If AA was present in more than equivalent amounts based on NBA the cooligomer composition became rich in AA units, indicating the lower reactivity of NBA compared to that of AA in the cooligomerization (No. 4–6). The melting point of **1** was 127–129° and was depressed as the NBA content in the cooligomer decreased.

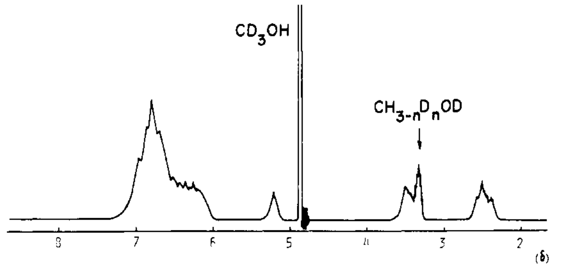


Figure 1. NMR spectrum of NBA–AA cooligomer in CD_3OD.

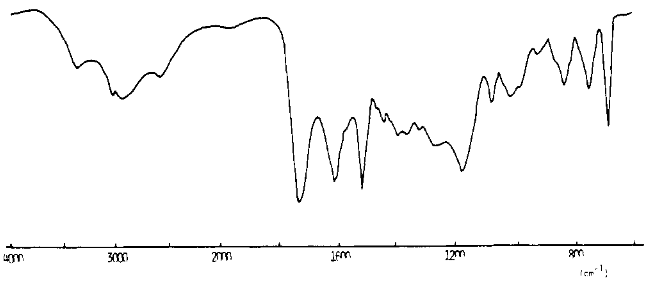


Figure 2. Ir spectrum of NBA–AA cooligomer (KBr).

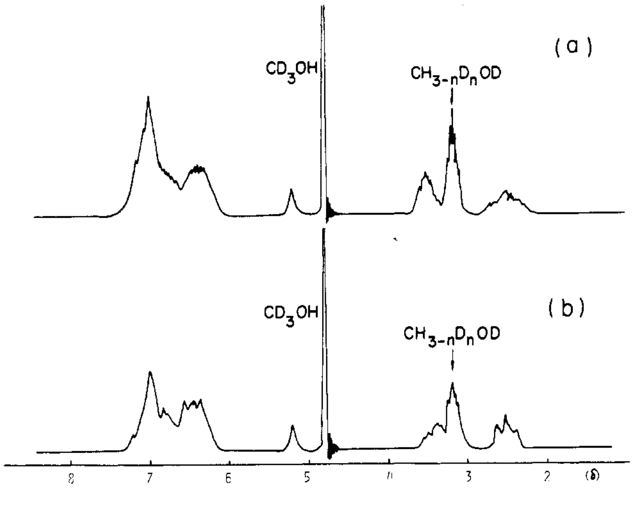


Figure 3. NMR spectra in CD_3OD of (a) alkaline hydrolysis product of NBA–AA cooligomer and (b) authentic sample of **2**.

The course of the cooligomerization of NBA with AA is considered to be analogous to our previous copolymerizations.[1-9] The genetic (monomeric) zwitterion **5** is the key intermediate which is formed followed by hydrogen transfer in the Michael adduct **4**. Species **5** is responsible for both initiation and propagation of the alternating cooligomerization. When NBA is not excess over AA, the reaction of **5** with AA occurred to yield homosequences of AA. This reaction corresponds to the AA polymerization catalyzed by amines.[13] Homosequences of NBA has never been produced because of the lower reactivity of NBA. This is the first case in our copolymerizations in which M_N is more reactive than the M_E.

To compare the reactivity of β-propiolactone (BPL) with AA the copolymerization of NBA with BPL was examined. Thus, only the homopolymerization of BPL took place as expected on the basis that BPL is much more susceptible to anionic polymerization.[3,4,7]

Cooligomerization of NBA with SAn. An equimolar mixture of the two monomers, 7.5 mmol of each, in 2.0 ml

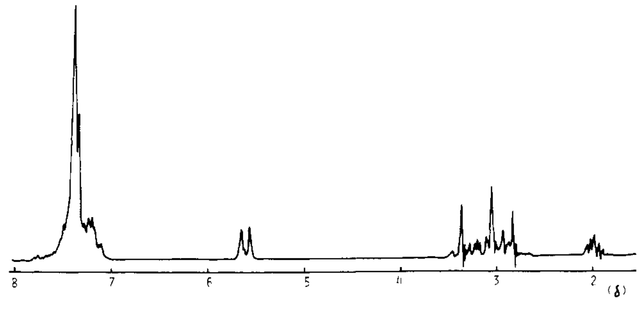


Figure 4. NMR spectrum of the NBA–SAn cooligomer in CD_3CN.

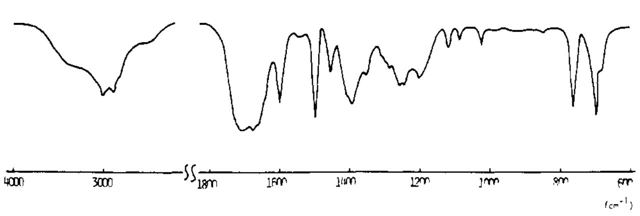


Figure 5. Ir spectrum of the NBA–SAn cooligomer (KBr).

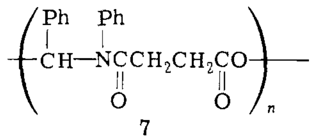
Table II
Effect of the Feed Monomer Ratio upon the Cooligomer Composition in the NBA–SAn Cooligomerization[a]

No.	Feed SAn/NBA molar ratio	Yield, %	Cooligomer composition NBA unit, %	
			From N	From NMR[b]
7	0.50	43		50
8	1.00	90	51	50
9	2.00	59		50
10	3.00	53		50

[a] The total amount of the charged NBA and SAn was 15.0 mmol in 2 ml of acetonitrile; reaction at 100° for 110 hr. [b] From the integrated ratio of peaks due to phenyl (10 H) and two methylene (4 H) protons.

of acetonitrile was kept at 100°. After 110 hr the reaction mixture was poured into a large excess of diethyl ether to precipitate polymeric material. The product was twice reprecipitated in the acetonitrile–diethyl ether system. The cooligomer was isolated and dried in vacuo to give 1.90 g (90% yield) of a pale yellow powder (mp 155°, molecular weight, 614). The elemental analysis yielded a nitrogen content of 5.02% for the copolymer. This value corresponds to an NBA content of 51% unit (the calculated value for the nitrogen content of a 1:1 composition = 4.98%).

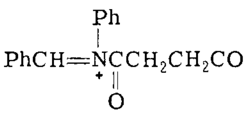
The NMR spectrum of the cooligomer (Figure 4) shows a broad signal at δ 7.6–7.1 for the phenyl protons (10 H), a doublet-like signal at δ 5.7–5.6 assignable to a methine proton (1 H), and complex peaks between δ 3.4 and 2.8 ascribed to protons of two methylene groups (4 H). The ir spectrum (Figure 5) clearly shows the presence of amide ($\gamma_{C=O}$ at 1680 cm^{-1}) and ester ($\gamma_{C=O}$ at 1720 cm^{-1}) groups. From these data the comonomer structure is reasonably assigned as an amide ester, **7**, an alternating arrangement of NBA and SAn.



$$-\!\left(\mathrm{\overset{Ph}{\overset{|}{C}}H{-}\overset{Ph}{\overset{|}{N}}\underset{\underset{O}{\|}}{C}CH_2CH_2\underset{\underset{O}{\|}}{C}O}\right)_n\!-$$

7

The relationship between the monomer feed ratio and the cooligomer composition was examined (Table II). In the cooligomerization of NBA with SAn a 1:1 cooligomer composition was obtained in every case regardless of the molar feed ratio of two monomers examined. A zwitterion **8** is considered to be the key intermediate for the alternating cooligomerization.



$$\mathrm{PhCH{=}\overset{Ph}{\overset{|}{\underset{+}{N}}}\underset{\underset{O}{\|}}{C}CH_2CH_2CO_2^-}$$

8

Experimental Section

Materials. NBA was prepared by the reaction of benzaldehyde with aniline,[14] mp 52° (lit.[14] 52°). AA was freshly distilled under nitrogen in the presence of a radical inhibitor of *p*-methoxyphenol. SAn was purified by recrystallization from chloroform. Acetonitrile was purified according to the ordinary procedure.

An authentic sample **2** was prepared as follows. NBA (2.0 g) was dissolved in 50 ml of benzene. Dry HCl gas was then introduced into the solution to form a precipitate of the hydrochloride salt of NBA (NBA·HCl). The salt was isolated by filtration and was recrystallized from an ethanol–benzene (5:95 vol %) mixture to give 1.3 g of a pale yellow needle-like crystal, mp 155° (lit.[15] 153–160°). An aqueous solution of the salt (0.50 g) was carefully neutralized with aqueous 1 *N* Na_2CO_3 at 0°. To the aqueous solution 0.17 g of AA and 0.003 g of *p*-methoxyphenol (radical inhibitor) were added. The mixture was allowed to react at 100° for 30 min. The aqueous and organic layers were separated and the organic layer was washed several times with water and dried in vacuo to give 0.48 g of a greenish powder, mp 67–68°. Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.38; H, 6.32; N, 5.16. Found: C, 70.32; H, 6.45; N, 5.20.

Cooligomerizations. All cooligomerizations were carried out under nitrogen. In a typical run, 7.5 mmol of NBA, 3.75 mmol of AA, and 0.02 mmol of *p*-methoxyphenol (radical inhibitor) were added at room temperature to 2.0 ml of acetonitrile in a glass tube. The tube was sealed and the mixture was kept at 100° for 118 hr. The tube was opened and the reaction mixture was poured into 100 ml of diethyl ether to precipitate the product. Unreacted NBA and AA were completely removed from the cooligomer. The precipitated product was dried in vacuo and analyzed by NMR, ir, and elemental analyses as well as by alkaline hydrolysis.

Alkaline Hydrolysis of the Product. To 0.10 g of cooligomer was added 1.0 ml of 10% aqueous NaOH solution and the mixture was refluxed for 20 hr. A trace amount of insoluble parts was removed by filtration. The filtrate was then neutralized with aqueous 0.1 *N* HCl. A precipitate was produced. It was separated from the solution and dried in vacuo to give 0.06 g of a greenish powder, mp 70°, the NMR spectrum of which was identical with that of the authentic compound (Figure 3).

Molecular Weight Determination. The molecular weight of the copolymer was measured by vapor pressure osmometry (Hitachi Perkin-Elmer Model 115) in dimethylformamide at 55°.

References and Notes

(1) Part VII: T. Saegusa, H. Ikeda, S. Hirayanagi, Y. Kimura, and S. Kobayashi, *Macromolecules*, **8**, 259 (1975).
(2) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **5**, 354 (1972).
(3) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **7**, 1 (1974).
(4) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **7**, 139 (1974).
(5) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **8**, 374 (1975).
(6) T. Saegusa, Y. Kimura, K. Sano, and S. Kobayashi, *Macromolecules*, **7**, 546 (1974).
(7) T. Saegusa, Y. Kimura, S. Sawada, and S. Kobayashi, *Macromolecules*, **7**, 956 (1974).
(8) T. Saegusa, *Pure Appl. Chem.*, **39**, 81 (1974).
(9) T. Saegusa, S. Kobayashi, Y. Kimura, and H. Ikeda, *J. Macromol. Sci., Chem.*, in press.
(10) K. Harada, Y. Mizoe, J. Furukawa, and S. Yamashita, *Makromol. Chem.*, **132**, 269 (1970).
(11) P. Ferruti, G. Audisio, G. Cottica, and A. Fere, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 451 (1974).
(12) M. M. Sprung, *Chem. Rev.*, **26**, 324 (1940).
(13) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **7**, 256 (1974).
(14) L. A. Bigelow and H. Eatough, "Organic Syntheses", Collect Vol. 1, Wiley, New York, N.Y., 1947, p 80.
(15) B. Witkop, J. B. Patrick, H. M. Kissman, *Ber.*, **85**, 949 (1952).