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Cationic Polymerization

Cationic Polymerization of n-Vinyl Carbazole initiated by Trityl Salts in Nitrobenzene

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Summary

The initiation mechanism in the cationic polymerization of N-vinyl carbazole by trityl salts in nitrobenzene has been investigated. An spectroscopic study of the reaction solutions indicates that the triphenylmethyl cation is not present at the end of the polymerization, the mechanism being not therefore similar to that proposed in CH_2Cl_2. A mechanism involving hydride ion abstraction is proposed.

Introduction

In a previous paper(RODRIGUEZ and LEON, 1983) we have presented the results obtained about the reaction mechanism in the cationic polymerization of N-vinyl carbazole(NVC) by triphenylmethyl salts in methylene dichloride. It was found that the initiation mechanism is not the addition of triphenylmethyl cation to the monomer as it was accepted up to now and as it occurs when the initiator is the cycloheptatrienyl cation (BOWYER et al., 1971); a mechanism was proposed involving formation of triphenylmethyl radical and a cation-radical from the monomer, being regenerated the Ph_3C^+ cation from the radical. Such a mechanism was proposed on the basis of the visible spectrum of Ph_3C^+ obtained at the end of the reactions, with absorbance values at 412 nm indicating that the cation almost totally has been regenerated.

Now we present a study of the initiation mechanism for this reaction in a solvent of higher dielectric constant as nitrobenzene.

Experimental

Reagents: The monomer, N-vinyl carbazole(Fluka, purum), was purified by standard techniques(BOWYER et al., 1971). The initiators, $Ph_3C^+AsF_6^-$(Merck) and $Ph_3C^+SbCl_6^-$(Aldrich Co.), were utilized directly as absorbance at 412 nm of solutions in CH_2Cl_2 indicated that purity was satisfactory; they were stored under dry N_2.

Solvent: The solvent, nitrobenzene, was twice distilled from CaH_2 under reduced pressure and stored over CaH_2. It was distilled before use.

Procedure: The polymerization reactions were carried out at 20°C, under dry N_2, using initiator concentrations from

2.10^{-5} to 9.10^{-5}M; conversion was total in all cases. The visible spectrum of solutions at the end of the polymerization was recorded by a Varian Techtron Spectrophotometer using quartz cells of 1 and 0.1 cm light path. In some cases a new addition of monomer solution was accomplished after the first reaction being obtained likewise total conversion.

Results and discussion

In order to prove if the initiation mechanism is the same in nitrobenzene as in methylene dichloride, which would be confirmed if the characteristic spectrum of the Ph_3C^+ cation(ANDERSON, 1930) is obtained at the end of the reaction, a previous study of $Ph_3C^+AsF_6^-$ and $Ph_3C^+SbCl_6^-$ solutions in nitrobenzene was accomplished. The visible spectrum of the Ph_3C^+ cation in nitrobenzene was somewhat modified with respect to that in H_2SO_4 or CH_2Cl_2; the absorption maximum at 435 nm is shifted to 440 nm and that at 412 nm do not appear but there is a shoulder at approx. 424 nm. This clearly indicates that some interaction exists between the triphenylmethyl cation and the solvent due to the polarity of nitrobenzene; the Lambert-Beer law is fulfilled and the absorption molar coefficient at 440 nm is $3.0.10^4$ $M^{-1}cm^{-1}$.

The spectrum obtained at the end of the reaction is not that of the Ph_3C^+ cation but it shows only an absorption maximum at 420 nm; there is however a small absorption at 440 nm (absorption maximum of Ph_3C^+ in this solvent) which could be due to Ph_3C^+ cation regenerated in small amount according to a mechanism similar to that in CH_2Cl_2; in order to prove it, purified and dried polymer solutions were analyzed and an identical spectrum was obtained with a small absorption at 440 nm also.

Figure 1 shows a plot of absorbance vs. concentration of monomer polymerized for final reaction solutions and purified polymer solutions and, as can be seen, the plot is linear; it must be noted that some experimental values correspond to reactions with successive monomer addition and another ones correspond to solutions of poly(N-vinyl carbazole) obtained by other triphenylmethyl salts in CH_2Cl_2, being all the values undistinguishable; the same behaviour was found for the small absorbance at 440 nm.

A posterior analysis of NVC and carbazole solutions in nitrobenzene revealed that their visible spectrum was identical to that of the polymer solutions and in Figure 1 the absorbance values vs. monomer and carbazole concentration for these solutions have been included. As can be seen, the plot is linear although the absorbance values are higher than those for polymer solutions.

All this allows us to conclude that the obtained spectrum is characteristic of an interaction between the carbazole group and nitrobenzene, which do not takes place in CH_2Cl_2(RODRIGUEZ and LEON, 1983). The difference in absorbance between monomer and carbazole solutions and polymer solutions can be due, in our opinion, to a different magnitude of interaction when the carbazole group is incorporated on the polymeric chain.

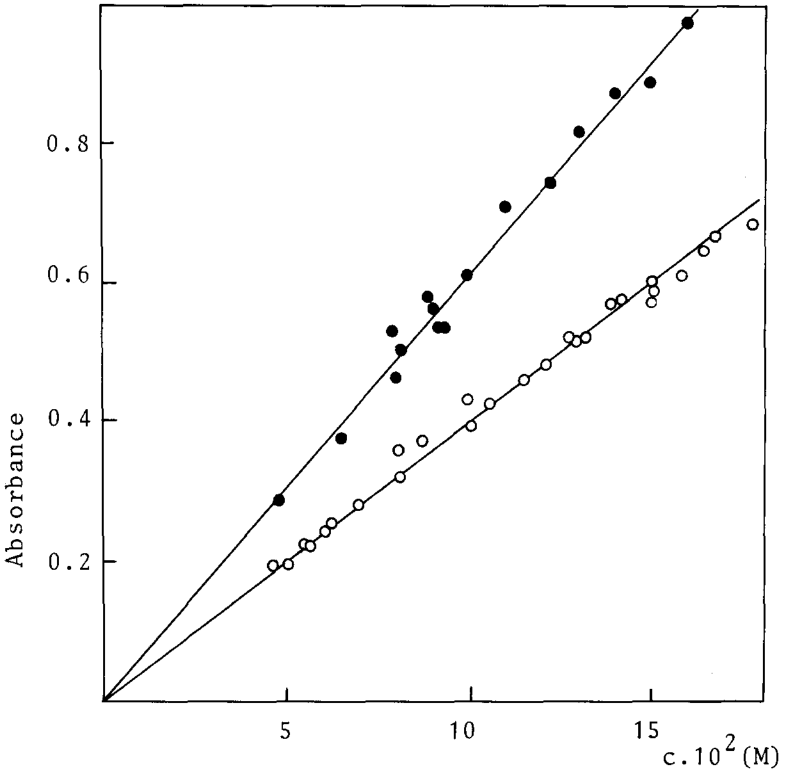

Figure 1.- Plot of basorbance vs. concentration (o-final reactions and purified polymer solutions; ●- NVC and carbazole solutions).

All these results allow us to conclude that the initiation mechanism in nitrobenzene is not the same taking place in CH_2Cl_2, then having two possible alternatives:

1.- Direct addition of the Ph_3C^+ cation to the monomer.
2.- Hydride ion abstraction from the monomer forming Ph_3CH.

To determine which is the mechanism in this case, several samples were synthesized with a small ratio $|M|/|I|$ and experiments were carried out in presence of methanol in order to obtain very short chains in which could be possible to detect the triphenylmethyl group incorporated to the polymeric chain by infrared analysis. The results were in all cases negative so that, in our opinion, the initiation mechanism is not the addition of the triphenylmethyl group to the monomer. This is not surprising taking into account that steric hindrance may prevent close approach to the central carbon atom of triphenylmethyl cation as in CH_2Cl_2. So, we think that the initiation mechanism in nitrobenzene is the hydride ion abstraction from the monomer being, on the other hand, this one a characteristic mechanism for reactions in which triphenylmethyl cation is involved(DAUBEN et al., 1960)(OLAH and SVOBADA, 1973).

The identification of Ph_3CH as a product of the reaction is difficult as its concentration will be very small.

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