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Polymerization of *N*-Vinylcarbazole in the Presence of β-Cyanoacrolein

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It was found that *N*-vinylcarbazole (VCZ) initiated the polymerization in the presence of β-cyanoacrolein (CAL) even in air at room temperature. The polymerization of VCZ induced by CAL was investigated in benzene at 60°C. Polymer formed was found to be VCZ homopolymer. The rate of polymerization attains to a maximum at the mole fraction of CAL of about 0.65 in the monomer mixture. The products obtained from the terpolymerization in the system of CAL-VCZ-Styrene in benzene at 60°C contain no CAL unit and exclusively consist of the VCZ component. The composition curve of the copolymer is contrasted with that of a radical initiated copolymer. In view of these results, as well as the *Q*-*e* values of both CAL and VCZ, it seems possible that the cationic polymerization of VCZ is induced by some donor-acceptor type interaction between VCZ and CAL.

Since the publication of papers by Scott *et al.* and Ellinger (1963) it has often been shown that the polymerization of *N*-vinylcarbazole (VCZ) is easily induced by electron acceptors, although the mechanism of the initiation is still a matter of controversy.[1]

We have observed that VCZ starts the polymerization immediately after mixing with β-cyanoacrolein (NC–CH=CH–CHO, CAL) even in air at room temperature. In the present note it is elucidated that the polymerization of VCZ is initiated cationically by some kind of interaction between a donor (VCZ) and an acceptor (CAL).

Experimental

Materials. CAL was prepared by dehydrogenation of β-cyanopropionaldehyde (CPA).[2,3] VCZ (B.A.S.F. Chemicals Ltd.) was recrystallized from methanol (mp 65.5—66°C) after distillation under a reduced pressure (bp 142—142.5°C/2 mmHg). Styrene (St) was washed with an aqueous solution of sodium thiosulfate, water, 5% aqueous solution of potassium hydroxide and then water, drying on anhydrous sodium sulfate, before distillation at reduced pressure. Bp 46.7—47.0°C/22 mmHg. Azobisisobutyronitrile(AIBN) was recrystallized from ethanol. Benzene was distilled after drying with sodium.

Polymerization. The polymerization at different compositions of VCZ and CAL was investigated in air at 60°C. Terpolymerization of VCZ, CAL and St was also carried out at different molar ratios of VCZ to St, at the constant molar ratio, VCZ : CAL, of unity, and at the total monomer concentration of 4 mol/*l* in benzene, in air and at 60°C. Resulting polymer was precipitated into a larger amount of methanol, purified by the reprecipitation in the system of benzene (solvent) - methanol (precipitant), and then dried at room temperature under vacuum.

Determination of Polymer Composition. Infrared absorption spectra were measured for polymerization products, which were compared with those for parent monomers and their homopolymers. No St homopolymer was extracted with use of carbon tetrachloride from the product of the terpolymerization.

Polymer compositions were determined from nitrogen contents by the Kjeldahl method for the products in VCZ-CAL system and by an elementary analysis using C.H.N. Corder (Yanagimoto Co., Ltd.) for those in VCZ-CAL-St system. There is a good agreement between the results obtained in the nitrogen analysis by these different methods.

Viscometry. Viscosity numbers, η_{sp}/c, of polymers were measured at the concentration of 0.3 g/100 m*l* in benzene at 25±0.05°C with use of an Ostwald viscometer.

Results and Discussion

The results of the preliminary test are shown in Table 1.

VCZ alone gives no polymer in the present conditions, but the addition of CAL results in the formation of the polymer in higher yield even in air at room temperature. There appears no influence of the presence of a radical initiator. The nitrogen contents of the products show the agreement with the value calculated for VCZ homopolymer (PVCZ). An agreement between the infrared spectra (KBr disk), as shown in Fig. 1, of the product and of PVCZ which was obtained by AIBN initiated polymerization, also indicates

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[1] J. Pac and P. H. Plesch, *Polymer*, **8**, 237 (1967).

[2] H. Sumitomo and K. Azuma, *J. Polymer Sci.*, **B4**, 883 (1966).

[3] S. Motoki, S. Satsumabayashi and T. Matsuda, This Bulletin, **39**, 1519 (1966).

TABLE 1. POLYMERIZATION OF VCZ IN THE PRESENCE OF CAL[a)]
EFFECTS OF SOLVENT AND RADICAL INITIATOR

Expt. No.	Monomer VCZ g	CAL g	CPA g	Mole fractn. of CAL (or CPA)	Wt. ratio of benzene : monomer	AIBM mol% to monomer	Temp. °C	Time hr	Convn. %	Nitrogen content[b)] %
101	0.48	—	—	—	2	—	24.0—24.5	3	0	—
102	0.48	—	—	—	2	0.5	24.0—24.5	3	0	—
130	0.48	0.21	—	0.5	—	—	27.5—27.9	3	34.6	7.22
131	0.48	0.21	—	0.5	—	0.5	27.5—27.9	3	34.2	7.24
134	1.93	0.81	—	0.5	2	—	27.5—27.9	5	1.5	7.23
135	1.93	0.81	—	0.5	2	0.5	27.5—27.9	5	1.0	7.25
—	1.93	—	0.83	0.5	—	—	21.5	3	0	—

a) In air.
b) Calculated for poly (*N*-vinylcarbazole), 7.25%.

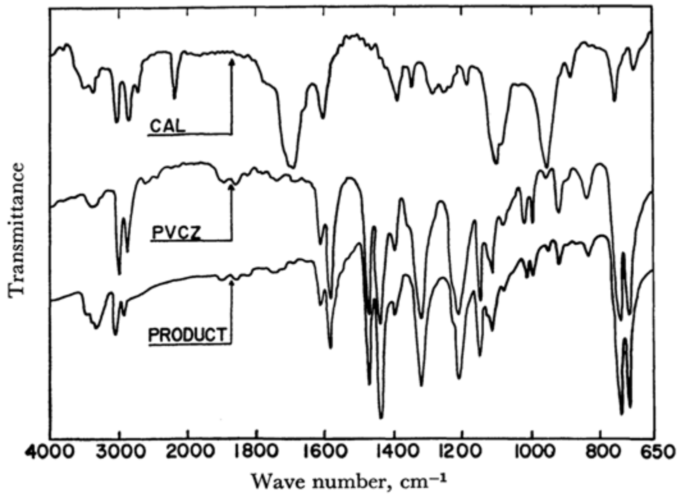

Fig. 1. Infrared absorption spectra of β-cyanoacrolein (CAL), poly(*N*-vinylcarbazole) (PVCZ) and a product obtained in the experiments shown in Table 1.

TABLE 2. POLYMERIZATION OF VCZ IN THE PRESENCE OF CAL[a)]
EFFECT OF COMPOSITION OF MONOMER MIXTURE

Expt. No.	Monomer VCZ g	CAL g	Mol fractn. of CAL	Time hr	Convn. %	Rate %/hr	η_{sp}/c[b)]
217	3.47	0.16	0.1	2.8	1.8	0.62	0.14
218	3.09	0.32	0.2	5.2	4.6	0.87	—
219	2.70	0.48	0.3	3.5	4.5	1.29	0.29
220	2.32	0.64	0.4	3.0	5.7	1.88	0.31
221	1.93	0.81	0.5	2.3	9.2	3.95	0.35
222	1.54	0.97	0.6	2.2	10.9	5.00	—
223	1.16	1.13	0.7	3.7	18.5	5.04	0.29
224	0.77	1.30	0.8	3.2	15.7	4.96	0.22
225	0.39	1.46	0.9	4.5	15.6	3.47	0.29

a) In benzene, [CAL]+[VCZ]=2mol/*l*, 60°C, in air.
b) Benzene, c=0.3 g/100 m*l*, 25°C. η_{sp}/c of radical initiated polymer, 1.1.

TABLE 3. CAL-VCZ-St TERPOLYMERIZATION[a)]

Expt. No.	Monomer VCZ g	CAL g	St g	Mol fractn. of VCZ in VCZ+St	Time hr	Convn. %	Mol fractn. of VCZ in copolymer[b)]
513	2.84	0.64	13.60	0.1	16	1.00	0.817
514	2.59	0.54	5.56	0.2	2	0.91	0.876
515	3.58	1.50	4.48	0.3	9	2.63	0.917
519	2.22	0.93	1.78	0.4	6	7.63	0.952
516	2.59	1.09	1.38	0.5	2	5.72	0.934
520	3.34	2.88	0.46	0.8	0.3	3.64	0.923
506	1.84	0.77	0.11	0.9	0.3	2.81	1.000

a) [CAL]+[VCZ]+[St]=4 mol/*l*, [CAL]/[VCZ]=1, benzene, in air, 60°C.
b) Determined by elementary analysis.

that no CAL unit was detectably incorporated into the polymer chain.

Figure 2 summarizes the results of the polymerization of VCZ in the presence of different mole fractions of CAL at the constant total monomer concentration of 0.4 mol/*l* in benzene at 60°C.

The polymerization starts without any induction period. The rate of polymerization seems to attain to a maximum at the mole fraction of CAL of about 0.65. Similar behaviors can be seen in Table 2 in which the polymerization is investigated at the total monomer concentration of 2 mol/*l*. All of the solution viscosity numbers, η_{sp}/c, of polymer are much lower than those of a radical polymer.

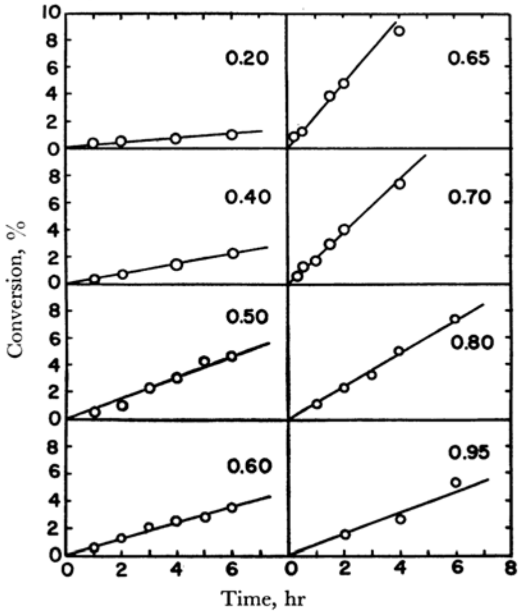

Fig. 2. Polymerization of VCZ in the presence of CAL.
Effect of composition in monomer mixture (numbers in figures show mole fraction of CAL).
[CAL]+[VCZ]=0.4 mol/*l*, benzene, 60°C, in air.

In Fig. 3 are plotted the rate as well as the viscosity numbers against the mole fraction of CAL in monomers to show the remarkable tendencies in graphical form. It is conceivable from these facts that there may be some donor-acceptor type of interaction between VCZ and CAL.

Table 3 includes the results of terpolymerization in the system of CAL-VCZ-St at the constant mole ratio of CAL to VCZ of unity in the total monomer concentration of 4 mol/*l* in benzene at 60°C.

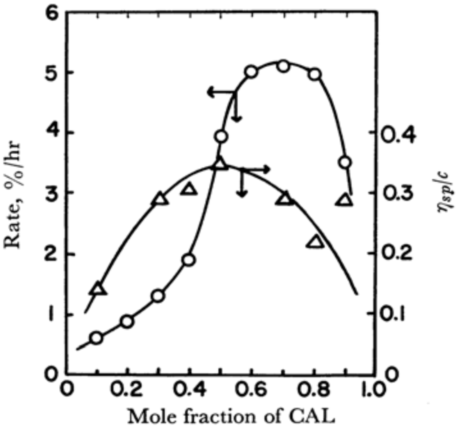

Fig. 3. Polymerization of VCZ in the presence of CAL.
Effect of composition in monomer mixture.
[VCZ]+[CAL]=2 mol/*l*, benzene, 60°C, in air.

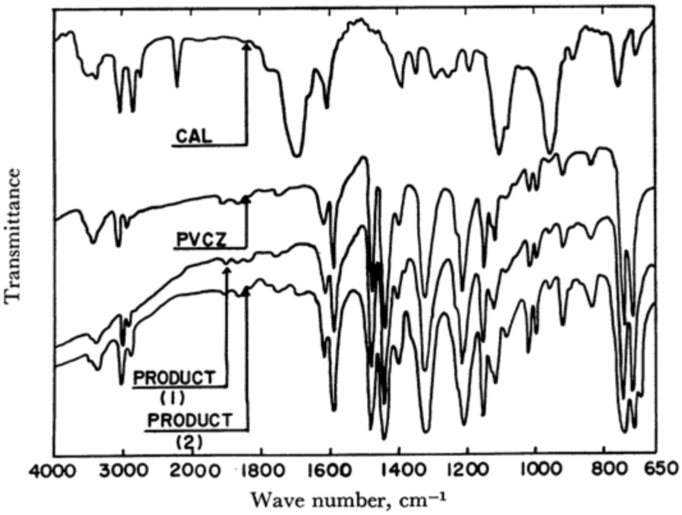

Fig. 4. Infrared absorption spectra of CAL monomer, PVCZ, a product (1) obtained from the experiments other than Expt. No. 513 and the product (2) obtained from Expt. No. 513.

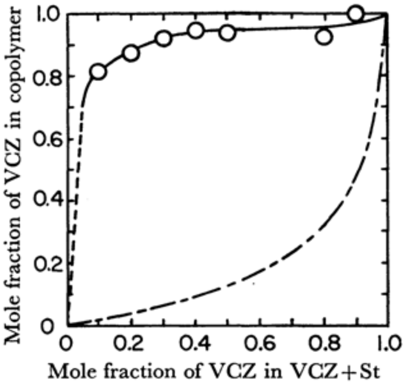

Fig. 5. Composition of copolymer as a function of monomer composition in CAL-VCZ-St system. [CAL]+[VCZ]+[St]=4 mol/*l*, [VCZ]/[CAL]=1, Benzene, 60°C, in air. ---: radical copolymerization of VCZ with St (R. Hart (1961)).

The infrared spectra of the Product 1, starting from the mole fraction of VCZ higher than 0.1 in the total amount of VCZ and St (any product excepting expt. No. 513), and of the Product 2 from that of 0.1, are compared with those of PVCZ and of CAL monomer in Fig. 4.

The spectra of both products are not different from that of PVCZ, excepting that an absorption by styrene appears slightly at 700 cm^{-1} in the spectrum of product 2, and do not represent any absorption peak of CAL.

In Fig. 4 the compositions of the copolymers obtained here are plotted against the monomer compositions. From the fact that the copolymers consist exclusively of the VCZ component and also that the curve is contrasted with that for the radical copolymer given by Hart,[4] it may be suggested that the copolymerization in the present system takes place cationically.

Q-e values of CAL are determined to be $Q=0.53$ and $e=2.07$[5] and those of VCZ are presented to be $Q=0.41$ and $e=-1.40$.[6] It seems possible, therefore, that there may exist some donor-acceptor type interaction between CAL and VCZ inducing the cationic polymerization of VCZ.

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[4] R. Hart, *Macromol. Chem.*, **47**, 134 (1961).

[5] I. Takemura and H. Sumitomo, This Bulletin, **42**, 634 (1969).

[6] G. E. Ham, ed., "Copolymerization," Interscience Publishers, New York (1964), p. 862.