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Solid-State Polymerization of N-Vinylcarbazole by Redox Catalyst

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Summary

A crystal of N-vinylcarbazole was polymerized by redox catalyst (ammonium persulfite/sodium bisulfate) in a suspended state in water and poly (vinyl carbazole) was obtained. The polymerization proceeded rapidly above 40°C without an induction period in the solid state. The molecular weight of the polymer increased with decreasing catalyst concentration and raising temperature. η_{sp}/c of polymer was in the range 0.04—0.07 and it was lower than that obtained in radiation-induced solid-state polymerization. Observation of the partially polymerized crystal through a polarizing microscope showed that the polymerization proceeded from the surface of the monomer crystal and that birefringence was observed in the polymer layer. In X-ray diffraction studies it was found that the polymer was crystalline.

It was found that N-vinylcarbazole (VCar) can be polymerized in the solid state by various metal halides [1–3] and that the polymerization proceeds from the surface of monomer crystal to the inner part.

In this paper the solid-state polymerization was carried out by a radical catalyst. Poly-VCar could be obtained in the solid state, and it was clarified by microscopic studies that the polymerization proceeded from a crystal surface into an inner part, similar to the case of cationic polymerization [3, 4].

The properties of polymers obtained in the solid state were examined by microscope and X-ray diffraction. Both results show that the polymer is produced in a crystalline state.

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On the basis of these kinetics and polymer properties, the mechanism of radical catalytic solid-state polymerization is discussed, compared with radiation-induced and cationic solid-state polymerization.

EXPERIMENTAL

Procedure

Solid-State Polymerization. The polymerization was initiated by adding the catalyst solution into the flask containing the monomer crystals at a constant temperature in air. The catalyst solution was composed of ammonium persulfate/sodium bisulfite (3:1), a small amount of the surface activator (sodium laurylsulfate), and 20 ml of water. The polymerization was stopped by adding methanol solution of hydroquinone and by cooling the reaction system. The polymer was dissolved in benzene and reprecipitated in methanol. The precipitated polymer was washed with hot water and methanol, and dried at 30°C in vacuo.

Solution Polymerization. The polymerization was initiated by pouring the aqueous catalytic solution into methanol solution of monomer. The polymer was insoluble in methanol and a resultant polymer was precipitated from the reaction system. Purification of the polymer was the same as in the case of solid-state polymerization.

Properties of the Polymer. The molecular weights of the polymer obtained were compared in η_{sp}/c (benzene solution, c: 1 g/100 ml) at 30°C.

A partially polymerized crystal was used as the sample for microscopic and X-ray studies. The polymer crystals was washed with water and dried. During the measurements polymerization did not proceed further.

A POH polarizing microscope (Nihon Kogaku) was used.

X-ray diffraction diagrams of the polymer were taken with a Shimadzu GX-II type diffractometer using 30-kV, 15-mA Ni-filtered CuKα rays.

Materials

VCar (Stein Hall Co. Ltd.) was purified by twice recrystallizing from distilled n-hexane. The purified monomer was stored in a dark and cool place.

Ammonium persulfate and sodium bisulfite (Guaranteed Reagent) were used without further purification.

RESULTS

Kinetic Results

The time-conversion curves of the solid-state polymerization by redox catalyst are shown in Fig. 1. As seen in Fig. 1, the polymerization proceeds rapidly above 40°C even in a suspended solid state in water without an induction period, and the rate of polymerization greatly increases with an increase in the polymerization temperature. Adding a catalyst solution to a monomer crystal, the colorless monomer crystal was turned to pale yellow in a few minutes.

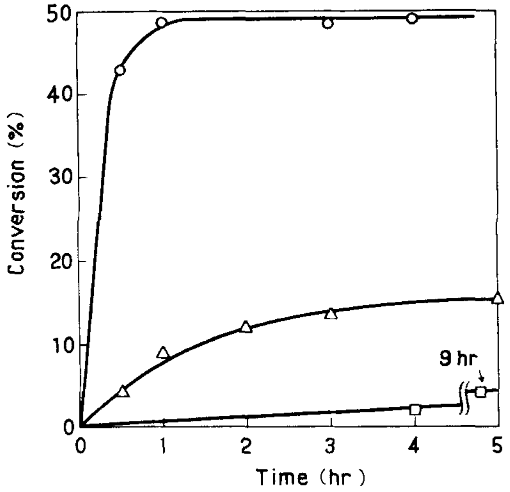

FIG. 1. Effect of temperature on solid-state polymerization of VCar initiated by redox catalyst. □, 30°C; △, 40°C; ○, 50°C; [APS]: 0.11 mol/liter; [M] (apparent): 1 g/20 ml.

VCar was not polymerized by the addition of a small amount of sulfuric acid, which was expected from the concentration of the catalyst. Therefore, it is concluded that the polymerization of VCar by a redox catalyst may proceed radically.

Figure 2 shows the relationship between the rate of polymerization and a catalyst concentration. As shown in Fig. 2, the rate of polymerization is not so greatly affected by the catalyst concentration at high concentration range.

The relations between the catalyst concentrations and η_{sp}/c of the polymer obtained at 40 and 50°C are shown in Fig. 3. In the cationic solid-state polymerization as reported in the previous

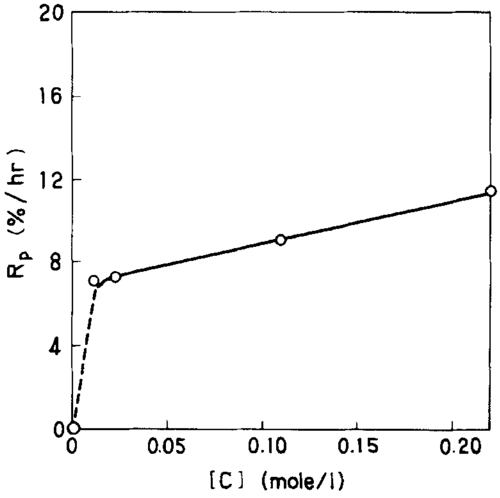

FIG. 2. Effect of catalyst concentration on rate of polymerization at 40°C. [M]: 1 g/20 ml.

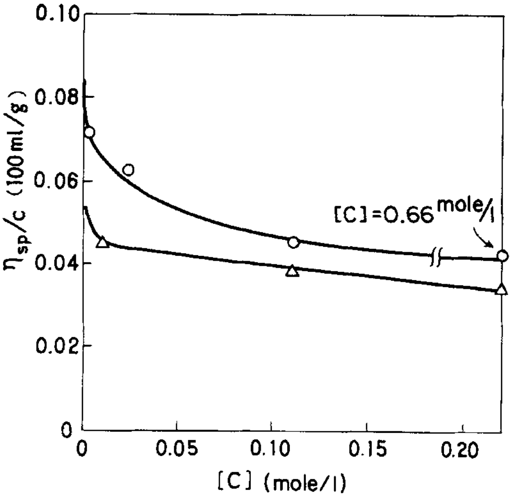

FIG. 3. Relationship between catalyst concentration and η_{sp}/c of resultant polymer obtained at ○, 50°C; △, 40°C. [M]: 1 g/20 ml.

papers [1–4], the catalyst concentration did not affect the molecular weight of the resultant polymer. In the catalytic radical solid-state polymerization, the molecular weight of the polymer increases with decreasing of the catalyst concentration and with raising of the polymerization temperature at the same catalyst concentration. The molecular weight of the polymer formed in the catalytic radical solid-state polymerization is large at low catalyst concentration, compared with cationic solid-state polymerization [1–4].

The solution polymerization was carried out in methanol–water to compare with the solid-state polymerization (Table 1).

Table 1. Solution Polymerization of VCar in MeOH/H_2O Mixture (19:1 Weight Ratio) by Redox Catalyst

Temp., °C	[C], mmoles/liter	Time, hr	Conversion, %	η_{sp}/c
40	2.2	3	9.2	—
	2.2	4	12.1	—
	11.0	0.5	2.5	—
	11.0	3	19.3	0.027
	11.0	5	20.3	0.028
	22.0	1	26.0	0.027
50	2.2	1	12.3	—
	2.2	3	16.4	0.023

Under this condition, only a low molecular weight polymer was obtained in the solution polymerization.

Properties of the Polymer

Infrared spectra of the products obtained in this polymerization system coincide with that of poly-VCar obtained in the ordinary radical polymerization.

The orientation of the polymer obtained in the radical solid-state polymerization was studied by the polarizing microscope and X-ray diffraction. For the microscopic observations and X-ray studies, a partially polymerized crystal with a plate-like shape was used. The surface and the section of the crystal were observed by microscope from the directions as shown in Fig. 4. Figure 5 shows many of the small cracks on the surface of the partially polymerized crystal [from the (a) direction in Fig. 4].

The polarizing photomicrograph of the section of the partially polymerized crystal [observed from the (b) direction in Fig. 4] is shown in Fig. 6. As seen in this photograph, the polymer layer is clearly distinguished from the unreacted residual monomer layer and the catalytic radical solid-state polymerization proceeds from

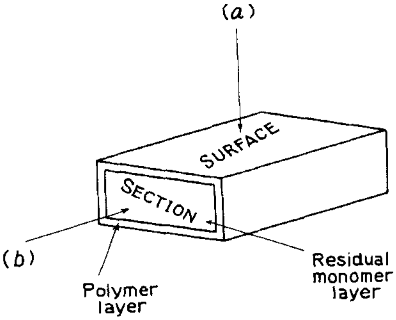

FIG. 4. Schematical diagram of partially polymerized crystal.

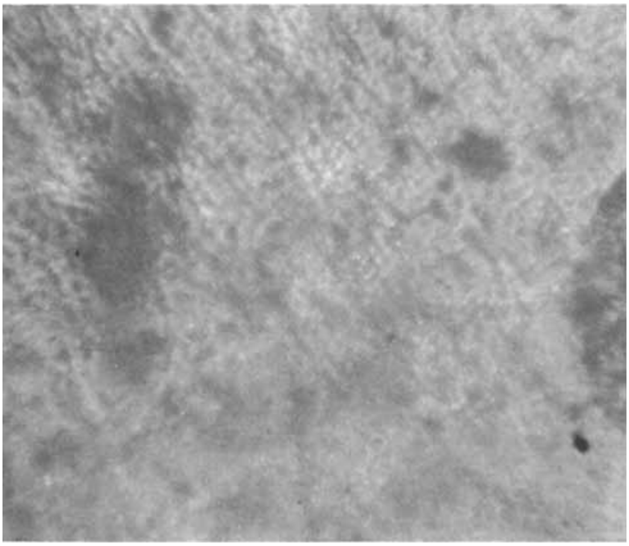

FIG. 5. Photomicrograph of the surface of the partially polymerized crystal.

the crystal surface to the inner part of the monomer crystal as well as cationic solid state [3]. Although the birefringence can be clearly observed as shown in Fig. 6, no birefringence was observed in the polymer, which was dissolved in benzene and reprecipitated from menthanol.

X-ray diffraction studies were also carried out. In cationic solid-state polymerization, irrespective of a kind of catalyst, X-ray diffraction patterns of the product show the only diffuse ring as

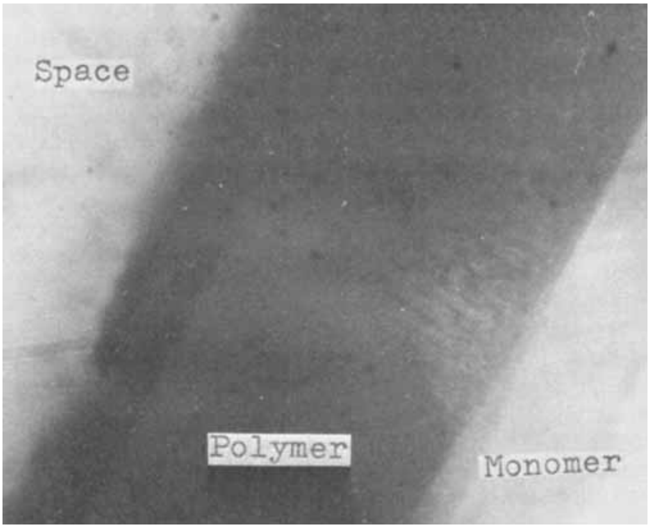

FIG. 6. Polarizing photomicrograph of the section of the partially polymerized crystal.

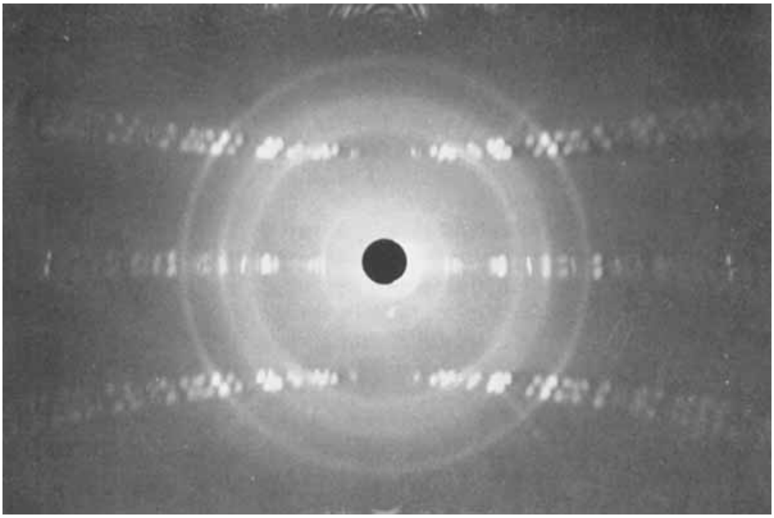

FIG. 7. X-ray diffraction pattern of the partially polymerized crystal. Spacing of crystalline rings: 1.61, 1.93, 2.23, and 4.71 Å.

due to the amorphous polymer and the spots as due to the residual monomer [1]. On the other hand, in catalytic radical solid-state polymerization, as shown in Fig. 7, the sharp rings due to the crystalline polymer can be observed in addition to a diffuse ring and spots. The spacing of the crystalline rings is calculated.

From these results it is found that the polymer formed by this procedure is more crystalline than the polymer produced in the cationic solid-state polymerization.

DISCUSSION

It is found that VCar can be easily converted to the polymer by a redox catalyst in the solid state and that the monomer crystal was apparently unchanged by the polymerization. The behavior of catalytic radical solid-state polymerizations are different from that in the radiation-induced solid-state polymerization of VCar [5—7]. Radiation polymerization is initiated in the inner part of a crystal where γ-rays pass through, while in catalytic solid-state polymerization the reaction proceeds from the crystal surface. This difference may affect the kinetic behavior.

There are three differences in the reaction rate between catalytic radical and radiation solid-state polymerization. They are (1) that the polymerization is accelerated in radiation solid-state polymerization, (2) that a long induction prevails before the onset of polymerization in radiation [5], and (3) that in catalytic solid-state polymerization the rate decreases gradually and polymer yield reaches the saturated value. These phenomena are explained as follows. In the radiation-induced solid-state polymerization, as mentioned by Morawetz [8] and Adler et al. [9], the polymer chains grow at the interface of a crystalline and an amorphous region. So the interface region increases with an increase of polymer yield and then the polymerization is accelerated. On the other hand, in catalytic solid-state polymerization, the polymerization is initiated as soon as the catalyst molecules are adsorbed on the crystal surface. But when the polymer layer becomes thicker, it is getting more difficult for the catalyst molecules to diffuse into the inner part of crystal and the rate of polymerization will decrease.

The molecular weight of the polymer produced is lower in catalytic solid-state polymerization than in the radiation-induced one [6]. It might be due to the fact that in catalytic solid-state polymerization it proceeds without disturbing the monomer crystal and that no further polymerization could have occurred as a result of volume shrinkage during polymerization, or chain transfer or termination reactions would occur.

In catalytic solid-state polymerization, the molecular weight of the polymer increases with raising temperature as well as in the radiation polymerization. This is due to the increase of the mobility of the monomer molecules with increasing the temperature.

The birefringence observed in the polymer layer obtained in radical solid-state polymerization is clearer than that in the cationic one. X-ray diffraction pattern shows that the polymer obtained in catalytic radical solid-state polymerization is crystalline.

There is no report which shows a formation of crystalline poly-VCar in solid-state polymerization. Otherwise, there are many papers that indicate that the crystalline and oriented polymer could be obtained in the radiation-induced and catalytic solid-state polymerization of cyclic monomers [10–12] but not of vinyl monomers. This might be considered to be due to the difference of a monomer structure. In cyclic compounds the shrinkage of volume by polymerization might be considered to be compensated by opening the rings.

Now, it is possible that even vinyl compound can be polymerized to give a crystalline polymer in the solid state. As catalytic solid-state polymerization proceeds from a crystal surface without disturbing the monomer crystal, the polymer may be crystallized. On the other hand, one of the reasons no crystalline polymer could be obtained in cationic solid-state polymerization might be the fact that the counteranions produced from the catalyst would disturb the alignment of monomer molecules in a crystal.

REFERENCES

[1] S. Okamura, T. Higashimura, and T. Matsuda, *Kobunshi Kagaku*, **22**, 180 (1965).

[2] S. Okamura, T. Higashimura, and T. Matsuda, *Kobunshi Kagaku*, **23**, 269 (1966).

[3] T. Matsuda, T. Higashimura, and S. Okamura, *Kobunshi Kagaku*, **24**, 165 (1967).

[4] T. Matsuda, T. Higashimura, and S. Okamura, *Kobunshi Kagaku*, **23**, 273 (1966).

[5] A. T. Restaino, R. B. Mesrobian, H. Morawetz, D. S. Ballantine, G. J. Dienes, and D. J. Metz, *J. Am. Chem. Soc.*, **78**, 2939 (1956).

[6] A. Chapiro and G. Hardy, *J. Chim. Phys.*, **59**, 71 (1962).

[7] J. Kroh and W. Pekala, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **12**, 419 (1964).

[8] H. Morawetz, *J. Polymer Sci.*, **C1**, 65 (1963).

[9] G. Adler, D. Ballantine, and B. Baysal, *J. Polymer Sci.*, **48**, 195 (1960).

[10] S. Okamura, K. Hayashi, and Y. Kitanishi, *J. Polymer Sci.*, **58** 925 (1962).

[11] J. B. Lando and V. Stannett, *J. Polymer Sci.*, **A3**, 2369 (1965).
[12] S. Okamura, E. Kobayashi, and T. Higashimura, *Makromol. Chem.*, **88**, 1 (1965).

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Zussammenfassung

Ein N-Vinylcarbazolkrystall, suspendiert in Wasser, wurde mittels eines Redoxkatalysators (Ammoniumpersulfit Natriumbisulfat) zu Polyvinylcarbazol polymerisiert. Die Polymerisation ging oberhalb von 40°C ohne Induktionsperiode im festen Zustand vor sich. Das Molekulargewicht des Polymeren stieg mit abnehmender Katalysatorkonzentration und steigender Temperatur an. Das Verhältnis η_{sp}/c des Polymeren war im Bereich von 0.04 bis 0.07 und damit geringer als bei strahlungsinduzierten Festkörperpolymerisationen. Eine Beobachtung des teilweise polymerisierten Krystals durch ein Polarisationsmikroskop zeigte, dass die Polymerisation von der Oberfläche des Monomerenkristalls ausging und dass in den polymerisierten Schichten Doppelbrechung auftrat. Röntgenographische Untersuchungen zeigten, dass das polymere Produkt krystallin ist.

Résumé

La polymérisation d'un cristal de N-vinylcarbazole à l'aide d'un catalyseur redox (persulfite d'ammonium bisulfate de sodium) en suspension dans l'eau permet d'obtenir le polyvinylcarbazole. La polymérisation procède rapidement au-dessus de 40°C, sans periode d'induction. La masse moléculaire du polymère augmente avec l'abaissement de la concentration du catalyseur et l'accroissement de la temperature. η_{sp}/c du polymère à l'échelle de 0.04—0.07 est plus bas que dans la polymérisation a l'état solide, induite par radiation. L'examen du cristal, partiéllement polymerisé, à l'aide d'un microscope polarisant, montre que la polymérisation procède de la surface du cristal monomère. On observe une birefringence dans la couche polymérique. On a trouvé par les études de la diffraction des rayons X que le polymère était cristallin.