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Vinyl Polymerization by Carbon Black. II. Modification of Carbon Black and Its Use in the Polymerization of N-Vinylcarbazole

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ABSTRACT

Modification of carbon black N220, ISAF-HM, by aprotonic and protonic acids uniquely improves its catalytic activity in relation to the polymerization of N-vinylcarbazole. The polymerization is first order in monomer and directly proportional to the weight of the catalyst. However, the molecular weights of the polymer do not depend significantly on the nature of the modification. Heat treatment of the catalysts at 500°C reduces the yield of polymer drastically. The activation energy of the polymerization by unmodified carbon black is 83 kJ/mol as compared to 71 kJ/mol for the modified catalyst. Modification by dialkylzinc (0.1 to 0.4 $\underline{M}$) produces stereoregularity as indicated by the MEK insolubility of the polymer.

INTRODUCTION

Carbon black has been used as a catalyst for the polymerization of a number of vinyl monomers such as styrene [1], isobutylvinylether [2], α-methylstyrene [3], and N-vinylcarbazole (NVC) [4, 5]. The mechanisms of these polymerizations range from free radical to

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cationic, although very recently Biswas and Haque proposed in Ref. 6 (to be regarded as Part I in the series) a novel electron transfer initiation mechanism involving unpaired electrons on the carbon black and lone pair heteroatoms on the appropriate vinyl monomer.

It has now been possible to improve the catalytic activity of carbon black by appropriate chemical treatment. This paper highlights the salient aspects of the chemical modification of Orient Black by protonic and aprotonic acids and by metal alkyls, and reports its catalytic activity in relation to the polymerization of NVC.

EXPERIMENTAL

Materials

Carbon black, Orient Black N220 (ISAF-HM), was supplied by Phillips Carbon Black Ltd., India. The specific surface area was 120 m^2/g (N_2-BET). NVC (BASF) was purified as described earlier and kept in the dark in a vacuum desiccator prior to use. Solvents were all A.R. grade materials and purified by standard methods. Dialkylzinc was supplied by M/S A. G. Schering and used in toluene solution.

Modification of Carbon Black

The carbon black samples were treated with thionyl chloride as an aprotonic acid and with protonic acids such as HNO_3, H_2SO_4, and $HClO_4$ at desired concentrations under selective conditions. The treated samples were made free of acid traces by repeated washings with deionized water. Finally the samples were dried at 100°C for 2 h and cooled in a dry glove box to ambient temperature prior to use. As before, the catalysts were used in 100 mesh size powder form. Modification with dialkylzinc was done according to reaction condition described in Table 3.

Polymerization

Polymerizations were conducted in stoppered Pyrex tubes (30 mL) under nitrogen atmosphere with constant shaking. The general procedures followed for pretreatment of reaction vessels, preparation of monomer solution in a dry glove box, and charging of reaction vessels with monomer solution in dry condition were essentially similar to those adopted earlier [7, 8]. At the end of a desired time interval, the polymerizations were quenched by adding a drop of pyridine. The polymers produced were quantitatively precipitated in methanol containing 5% (v/v) HCl. The precipitate was filtered, washed free of any residual monomer by Ellinger's procedure [9], and dried to constant weight at 50°C.

Relative Viscosity

η_{rel} values of 1% solutions of the polymers in benzene were determined at 25°C using an Ostwald viscometer.

In a few cases the molecular weights were measured with a vapor pressure osmometer.

Heat Treatment of Modified Catalyst

In all the kinetic runs carbon black samples were preheated at 120°C for 2 h in vacuum, subsequently cooled to ambient temperature, and finally used in the polymerizations. To examine the effect of preheating temperature on the activity, a few samples were preheated to 500°C for 2 h in vacuum and cooled to ambient temperature before use.

pH of Modified Carbon Black (Slurry)

pH measurement of the aqueous slurries of the modified carbon blacks was made in a Digital pH meter using a glass electrode.

Index of Sterospecificity Measurement

The percentage (by weight) of the MEK insoluble fraction of PNVC was determined following the procedure of Hirata and Tani [10] and used as a measure of index of sterospecificity, I_s.

IR Spectrum

The IR spectra of the fractions of PNVC, soluble and insoluble in MEK, were recorded in a Perkin-Elmer 237B spectrophotometer in nujol.

X-Ray Diffraction Pattern

X-ray diffraction patterns were measured with a Dorn I (USSR) x-ray diffractometer with Mo target (λ = 0.711 Å) at 40 kV operation voltage and 19 mA current using a zirconium K_α filter.

RESULTS AND DISCUSSION

General Characteristics of the Polymerization

Figures 1 and 2 represent some typical characteristic time-conversion curves for the polymerization of NVC by carbon black modified

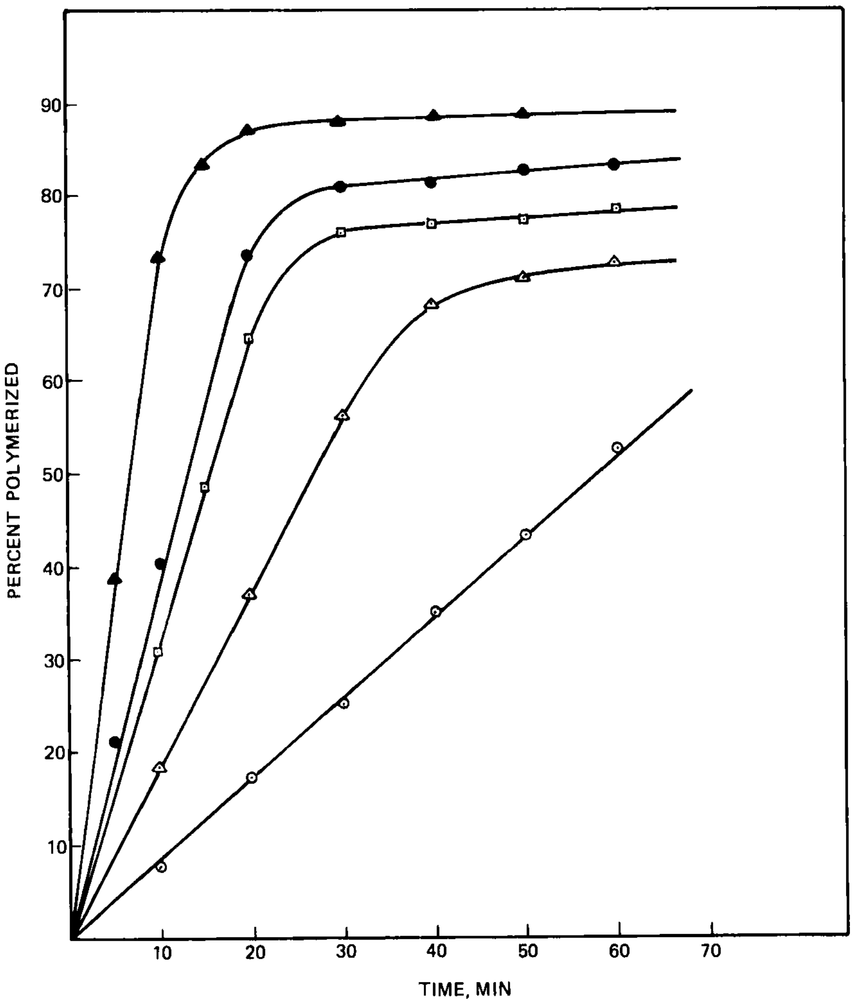

FIG. 1. Time-conversion curves for the polymerization of NVC in toluene at 60°C. [NVC] = (10%) and carbon black (0.03 g/2 mL) modified with: unmodified (○), 50% $SOCl_2$ (△), 1.7 N H_2SO_4 (□); 1.7 N HNO_3 (●), and 1.7 N $HClO_4$ (▲).

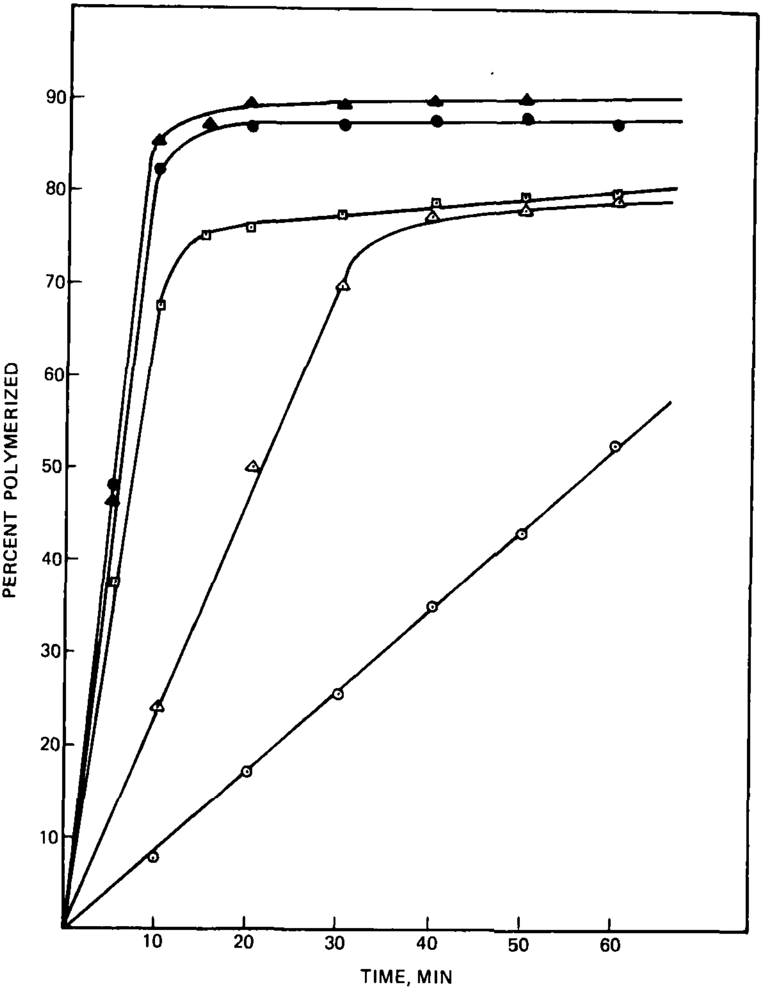

FIG. 2. Time-conversion curves for the polymerization of NVC in toluene at 60°C. [NVC] = 10% and carbon black (0.03 g/2 mL) modified with: unmodified (○), 100% $SOCl_2$ (△), 4.25 N H_2SO_4 (□), 4.25 N HNO_3 (●), and 4.25 N $HClO_4$ (▲).

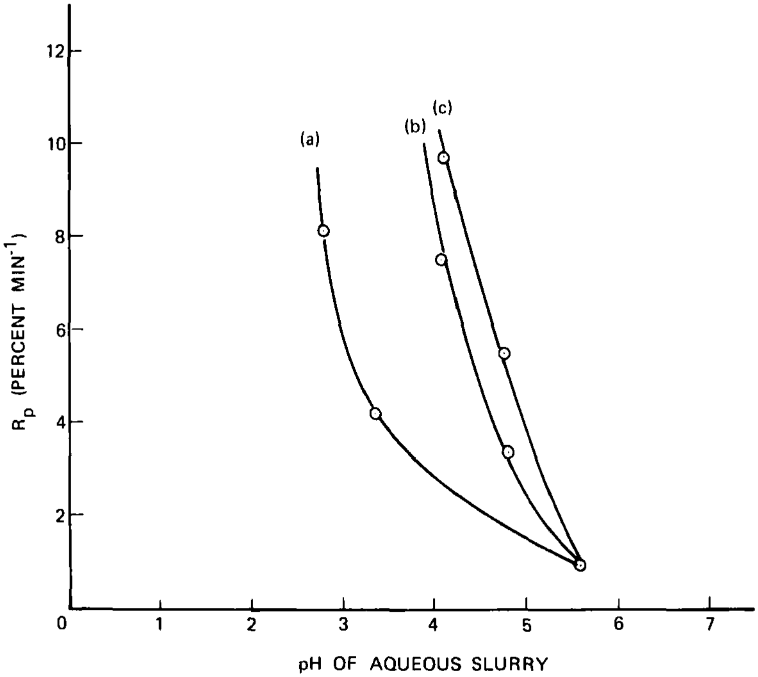

FIG. 3. Dependence of the rate of polymerization on the pH of aqueous slurry of carbon black modified with: HNO_3 (a), H_2SO_4 (b), and $HClO_4$ (c).

with protonic and aprotonic acids of two different concentrations. These data clearly indicate that modification with these acids indeed improves the catalytic efficiency of the Orient Black in the order $HClO_4 > HNO_3 > H_2SO_4$, the acid concentrations used for modification being 4.25 and 1.7 $\underline{N}$, respectively, in all cases.

Figure 3 shows that the rate of polymerization increases with increasing pH of the aqueous slurry of the acid-modified carbon black sample.

The above trend is apparently consistent with acid strength, which also reflects the oxidizing capacity. Nemerovets [11] reported on the oxidative modifications of carbon black by H_2O_2, air, nitric acid, sulfuric acid, and their mixtures. It appears that such an oxidative modification increases the concentration of the surface COOH groups, phenolic OH, and lactone groups present on the carbon black surface. As a result, the initiating capacity of this modified black will be expected to increase. This observation need not be taken to contradict the proposed electron transfer initiation reaction [6] between $\underset{\cdot\cdot}{\overset{\diagdown\,\diagup}{N}}$ and the unpaired electrons on the carbon black surface inasmuch as initiation by surface carboxyl groups cannot be ruled out [6] completely. However, to what extent such oxidative modifications would affect the electron spin concentration on the carbon black surface and hence the electron transfer mechanism remains, as yet, an open question which is now receiving attention.

Effect of Heat Treatment Temperature on the Carbon Black Activity

It has been reported [6] that the polymerization initiating activity of carbon black decreases with increasing heat treatment temperature of the catalyst, and almost becomes negligible at a preheating temperature of ~ 500°C. With the modified black a similar trend is observed although some activity, though very small, is realized (Table 1). Heat treatment is known [12, 13] to affect the concentration of surface COOH and other groups as is the spin concentrations of the unpaired electrons; both of these factors can be responsible for the observed loss of initiating activity of the black [6].

Dependence of Rate on Monomer Concentration

Figure 4 shows that the polymerization is first order in [NVC] in the range studied. A similar trend was realized with the polymerization of this monomer by unmodified carbon black [6] and also by molecular sieve catalysts [14-16].

Dependence of Rate on Catalyst Concentration

Figure 5 shows that the rate of polymerization exhibits a first-order dependence on the concentration (weight) of carbon black modified both with 1.7 N HNO_3 and 1.7 N H_2SO_4. Significantly, a similar trend was observed during polymerization of this monomer by unmodified carbon black [6]. This feature implies that oxidative modification does not significantly affect the mode of initiation while modifying the concentration of active entities responsible for the polymerization.

Molecular Weight Trends

η_{rel} values of the polymers prepared with modified carbon black do not reveal any significant difference (Table 2).

TABLE 1. Effect of Heat Treatment Temperature of Modified Carbon Black on the Polymerization of NVC[a]

Type of modification of carbon black	% Polymer yield[b]	Time (h)
Unmodified	53.1[c]	1
Unmodified	-	5
4.25 N HNO_3	88.1[c]	1
4.25 N HNO_3	8.2	3
4.25 N HNO_3	21.2	5
4.25 N H_2SO_4	78.0[c]	1
4.25 N H_2SO_4	2.6	3
4.25 N H_2SO_4	4.3	5
4.25 N $HClO_4$	90.5[c]	1
4.25 N $HClO_4$	-	5
100% $SOCl_2$	78.8[c]	1
100% $SOCl_2$	-	5

[a] 10% (w/v) NVC and 0.03 g carbon black in toluene (2 mL) in each polymerization run at 60°C under nitrogen.

[b] Heat treatment temperature of carbon black = 500°C (in vacuo) for 2 h.

[c] Heat treatment temperature of carbon black = 120°C (in vacuo) for 2 h.

Activation Energy

Conventional log rate versus 1/T plots for the polymerization of NVC by unmodified and modified carbon black are presented in Fig. 6 from which the overall activation energies can be calculated as 83 and 71 kJ/mol, respectively, for the system under consideration. It is reasonable to assume that over the temperature range studied (45 to 70°C) there would not be any significant loss of initiating moieties through decarboxylation and related reactions so that the rate tends to increase with temperature.

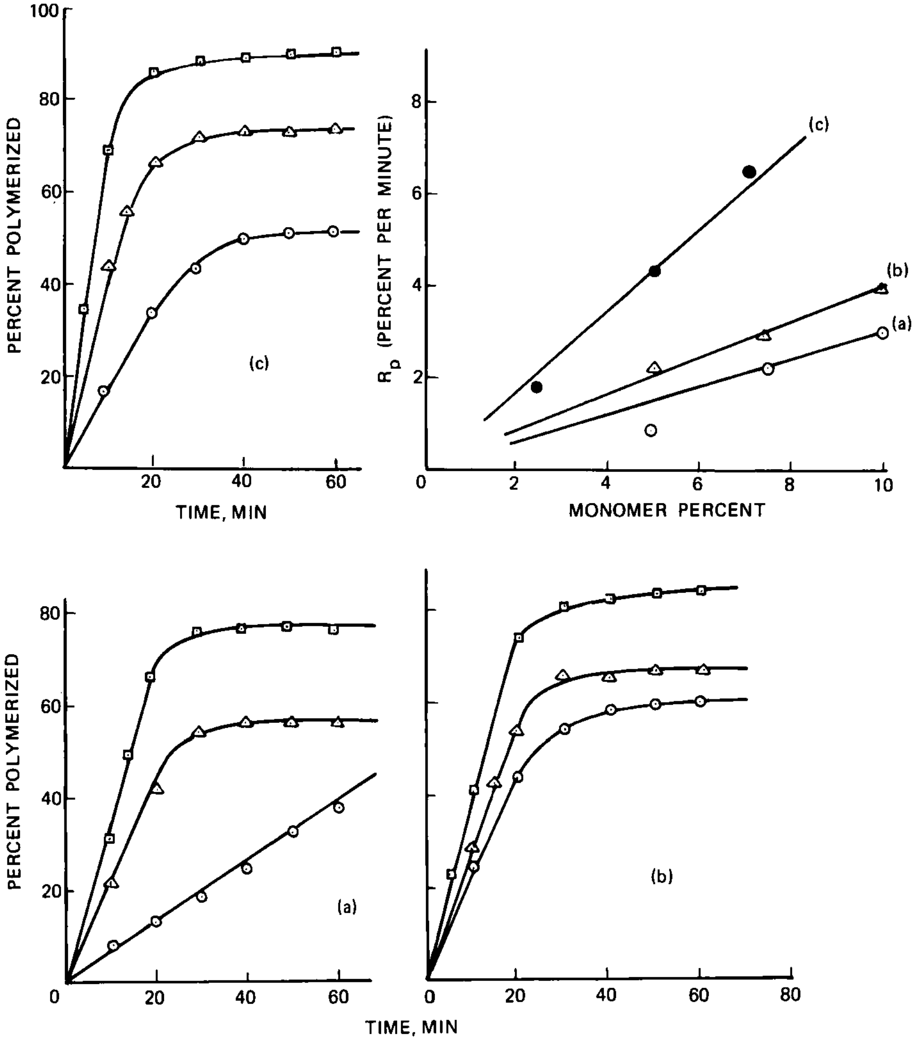

FIG. 4. Effect of NVC concentration on the yield and rate of polymerization. Carbon black (0.03 g/2 mL) modified with: 1.7 N H_2SO_4 (a), 1.7 N HNO_3 (b), and 1.7 N $HClO_4$ (c).

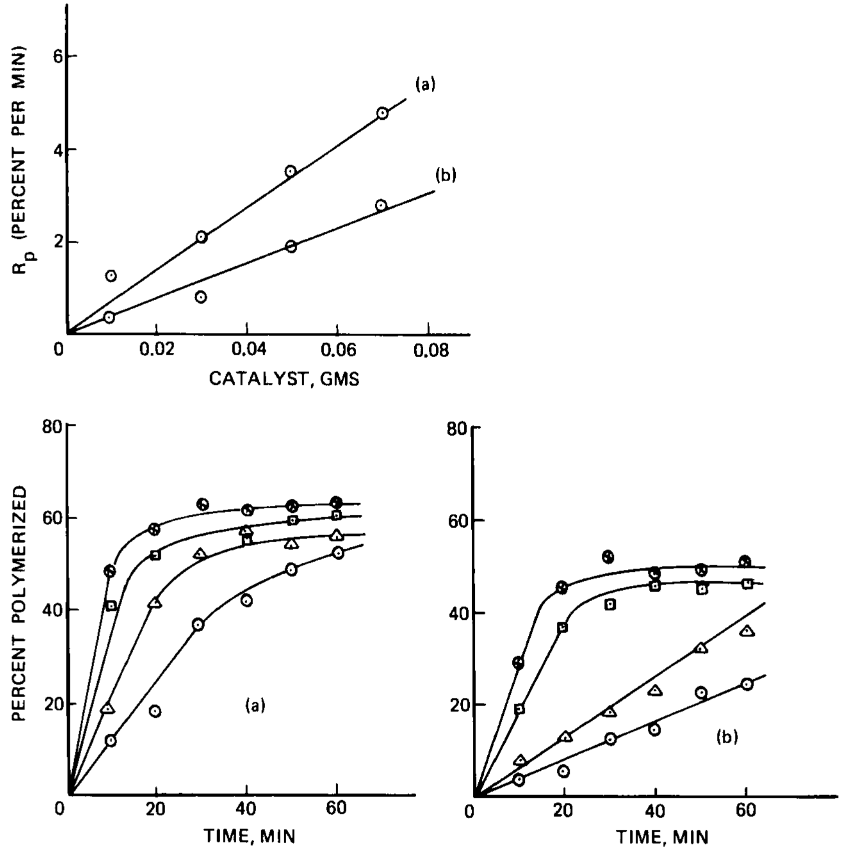

FIG. 5. Effect of modified carbon black on the yield and rate of polymerization. [NVC] = 5% in toluene; carbon black = 0.01 g (⊙), 0.03 g (△), 0.05 g (⊡), and 0.07 g (⊗) modified with 1.7 N HNO_3 (a) and 1.7 N H_2SO_4 (b)

Modification by Metal Alkyls

Treatment of $SOCl_2$-modified carbon black with dialkylzinc brings about a novel modification of the catalyst in NVC polymerization. Table 3 presents relevant data on the effect of modification of carbon black by dialkylzinc under selective conditions, notably in the presence of dialkylzinc where a certain fraction of PNVC produced remains insoluble in methyl ethyl ketone (MEK). Biswas and Mishra

TABLE 2. Variation of η_{rel} with Modification of Carbon Black[a]

Modified with	Concentration	η_{rel}
Unmodified	-	1.12
HNO_3	1.70 N	1.14
HNO_3	4.25 N	1.20
H_2SO_4	1.70 N	1.15
H_2SO_4	4.25 N	1.10
$HClO_4$	1.70 N	1.11
$HClO_4$	4.25 N	1.10
$SOCl_2$	50%[b]	1.08
$SOCl_2$	100%	1.11

[a] 2 mL of 10% (w/v) NVC and 0.03 g catalyst used in each polymerization run and the product after 1 h was used for measurement of η_{rel}.
[b] 50% in benzene solvent.

[17, 18] reported the formation of similar MEK-insoluble PNVC during polymerization of NVC by the $ZnEt_2/CoCl_2$-pyridine/quinoline catalyst system. Thus, it appears that dialkylzinc modifies the carbon black to a stereoregulating catalyst. The mode of aging and the reaction conditions appear to affect the properties of NVC. Table 3 suggests that monomer aged with dialkylzinc followed by addition of modified carbon black gives, in general, a better polymer yield and I_s values between 24 to 70%, compared to a lower polymer yield and a higher I_s range of 13 to 82% when the catalyst is aged with dialkylzinc followed by monomer addition. Detailed characterization of the MEK-soluble and -insoluble fractions is under progress. The molecular weight of the MEK-insoluble fraction (29,000) is significantly higher than that for the MEK-soluble part (6,000). However, x-ray diffraction patterns of these two polymers do not reveal any conspicuous differences in crystallinity (Fig. 7), and their IR spectra are virtually the same.

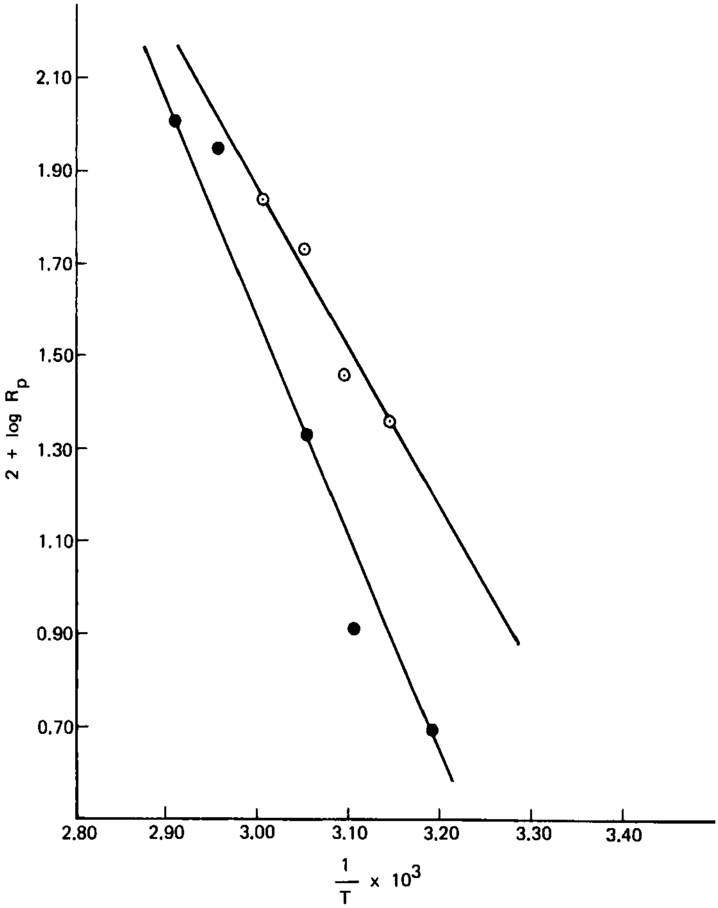

FIG. 6. Temperature dependence of the rate of polymerization of NVC by carbon black; modified with 1.7 N H_2SO_4 (⊙) and unmodified (●).

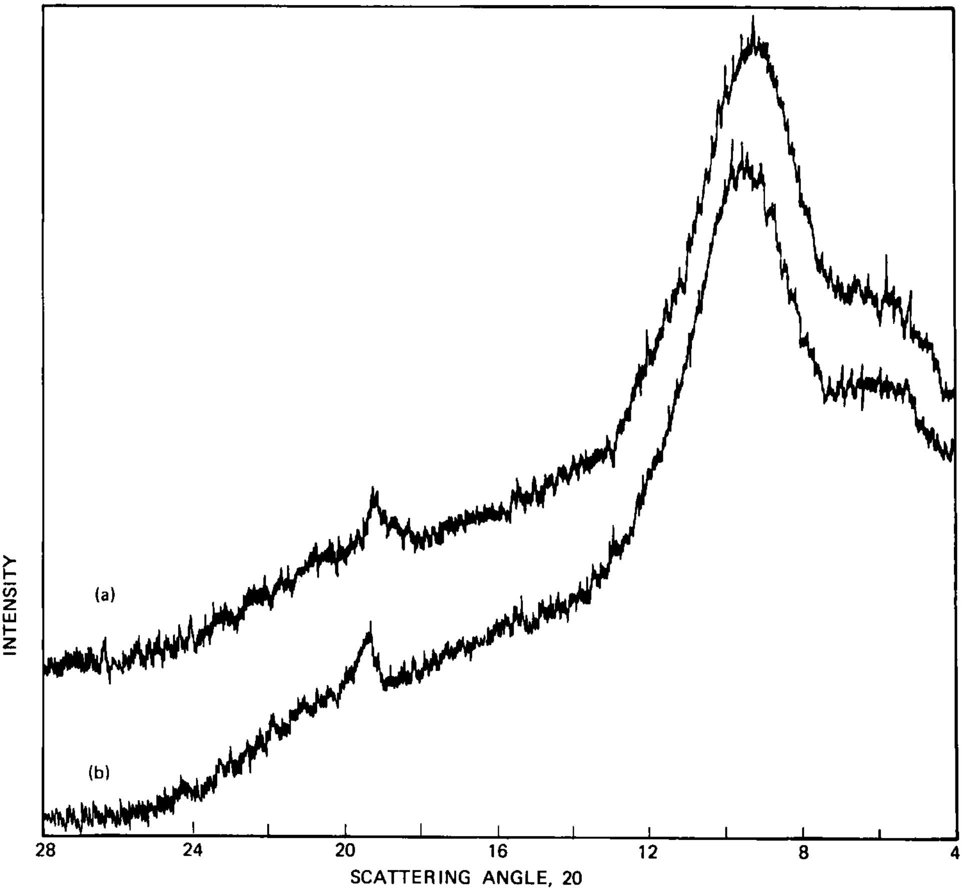

FIG. 7. X-ray diffraction pattern of PNVC. Soluble in MEK (a) and insoluble in MEK (b).

TABLE 3. Polymerization[a] of NVC by $ZnEt_2$-$SOCl_2$ Modified Carbon Black

Weight of the catalyst (g)	Monomer (NVC) % (w/v)	Concentration of $ZnEt_2$ (mol/L)	Mode of aging[b]	PNVC formed in 60 min (%)	I_s
-	10	0.2-0.4	c	-	-
0.03	10	0.4	c	2.2	-
0.03	10	0.4	c	2.5[e]	-
0.03	10	0.4	c	3.2[f]	-
0.03	10	0.4	c	6.5[g]	-
0.03	10	0.2	c	30.7	82
0.03	10	0.1	c	66.0	35
0.05	10	0.2	c	24.2	20
0.07	10	0.2	c	15.0	13

0.03	15	0.4	d	77.3	61
0.03	10	0.4	d	60.5	70
0.03	5	0.4	d	57.3	57
0.03	15	0.2	d	42.6	47
0.03	10	0.2	d	33.6	28
0.03	5	0.2	d	10.0	24
0.05	10	0.2	d	24.0	42
Carbon black (unmodified)	10	0.2	c	-	-

[a] All polymerizations were carried out at 60°C in nitrogen with constant shaking.

[b] Toluene solution of $ZnEt_2$ was used and aged for 1 h under nitrogen atmosphere.

[c] Catalyst aged with toluene solution of $ZnEt_2$.

[d] Monomer aged with toluene solution of $ZnEt_2$.

[e,f,g] Polymerizations conducted in 80, 100, and 120 min, respectively.

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