of the ethylene monomer to the catalytic site.

A similar explanation may be advanced for the relative catalytic activities of the initiators derived from polystyrene (*Table 2b*) in which an inverse relationship was found between the activity and the degree of substitution of the metal alkyl component. The greater bulk of polystyrene chains makes steric factors more important, such that the least bulky component, LiR, has the greatest activity, whereas the most bulky, AlR_3, is very much less.

If the assumption be accepted that the non-extractable homopolystyrene or polyisoprene from the products of these polymerizing systems is due to block copolymer formation, then these experiments demonstrate the feasibility of preparing such copolymers by this means. There remains a possibility, however, that the unextractable homopolymer is physically entrapped within the polyethylene matrix rather than chemically bound thereto. The following observations, nevertheless, make the latter explanation unlikely: (a) the homopolymer is soxhlet extracted rapidly by benzene, but after about 24 h no further material is solubilized, (b) the fraction of extractable material is reproducible in repeat experiments, (c) the catalyst efficiency increases with r, which means that the fraction of extractable polymer *decreases* as the proportion of the polymer derivative added *increases*.

Absolute confirmation of block copolymer formation can best be obtained by high temperature g.p.c., a technique to which we currently have no access. Nevertheless, these materials will be examined in this way in the future, when a fuller report will be made on the kinetics of the process and characterization of the products.

Lastly, it should be noted that the efficiencies quoted refer exclusively to the conversion of the polymer ligands into block copolymers. No assessment has been made of the molar per cent of block copolymer in the product. This could be 100% in the solvent extracted material if no chain transfer reactions took place during ZN polymerization, down to a low figure if such reactions were prevalent.

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Stereospecific polymerization of *N*-vinylcarbazole by $ZnEt_2/CoCl_2$–pyridine catalyst system

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Introduction

Little established work on the stereospecific polymerization of N-vinylcarbazole at ambient temperature has been reported. Some of the work reported[1] is irreproducible and has been contradicted[2]. In the course of our work on the development of sterospecific catalyst systems based on oxychloride–metal alkyl combinations[3,4], we have observed that cobalt chloride pyridine complex is particularly effective in presence of zinc diethyl in producing stereoregular poly(*N*-vinylcarbazole) at room temperature. A cobalt chloride–pyridine–$AlEt_2Cl$ catalyst system has been used for the *cis*-polymerization of butadiene and isoprene[5]. Interestingly, the molecular weights of poly(*N*-vinylcarbazole) produced under these conditions are much higher than those reported by us for the aprotonic acids[6,7], Grignard reagent[8,9] and the metal oxide[10,11] initiated polymerization of this monomer. This communication highlights some relevant observations on this system.

Experimental

Monomers. *N*-vinylcarbazole (NVC), (BASF — West Germany), styrene (S) ICI. Plastics Division and iso-butyl vinylether (IBVE) E. Merck were purified, distilled and preserved following standard techniques[6,12,13].

Preparation of the catalyst. The hydrocarbon soluble cobalt chloride pyridine complex was prepared by adding a calculated amount of pyridine to a known quantity of anhydrous cobalt chloride[14] in a pyrex test-tube under nitrogen atmosphere. The deep blue complex formed was freely soluble in toluene and was stable for a considerable period (one month). Solutions of desired concentration were prepared conventionally. All dilutions and handling

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were performed in a dry glove-box under nitrogen atmosphere.

Diethyl zinc ($ZnEt_2$) Schering AG. was diluted with toluene to the necessary concentrations.

Polymerization. Polymerization of NVC was conducted in stoppered pyrex reaction vessels under nitrogen. In a typical run with NVC appropriate quantities of monomer and cobalt chloride solution were allowed to age for a definite time under nitrogen and then the polymerization was initiated by injecting a requisite quantity of toluene solution of $ZnEt_2$. The extent of polymerization was observed gravimetrically by precipitating the polymers in excess methanol containing 5% (V/V) HCl and removing solvents and unreacted monomer[3,15].

Intrinsic viscosity. Intrinsic viscosities of polymers were determined in benzene solution at 25°C and molecular weights were calculated using the equation[16] $[\eta] = KM^{\alpha}$; where $K = 3.35$ and $\alpha = 0.58$.

Index of stereospecificity. As a measure of stereospecificity the value of index of stereospecificity (*IS*) defined by Hirata and Tani[17] as the percentage of the weight of methyl ethyl ketone (MEK) insoluble fraction against the total polymer yield was considered. Fractionation of the polymer was carried out by following the procedure of Hirata and Tani.

N.m.r. characterization. ^{13}C n.m.r. spectra of polyNVC were taken on a varian CFT 20 spectrometer in C_6H_6/C_6D_6 mixtures.

X-ray analysis. X-ray diffraction analysis of the polymers were made on APOH I X-ray diffractometer with Cu-target ($\lambda = 1.542$) at 30 KV operation voltage, and 18 m.a. current using Nickel filters.

Results and Discussion

General features and solubility characteristics. *Figure 1* presents some typical percentage polymerization *vs.* time curves for the polymerization of NVC by $ZnEt_2/CoCl_2$–Py system. Alone $ZnEt_2$ (upto 0.3M) or $CoCl_2$–Py (3.4×10^{-7}M) did not initiate the polymerization. The polymerizations are not attended by any typical colour development indicating that charge-transfer interactions[18,19] are not important in the present system. The polymers are freely soluble in benzene but leave some insoluble fraction when treated with methyl ethyl ketone (MEK). This behaviour is typical of this catalyst combination. Significantly, aprotonic acid and charge-transfer polymerizations of NVC have not been reported to produce such MEK insoluble fractions, all the polymers being however, freely soluble in benzene, MEK and other solvents. Since insolubility in ketonic solvents is often regarded as a first criterion for sterospecific vinyl polymers[20–24], it is suggested that $CoCl_2$–Py system in combination with $ZnEt_2$ induces the stereoregular polymerization of NVC in this case, at ambient temperatures.

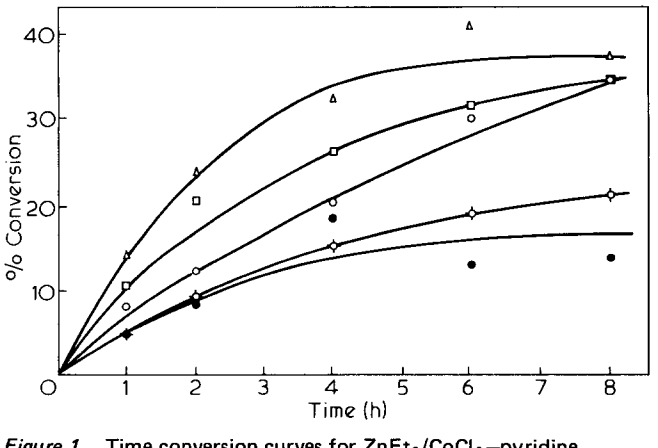


Figure 1 Time conversion curves for $ZnEt_2/CoCl_2$–pyridine catalysed polymerization of NVC in toluene at 32°C. [NVC] = 0.1 M; $[CoCl_2] = 3.4 \times 10^{-7}$ M; $[ZnEt_2]$ = ⊙: 0.1 M; ☆: 0.075 M; ⊡: 0.2 M; $[ZnEt_2]$ = 0.1 M; $[CoCl_2] = 3.4 \times 10^{-7}$ M; [NVC] = ●: 0.075 M; △: 0.3 M

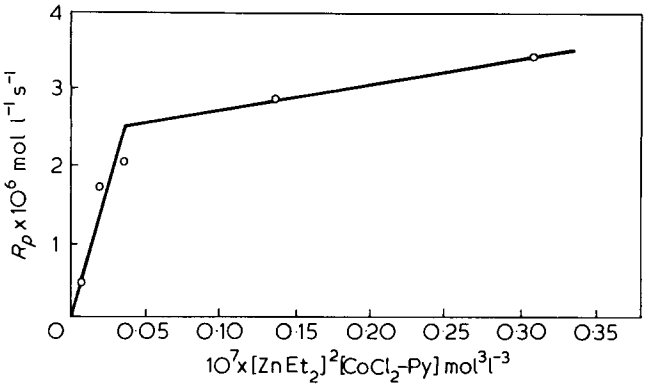


Figure 2 Dependence of R_p on $[ZnEt_2]^2/[CoCl_2]$ ratio in toluene at 32°C

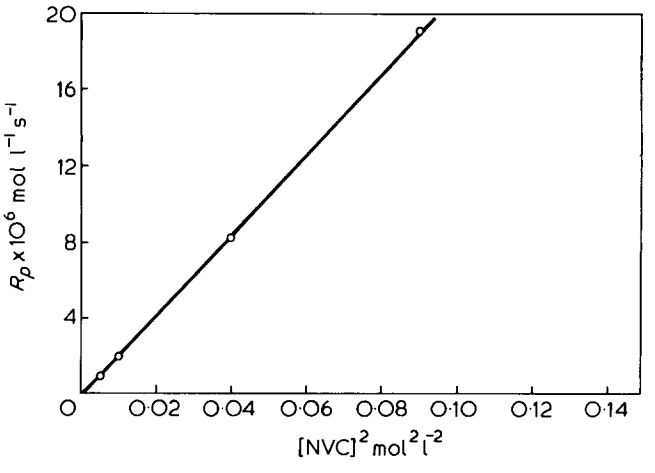


Figure 3 Dependence of R_p on $[NVC]^2$ in toluene at 32°C

Dependence of rate on $ZnEt_2$ and $CoCl_2$–Py concentration. *Figure 2* shows that at a fixed NVC concentration the rate correlates with the product $[ZnEt_2]^2[CoCl_2\text{–}Py]$ up to a certain value, changing slowly thereafter with increasing $ZnEt_2$ concentration. This implies that the catalyst complex responsible for the polymerization may involve two molecules of $ZnEt_2$ and one of $CoCl_2$–Py. The deviation of the rate from this relation at high $ZnEt_2$ may be due to termination of growing carbonium ions by $ZnEt_2$. At fixed concentrations of $ZnEt_2$ (0.1 M) and $CoCl_2$–Py (3.4×10^{-7} M) the rate of polymerization appears to be second order with respect to NVC concentration (see *Figure 3*).

Characterization of methyl ethyl ketone (MEK) insoluble poly(N-vinylcarbazole). ^{13}C n.m.r. spectra: *Figure 4* shows the ^{13}C n.m.r. spectrum of the MEK insoluble polyNVC. The methine carbons are clearly shown to be

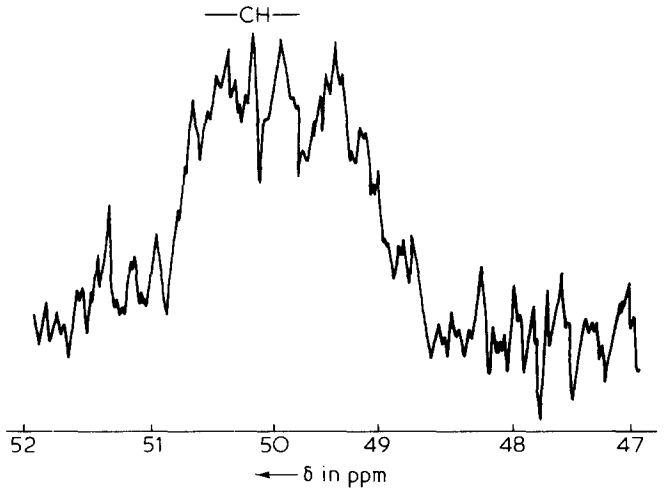


Figure 4 Methine (—CH—) resonance spectrum (^{13}C n.m.r.) of poly(NVC) prepared by the $ZnEt_2/CoCl_2$—pyridine catalyst system

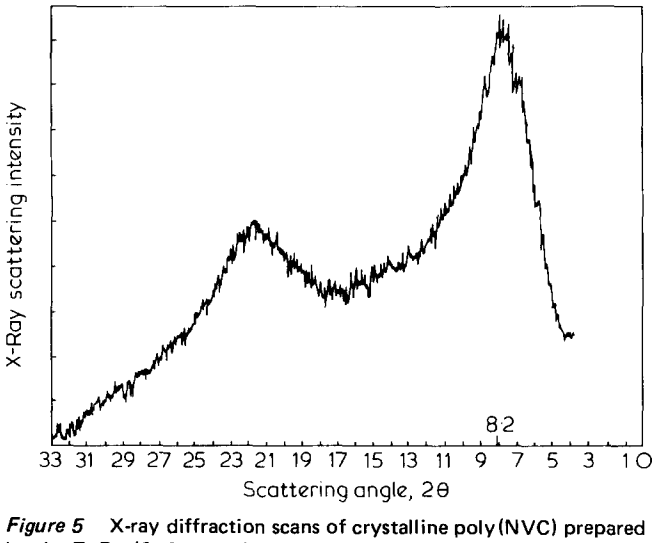


Figure 5 X-ray diffraction scans of crystalline poly(NVC) prepared by the $ZnEt_2/CoCl_2$—pyridine catalyst system

split into a triplet corresponding to chemical shifts 49.43, 49.85 and 50.63 p.p.m. respectively.

Kawamura and Matsuzaki[25] showed that methine carbons of polyNVC obtained with AIBN in toluene at 80°C were split into a triplet corresponding to chemical shifts 49.2, 49.65 and 50.3 p.p.m., while those of polymers obtained with $BF_3.OEt_2$ in toluene at −78°C into a doublet (49.35 and 50.10 p.p.m.). These authors tentatively presumed that the radical (AIBN) initiated polyNVC possesses a syndiotactic rich structure and the $BF_2.Et_2O$ initiated polyNVC an isotactic rich structure. PolyNVC with 35–50% crystallinity gives a spectrum intermediate between the two in respect of the methine carbon splitting and is suggested to possess a stereoblock configuration. On the basis of these observations the polyNVC prepared with the $ZnEt_2$–$CoCl_2$–Py system appears to possess a stereoblock configuration.

X-ray characterization. X-ray diffraction traces for MEK insoluble fraction are shown in *Figure 5*. The crystalline peak at $2\theta = 8.2°$ represents an interplaner spacing of 10.78 Å and is very similar to, though somewhat less sharp, than that reported by Penwell for a crystalline poly(NVC) sample[26].

Thermal characteristics. D.t.a., d.t.g. and t.g. of poly(NVC) obtained by the $ZnEt_2/CoCl_2$–Py catalyst system have been compared in *Table 1* with the corresponding data for aprotonic acid ($POCl_3$ and $AlCl_3$) initiated polyNVC. The former is conspicuously characterized by a sharp endothermic peak at 460°C, which is absent in the latter and may be due to the melting of the crystallites.

Factors affecting the index of stereospecificity (IS). Effect of ageing: Two ageing procedures were followed (a) NVC was aged with $CoCl_2$–Py for a definite time (5 min to 90 min) followed by the addition of the $ZnEt_2$; (b) $ZnEt_2$ was aged with $CoCl_2$–Py (5 min to 90 min) followed by the addition of the monomer. It may be observed from *Table 2* that with procedure (a) the percentage of poly(NVC) formed increases systematically

Table 1 Comparison of thermal characteristics of PolyNVC

Polymerization system	Thermal characteristics										
	d.t.a.		d.t.g.		Temperature (°C) of % weight loss on heating (10°C/min)						
					0	20	40	60	80	95	0°C
	Endo peak	Exo peak	Endo peak	Exo peak							
NVC–$ZnEt_2/CoCl_2$–Py/ toluene	460°C	500°C	455°C	–	upto 200°	400	460	500	520	580	
NVC–$POCl_3$/benzene	–	340°C 525°C	500°C		200	410	450	500	540	700	
NVC/$AlCl_3$/chlorobenzene	–	450°C	500°C		75	450	480	500	520	600	

Table 2 Effect of ageing[a]

No. of observation	$[ZnEt_2]$ in mol l^{-1}	$\frac{[ZnEt_2]}{[CoCl_2]} \times 10^{-7}$	[NVC] in mol l^{-1}	Mode of ageing	% Poly(NVC) formed at different ageing time Time in min			Molecular weight	Index of stereo-specificity
					5	60	90		
1	0.2	0.06	0.1	a	15	72	33	37230	47
2	0.1	0.03	0.2	a	38	55	40	12940	80
3	0.1	0.03	0.1	b	53	53	51	10000	78
4	0.1	0.03	0.2	b	35	33	31	8784	80

[a] In all cases the polymerizations were carried out at 32°C using toluene as solvent

over the first 60 min. but registers a fall at 90 min onwards. However, with (b) a limiting conversion is reached during the first 5 min showing finally a tendency to fall, but the fall is not as conspicuous as with procedure (a). The molecular weights are usually higher with (a). The amount of MEK insoluble fraction is high in (b) and not dependent on NVC concentration, whereas the same is low at low NVC concentration and tends to increase with the increase in NVC concentration. In the present work, procedure (a) was followed in all the experiments.

Effect of temperature. The index of stereospecificity consistently decreases with increasing temperature as is usually observed.

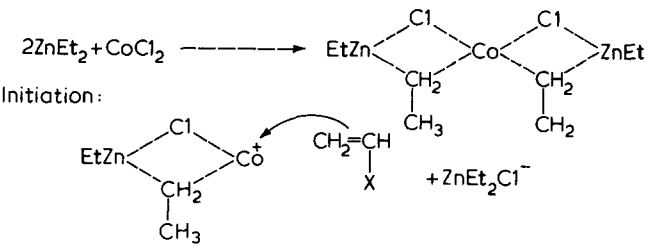
Molecular weight trends. Molecular weights of polyNVC obtained with this catalyst system fall within the range 12–37 000 under various conditions. Significantly, these values are higher than those obtained with conventional aprotonic acid initiators. It is possible[27] that very large differences in properties could arise in this region due to molecular weight differences. However, it has been observed in the present context that a thermally polymerized high molecular weight ($=10^6$) sample of polyNVC is as freely soluble in benzene and in MEK as is an aprotonic acid initiated polyNVC of much lower molecular weight ($=10^4$). Hence MEK insolubility in this case does not appear to be associated with molecular weight differences alone but is rather consistent with the suggested stereochemical differences in the polymer sample.

A remarkable feature is that the degree of polymerization increases with $[ZnEt_2]/[CoCl_2\text{–Py}]$ to a maximum value and falls thereafter. This trend possibly implies that the catalyst eliminates[28] some of the basic adventitious impurities from the system. The degree of polymerization also increases with increase in monomer concentration to a constant limiting value when monomer transfer assumes dominance.

Variation of the cobalt complexing ligand. Biswas and Mishra recently reported[29] that a change in the complexing ligand from pyridine to quinoline also affords a polyNVC with comparable solubility and other physical as well as kinetic characteristics. Hence, the observed effects appear to be rather specific for the $ZnEt_2$–$CoCl_2$–(complexing agent) based homogeneous catalyst system.

Monomer selectivity of $ZnEt_2/CoCl_2$–Py initiator system. Iso-butyl vinyl ether upto a concentration of 5 to 6M could not be polymerized in solution by either $ZnEt_2$ or $CoCl_2$–Py complex or their combination in (1–24 h) even at low temperatures (0°C). Styrene (2–6 M) was not polymerized either by $ZnEt_2$ or $CoCl_2$–Py alone, while their combination yielded a polystyrene of very high molecular weight ~75 000), but of very low yield (5% in 24 h) which made kinetic studies rather difficult under these conditions. Significantly, the polystyrene formed did not reveal any stereospecific character.

Reaction mechanisms. By analogy with the $AlEt_2Cl$–$CoCl_2$–pyridine homogeneous catalyst system[30] it is clear that, in the present system the $ZnEt_2$ forms with $CoCl_2$ in pyridine a soluble organo-cobalt complex responsible for the polymerization. Since, NVC is more susceptible to cationic polymerization an ionic complex[30] is possibly involved. The following scheme of polymerization is therefore tentatively suggested.



This mechanism is consistent with the observed dependence of rate on the catalyst complex and the monomer respectively.

The observed monomer specificity of the catalyst system appears to be consistent with the basicity of the monomer moiety which determines the extent of stereospecific coordination of the monomer with the cobalt complex.

Conclusion

$ZnEt_2/CoCl_2$–pyridine complex catalyst system polymerizes NVC to a stereoregular polymer. The reactions are feasible at ambient temperature and can be accomplished with a remarkably low $CoCl_2$–pyridine complex concentration ($\simeq 10^{-7}$ M).

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