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NEUTRAL SALT EFFECT IN THE POLYMERIZATION OF *N*-VINYLCARBAZOLE BY TRITYL CATION IN NITROBENZENE†

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ABSTRACT

The polymerization of *N*-vinylcarbazole in the presence of the $PhCH_2(CH_3)_3N^+SbF_6^-$ salt has been studied at different temperatures (293 and 308 K) in nitrobenzene. An increase in k_p at high $[salt]/[I]_0$ ratios has been observed which can be explained by the strong interactions of the nitrobenzene solvent with the monomer and the propagating species.

INTRODUCTION

One of the main problems in cationic polymerization is the ionic association of the propagating species. The apparent reactivity of a monomer cannot be determined without considering the possible effects of initiator and solvent, which determine the nature of the propagating species. This is a decisive factor for several kinetic parameters such as propagation and termination, transfer rate constants, reactivity ratios in copolymerization, etc.

The study of the addition of inner salts on the polymerization process gives information about the nature of the propagating species. Several authors [1–4] found that inner salts in cationic polymerization of vinyl monomers affect the

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†In memory of Prof. G. M. Guzmán.

polymerization rate and the molecular weight. These effects are more important in low polarity media and can be attributed to the following factors:

1. Effects on the ionic strength
2. Counterion exchange
3. Participation in the polymerization as a cocatalyst
4. Participation in termination reactions

In previous work [5] the polymerization of *N*-vinylcarbazole has been studied in nitrobenzene at 293 K using trityl salts as initiators. These initiators are stable and easy to use because they do not need a cocatalyst. It was concluded from kinetic measurements that termination reactions were not determinant and the propagation rate constant was independent of the initiator and the salt counterion initial concentrations. Several experiments were carried out in the presence of $PhCH_2(CH_3)_3N^+$-SbF_6^- salt at concentrations slightly higher than the initiator concentration. These studies suggested that the propagation reaction took place by a free ion mechanism.

We also investigated [6] the strong interaction that nitrobenzene has with the *N*-vinylcarbazole and the propagating cation respectively. The values of molar absorption were determined in each case. In consequence, the predominant species in the reaction media are unpaired propagating cations, Pn^+, which interact strongly with solvent molecules. Recently [7], this behavior has been described in other systems using nitrobenzene as solvent.

The purpose of this work was to study the influence of the $PhCH_2(CH_3)_3N^+$ SbF_6^- salt at high [salt]/[initiator] ratios, at 293 and 308 K, in the *N*-vinylcarbazole polymerization process using nitrobenzene as solvent. These results are compared with those obtained from a salt-free system studied at 308 K.

EXPERIMENTAL

The monomer *N*-vinylcarbazole (Fluka Purum) and the initiator, Ph_3C^+-$SbCl_6^-$ (Aldrich), were purified and stored as described previously [8]. The salt, $PhCH_2(CH_3)_3N^+SbF_6^-$ (Aldrich), was recrystallized from methylene dichloride and stored under dry N_2. The solvent, nitrobenzene (Carlo Erba), was distilled under reduced pressure in the presence of calcium hydride.

The polymerization reactions were carried out under dry N_2. They were followed by adiabatic calorimetry as described in Ref. 8.

The molecular weights of the samples were determined by gel permeation chromatography using a Waters chromatograph equipped with two Shodex columns and tetrahydrofuran as solvent at 298 K. The columns were calibrated with monodisperse polystyrene samples, and the poly(*N*-vinylcarbazole) calibration was obtained by the universal calibration method [9].

RESULTS AND DISCUSSION

Preliminary experiments with no initiator were carried out in order to make sure that the $PhCH_2(CH_3)_3N^+SbF_6^-$ salt did not initiate the polymerization reaction.

The *N*-vinylcarbazole polymerization was studied at 293 and 308 K using the trityl cation as initiator at different salt concentrations. The kinetic behavior is similar to that observed in nitrobenzene at 293 K without salt [5] or in methylene dichloride [8]. The reactions were very fast and complete as deduced from the relation between the temperature rise and the monomer consumption as verified by gravimetry. The kinetics were found to be first-order reaction with respect to monomer concentration:

$$-d[M]/dt = k_1[M] \qquad (1)$$

The plot of $\ln([M]_0/[M])$ vs time (Fig. 1) shows how the addition of salt affects the polymerization rate (the monomer and initiator concentrations were similar in both experiments). This plot is linear in all cases up to high monomer conversion, which indicates that there was not an appreciable loss of active centers during polymerization. The brief induction period observed is associated with an initiation step which is slower than the propagation one.

Disregarding the loss of active centers and taking into account the quantitative action of the trityl cation, the propagation rate constant, k_p, was calculated as

$$k_p = k_1/[I]_0 \qquad (2)$$

where $[I]_0$ is the initial trityl cation concentration and k_1 is the slope of the first-order reaction plot. Tables 1 and 2 show the values of k_p at both temperatures. The results obtained at 308 K in the absence of salt are also presented in Table 2.

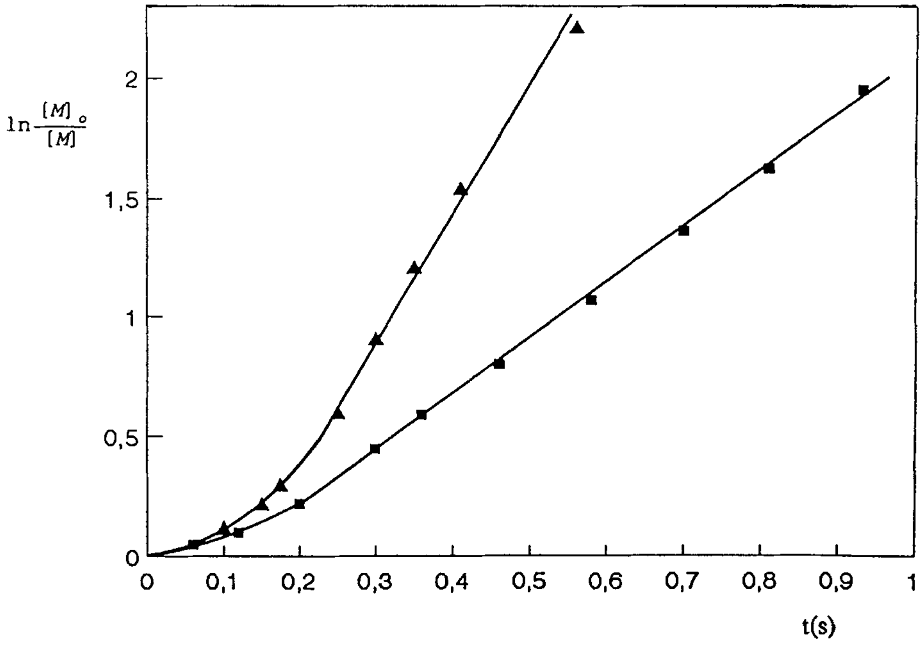

FIG. 1. First-order plots: (▲) $[I]_0 = 2.53 \times 10^{-5}$ M, $[M]_0 = 5.90 \times 10^{-2}$ M, [salt] = 1.09×10^{-2} M; (■) $[I]_0 = 2.40 \times 10^{-5}$ M, $[M]_0 = 6.06 \times 10^{-2}$ M.

Polymerization at 293 K

Table 1 shows the results obtained for experiments carried out in the presence of the salt. Previous experiments [5] carried out with lower salt concentrations and without salt at 293 K determined that k_p was independent of $[I]_0$, giving a mean k_p value of $0.89 \times 10^5\ M^{-1} \cdot s^{-1}$.

By comparing the k_p values from both experiments ($k_{p_{ns}}$ and $k_{p_{salt}}$), it can be seen that the $k_{p_{salt}}$ values shown in Table 1 for high $[\text{salt}]/[I]_0$ ratios (>200) are higher than those for $k_{p_{ns}}$. This fact is clearly observed in Fig. 2. The dashed line corresponds to salt-free experiments, and the values which appear on that line correspond to low $[\text{salt}]/[I]_0$ ratio experiments. As can be seen, $k_{p_{salt}}$ increases (up to two or three times), indicating that the propagating species are more reactive in the presence of the salt. From all experiments at $[\text{salt}]/[I]_0 > 200$, a mean value of $k_{p_{salt}} = 2.4 \times 10^5\ M^{-1} \cdot s^{-1}$ can be estimated. However, two trends can be observed:

1. At $[I]_0 \geq 2 \times 10^{-5}$ M (Expt. 3-7), there is a mean value of $k_{p_{salt}} = 1.8 \times 10^5\ M^{-1} \cdot s^{-1}$,
2. At $[I]_0 \approx 1 \times 10^{-5}$ M (Expt. 8-13), there is a mean value of $k_{p_{salt}} = 2.9 \times 10^5\ M^{-1} \cdot s^{-1}$.

We conclude that in the interval of $[I]_0$ studied, the lower the value of $[I]_0$, the more reactive are the propagating species and the higher is the value of $k_{p_{salt}}$.

The observed increase in $k_{p_{salt}}$ at high salt concentrations cannot be explained by a counterion effect since the type of counterion does not affect this polymerization. On the other hand, as the polymerization takes place by unpaired cations, the

TABLE 1. Polymerization at 293 K in the Presence of Salt

Expt.	$[M]_0 \times 10^2$, M	$[I]_0 \times 10^5$, M	[Salt] × 10^3, M	$k_p \times 10^{-5}$, $M^{-1} \cdot s^{-1}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
1	5.82	3.02	3.41	0.88	12.0	2.7
2	5.75	3.00	5.07	1.3	10.4	2.5
3	5.70	3.00	7.12	1.6	12.1	2.5
4	5.90	2.53	10.9	2.0	12.2	2.5
5	5.76	2.01	10.1	1.8	11.7	2.4
6	5.81	1.99	13.6	1.7	–	–
7	5.77	1.99	6.20	1.8	12.0	2.7
8	5.65	1.25	5.44	2.7	13.0	2.6
9	5.73	1.04	2.96	2.4	–	–
10	5.66	1.01	3.25	2.8	13.3	2.6
11	5.74	1.01	3.42	2.9	12.9	2.5
12	5.77	0.980	6.07	3.3	–	–
13	5.92	0.740	3.70	3.4	12.7	2.9
14	11.6	4.93	0.169	1.1	20.0	3.8
15	11.0	3.97	0.041	0.82	16.3	3.8
16	12.0	3.94	0.224	0.88	19.4	3.9
17	11.3	2.42	0.383	1.2	18.6	3.8

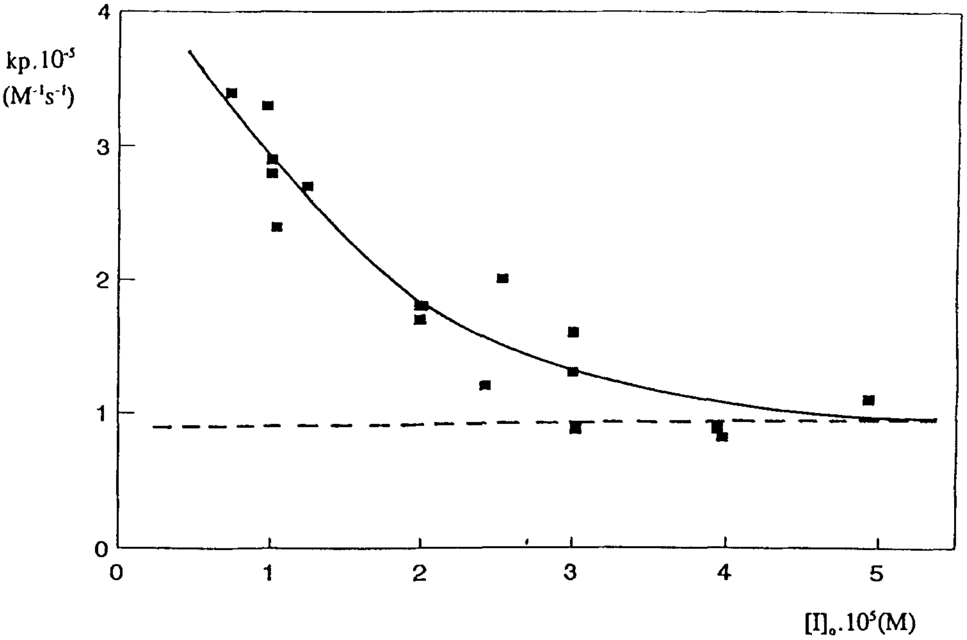

FIG. 2. k_p values as a function of $[I]_0$ at 293 K: (——) in the presence of added salt, (---) without added salt.

salt effect cannot be explained in terms of an equilibrium shift. In our opinion, the observed $k_{p_{salt}}$ values are a consequence of the increase in the ionic strength which modifies the strong interactions of nitrobenzene with both the monomer and propagating cations [6], and, in consequence, both species become more reactive. The interactions will be stronger in the transition state, so the final product is obtained at a higher rate. This means that the addition of the salt leads to a less solvating media which enhances the transition state with respect to the initial one, resulting in a faster reaction. The effect of the salt is greater the lower $[I]_0$ is; this can be explained by considering that at lower propagating species concentrations, the effect of a high salt concentration is more important.

Polymerization at 308 K

The results obtained from the polymerization process at 308 K (Table 2) shows a different behavior. For experiments in the absence of salt, there is a dependence between $k_{p_{ns}}$ and $[I]_0$ (Fig. 3). The same dependence is observed in experiments carried out with added salt. However, it is not possible to establish a clear relation between the two types of experiments. It was expected that at 293 K the polymerization would occur by an unpaired cations mechanism; nevertheless, k_p varies with $[I]_0$ (Fig. 3). This can be explained as follows: At the reaction conditions there is a shift toward the left in the ion pair = free ions equilibrium produced by $[I]_0$ variations. The reactivities of both propagating species are very different [8], therefore, a small change in the proportion of ion pairs gives rise to a perceptible

TABLE 2. Polymerization at 308 K

$[M]_0 \times 10^2$, M	$[I]_0 \times 10^5$, M	[Salt] × 10^3, M	$k_p \times 10^{-5}$, $M^{-1} \cdot s^{-1}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
5.61	7.57	–	0.59	12.8	2.4
5.60	7.22	–	0.63	12.7	2.5
5.51	6.39	–	0.74	9.84	2.3
5.62	5.40	–	1.1	10.4	2.5
5.51	4.95	–	0.88	8.44	2.5
5.58	4.16	–	0.87	–	–
5.63	4.05	–	1.4	11.3	2.4
5.57	3.59	–	1.2	8.96	2.4
5.59	3.22	–	1.2	9.37	2.2
5.65	1.85	–	2.3	9.76	2.4
5.62	1.32	–	2.8	8.27	2.2
5.61	0.751	–	3.1	8.20	2.2
5.68	2.63	12.5	2.1	8.23	2.3
5.47	2.50	0.241	1.8	8.48	2.0
5.59	2.39	2.21	1.9	7.72	2.0
5.78	2.30	0.055	1.5	7.95	1.9
5.92	2.10	10.3	2.4	7.94	2.2
5.73	1.46	41.2	3.2	8.06	1.9
5.38	0.771	14.2	3.3	7.59	2.0

effect on k_p. We conclude that this system at 308 K is not suitable for the study of the salt effect since it occurs simultaneously with the aforementioned shift.

Tables 1, 2, and 3 show the molecular weight (M_n) and molecular weight distributions (M_w/M_n) of several samples at both temperatures. The polymers obtained at 293 K in the absence of salt have molecular weights slightly higher than those obtained at 308 K. This is caused by an increment of the transfer process at this temperature. At 293 K we can estimate a slow decrease of the molecular weight as $[I]_0$ increases, but this influence cannot be directly observed at 308 K due to the shift in the ion pairs = free ion equilibrium with $[I]_0$ variations.

Comparing these values with those obtained in the systems with salt at both temperatures, it can be deduced that the addition of salt leads to polymers with lower molecular weights. As indicated above, the addition of salt gives rise to a higher reactivity of monomer and propagating species. Therefore, monomer transfer processes are enhanced, resulting in a decrease of molecular weight.

CONCLUSIONS

The cationic polymerization of *N*-vinylcarbazole in nitrobenzene is a complex process. First, the proportion of unpaired propagating species is greater than in a low polarity media. However, as we previously indicated [6], the propagating spe-

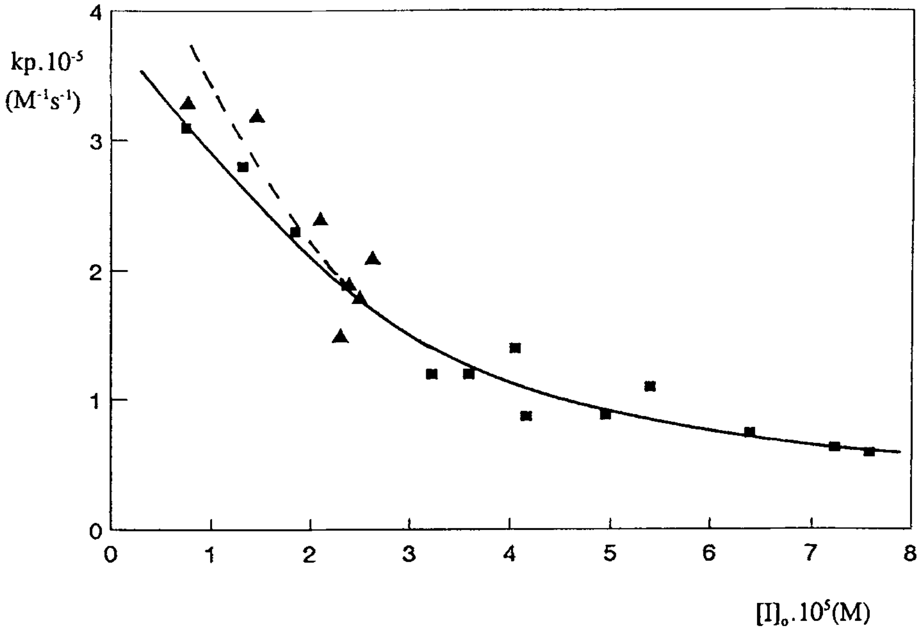

FIG. 3. k_p values as a function of $[I]_0$ at 308 K: (▲) in the presence of salt, (■) without salt.

TABLE 3. Molecular Weights at 293 K in the Absence of Salt

$[M]_0 \times 10^2$, M	$[I]_0 \times 10^5$, M	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
6.10	8.00	12.6	3.4
6.05	5.73	13.3	3.6
6.05	5.35	15.2	3.2
6.10	4.03	17.0	2.8
6.04	2.97	14.6	3.1
6.06	2.40	14.0	2.9
6.06	1.51	17.2	3.2
6.87	2.27	19.7	3.2
6.89	0.91	19.6	3.2
6.83	0.74	20.2	3.3
6.94	1.05	17.3	3.2
6.97	5.68	14.8	2.9
7.02	3.71	15.4	3.2
7.13	2.21	18.7	2.9
9.53	5.95	17.0	3.8
10.9	3.04	23.4	4.1
11.0	2.25	24.8	3.5

cies and the monomer interact strongly with the solvent, thus k_p cannot be considered as the propagating rate constant by free ions, k_p^+. The increased reactivity of the propagating species in the presence of salt can be explained on the basis of a small change in that interaction.

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