Technology Section

EFFECT OF ADDITIVES ON THE POLYMERIZATION OF N-VINYLCARBAZOLE INITIATED BY MERCURIC CHLORIDE IN CHLOROBENZENE SOLUTION

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The effect of different additives on the rate of polymerization of *N*-vinylcarbazole initiated by mercuric chloride in chlorbenzene and on the molecular weight of the polymers was studied. The chain-transfer coefficients with monomer, water and phenylacetate were found to be much higher than those with quinone and anthracene.

By spectroscopic analysis showed no formation of a complex between monomer and catalyst. The oligomers obtained in the presence of esters and water and chain-transfer agents showed the absorptions of carbonyl and hydroxyl groups respectively, indicating incorporation of the chain-transfer agent. All mechanisms put forward were in agreement with the experimental results.

Key words: Polymerization, Mercuric Chloride, Solution.

INTRODUCTION

It has been reported by L.P. Ellinger (1-4) that the polymerization of *N*-vinylcarbazole by free radical initiators, especially azobisisobutyronitrile, yields polymers of higher molecular weights than by thermal polymerization. The polymerization was retarded and the molecular weight of the polymer was lowered by added anthracene comparable to the initiator's concentration, but this effect soon showed saturation at higher anthracene concentrations. On the other hand, phenanthrene has a slight inhibiting effect which increases with concentration, the polymerization being almost completely inhibited at very high phenanthrene concentrations. Ellinger explained the effect of anthracene and phenanthrene on *N*-vinylcarbazole polymerization in terms of the formation of an intermediate complex between the aromatic hydrocarbon and the growing polymer chain.

Plesch *et al.* [5] studied the effect of water, a cation inhibitor, on the polymerization of *N*-vinylcarbazole catalysed by tetranitrobenzene in nitrobenzene solution. They concluded from their results that water did not play an active role as monomer itself in the chain breaking reaction in spite of the fact that the polymerization of *N*-vinylcarbazole by tetranitrobenzene was supposed to be cationic in nature.

This work was undertaken to clarify the fate of radical-cation produced by the action of oxidizing metal salt,

mercuric chloride on *N*-vinylcarbazole. The polymerization of *N*-vinylcarbazole initiated by mercuric chloride in chlorobenzene solution were carried out with and without added well known radical inhibitors such as quinone and anthracene and cation inhibitors such as water and phenylacetate and the results are presented here.

MATERIALS AND METHODS

Phenylacetate . Phenylacetate (BDH Laboratory Reagent), graded 99% ester by saponification was further purified by successively washing with a solution saturated with $NaHCO_3$ and NaCl and dried. It was then fractionally distilled twice and a middle fraction was collected over silica gel in a flask equipped with a break seal. This flask containing phenylacetate was then joined to the high vacuum line through a metal valve for further use in polymerization experiments.

Benzylacetate, benzylbenzoate, ethylphenylacetate and ethylbenzoate: The commercial products of benzylacetate benzylbenzoate, ethylphenylacetate and ethylbenzoate (BDH Laboratory Reagents) were purified, following the same procedure as described for phenylacetate.

Anthracene. The commercial anthracene (BDH Laboratory Reagent) was recrystallized from chlorobenzene. The anthracene thus recrystallized was dried in a vacuum oven at 40° and stored in an anhydrous atmosphere. Just before each polymerization experiement, the anthracene was thoroughly dried in the polymerization device under high vacuum conditions ($\cong 10^{-4}$ torr) for three hr.

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Quinone. The commercial quinone (BDH Laboratory Reagent) was three times recrystallized from *n*-hexane. The recrystallized quinone was dried and stored as mentioned for anthracene.

Preparation of water phials. Distilled water freed from carbon dioxide by boiling was used to prepare the water phials using the procedure described by Biddulph *et al.* [6].

Infrared spectra. The infrared spectra were run on Perkin-Elmer Model 257 Spectrophotometer. The spectra were measured on polymer film deposited on sodium chloride plates from benzene solution.

RESULTS

(1) *Effect of water on the polymerization of N-vinylcarbazole initiated by mercuric chloride in chlorobenzene solution.* The effect of added water in the polymerization of N-vinylcarbazole initiated by mercuric chloride in chlorobenzene solution were carried out under high vacuum conditions ($\cong 10^{-4}$ torr) at 25°. The dilatometer was used to measure the kinetics of polymerizations as described in this author's earlier paper [7].

The polymerization experiments were carried out using initial N-vinylcarbazole concentration, $m_o = 0.3$ M and initial mercuric chloride concentration, $C_o = 8.33 \times 10^{-4}$M and added water concentration, W_o was varied from 4.16×10^{-4} to 5.27×10^{-3}M. Fig. 1 shows the effect of added water on the first order rate constant, k (Table 1). The rate constant falls asymptotically towards a rather low value over the added water concentration studied.

Fig. 1 shows the decrease of molecular weight $\overline{DP}$ with initial added water concentration. This fact indicates that chain breaking with water is very important.

(ii) *Effect of phenylacetate on the polymerization of N-vinylcarbazole initiated by mercuric chloride in chlorobenzene solution.* The polymerizations of N-vinylcarbazole catalysed by mercuric chloride in chlorobenzene solution with added phenylacetate, a chain transfer agent, were carried out under high vacuum conditions ($\cong 10^{-4}$ torr) to establish its effect on the rate of polymerization. In these polymerization experiments, N-vinylcarbazole ($m_o = 0.3$M) and mercuric chloride ($C_o = 8.33 \times 10^{-4}$M) concentrations were kept constant while the concentration of phenylacetate was varied from 0.05 to 1.0. All the experiments were carried out at 25°.

Fig. 2 shows the dependence of the first order rate constant, k, on initial phenylacetate concentration (E_o) (Table 1). The curve exhibits a minimum at about $E_o = 0.07$M. The k, increases rapidly from $E_o = 0.07$ M to 0.22M and beyond that it increases slightly with the increase in concentration of phenylacetate.

Fig. 2 shows the effect of E_o on $\overline{DP}$ of polymers measured at complete conversion. The behaviour of phenylacetate with respect to $\overline{DP}$ does indicate its importance as a chain breaking agent in the polymerization system studied. The minimum found in the polymerization rate constant, k - phenylacetate concentration, E_o graph is supported by the degree of polymerization, $\overline{DP}$ phenylacetate,

Table 1. Experimental data for the polymerization of N-vinylcarbazole initiated by mericuric chloride in chlorbenzene solution with added water, phenylacetate, anthracene and quinone carried out under vacuum (10^{-4} torr) at 25°.
Initial mercuric chloride concentration = 8.33×10^{-4}M.

No.	$10^4 W_o$ M	E_o M	$10^4 An_o$ M	$10^4 Q_o$ M	$10^2 k$ (min.$^{-1}$)	$\overline{DP}$
158	52.71	—	—	—	4.13	28
157	37.65	—	—	—	3.37	36
156	22.59	—	—	—	4.89	62
88	16.66	—	—	—	5.07	83
89	8.33	—	—	—	5.56	133
86	4.16	—	—	—	7.44	166
179	—	—	—	—	8.03	203
161	—	0.900	—	—	14.94	42
164	—	0.700	—	—	13.43	64
162	—	0.500	—	—	11.51	100
144	—	0.250	—	—	10.74	160
137	—	0.250	—	—	11.21	231
163	—	0.200	—	—	9.21	178
138	—	0.125	—	—	5.83	201
160	—	0.100	—	—	5.52	218
139	—	0.050	—	—	5.18	242
203	—	—	22.50	—	2.62	100
202	—	—	17.50	—	3.11	130
96	—	—	12.49	—	3.83	172
93	—	—	8.33	—	4.60	212
95	—	—	4.16	—	5.75	245
201	—	—	2.10	—	7.12	250
205	—	—	—	20.60	3.75	137
90	—	—	—	16.66	4.10	182
91	—	—	—	8.33	5.90	196
92	—	—	—	4.16	6.90	209
204	—	—	—	1.90	7.55	215

W_o = Initial added water concentration.
E_o = Initial added phenylacetate concentration.
An_o = Initial added anthracene concentration.
Q_o = Initial added quinone concentration.
$\overline{DP}$ = Degree of polymerization.

Table 2. Experimental data for the preparation of *N*-vinylcarbazole oligomers in the presence of chain transfer agents catalysed by mercuric chloride, carried out in an open systems at 25°.

No.	m_0 M	$10^4 C_0$ M	CTA	CTA M	Solvent	$\overline{DP}$	$\overline{DP}$	>C = 0 Absorption (Wave number, cm^{-1})	− OH Absorption (Wave number, cm^{-1})
97	0.3	8.33	Ph−Act.	1.5	φcl	12	4	1725	3420
98	0.15	”	”	2.0	”	9	4	1725	3410
106	0.30	”	Benz−Act	1.5	”	7	−	1723	3415
112	0.10	”	”	1.33	”	6	−	1725	3410
103	0.30	”	Eth-Ph-Act.	1.5	”	12	−	−	−
120	0.15	16.60	−	−	Benz-Act.	8	−	1725	3410
114	0.50	8.33	−	−	Benz-Bent.	8	5	1722 & 1380	3420
122	0.20	33.20	−	−	Eth-Ph-Act.	11	7	1724	3415

Here m_0 = initial *N*-vinylcarbazole concentration, C_0 = initial mercuric chloride concentration, CTA = chain-transfer agent, $\overline{DP}$ = degree of polymerization, Ph-Act. = Phenylacetate, ϕol = chlorobenzene, Benz-Act. = benzylacetate, Eth-Ph-Act. = ethylphenylacetate, and Benz-Bent. = benzylbenzoate.

E_0 graph (Fig. 2) which shows a maximum at approximately the same concentration range of phenylacetate.

(iii) *Effect of quinone and anthracene on the polymerization of N-vinylcarbazole initiated by mercuric chloride in chlorobenzene solution.* The polymerization of *N*-vinylcarbazole initiated by mercuric chloride in chlorobenzene solution was carried out with added quinone and anthracene, the radical scavengers using the same conditions and techniques as described for the polymerization experiments carried out with added water and phenylacetate, to establish their effect on the polymerization rate constant, k, and degree of polymerization, $\overline{DP}$ · In these polymerization experiments the concentrations of *N*-vinylcarbazole (m_0 = 0.3M) and mercuric chloride (C_0 = 8.33 x 10^{-4}M) were kept constant whereas the concentrations of quinone (Q_0) and anthracene (An_0) were varied from 1.9 x 10^{-4} to 20.6 x 10^{-4}M and 2.1 x 10^{-4} to 22.5 x 10^{-4}M, respectively (Table 1). Fig. 3 shows the effect of initial quinone (Q_0) and initial anthracene (An_0) concentrations on the first order polymerization rate constant, k. The rate constant, k, appears to decrease asymptotically towards a rather low value over the concentrations range studied for these radical scavengers. Fig. 3 shows a slight increase of the molecular weight ($\overline{DP}$) at a relatively low concentration and then decreases with respect to the added quinone and anthracene concentrations.

(iv) *Effect of phenylacetate on the polymerization of N-vinylcarbazole initiated by $BF_3O(C_2H_5)_2$ in chlorobenzene solution.* The polymerization of *N*-vinylcarbazole initiated by $BF_3O(C_2H_5)_2$ in chlorobenzene solution were carried out with added phenylacetate at 25° and under
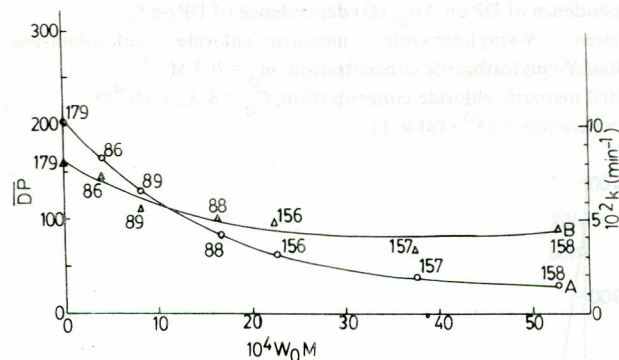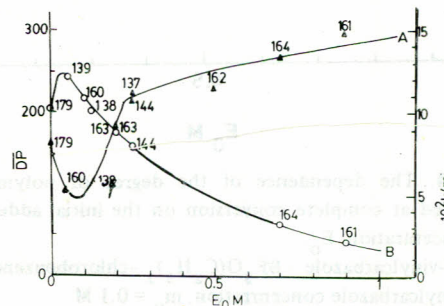

Fig. 1. The dependence of the first-order rate constant, k and the degree of polymerization, $\overline{DP}$ measured at complete conversion on the initial added water concentration, W_0. (A) dependence of k on W_0, (B) dependence of $\overline{DP}$ on Wo. System = *N*-vinylcarbazole - mercuric chloride - chlorobenzene. Initial *N*-vinylcarbazole concentration, m_0 = 0.3 M. Initial mercuric chloride concentration, C_0 = 8.33 x 10^{-4}M Temperature = 25° (Table 1).

Fig. 2. The dependence of the first-order rate constant, k and the degree of polymerization, $\overline{DP}$ measured at complete conversion on the initial added phenylacetate concentration, E_0 (A) dependence of k on E_0, (B) dependence of $\overline{DP}$ on E_0. System : *N*-vinylcarbazole - mercuric chloride - Chlorobenzene. Initial *N*-vinylcarbazole concentration, m_0 = 0.3M. Initial mercuric chloride concentration, C_0 = 8.33 x 10^{-4}M. Temperature = 25° (Table 1).
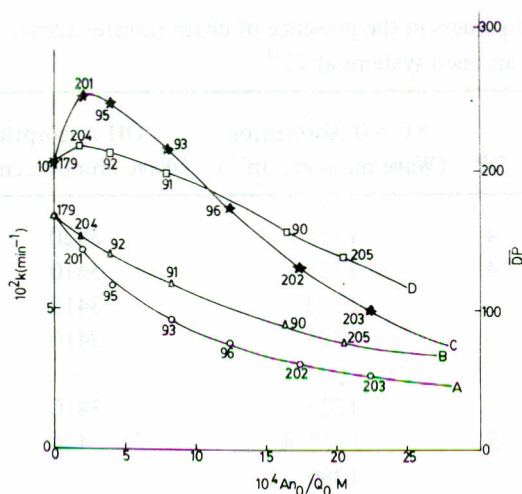
Fig. 3. The dependence of the first-order rate constant, k and the degree of polymerization, DP measured at complete conversion on th initial added anthracene, An_o/quinone, Q_o concentration. (A) dependence of k on An_o, (B) dependence of k on Q_o, (C) dependence of DP on An_o, (D) dependence of DP on Q_o
System : N-vinylcarbazole - mercuric chloride - chlorobenzene.
Initial N-vinylcarbazole concentration, m_o = 0.3 M
Initial mercuric chloride concentration, C_o = 8.33 x 10^{-4}M.
Temperature = 25° (Table 1).
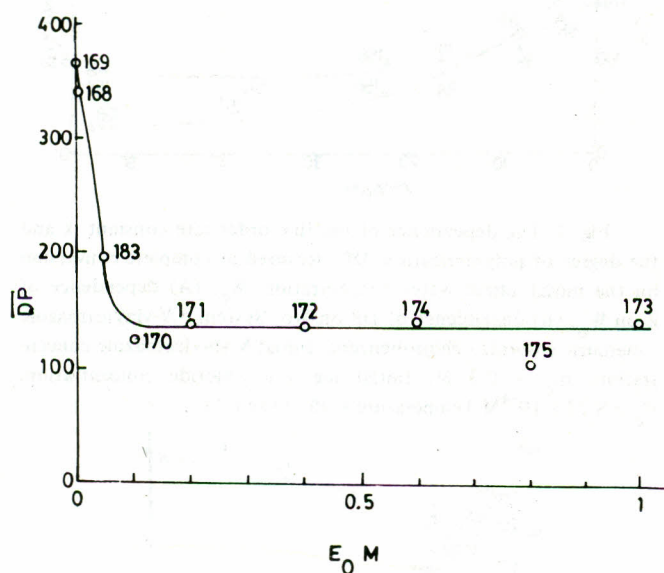
Fig. 4. The dependence of the degree of polymerization, DP measured at complete conversion on the initial added phenylacetate concentration, E_o.
System : N-vinylcarbazole $-BF_3O(C_2H_5)_2$ -chlorobenzene.
Initial N-vinylcarbazole concenrration, m_o = 0.1 M
Initial $BF_3O(C_2H_5)_2$ concentration, C_o = 9.5 x 10^{-5}M.
Temperature = 25°

high vacuum. conditions ($\cong 10^{-4}$torr). As mentioned in my previous paper [7] it was not possible to measure the polymerization kinetics for this system, because the reac-

tions were rapid to measure using the available techniques. Therefore, only polymers were recovered after the reaction was stopped and their molecular weights were measured. The concentrations of N-vinylcarbazole, (m_o = 0.1M) and $BF_3O(C_2H_5)_2$ ($C_o \cong 9.5$ x 10^{-4}M) were kept constant whereas the concentration of phenylacetate, (E_o) varied from 0.05 to 1.0 M. in these experiments. Fig. 4 shows the degree of polymerization ($\overline{DP}$) of the polymers as a function of the initial concentration of phenylacetate, E_o. This behaviour is very peculiar, because it seems to lead

to the conclusion, according to the theoretical treatment given by P.H. Plesch [8] that phenylacetate itself is not a chain breaker or is a very weak chain breaker, but can form an active chain breaking agent by combination with something present in the sytem. In the N-vinylcarbazole mercuric chloride system, phenylacetate proved to be a very active chain breaking agent, reducing the $\overline{DP}$ to very small values (see Fig. 2). The different behaviour of phenylacetate with respect to N-vinylcarbazole - mercuric chloride and N-vinylcarbazole-$BF_3O(C_2H_5)_2$ systems suggests that the activity of phenylacetate as a chain breaking agent is strictly dependent on the nature of the catalyst. These findings agree to the fact that if a catalyst is so active as to give very high values for the propagation costant then the influence of the chain breaking agent will become proportionally less important. These results have demonstrated that $BF_3O(C_2H_5)_2$ gives very high rates of polymerization and this can probably explain why in this case phenylacetate has a negligible activity as a chain breaking agent.

(v) *Identification of terminal groups of N-vinylcarbazole oligomers by IR spectroscopy.* In order to gain some more information about the polymerization mechanism of N-vinylcarbazole initiated by mercuric chloride, IR spectroscopic techniques were employed to determine the nature of terminal groups in N-vinylcarbazole oligomers prepared using various well known chain-transfer agents.

A group of esters was selected with respect to their activity as chain-transfer agent and their functional groups. All oligomerization experiments were carried out in open system at 25°. In some experiments the ester was used as chain-transfer agent as well as a medium of oligomerization. The reaction mixture was always quenched with methanol after 20 hr. The oligomers thus obtained were then fractionated using propanol or acetonitrile: methylene dichloride mixture (5:1) as a solvent to obtain oligomers of relatively low molecular weight. These oligomers were purified and dried under high vacuum conditions ($\cong 10^{-4}$ torr) for six hours and then analyzed by IR spectroscopically. All the experimental data is given in Table 2.

The absorption for OH group in the IR spectra of the oligomers seems to indicate that water was present in small amount in the reaction mixtures (open system technique). It means that water as well as esters behaved as an active chain-transfer agents in the oligomerization experiments (Table 2). This was also proved by the polymerization experiments carreid out under high vacuum conditions with and without added water and phenylacetate respectively. It is also worth mentioning here that the oligomers fractionated by propanol as well as by acetonitrile-methylene chloride mixture give the identical IR spectra. It could be concluded that the OH group as well as the carbonyl group present in all the IR spectra are derived from the oligomers. All the above mentioned experiments demonstrate that it was not possible to obtain very low molecular weight oligomers (dimer, trimer) with all the chain transfer agents used. Therefore, the oligomers were fractionated and thus oligomers of relatively low molecular weight were isolated. Nevertheless, all NMR spectra of the oligomers including those of the lower molecular weight did not give good resolution and proved to be useless for drawing any firm conclusions with respect to their structure.

DISCUSSION

The decrease in molecular weights, $\overline{DP}$ of the polymers recovered from the polymerization experiments of *N*-vinylcarbazole initiated by mercuric chloride in chlorobenzene solution with added water and phenylacetate suggest that both water and phenylacetate act as strong chain-transfer agents in this polymerization system. Therefore, in order to calculate the chain breaking constant with respect to water/phenylacetate, a mathematical equation was derived as follows:

Assuming

Rate of propagation, $R_p = k_p m^* m$

where m^* and m are concentrations of consumed and residue monomer, respectively and

Rate of Termination, $R_t = k'_m m^* m + k_w W m^*$

where W is the concentration of added water.

$\therefore$ Number of repeated monomer units, $\overline{N} = \dfrac{k_p m}{k'_m m + k_w W}$

$$\overline{P} = \int dm / \int \frac{1}{\overline{P}} \, dm \quad \dots \dots \dots (1)$$

where $\overline{P} = N + 1$ (unity is not ignored due to low degree of polymerization). If w is constant, the intergrted form of the equation (1) from m_o to m gives equation 2 :

$$\frac{1}{\overline{P}} = \frac{K'_m}{k'_m + k_p} + \frac{k_p k_w W}{(k'_m + k_p)2} \cdot \frac{1}{(m - m_o)}$$

$$\text{In} \quad \frac{k_w W + (k'_w + kp)m}{k_w W + (k'_m + k_p)m_o} \quad \dots \dots \dots (2)$$

Equation (2) describes the change of degree of polymerization, $\overline{P}$ with conversion. In order to use this equation for degree of polymerization at complete conversion, $\overline{DP}$ it is simplified by assuming that

$$k_p \gg k'_m \text{ and } k_p m_o \gg k_w W$$

Taking m = 0, equation (2) reduces to equation (3)

$$\frac{1}{\overline{DP}} = \frac{k'_m}{k_p} - \frac{k_w W}{k_p} \frac{1}{m_o} \text{In} \frac{k_w W}{k_p m_o} \quad \dots \dots (3)$$

To simplify the matter the values of 1/DP are plotted against W, which gives a curve (Fig. 5). The slopes drawn at different values of W on this curve give the values of d(1/DP)/dw at those values of w. The values of d(1/DP)/dw are plooted against log w, (Fig. 6). This gives the values of k_w/k_p according to equation (4), which is a differential form of equation (3) with respect to W when m_o is a constant (m_o is constant in all the experients with added water).

$$d(1/DP)/d_w = \text{constant} - (k_w/k_p m_o) \text{ In } w \text{ or}$$
$$d(1/DP)/d_w = \text{constant} - 2.303 \frac{k_w}{k_p m_o} \log w \quad \dots \dots (4)$$

The values of k_w/k_p as calcullated from Fig. 6 is equal to 0.45.

Phenylacetate is also used as a chain-transfer agent in this work and the same procedure is adopted to evaluate the chain breaking constant with respect to phenylacetate as adopted to determine the chain breaking constant with water. The symbol E is used in equation (4) instead of w.

Fig. 7 shows the curve drawn by plotting $1/\overline{DP}$ against E_o and Fig. 8 shows the plot of $d(1/\overline{DP})/dE_o$ against log E_o. The value calculated from Fig.8 for K_E/k_p is 7.6×10^{-3}.

Polymerization in the presence of radical scavengers, quinone and anthracene, showed a slight decrease in the molecular weight of the polymers with an increase in initial concentration of quinone and anthracene. But no attempts have been made to evaluate the chain breaking constants with respect to these chain transfer agents, mainly due to insufficient data.

Kinetics and mechanisms. Since in the system chlorobenzene-mercuric chloride the radical function may not be deactivated at once as is believed to happen in the
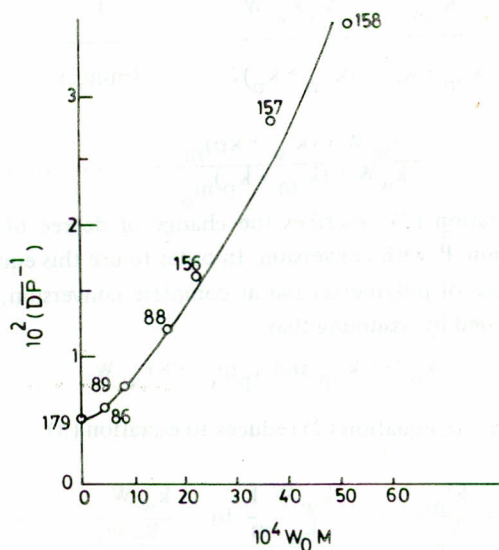
Fig. 5. The dependence of the inverse degree of polymerization -1/DP-1 on the initial added water concentration W_0 (W in equation 3). System: N-vinylcarbazole-mercuric chloride-chlorobenzene.
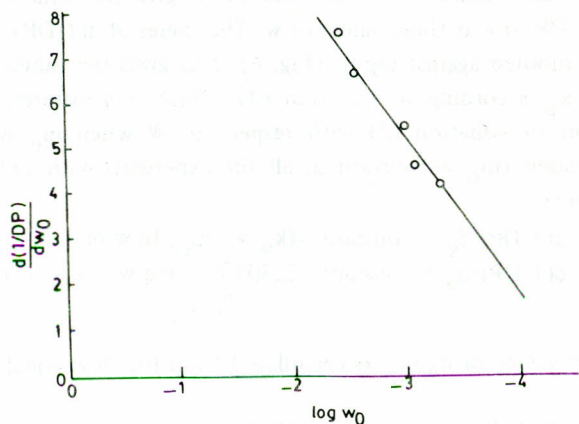
Fig. 6. The dependence of the $d(1/DP)/dw_0$ on logarithm of the initial added water concentration, W_0 (W in equation 4). System: N-vinylcarbazole-mercuric chloride-chlorobenzene.
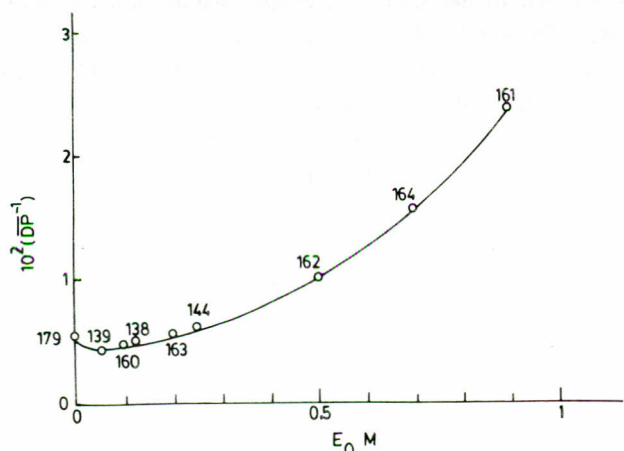
Fig. 7. The dependence of the inverse degree of polymerization, -1/DP-1 on the initial added phenylacetate concentration E_0 (E_0 instead of W in equation 3).
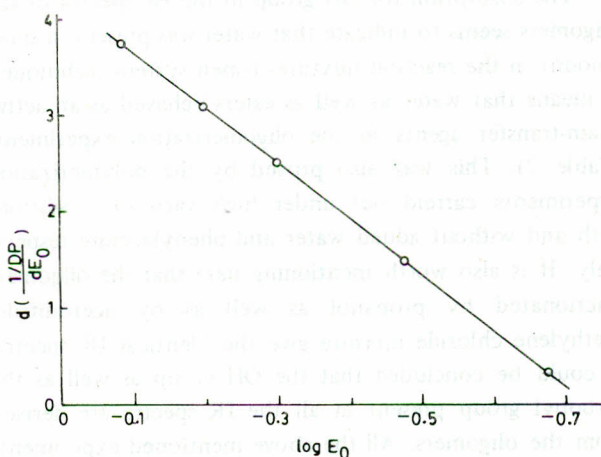
Fig. 8. The dependence of the $d(1/DP)d E_0$ on logarithm of the initial added phenylacetate concentration, E_0 (E_0 instead of W in equation 4).

System: N-vinylcarbazole- mercuric chloride - chlorobenzene.

nitrobenzene-tetranitromethane system [5] a propagation by a radical mechanism may be considered. Such a mechanism is also indicated by the decrease in the rate of polymerization and of the $\overline{DP}$ by radical inhibitor such as quinone or anthracene and by the fact that when the amount of water is increased, the rate tends to a limiting value which is different from zero. Another circumstantial evidence supporting a radical propagation is furnished by the experiments carried out in the presence of phenylacetate and other chain-transfer agents. In these experiments it was not possible to get oligomers of very low degree of polymerization, possibly because of the uncontrolled radical propagation. The fate of the radical function may be deactivated sooner or later in different ways, by combination with another chain to give a bication, by interaction with any radical scavenger or by neutralization on the walls of the reaction vessel.

Neutralization of radical end
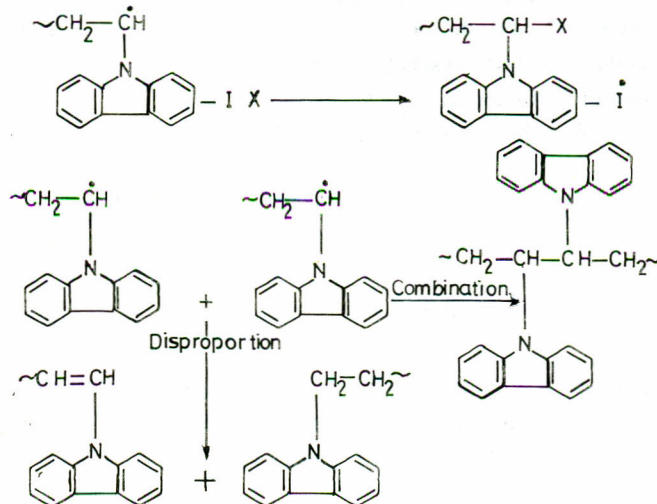
Here IX represents a molecule of radical inhibitor (intentionally added or an impurity), and I' is a radical too stable to propagate the reaction; X may be a hydrogen atom.

The propagation by the radical end is of course related to the question wheather the neutralization reactions are happening very rapidly, just after mixing the monomer and catalyst or wheather they are quite slow. In other words, the longer the life of the active radical, the more likely is the propagation by a radical.

Chain breaking reactions for the cationic end : The experimental results obtained by carrying out the polymerizations in the presence of water and esters can be interpreted by assuming that these chain-transfer agents interfere only with the cationic end of the chains:

Chain transfer with water

~CH$_2$-CH + HOH → ~CH$_2$-CH-OH + CH$_3$-CH

Chain transfer with ester
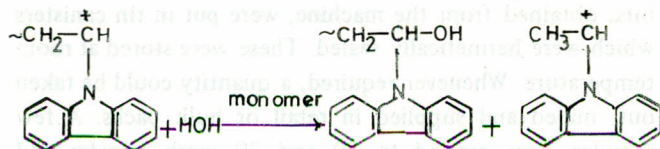
~CH$_2$-CH + RCOOR' → ~CH$_2$-CH-OR' + CH-CH$_2$C-R'
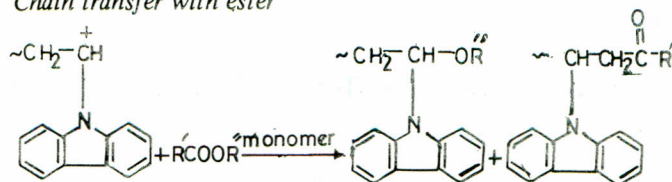
These reactions are in agreement with the evidence obtained by spectroscopic analysis of the oligomers prepared in open system, in the presence of intentionally added chain-transfer agents. As previously described, these oligomers show the presence of carbonyl an hydroxyl groups which indicate the incorporation of the chain-transfer agents (ester or/and water) into the oligomer molecule.

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