

## Kinetics of the Cationic Polymerization of N-Vinylcarbazole by Trityl Salts in Nitrobenzene

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### Summary

The cationic polymerization of N-vinylcarbazole by trityl salts in nitrobenzene at 20°C has been studied. The  $k_p$  values are independent of initiator concentration and an average value of  $8.9 \cdot 10^4 \text{M}^{-1} \text{s}^{-1}$  has been obtained which, according to the reaction conditions, has been interpreted in terms of propagation by free ions.

### Introduction

Trityl salts have proved to be very efficient initiators in the cationic polymerization of reactive olefins (BAWN et al. 1964; ELEY and RICHARDS, 1949; BONNER et al., 1958; HIGASHIMURA et al., 1967) as they allow for complete characterization of the catalyst system and give rapid and highly reproducible polymerizations. Previous studies (ROONEY, 1976; RODRIGUEZ and LEON, 1983) have demonstrated that the use of these catalysts ( $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$  and  $\text{PF}_6^-$  as counteranions) in the polymerization of N-vinylcarbazole (NVC) in  $\text{CH}_2\text{Cl}_2$  allows the determination of the absolute reactivity of the N-vinylcarbazole cation, that means the rate constant for propagation by free ions. However, its determination in a direct manner has not been possible except using extrapolation methods. In our opinion it could be possible to obtain  $k_p^+$  directly if the reaction was conducted in a solvent of higher dielectric constant in which the propagating species will be present as free ions almost entirely. So, in this paper we report on the study of the polymerization of N-vinylcarbazole by  $\text{Ph}_3\text{C}^+$  ( $\text{AsF}_6^-$ ,  $\text{SbCl}_6^-$  and  $\text{SnCl}_5^-$  as counteranions), at 20°C, in nitrobenzene.

### Experimental

**Reagents:** The monomer, N-vinylcarbazole (Fluka, purum) and the initiators,  $\text{Ph}_3\text{C}^+\text{AsF}_6^-$  (Merck),  $\text{Ph}_3\text{C}^+\text{SbCl}_6^-$  (Aldrich Co.) and  $\text{Ph}_3\text{C}^+\text{SnCl}_5^-$  (Aldrich Co.), were purified and stored as described previously (RODRIGUEZ and LEON, 1983). The salt  $\text{PhCH}_2^-(\text{CH}_3)_2\text{N}^+\text{SbF}_6^-$  was recrystallized from methylene dichloride and stored under dry  $\text{N}_2$ .

**Solvent:** Nitrobenzene (Merck) was twice distilled under reduced pressure in presence of  $\text{CaH}_2$  being its conductivity always lower than  $10^{-8} \Omega^{-1} \text{cm}^{-1}$ .

**Procedure:** Polymerizations were carried out at 20°C, under dry  $\text{N}_2$ , by an adiabatic calorimetric technique previously described (RODRIGUEZ and LEON, 1983).

### Results and discussion

Reactions were very fast and conversion was total in all cases as deduced from the linear relationship between the variation of temperature of the reaction mixture and the monomer concentration; it was gravimetrically verified as polymer yields were quantitative. A plot of  $\ln(|M|_0/|M|)$  vs. time (Figure 1) shows and induction period, as in  $\text{CH}_2\text{Cl}_2$  (RODRIGUEZ and LEON, 1983), i.e. the initiation is slower than propagation which is first order in monomer until practically total conversion indicating that there is no appreciable loss of active centres during the reaction.

From the slope of these linear plots, the  $k_{app}$  values were determined and, assuming that the initiator acts quantitatively and there is no loss of active centres so that  $[\text{propagating species}] = |I|_0 = \text{cte}$ , the  $k_p$  values were obtained from  $k_p = k_{app}/|I|_0$ . As can be seen in Table 1, which shows the  $k_p$  values in nitrobenzene, there is no dependence between  $k_p$  and  $|I|_0$  in the range of initiator concentrations used; therefore, an average value of  $k_p$  can be estimated:

$$k_p = 8.9 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$$

Taking into account that a dissociation equilibrium exists between free ionic and ion-paired species, the constancy in  $k_p$  (which would include both contributions) can be due to two possible causes: either the ion-pairs are similarly reactive than free ions, which implies that an equilibrium displacement will not affect significantly the  $k_p$  value, or in the range of initiator concentrations utilized only one species exists and  $k_p$  is an absolute value of the rate constant.

Previous studies of this polymerization in  $\text{CH}_2\text{Cl}_2$  (RODRIGUEZ and LEON, 1983) made evident that the reactivity of ion-pairs from N-vinylcarbazole was several orders of magnitude lower than that of free ions so that any displacement of the dissociation equilibrium would be clearly observed. On the other hand, a study of the dissociation equilibrium of  $\text{Ph}_3\text{C}^+\text{AsF}_6^-$  in nitrobenzene (ALAEZ and LEON) gives a dissociation constant,  $K_d = 8.4 \cdot 10^{-3}$ , and assuming that the polymeric ion-pairs and the initiator salt are similarly dissociated (BOWYER et al., 1971a and 1971b; RODRIGUEZ and LEON, 1983), it results that in our system the predominant species are free ions in proportion always higher than 99%: therefore, the  $k_p$  value is really  $k_p^+$ , the propagation rate constant by free  $\text{P}^+$  ions. This is logical since nitrobenzene has a high dielectric constant ( $\approx 36$ ), being moreover the  $k^+$  value in this solvent smaller than that in  $\text{CH}_2\text{Cl}_2$  (RODRIGUEZ and LEON, 1983) as would be expected from the transition state theory.

Several experiments were performed in presence of a neutral salt,  $\text{PhCH}_2(\text{CH}_2)_3\text{N}^+\text{SbF}_6^-$ , which by itself is not capable to initiate the polymerization as was verified. The action of a neutral salt on the cationic polymerization has been interpreted in terms of a counterion exchange and a change in ionic strength (TAZUKE et al., 1972; MASUDA and HIGASHIMURA, 1971; MASUDA et al., 1972; LEON et al., 1980). In our case, however, the  $k_p$  values obtained (Table 2) are not influenced by the addition of the salt; this fact agrees with our previous

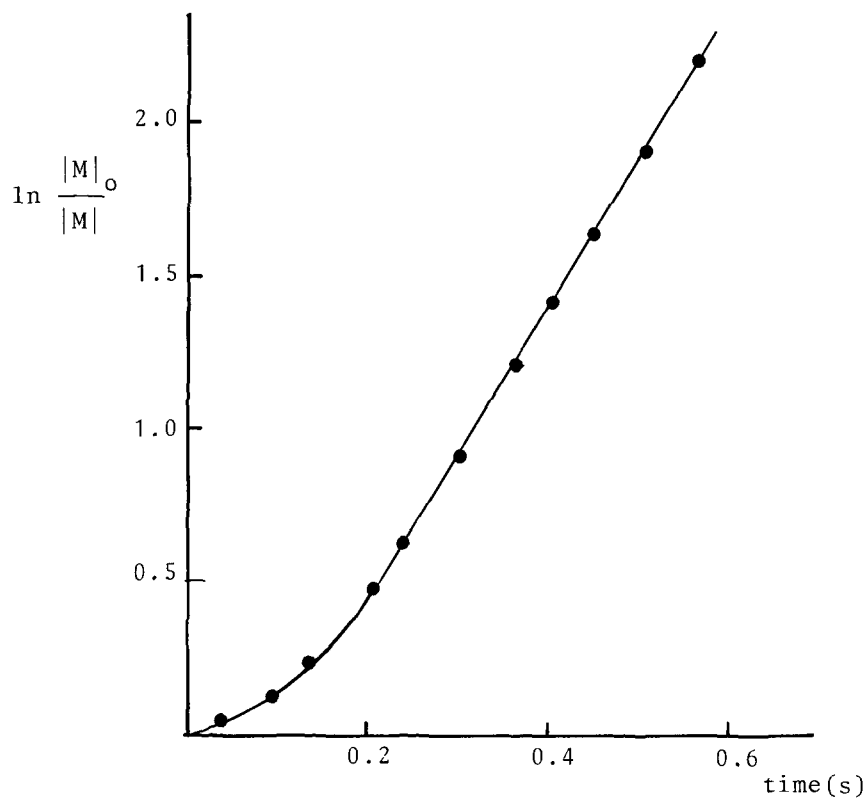


Figure 1.- Typical first order plot. ( $|NVC| = 0.061$  M;  $|I|_0 = 8.00 \cdot 10^{-5}$  M).

Table 1.- Polymerization of NVC at 20°C

Initiator	$ M _0 \cdot 10^2$ (M)	$ I _0 \cdot 10^5$ (M)	$k_{app}$ ( $s^{-1}$ )	$k_p \cdot 10^{-5}$ ( $M^{-1}s^{-1}$ )
$Ph_3C^+AsF_6^-$	6.10	8.00	4.76	0.60
"	6.05	5.73	2.95	0.51
"	6.04	2.97	3.23	1.1
"	6.06	2.40	2.29	0.96
"	6.06	1.51	1.50	1.0
"	6.10	4.03	2.70	0.67
"	7.13	2.21	2.34	1.1
$Ph_3C^+SbCl_6^-$	7.02	3.71	2.92	0.79
"	6.94	1.05	0.91	0.87
"	6.97	5.68	4.78	0.84
"	6.89	0.91	1.03	1.1
"	9.53	5.95	5.17	0.87
"	11.0	2.25	2.67	1.2
$Ph_3C^+SnCl_5^-$	6.05	5.35	3.42	0.64
"	6.87	2.27	2.82	1.2
"	6.83	0.74	0.70	0.94
"	10.9	3.04	2.40	0.79

Table 2. Polymerization in presence of  $\text{PhCH}_2(\text{CH}_3)_3\text{N}^+\text{SbF}_6^-$ 

Initiator	$ \text{M} _0$ (M)	$ \text{I} _0 \cdot 10^5$ (M)	$ \text{salt} _0 \cdot 10^5$ (M)	$k_p \cdot 10^{-5}$ ( $\text{M}^{-1}\text{s}^{-1}$ )
$\text{Ph}_3\text{C}^+\text{SbCl}_6^-$	0.110	3.97	4.07	0.82
"	0.120	3.94	22.4	0.88
"	0.113	2.42	38.3	1.2
$\text{Ph}_3\text{C}^+\text{SnCl}_5^-$	0.112	2.40	49.0	0.87
$\text{Ph}_3\text{C}^+\text{AsF}_6^-$	0.116	4.93	16.9	1.1

conclusion that the predominant species are free ions. So, as the anions employed are fairly stable, the first effect is not expected in our system; moreover, it could not be observed if the counterion is far from the propagating polymeric cation. On the other hand, an important change in ionic strength, caused by the addition of the salt, does not affect the rate constant. All these results confirm our conclusion that free ions are the propagating species in this system.

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