

MECHANISM OF N-VINYLCARBAZOLE POLYMERIZATION CATALYZED BY MERCURIC CHLORIDE IN CHLOROBENZENE SOLUTION

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(Received March 13, 1986; revised June 14, 1988)

The polymerization of N-Vinylcarbazole initiated by mercuric chloride in chlorobenzene solution were done under high vacuum conditions ($\approx 10^{-4}$ torr) at 25°C, and the rates of reactions were followed dilatometrically. All the polymerization reactions gave first order plots after a short acceleration period. The rate of polymerization was found to be proportional to $C_0 m_0^2$, $C_0 m_0$ and $C_0^3 m_0$ depending on the initial monomer, m_0 and catalyst, c_0 concentration. The polymerization of N-Vinylcarbazole initiated by mercuric chloride in chlorobenzene solution was believed to be stepwise reaction. The molecular weights of all the polymers, determined at complete conversion, were independent of C_0 and increased with the increase in m_0 . Therefore, it was concluded that the chain breaking reactions with monomer were predominant reactions in this polymerization system. It was believed that a charge transfer complex between N-Vinylcarbazole and mercuric chloride was formed, which under favourable conditions dissociated into radical-ions. The radical-cation carrying N-Vinylcarbazole thus formed, successively reacted with another molecule of N-Vinylcarbazole to dissociate radical and cation ends for propagation. Therefore, it was suggested that the polymerization of N-Vinylcarbazole initiated by mercuric chloride in chlorobenzene solution was of radical-cationic in nature.

Key words: Polymerization of N-Vinylcarbazole, Mechanism of N-Vinylcarbazole polymerization.

INTRODUCTION

The kinetics of polymerization and the molecular weights of the polymers formed from N-Vinylcarbazole catalyzed by organic electron acceptor type catalyst such as tetranitromethane in nitrobenzene solution has been reported by Pac and his coworker [1]. They suggested that the polymerization was cationic in nature because the radical function would be rapidly inactivated by the catalyst which is a well known radical scavenger as well, and that the chain breaking by monomer was predominant in comparison with that of water. The kinetics of polymerization were explained in terms of a slow initiation by ionogenic dissociation of the charge-transfer complex between monomer and catalyst and a termination by monomer maintaining an almost constant, very low, concentration of rapidly growing chains.

The polymerization of N-Vinylcarbazole by inorganic electron acceptors such as Fe^{3+} , Cu^{2+} , and Ce^{4+} salts have also been reported in the literature [2-4] which were mainly concerned with the chemical aspects of the polymerizations. These authors [3-4] reported the formation of an

ion-radical by electron transfer between the oxidizing metal salts and various carbazole derivatives. Therefore, they suggested that the mechanisms of initiation for the polymerization of N-Vinylcarbazole by oxidizing metal salts were of electron transfer type in nature. However, they reported that the polymerization of N-vinylcarbazole initiated by the oxidizing metal salts in solvents of different polarity was of a cationic in nature. They supported this cationic mechanism by their work on the copolymerization of N-vinylcarbazole with styrene and subsequently comparing the polymerization of N-vinylcarbazole with that of Vinylpyridine using the same catalyst-solvent system. In another words these authors [3-4] ignored altogether the role of radical formed in the initiation reaction for the polymerization of N-vinylcarbazole initiated by the oxidizing metal salts. The cationic polymerization of N-vinylcarbazole initiated by the stable cationic metal salts [5-7] such as triphenylmethylhexafluoroantimonate, aluminium chloride [8] and a cationic coordination polymerization has also been reported when the polymerization was initiated by the stable mixed metal salts such as $Zn Et_2/Co Cl_2$ -pyridine complex [9] and $Zn Et_2/Co Cl_2$ -quinoline complex [10]. Therefore, it seems very unlikely that the polymeri-

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zation of N-vinylcarbazole initiated by oxidizing metal salts propagates only by simple cationic mechanism.

As it is clear that there is considerable confusion about the mechanism of polymerization of N-vinylcarbazole initiated by oxidizing metal salts. Therefore, this work is undertaken to study the polymerization of N-vinylcarbazole initiated by mercuric chloride in chlorobenzene solution and I wish to report that mercuric chloride initiated polymerization of N-vinylcarbazole propagates both by radical as well as by cationic mechanisms.

MATERIALS

N-Vinylcarbazole. N-vinylcarbazole (Koch light) was recrystallized four times from pure n-hexane. The N-vinylcarbazole thus obtained, about 60% of the starting material was finally dried in a vacuum oven at 30°C for 24 hours. The melting point of this N-vinylcarbazole, determined by a polarisation microscope was 66.5°C compared with literature [11] values ranging between 61 to 67°C. Just before each polymerization experiment N-vinylcarbazole was thoroughly dried in the polymerization device under a vacuum of about 10^{-4} torr at room temperature for three hours.

Mercuric chloride. Mercuric chloride (May and Baker pure product) was recrystallized thrice from pure chlorobenzene. The total yield after repeated recrystallization was about 50% of the starting material. This mercuric chloride was thoroughly dried under high vacuum conditions for three hours in the polymerization device, just before each polymerization experiment.

Borontrifluoride etherate. The commercial product of $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ (a generous gift from B.P.) was fractionally distilled under high vacuum conditions, and generous amounts were discarded as head and tail fractions. A middle fraction about 40% of the starting material was collected in a flask equipped with break seal. The boiling point of this middle fraction was 50°C (16 torr) compared with the value of 48.5°C (15 torr) as calculated by the following equation given in the literature [12] for the temperature dependence of the vapour pressure P:

$$\log P(\text{mm}) = -\frac{2845}{T} + 10.02$$

This flask was sealed off after freezing its contents and was used for the preparation of $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ phials.

Preparation of $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ phials. The flask containing the middle fraction of $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ prepared as mentioned above was joined to vacuum line. The content of flask was thoroughly degassed by repeated freezing and thawing. A middle fraction was collected into the phial.

This was sealed off and its contents were determined by Rutherford's mid point method [13]. This phial was further used to prepare the phials containing the solution of $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ in chlorobenzene by using the tipping device [13].

Chlorobenzene. The chlorobenzene (BDH Laboratory Reagent) was purified by successive shaking with aqueous sodium hydroxide, water and sulphuric acid until the acid no longer became coloured. It was finally washed several times distilled water, dried over phosphorus pentoxide and fractionally distilled in an anhydrous atmosphere at ordinary pressure. The middle fraction about 70% of the starting material was collected at 131 to 132°C. This fraction was then rapidly transferred into the solvent reservoir containing freshly activated molecular sieves. The reservoir was closed with a mercury seal and pumped out by opening the metal valve connecting it to the vacuum line. The chlorobenzene was degassed thoroughly under high vacuum at room temperature, and then refluxed under vacuum for a few days. The purity of this chlorobenzene was checked by gas chromatography on a Perkin Elmer F 11 apparatus by using a column filled with SE 30 on chromosorb P, pure nitrogen as a carrier gas and a temperature of 120°C. A single sharp peak of chlorobenzene was always obtained.

EXPERIMENTAL

The dilatometer and the filling assembly. The dilatometer used in the experiments to measure the kinetics of polymerization consisted of a bulb with a capillary (A) joined through a sloping side arm to the large tube (B) which is further joined through a side arm to another large tube (C) (Figure 1). Weighed amounts of N-vinylcarbazole, monomer and mercuric chloride, catalyst were placed into tubes (B) and (C) respectively, which were then closed by sealing the tops. The dilatometer assembly was then joined to the solvent filling assembly by the tube (D) (Fig. 1). It was then evacuated for three hours at about 10^{-4} torr, the required volume of solvent from the burette (E) was run into the dilatometer assembly. The residual solvent on the walls was removed and solidified in tubes (B) and (C) and cooling their lower parts with liquid nitrogen and warming up the solvent path with a warm air. The dilatometer assembly was then sealed off from the vacuum line point (F), and the frozen parts of the tubes were immersed in methanol. The monomer and catalyst were dissolved in the melted solvent, and the whole apparatus was immersed in the thermostat ($25 \pm 0.01^\circ\text{C}$). When temperature equilibrium was reached, the contents were well mixed and tipped into the dilatometer and the whole assembly was

placed quickly back into the thermostat. The change in level of meniscus in the capillary of dilatometer was followed by a cathetometer to measure the kinetics of Polymerization reaction. The relation between contraction in (mm) and conversion was established by weighing of the polyvinylcarbazole formed. The polymer yield and the initial amount of monomer agreed to within 1 to 2%. The abbreviation used L_{∞} & L_t are the final and at time t dilatometer readings, respectively.

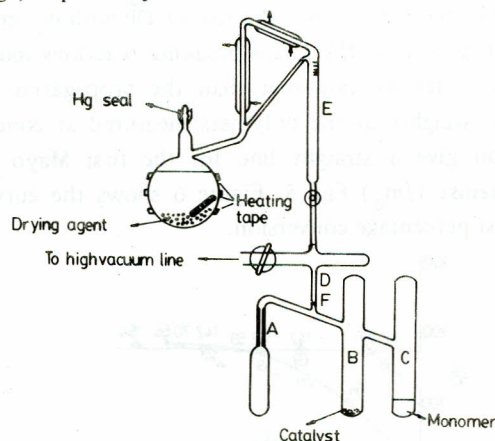


Fig. 1. Assembly for filling dilatometer (A) with charging arms (B) and (C) and chlorobenzene reservoir and burette (E).

Polymer isolation. After the polymerization had stopped, the solution was tipped back from the dilatometer to the side tubes. These tubes were opened and the contents were poured into an excess of 95% ethanol to precipitate the polymer. This polymer was filtered off, reprecipitated from methylene dichloride by ethanol and dried in a vacuum oven at 60°C for several hours. The polymers used for the spectroscopic analysis were purified by reprecipitating them several times and drying them under high vacuum conditions ($\approx 10^{-4}$ torr) at 30°C for at least 10 hours.

Molecular weight determination. Molecular Weights of the polymers were determined by using a Vapour-Pressure osmometer and a Membrane osmometer depending on the molecular weight of the polymer.

The molecular weights lower than 20000 were conveniently determined by using a Mechrolab Vapour Pressure osmometer Model 301. A employing a non aqueous probe running at 37°C. The instrument was calibrated with a concentration series of known solute. Molecular weights were measured at three different concentrations (c.g./l) and subsequently from the slope of the $\Delta T-C$ plot compared with the slope of the calibration curve. Dioxane was used as solvent on this apparatus. The molecular weights greater than 20000 were most conveniently determined

with a High Speed Membrane osmometer 18562 A running at 30°C. Toluene was used as a solvent in this apparatus. Molecular weights were measured at three to five different concentration (c.g/l). A plot of π/C against C was constructed and from the intercept at $C=0$, the molecular weight M_n was calculated by the formula: $RT/(\pi/C)_0 = M_n$ where R = gas constant, T = absolute temperature, π = osmotic pressure; and C = concentration in grams per litre (c.g/l).

Polymerization of *N*-vinylcarbazole in chlorobenzene solution catalysed by mercuric chloride. All the polymerization experiments were carried out under high vacuum conditions ($\approx 10^{-4}$ torr). The polymerizations were carried out at 25°C with initial *N*-vinylcarbazole concentration, m_0 varying from 0.1 to 0.4 and initial mercuric chloride concentration, C_0 varying from 1.77×10^{-4} to 19.42×10^{-4} M. All the experimental data are summarised in Table 1. Figure 2 shows the conversion curves (percentage conversion of vinylcarbazole to polyvinylcarbazole) against time at constant m_0 with varying C_0 , and at constant C_0 with varying m_0 . After a short acceleration period all the reaction curves give first order plots. The polymerizations were always complete. Figure 3 shows that the first order rate constant k is increasing with the increasing in m_0 from 0.10 to 0.25 M and it is independent of it from 0.25 to 0.40 M, but it is increasing linearly with C_0 . The kinetic

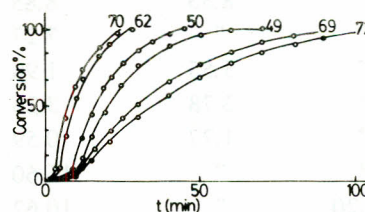


Fig. 2. The conversion curves (percentage conversion of vinylcarbazole into polyvinylcarbazole) against time, t at constant initial monomer concentration, m , with varying initial catalyst concentration, C , and at constant C , with varying m . (Table 1).

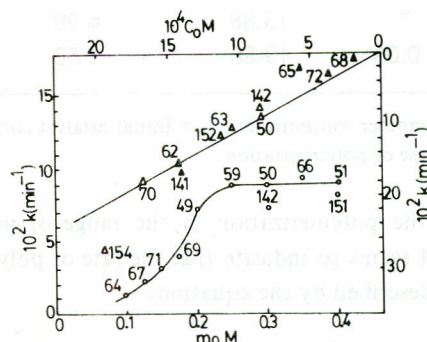


Fig. 3. The dependence of the first order rate constant k on initial monomer concentration, m , when initial catalyst concentration, $C = 8.33 \times 10^{-4}$ M (\circ) and on C , when $m = 0.3$ M (Δ). System vinylcarbazole mercuric chloride - chlorobenzene (Table 1).

Table 1. The experimental data for the polymerization of N-vinylcarbazole initiated by mercuric chloride in chlorobenzene solution carried out under vacuum (10^{-4} torr), and at 25°C .

No.	m. M	$10^4 C_0$ M	$10^2 k$ (min. $^{-1}$)	\overline{DP}
51	0.400	8.33	9.00	—
151	"	"	8.01	—
66	0.350	"	9.20	184
50	0.300	"	8.85	228
142	"	"	7.27	178
59	0.250	"	8.88	172
49	0.200	"	7.24	140
69	0.175	"	3.29	148
71	0.150	"	3.16	124
67	0.125	"	2.25	—
64	0.100	"	1.23	104
154	0.3	19.43	27.41	182
70	"	16.66	18.10	180
62	"	13.88	15.83	—
141	"	"	16.96	154
63	"	11.10	10.59	365
152	"	"	10.90	176
50	"	8.33	8.85	228
142	"	"	7.27	178
65	"	5.55	1.98	306
72	"	3.78	3.26	172
68	"	1.77	0.59	142
141	"	"	16.60	154
75	0.20	"	10.62	180
76	0.15	"	7.62	130
74	0.10	22.21	33.00	—
155	"	"	27.79	114
78	"	16.66	15.40	112
73	"	13.88	6.90	127
77	0.05	13.88	2.52	75

m. = Initial monomer concentration; c. = Initial catalyst concentration; \overline{DP} = Degree of polymerization.

analysis of the polymerization in the range of m_0 from 0.1 to 0.2 M seems to indicate that the rate of polymerization can be described by the equation:

$$-\frac{dm}{dt} = km = k_2 C_0 m_0^2 m$$

where $k = k_1 C_0$ and $k_1 = k_2 m_0^2$ and in the range from 0.25 to 0.40 M by the equation:

$$-\frac{dm}{dt} = km = k_1' C_0 m$$

where $k = k_1 C_0$. The reproducibility of the rate of polymerization was very good.

Figure 4 shows the dependence of degree of polymerization, \overline{DP} of the polymers measured at complete conversion, on m_0 and C_0 . The independence of \overline{DP} on C_0 means that chain breaking reaction with catalyst, mercuric chloride or catalyst fragments are unimportant in this system. On the other hand, the rise of \overline{DP} with m_0 implies that at least one of the chain breaking reactions must be of lower order in monomer than the propagation. The molecular weights of the polymers measured at complete conversion give a straight line for the first Mayo Plot, ($1/\overline{DP}$ against $1/m_0$) Fig. 5. Figure 6 shows the curve of \overline{DP} against percentage conversion.

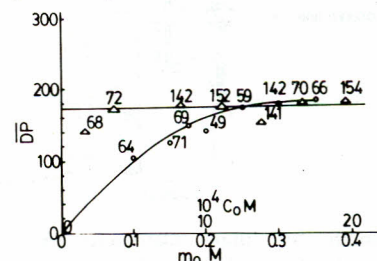


Fig. 4. The dependence of the degree of polymerization, \overline{DP} measured at complete conversion on initial monomer concentration, m , when initial catalyst concentration, $C_0 = 8.33 \times 10^{-4}$ M (—○—) and on C_0 when $m = 0.3$ M (—△—), System vinylcarbazole — mercuric chloride — chlorobenzene (Table 1):

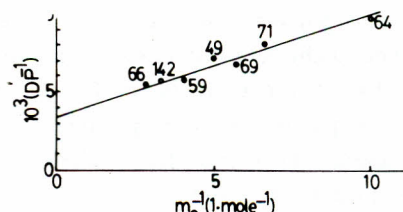


Fig. 5. The first Mayo plot ($1/\overline{DP}$ against $1/m_0$) for the degree of polymerization, measured at complete conversion. System vinylcarbazole — mercuric chloride — chlorobenzene (Table 1):

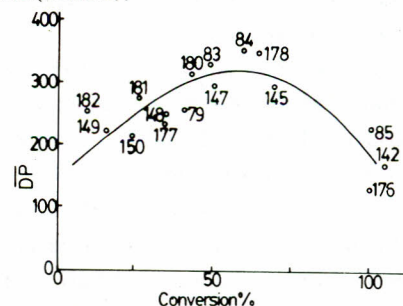


Fig. 6. The dependence of the degree of polymerization, \overline{DP} on conversion. System vinylcarbazole-mercuric chloride — chlorobenzene.

In order to support the above mentioned kinetic results, another set of polymerization experiments were carried out using m_0 varying from 0.05 to 0.30 M and C_0 varying from 8.33×10^{-4} to 22.2×10^{-4} M. The experimental results polymerization reactions increases linearly with m_0 at constant C_0 and it is increasing with increasing C_0 at constant m_0 . The rate of polymerization is described by the equation:

$$-\frac{dm}{dt} = km = k_2 m_0 C_0^3 m$$

where $k = k_1 C_0^3$ and $k_1 = k_2 m_0$

The molecular weights (\overline{DP}) of these polymers measured at complete conversion are consistent with the above mentioned results for molecular weights, as it is clear that the \overline{DP} is independent of the C_0 and increases with m_0 (Table 1).

Polymerization of N-vinylcarbazole in chlorobenzene solution catalysed by $BF_3O(C_2H_5)_2$. $BF_3O(C_2H_5)_2$ is a well known cationic catalyst, therefore, it was tried to polymerize *N*-vinylcarbazole in order to find some interesting results to compare with those previously obtained with mercuric chloride. All the polymerizations were carried out under high vacuum conditions ($\approx 10^{-4}$ torr) and at 25°C. The polymerization techniques used in this system were similar to those described for the mercuric chloride system, with the only exception that the catalyst $BF_3O(C_2H_5)_2$ was used in phials. The catalyst phial was broken magnetically in each experiment.

It was not possible to measure the chemical kinetics for the system vinylcarbazole – $BF_3O(C_2H_5)_2$, by using a dilatometer, because with the catalyst concentration used, the reactions were very fast and went to completion within a few seconds. Hence this work only deals with the molecular weights of the polymers determined after complete conversion.

Figure 7 shows the dependence of \overline{DP} on m_0 (Table 2). The increase in \overline{DP} with m_0 implies that at least one of the chain breaking reactions must be of lower order in monomer than the propagation. This behaviour is similar to that already found for the polymerizations carried out by mercuric chloride. Figure 7 also shows the first Mayo Plot, $1/\overline{DP}$ against $1/m_0$.

DISCUSSION

From the molecular weight measurements, the following conclusions concerning the propagation and chain breaking reactions are drawn:

(a) Neither catalyst, nor any species whose concentration is proportional to that of the catalyst, plays any important role in chain breaking reactions.

(b) The chain breaking with monomer is a predominant reaction and it must be of the same order in monomer as the propagation.

(c) One of the chain breaking reactions must be of lower order in monomer than the propagation. Because of the increase in molecular weight with m_0 , the propagation cannot be of zero order in monomer, therefore, the propagation must be of first order with respect to the

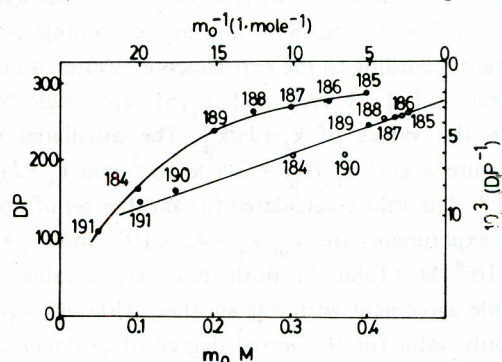


Fig. 7. The dependence of the degree of polymerization, \overline{DP} measured at complete conversion on initial monomer concentration, m . (—o—). The first Mayo plot ($1/\overline{DP}$ against $1/m$) for the degree of polymerization, measured at complete conversion (—o—). System vinylcarbazole – $BF_3O(C_2H_5)_2$ – chlorobenzene. (Table 2).

Table 2. The experimental data for the polymerization of *N*-vinylcarbazole initiated by $BF_3O(C_2H_5)_2$ in chlorobenzene solution carried out under vacuum ($\approx 10^{-4}$ torr) at 25°C.

No.	m M	$10^5 C$ M	\overline{DP}
185	0.40	6.78	293
186	0.35	6.90	280
187	0.30	6.75	272
188	0.25	6.75	267
189	0.20	6.76	239
190	0.15	6.77	161
168	0.10	9.40	344
169	"	9.41	367
184	"	6.84	162
192	"	4.25	119
193	"	2.73	104
191	0.05	6.80	108

m = Initial monomer concentration; c = Initial catalyst concentration; \overline{DP} = Degree of polymerization.

monomer. If the propagation is of first order in monomer, then according to (b) the transfer or termination with monomer must be of the same order. It should be noted that the termination by monomer must be unimportant, because all the polymerizations were complete. The values of k_m/k_p and $(k_t + J)/k_p$ are calculated from the first Mayo Plot (Figure 5) using the equation:

$$\frac{1}{DP} = \frac{k_m}{k_p} + \frac{1}{k_p m_0} (k_t + k_c [C] + k_a [A] + k_s [S] + J) \quad (1)$$

The chain breaking with catalyst, co-catalyst, co-catalyst (not used) and with solvent are unimportant in this system according to the experimental results, therefore, the terms $k_c [C]$, $k_a [A]$ and $k_s [S]$ are neglected to calculate the values of $(k_t + J)/k_p$. The calculated values from Figure 5 are: $k_m/k_p = 3.5 \times 10^{-3}$ and $(k_t + J)/k_p = 6.5 \times 10^{-4}$. The values calculated for another set of polymerization experiments are: $k_m/k_p = 4.2 \times 10^{-3}$ and $(k_t + J)/k_p = 4.5 \times 10^{-4}$ M. (Table 1). Both these sets of values are in reasonable agreement with one another. Although equation (1) is only valid for the initial degree of polymerization, the values of k_m/k_p and $(k_t + J)/k_p$ obtained by using this equation give the approximate values of these chain breaking coefficients. These results demonstrate that the chain breaking reaction with monomer is dominant. The fact that straight lines were obtained for first order Mayo Plots confirm the suggested chain breaking mechanisms. No conclusion can be made about the term $(k_t + J)/k_p$ which describes chain breaking by unimolecular termination (k_t) and by substances whose concentration is practically constant through out the reaction, of which the residual water may be an example. The values calculated for k_m/k_p and $(k_t + J)/k_p$ are 2.6×10^{-3} and 3.6×10^{-4} M, respectively for the system N-vinylcarbazole - $(C_2H_5)_2 O BF_3$ (Figure 7). These results may indicate that the chain breaking reactions with $(C_2H_5)_2 O BF_3$ as a catalyst are relatively less important with respect to the propagation than in the mercuric chloride system, although the differences are really too small to permit firm conclusions. The analysis of the results show that in all the range of $(C_2H_5)_2 O BF_3$ concentration studied the \overline{DP} is increasing with C. This fact can be explained as previously suggested by P.H. Plesch, [14] as due to the presence of a chain breaking agent G, which can form a complex with the catalyst and assuming that both this agent and the complex behave as chain breaking agents.

The dependence of molecular weight on the percentage conversion (Figure 6) seems to indicate that the initiation is faster than the growth. In such a system the average

degree of polymerization \overline{DP} is shown by the equation (2) [15],

$$\overline{DP} = \frac{(m_0 - m)}{\alpha C_0 + (k_z/k_p) Z \ln (m_0/m)} \quad (2)$$

Equation (2) implies that the degree of polymerization increases with the conversion to a limiting value and thereafter it decreases again. Owing to the fact that this is in agreement with the results I obtained, therefore, I have applied this equation to analyze the dependence of molecular weight on conversion. Figure 8 shows the plot of

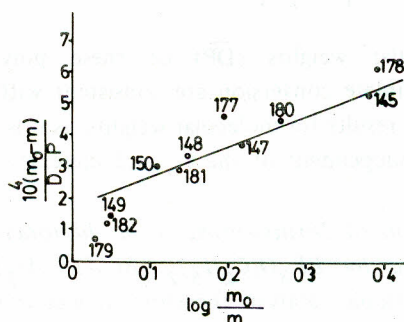
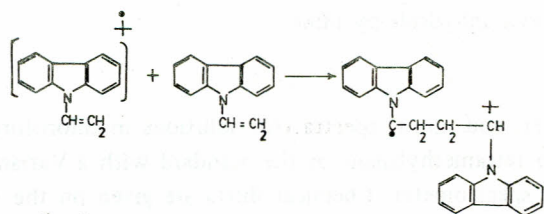
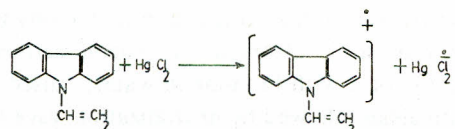


Fig. 8. The plot of $(m_0 - m)/P$ against $\log (m_0/m)$ according to equation 2 [15].

$(m_0 - m)/DP$ against $\log (m_0/m)$. The values obtained from this plot are $(k_z/k_p)Z = 4.2 \times 10^{-4}$ M and $\alpha = 0.23$ (the values of $(m_0 - m)/\overline{DP}$ and $\log m_0/m$ are calculated from the results of Figure 6). As it is clear that the polymerization of N-vinylcarbazole initiated with mercuric chloride in chlorobenzene solution obeys the rules of equation (2), therefore, it can be concluded that it is a step-wise polymerization.

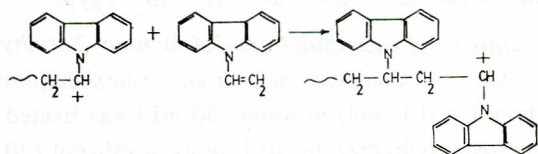
Kinetics and mechanism. All the polymerization reactions give first order plots after a short acceleration period. No doubt, the polymerization systems studied appear rather intractable from a kinetic point of view, since in different ranges of catalyst and monomer concentrations different equations are required to describe the dependence of the rate of polymerization on the initial monomer and catalyst concentrations. But it can be suggested tentatively, that this behaviour may be due to the great complexity of the systems studied and in particular to the possibility that the propagation can take place by both radical and cationic mechanisms. Depending on the conditions, mainly on the ranges of initial monomer and catalyst concentrations, these two types of propagating ends may be of different relative importance; thus altering the overall results. Therefore, the following reactions are to be considered only as possible routes for the polymerization studied throughout the present work because they are not in conflict with the experimental results.

Initiation. It is believed that a charge transfer complex between N-vinylcarbazole and mercuric chloride is formed. Such a complex, under favourable conditions, can dissociate into radical-ions. The radical-cation carrying N-vinylcarbazole thus formed, under favourable conditions, can react with another molecule of N-vinylcarbazole to dissociate radical and cation ends for propagation. I would like to emphasize here that neither the catalyst nor the solvent have to be considered as strong inhibitors for a radical polymerization in this work.

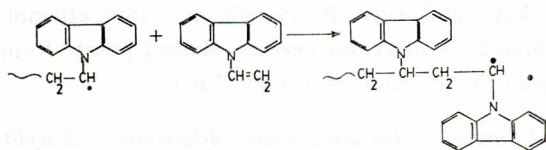


Propagation:

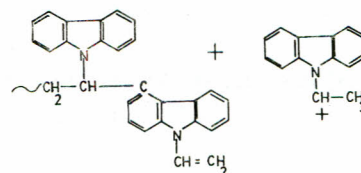
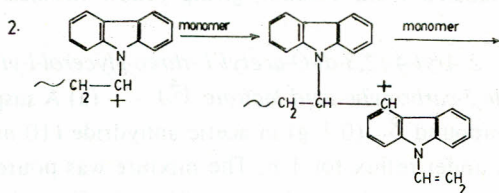
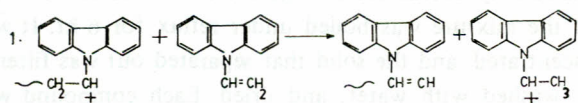
Propagation by cationic end:



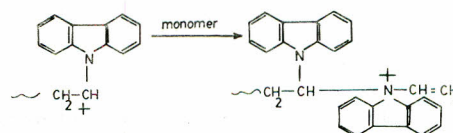
Propagation by radical end:



The chain-transfer with monomer may be explained in two different ways as follows:



Termination with monomer may be explained as follows



The above mentioned schemes represent the obvious possibilities for the polymerization of N-vinylcarbazole initiated by mercuric chloride in chlorobenzene because they are not in conflict with the experimental results.

Acknowledgement. The author is grateful to Professor H.D. Springall in whose Department this work was originally started.

REFERENCES

1. J. Pac and P.H. Plesch, *Polymer (London)*, **8**, 237, (1967).
2. C.H. Wang, *Chemistry and Industry*, **751**, (1964).
3. S. Tazuke, K. Nakagawa and S. Okamura, *Polymer letters* **3**, 923, (1965).
4. S. Tazuke, T.B. Tjoa and S. Okamura, *J. Polym. Sci. Part A-1*, **5**, 1911, (1967).
5. J.M. Rooney, *J. Polym. Sci., Symposium No. 56*, **47**, (1976).
6. J.M. Rooney, D.R. Squire and V.T. Stannett, *J. Polym. Sci; Poly. Chem. ed*, **14**, 1877, (1976).
7. J.M. Rooney, *Makromol. Chem*; **179**, 165, (1978).
8. M. Biswas and G.C. Mishra, *Makromol. Chem.* **182**, 261, (1980).
9. M. Biswas and G.C. Mishra, *Polymer*, **22**, 1319, (1981).
10. M. Biswas and G.C. Mishra, *J. Polym. Sci; Polym. Chem. Ed*; **19**, 3081, (1981).
11. Copenhaver, Bigelow, *Acetylene and Carbon Monoxide Chemistry* (Reinhold, New York, 1949).
12. H.S. Booth and D.R. Martin, *Boron Trifluoride and its Derivatives USA*, (1).
13. R.P. Rutherford, *Chemistry and Industry*, 1614, (1962).
14. P.H. Plesch, *J. Chem. Soc*; **16**, 104, (1964).
15. T. Kagiya, M. Izu and K. Fukui, *Bull. Chem. Sic; Japan*, **40**, 1045, (1967).