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The initiation process in the polymerization of *N*-vinylcarbazole and 3-1,9-*N*-vinylcarbazole by trityl salts

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SUMMARY

The initiation mechanism in the cationic polymerization of N-vinylcarbazole and 3-I,9-N-vinylcarbazole by trityl salts in nitrobenzene, methylene chloride and chlorobenzene has been studied. Spectroscopic studies and molecular weight analysis show that the polymerization mechanism depend on the used solvent.

INTRODUCTION

In previous papers(RODRIGUEZ et al., 1983a)(BILBAO et al., 1983) the results about the reaction mechanism in the cationic polymerization of N-vinylcarbazole(NVC) by trityl salts in methylene chloride and nitrobenzene have been presented. So, in methylene chloride spectroscopic studies from solutions at the end of the polymerization revealed the presence of trityl cation in concentration similar to that of the initial salt. A mechanism was proposed involving regeneration of trityl cation through the formation of a trityl radical and a monomeric cation radical, which dimerizes forming a dication, being this one the propagating species in the system.

When the reaction is carried out in nitrobenzene, the characteristic spectrum of trityl cation is not obtained at the end of the polymerization and the proposed mechanism implies the abstraction of a hydride ion from the monomer forming triphenylmethane and a monomeric cation which is the propagating species in the system.

In this paper we have studied the initiation mechanism for NVC in chlorobenzene, the dielectric constant of which is smaller than that of methylene chloride, and likewise it has been investigated the initiation mechanism for 3-I,9-N-vinylcarbazole(3I9NVC) in the same solvents.

EXPERIMENTAL

Reagents: N-vinylcarbazole(Fluka, purum) and 3-I,9-N-vinylcarbazole were purified by standard techniques(BOWYER et al.,1971).
Trityl salts, $Ph_3C^+AsF_6^-$(Merck) and $Ph_3C^+SbCl_6^-$(Aldrich), were utilized without further purification since its purity was considered adequate(RODRIGUEZ et al.,1983b). They were stored under dry N_2 and at low temperature.

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Solvents: Nitrobenzene was twice distilled from CaH_2.It was distilled before use.
Methylene chloride and chlorobenzene were purified by standard techniques (BOWYER et al.,1971)(RIDDICK et al.,1970) and distilled before use.
Tetrahydrofuran(THF) was distilled from CaH_2 and stored in the dark and under dry N_2. Peroxides from THF were removed before distillation.
Procedure: The polymerizations were carried out at 20°C, under dry N_2; concentrations ranged between $2.10^{-5}M-7.10^{-5}M$ and $3.10^{-2}M-12.10^{-2}M$ for trityl salts and monomer solutions, respectively.Conversion was total in all cases. The visible spectrum of solutions at the end of the polymerization was recorded on a Shimadzu UV-240 spectrophotometer using quartz cells of 1 and 0.1cm light path. When chlorobenzene was the utilized solvent, the visible spectrum of the initiator solution at the same concentration as in the polymerization system was also recorded.

Molecular weights of the samples were measured on a Waters Gel Permeation Chromatograph(GPC) with columns of 5.10^2, 10^3, 10^4, 10^5 and 10^6A of pore size, using THF as solvent, at 298K.The GPC columns were calibrated with monodisperse samples of polystyrene (RODRIGUEZ et al.,1983a) and from it the particular calibration for PNVC and P3I9NVC was obtained.

RESULTS AND DISCUSSION

Polymerizations in chlorobenzene and methylene chloride:The visible spectrum obtained from final solutions in the polymerization reactions of NVC and 3I9NVC in chlorobenzene, and of 3I9NVC in methylene chloride show the characteristic shape of trityl cation with two absorption maxima at 412nm and 435nm (ANDERSON,1930); this fact lead us to the conclusion that the initiation mechanism is the same as for NVC in methylene chloride(RODRIGUEZ et al.,1983a). However, the absorbance intensities for initiator solutions in chlorobenzene were lower than those in methylene chloride and moreover the absorbance decreased with time indicating that trityl cation is very unstable in that solvent.
Polymerizations in nitrobenzene:Spectroscopic analysis from final reaction solutions in the polymerization of 3I9NVC in nitrobenzene indicates that the initiation mechanism is the same as for NVC in this solvent(BILBAO et al.,1983).
Molecular weight analysis: The average molecular weights, M_w and M_n, as well as the polydispersity(I) of synthesized samples are shown in Tables 1 and 2.

TABLE 1
Molecular weights of PNVC

Solvent	[M] (M)	[I].10^5 (M)	$\bar{M}_w.10^{-4}$	$\bar{M}_n.10^{-5}$	I
CH_2Cl_2	0.063	4.57	72.0	22.0	3.3
"	0.063	9.25	40.0	9.8	4.1
"	0.125	4.22	91.0	25.0	3.6
$PhNO_2$	0.061	0.936	5.2	1.4	3.7
"	0.070	5.68	4.6	1.1	4.2
"	0.061	7.96	5.7	1.4	4.1
PhCl	0.058	5.44	11.8	3.6	3.3
"	0.110	4.87	22.5	9.2	2.4
"	0.052	7.76	9.3	3.0	3.1

TABLE 2
Molecular weights of P3I9NVC

Solvent	[M] (M)	[I].10^5 (M)	$\bar{M}_w.10^{-4}$	$\bar{M}_n.10^{-5}$	I
CH_2Cl_2	0.033	7.02	21.5	9.38	2.3
$PhNO_2$	0.038	6.90	3.94	1.21	3.3
PhCl	0.031	7.13	7.19	1.12	6.4

The results of this analysis allows us to corroborate the proposed mechanisms. So, the lower molecular weights for PNVC and P3I9NVC are obtained in nitrobenzene as solvent. This is logical bearing in mind that the propagation occurs in this case through a cation.In methylene chloride or chlorobenzene the propagation takes place by a dication and then molecular weights will be higher.On the other hand, molecular weights in chlorobenzene are lower than that in methylene chloride which can be explained taking into account that chlorobenzene have a smaller dielectric constant than methylene chloride.Therefore, in chlorobenzene the equilibrium

propagating ion pairs=propagating free ions

is displaced to the left so that transfer reactions will be more important and some chains will propagate only by one end lowering the molecular weight.

Figure 1 shows the obtained chromatograms for some samples of PNVC obtained in similar conditions of monomer and initiator concentrations. The most remarkable characteristic is the monodal molecular weight distributions obtained in nitrobenzene and the bimodal ones obtained in chlorobenzene or methylene chloride. These results are in agreement with the proposed mechanism in each solvent; so, in nitrobenzene the propagating species is a cation.In methylene chloride or chlorobenzene however, the propagating species is a dication but due to transfer reactions some active centres will be lost and therefore some chains will propagate by two ends and some ones only by one end. This implies the existence of a mixture of two polymers in the system one of which has a higher molecular weight than the other and, in consequence, the molecular weight distributions are bimodal.Likewise, when comparing the obtained chromatograms in methylene chloride with those in chlorobenzene it can be seen that in the latter solvent the highest peak corresponds to the lower molecular weight while in methylene chloride corresponds to the higher molecular weight. This is in agreement with the fact that in chlorobenzene the transfer processes are very important and so, there will be more chains growing by one end than by both ends.

In our opinion the different initiation mechanism taking place in nitrobenzene with respect to that in methylene chloride and chlorobenzene is due to the strong interaction existing between nitrobenzene and both monomer and propagating cation(BILBAO et al.,1983). Due to this interaction the formation of a charge transfer complex is less favoured so that the initiation occurs by hydride ion abstraction from the monomer being the propagating species a cation.

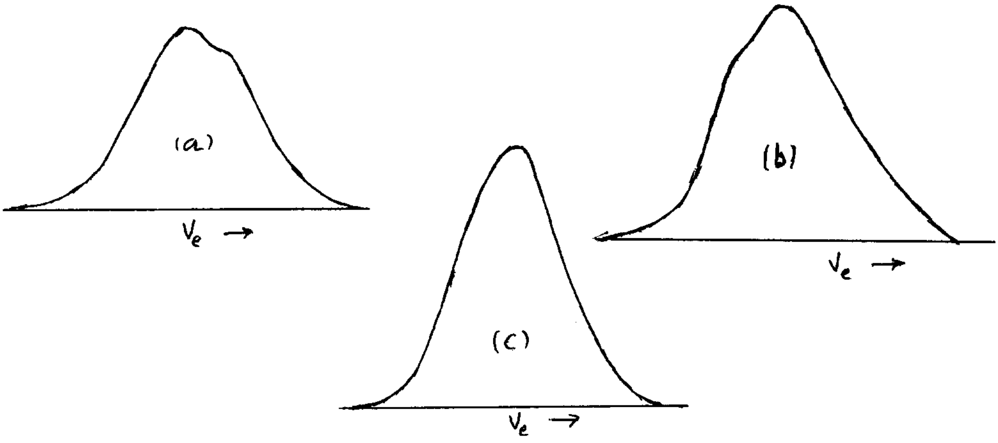

Figure 1.-Typical chromatograms in: a)methylene chloride; b)chlorobenzene; c)nitrobenzene

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