Charge-transfer complexes as polymerization inhibitors: 2. Studies on the mechanism of inhibition of the radical polymerizations of acrylonitrile and vinyl acetate using the amine–chloranil complexes

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The mechanism of inhibition of the bulk and solution polymerizations of acrylonitrile (AN) and vinyl acetate (VA) has been investigated using the charge-transfer complexes of triethylamine (TEA) and *N,N*-dimethylaniline (DMA) with chloranil. Complete inhibition is achieved by the complexes of both amines for the polymerizations of both monomers. The greater inhibiting efficiency of the TEA complexes is explained in terms of their greater stabilities. The results support the idea that inhibition by quinones involves electron-transfer from the polymeric radicals to the quinone forming molecular complexes of polymeric cations and semiquinone anions. The latter are the actual inhibitors so that the efficiency of inhibition depends on the feasibility of their formation which is determined by the stability of the complexes formed. The nature of the inhibition reaction products is determined by the extent to which the semiquinone anions are found as kinetically independent species in the polymerizing system. The mechanism suggested accounts for the great differences in the inhibiting powers of quinones for the polymerizations of various monomers.

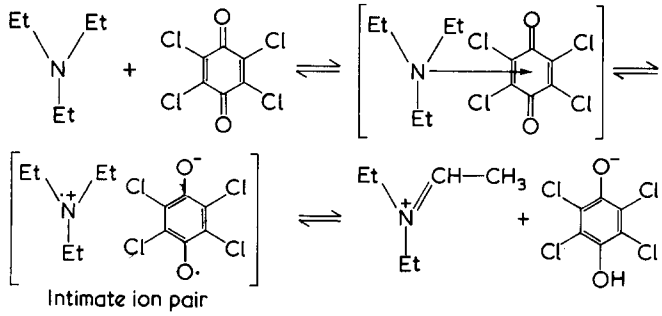
INTRODUCTION

The elucidation of the mechanism of inhibition and retardation in radical polymerizations by quinones has been the subject of extensive studies and much controversy. However, no single mechanism has been able to account for the great differences in the inhibiting power of a particular quinone for the polymerizations of different monomers nor for the nature of the inhibition reaction products[1–5].

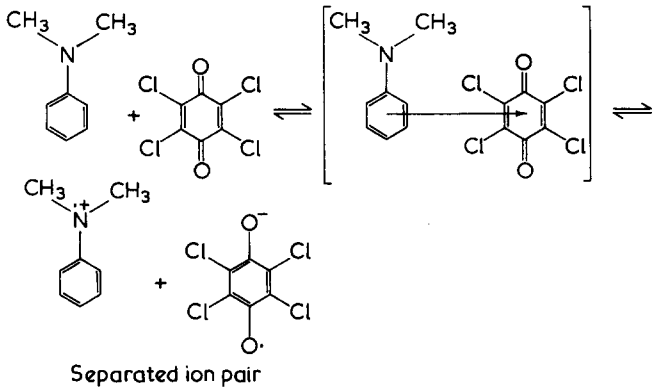
It has been shown that while the efficincy of inhibition is determined by the electron-donating power of the growing radicals and the redox potential of the quinone, the nature of the inhibition reaction products depends on the structure of the quinone used as well as on the polarity of the reaction medium. Thus while quinonoid products are usually formed from parent quinones having at least one hydrogen atom in the quinone nucleus, both for electron-rich as well as electron-deficient monomers, the formation of similar products from fully substituted quinones, such as chloranil, is determined by the nature of the monomer and the polarity of the reaction medium[6,7]. These facts have led to the idea that the inhibition reaction involves electron-transfer from the growing chains to the quinone with the formation of molecular complexes of macrocations and semiquinone anions. The latter are the actual inhibiting species so that the efficiency of inhibition will be determined by the feasibility of their formation in the polymerizing system. The nature of the inhibition products, on the other hand, will depend on the stability of these complexes and the extent to which the semiquinone anions are found as kinetically independent species in the reaction medium. If this is actually the case, the efficiency of inhibition should be greatly increased if the polymerization is carried out under conditions which favour the formation of semiquinone anions in concentrations higher than in the normal inhibition reaction. In other words, the inhibiting power of a particular quinone should be greatly improved if it is possible to introduce it into the polymerizing system, at least partly, in the semiquinone anion form. In order to accomplish this, use was made of the fact that chloranil forms charge-transfer complexes with a wide variety of strong electron-donors including DMA[8] and TEA[9]. The nature and stability of these complexes are determined by a number of factors including the type of the orbitals, of both the donor and the acceptor, which participate in the complex formation, the ionization potential of the donor, the electron affinity of the acceptor and finally the extent of attraction between the complex partners. On subsequent reactions, the complexes dissociate into pairs of radical ions involving semiquinone anions and radical cations. The degree of separation of the ion pairs will be determined by the stability of the radical cation.

TEA and DMA belong to different classes of electron-donors. While the former is purely an n-donor, the latter is, at least partly, of the π-type[10]. The complexes of both amines with chloranil will accordingly be of different stabilities. Thus while the more stable complexes of TEA form

only intimate pairs of radical ions[8]:



The corresponding species in case of DMA are sufficiently stable to exist separately in solution[9]:



The complexes of the two amines with chloranil might therefore correspond to the complexes which are formed in the reaction of the different polymeric radicals with the same quinone during the inhibition process. In this respect TEA might be compared with the radicals of vinyl acetate while DMA with the monomers whose radicals are conjugated with double or triple bonds as in the case of styrene and AN, respectively.

In the previous papers[11,12] the effect of the complexes of both amines with chloranil on the polymerizations of methyl methacrylate and styrene have been reported. In the present study the results of the use of these complexes for the inhibition of the polymerizations of AN and VA are given. The two monomers differ greatly not only in the electron-donating powers of their derived radicals but also in the nature of their atomic orbitals which allows the possibility of investigating the influence of the monomer structure on the efficiency of inhibition by a particular quinone.

EXPERIMENTAL

Materials

The monomers, the amines and solvents were twice distilled at reduced pressure under nitrogen. The sensitizer, azoisobutyronitrile (AIBN) and chloranil were purified by crystallization.

Reactions

AIBN (2×10^{-3} mol) and chloranil (5×10^{-4} mol) were used per mole monomer. The amines were taken in the amounts of 0.5, 1.0 and 5.0 moles per mole chloranil. On mixing the solutions of the amines and chloranil in the monomer a blue colour was developed in the case of DMA and a green colour in the case of TEA. The intensities of the colours increased on increasing the amine ratios. The complexes of the different amine ratios are designated as complexes-I, II and III, respectively. The polymerizations in benzene and acetonitrile were carried out in solutions of 1:1 monomer–solvent ratio by vol. The kinetics of the polymerizations were followed dilatometrically at 60° ± 1°C. On heating, the colours gradually disappeared. This was followed by the development of a violet colour in the case of DMA and a brown colour for TEA. The intensity of the developed colours reached a maximum at the highest amine ratios. The colours were particularly intense in the case of the polymerizations in acetonitrile. On the other hand, no colours were developed in benzene.

At ~15% conversion, the polymerizations were stopped and the low molecular weight products formed during the inhibition periods were isolated. This was achieved for AN by filtration of the polymer formed and its washing with ethyl alcohol. In the case of VA, on the other hand, the polymers were precipitated by cold petroleum ether 60°/80°C and filtered. The filtrates and washings of both monomers were distilled under nitrogen and the viscous residues formed were tested for the quinonoid nature both by the Craven test[13] and by i.r. spectra. Moreover, in the case of VA, the residue was further examined for combined nitrogen and halogen.

RESULTS AND DISCUSSION

The conversion–time plots of the bulk polymerizations of AN and VA in the presence and in the absence of the charge-transfer complexes of both amines with chloranil are shown in *Figures 1–4*. The results reveal that the efficiency of inhibition depends not only on the nature of the monomer but equally on that of the amine as well as on its ratio rela-

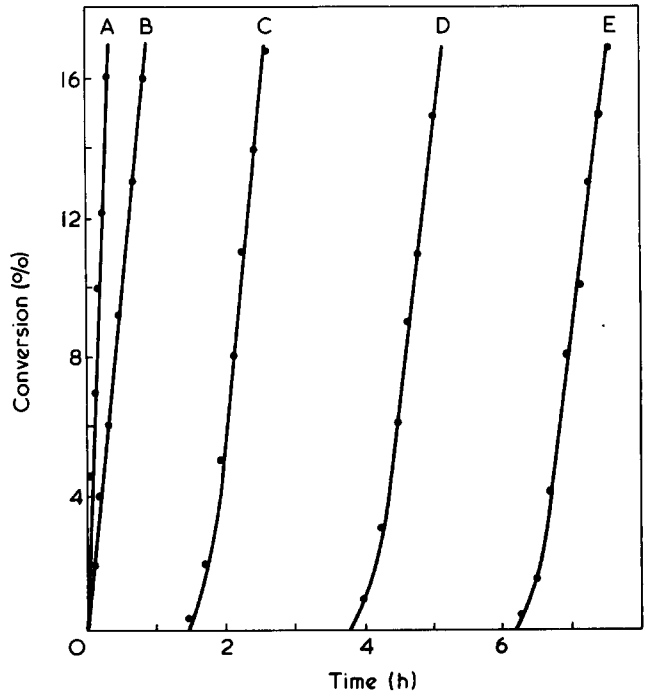


Figure 1 Conversion–time plots of bulk polymerizations of AN: A, AIBN alone; B, 5×10^{-4} mol TEA alone; C, TEA–chloranil complexes-I; D, TEA–chloranil complexes-II; E, TEA–chloranil complexes-III

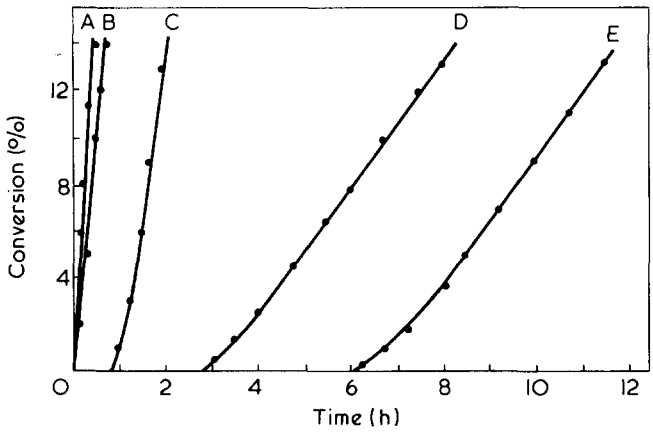


Figure 2 Conversion–time plots of bulk polymerizations of AN: A, 5 X 10^{-4} mol DMA alone; B, chloranil alone; C, DMA–chloranil complexes-I; D, DMA–chloranil complexes-II; E, DMA–chloranil complexes-III

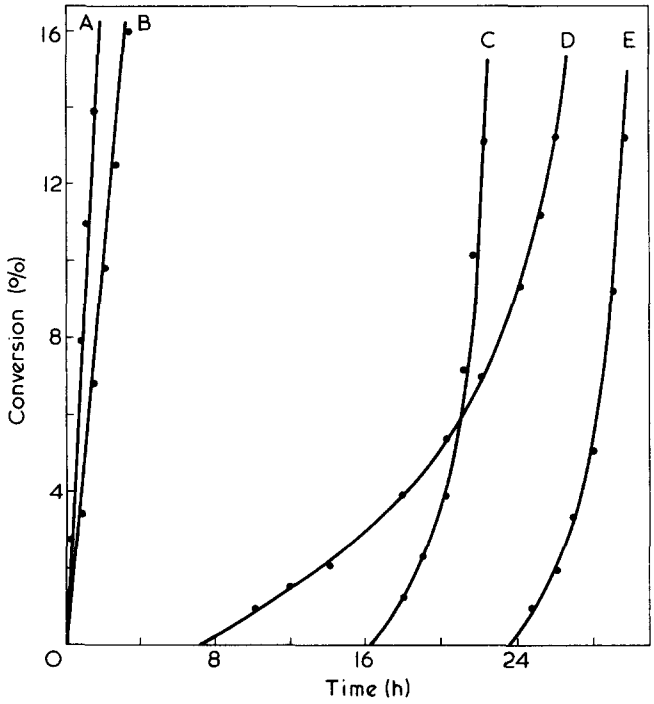
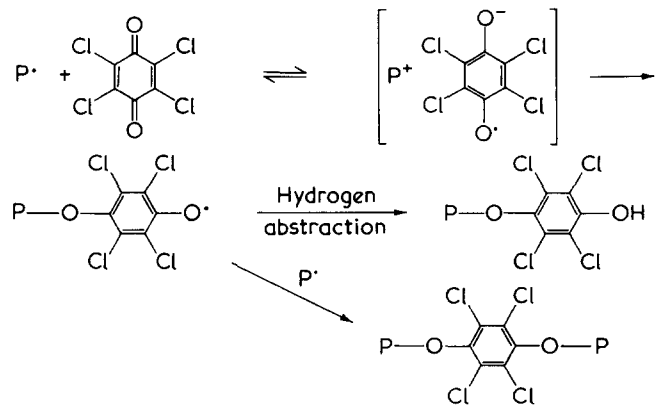


Figure 3 Conversion–time plots of bulk polymerization of VA: A, AIBN alone; B, 5 X 10^{-4} mol TEA; C, complex-I; D, complex-III; E, complex-II

tive to chloranil. Thus while the amines and chloranil when used separately only slightly retard the polymerization of AN, complete suppression of the growth reactions is achieved by chloranil alone in the case of VA. The complexes of both amines with chloranil, on the other hand, exhibit a strong inhibiting effect for the polymerizations of both monomers. The polymeric products formed during the induction periods in the presence of chloranil alone or its complexes with both amines are quinonoid in the case of AN and non-quinonoid for VA. This fact together with the absence of combined nitrogen in these products in the case of VA indicates that though the amine partners of the complexes are involved in the inhibition reactions they are not incorporated into the polymeric structures which suggests that the mechanism of inhibition by chloranil alone or its complexes is most probably the same. The appreciable difference in efficiency is therefore attributable to the difference in the extent to which chloranil is transformed into the active species responsible for inhibition in both cases.

The most acceptable mechanism which can account for these facts is one based on electron-transfer from the macroradicals to the quinone molecules with the formation of molecular complexes involving macrocations and semiquinone anions as represented by the following equations in which P$^{\bullet}$ represents a growing chain:



The greater electron-donating power of the VA radicals together with the σ-nature of the orbitals in which reside the odd electrons account for the formation of more stable complexes which on dissociation form only intimate ion pairs where the semiquinone anions are not found as kinetically independent species in the reaction medium. This leads to their mutual interaction with the macrocations, rather than with the growing chains, with the formation of oxygen radicals. The latter are insufficiently reactive to initiate the polymerization of the unreactive VA monomer which accounts for the complete suppression of the growth reactions in this case.

On the other hand, the electron-deficiency of the AN radicals together with the partly π-character of their orbitals account for the lower affinity of the growing chains to complex formation with the quinone. Moreover, the complexes

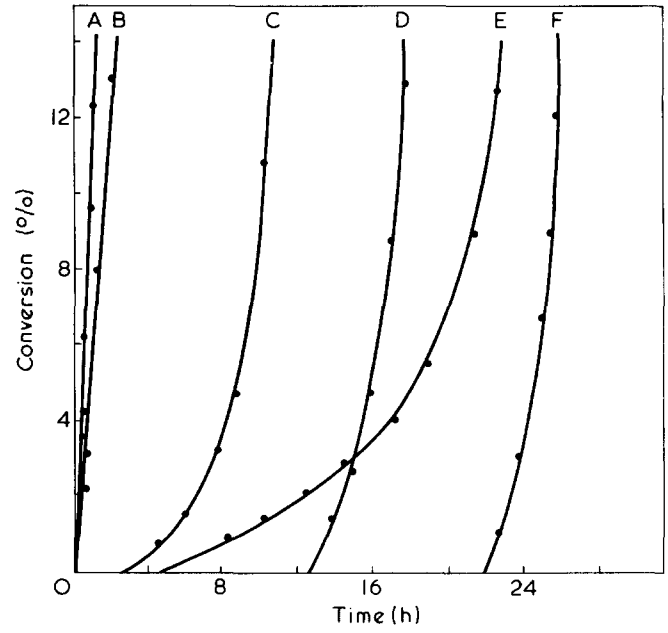
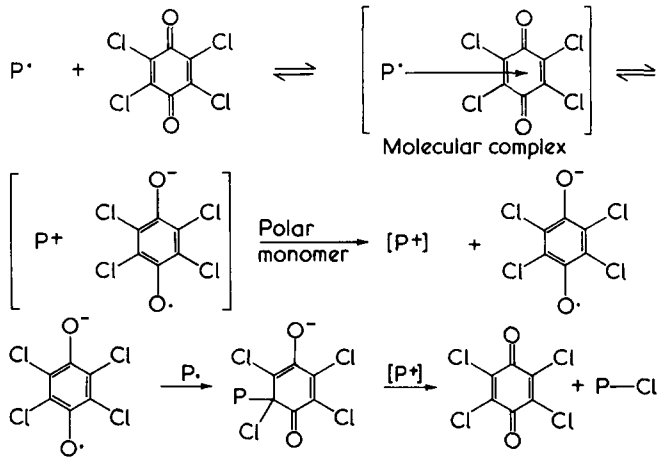
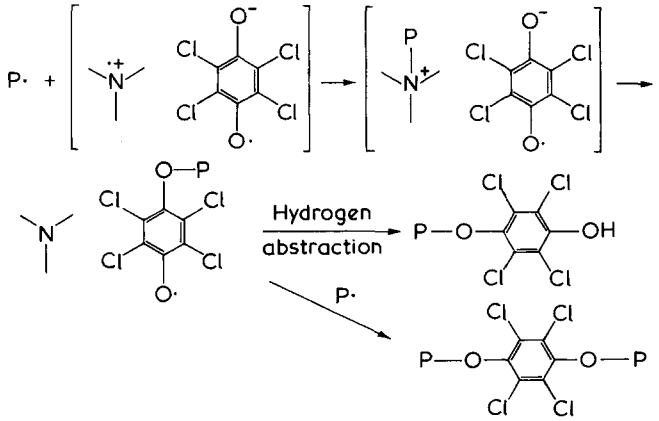


Figure 4 Conversion–time plots of bulk polymerization of VA: A, AIBN alone; B, 5 X 10^{-4} mol DMA; C, chloranil alone; D, complex-I; E, complex-III; F, complex-II

formed are relatively unstable and dissociate to form separated ion pairs. The dissociation is favoured by the high polarity of the solvent which affords the stabilization of the polymeric cations through solvation. The presence of the semiquinone anions as kinetically independent species in the reaction medium permits their preferential interaction with the growing chains, rather than with the solvated polymeric cations, with the eventual formation of quinonoid products. The low concentration of the semiquinone anions formed under these conditions accounts for chloranil acting only as retarder in this case:

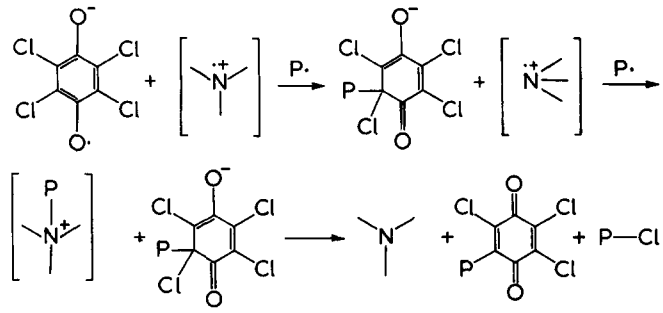


The aforementioned discussion leads to the conclusion that the semiquinone anions are the actual inhibiting species and that the efficiency of inhibition is determined by their concentration which in turn is dependent on the stability of the complexes formed between the growing chains and the quinone used. Evidence supporting this conclusion would be obtained if the replacement of the polymeric radicals by other electron donors of various complexing powers with chloranil resulted in a change in the efficiency of inhibition in the outlined directions. This can be seen from the effect of the complexes of both amines on the polymerizations of both monomers. The greater inhibiting efficiency achieved in the case of VA relative to AN and the TEA complexes relative to the corresponding DMA analogues supports the validity of the conclusion that the stability of the complexes is the factor which determines the efficiency of inhibition. Thus although the ionization potential of DMA (7.14 eV) is slightly lower than for TEA (7.5 eV), the complexes of the latter are more stable. This was proved from the absorption bands of the complexes of both amines in ethanol which correspond to 6600 Å for complexes of TEA compared with 5900 Å for those of DMA. The mechanism of inhibition of the VA polymerization in presence of the amine complexes may accordingly be represented by:



The macroradicals due to their nucleophilic nature will be preferentially directed towards combination with the more electron-deficient radical cations. The subsequent reactions of the resulting ammonium ion with the semiquinone anion leads to the liberation of the free amine and the formation of an oxygen radical which is terminated either by combination or disproportionation with a growing chain. This implies that although both partners of the complex are involved in the suppression of the growth reactions, the role of the amine is restricted to the transformation of chloranil into the semiquinone anion form which is the actual inhibiting species.

On the other hand, in the case of AN the inhibition reaction in the presence of the amine complexes may be represented by:



The electron-deficient growing radicals will combine with the electron-rich semiquinone anions. The solvated amine radical cations, on the other hand, will react by virtue of their instability. The stabilization of the ammonion ion by solvation probably leads to its interaction with the quinone adduct only at a later stage of the inhibition process. In the other case, the liberated amine would have participated in complex formation with the unreacted chloranil so that no gradual increase in the inhibiting efficiency would have been observed on increasing the amine ratio.

Another supporting evidence for the proposed mechanism can be obtained from the results of the polymerizations in solution given in *Figures 5–8*. The effect of the solvent is clearly restricted to its influence on the stability of the amine complexes. The results reveal that greater inhibiting efficiencies are obtained for both monomers when the less stable DMA complexes are used in the polar solvent. In this case the solvent reinforces the stabilization of the complexes which accordingly increases the possibility of their formation. On the other hand, the polar solvent facilitates the dissociation of the TEA complexes by affording stabilization, through solvation, to the resulting unstable unsaturated amine cation which subsequently reacts with tetrachlorohydroquinone to form *N,N*-diethyl amino vinyl trichloro *p*-benzoquinone responsible for the brown colour observed[8]. The consumption of the semiquinone anions in side reactions other than with the growing chains accounts for the absence of the induction periods when the TEA complexes are used in the polar solvent. In the case of DMA, the semiquinone anions are known to be involved in similar side reactions leading to the formation of the crystal violet cation[9]. As these reactions are favoured in polar media and in presence of excess amine their effect is manifested in the retardation which follows the induction periods only in case of AN for complexes DMA-II and III.

One point of difference exists between AN on one hand and VA, styrene[12] and methyl methacrylate[11] on the other hand. Thus while the gradual increase in the amine–chloranil

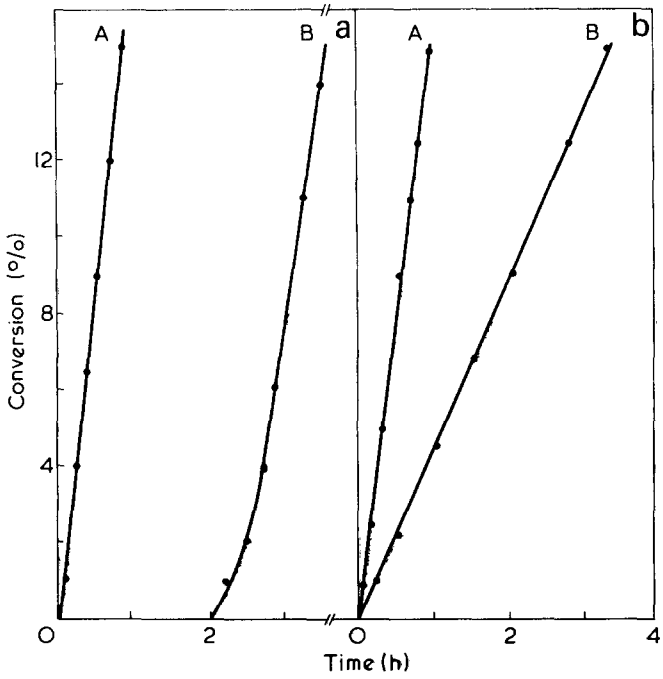


Figure 5 Conversion–time plots of solution polymerizations of AN: (a) in benzene; (b) in acetonitrile. A, 5 X 10^{-4} mol TEA; B, TEA–chloranil complexes-I

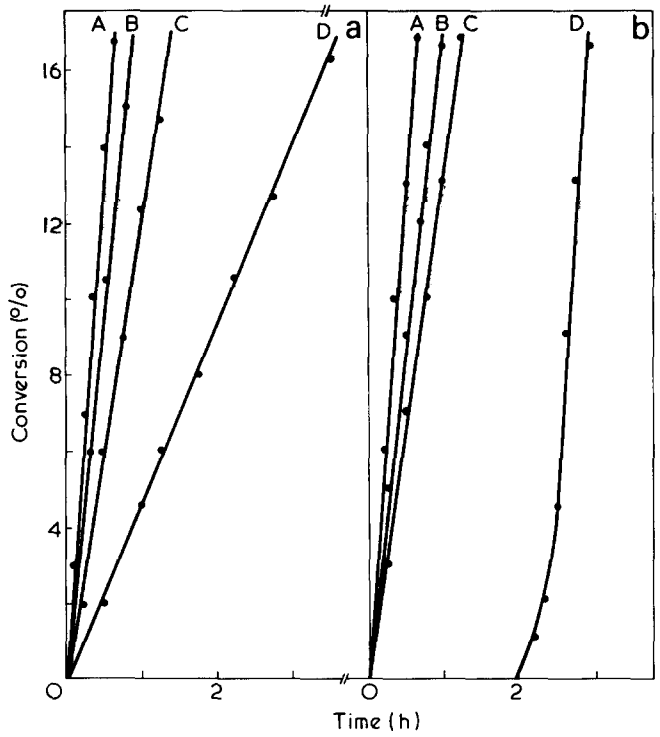


Figure 6 Conversion–time plots of solution polymerizations of AN: (a) in benzene; (b) in acetonitrile. A, AIBN alone; B, 5 X 10^{-4} mol DMA alone; C, chloranil alone; D, DMA–chloranil complexes-I

ratio is accompanied by an increase in the inhibiting efficiency for both amines in case of AN, the reverse is true for the other monomers. The most probable explanation that may be offered is that the quinonoid products formed in case of AN are of sufficiently high redox potential, due to the strong electron-withdrawing nitrile groups, that they are still capable of complexing with the excess amine with the eventual formation of quinonoid products having more than polymeric chain per quinone nucleus.

According to the mechanism suggested in this paper, it is now possible to afford a plausible explanation for the earlier observation that AN in low concentration completely suppresses the emulsion polymerization of VA while at higher concentrations it merely retards the growth reactions[14]. In this case AN fulfils the role of the electron-acceptor, so that electron-transfer from the VA growing chains to the AN molecules results in the formation of molecular complexes of VA macrocations and AN radical anions. The transformation of the growing macroradicals into macrocations is responsible for the full suppression of the growth reactions. Moreover, the mutual interaction of the complex partners results in the formation of electron-deficient nitrile radicals

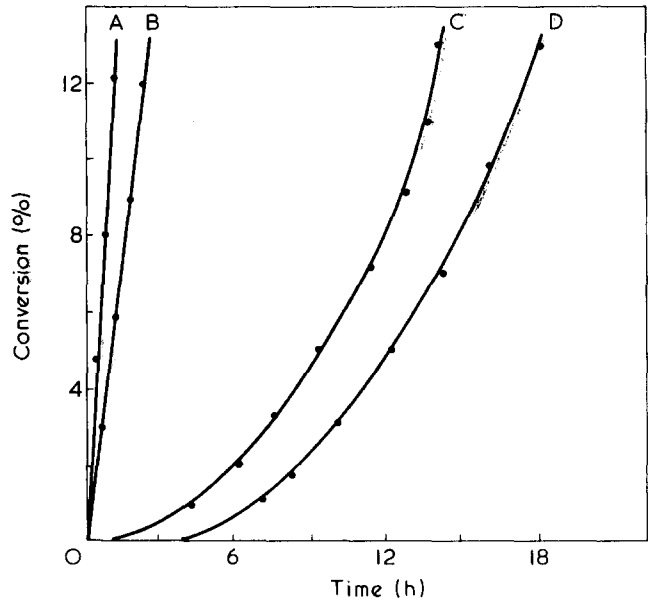


Figure 7 Conversion–time plots of sensitized polymerization of VA in acetonitrile: A, AIBN alone; B, 5 X 10^{-4} mol DMA; C, chloranil alone; D, complex-II

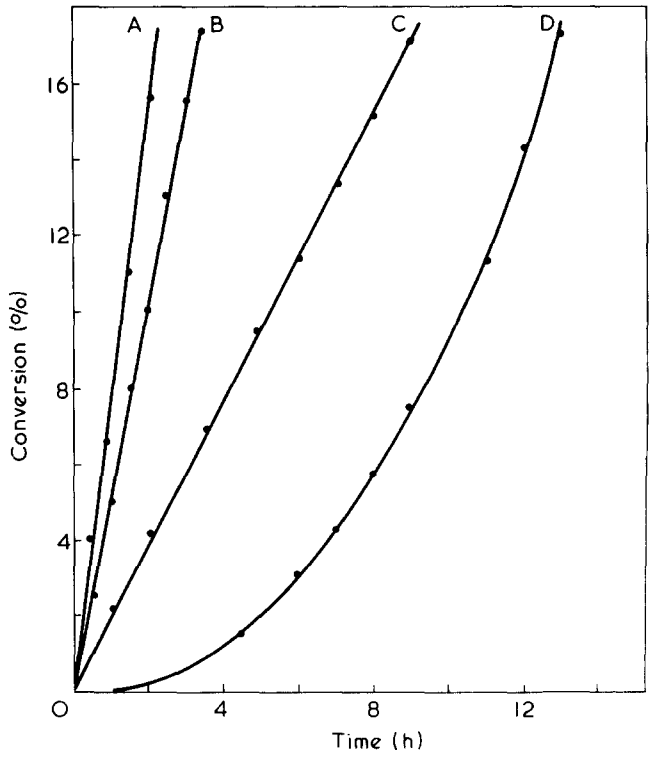
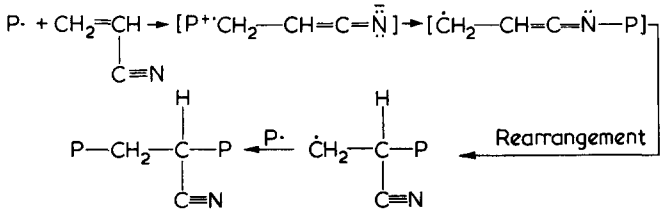
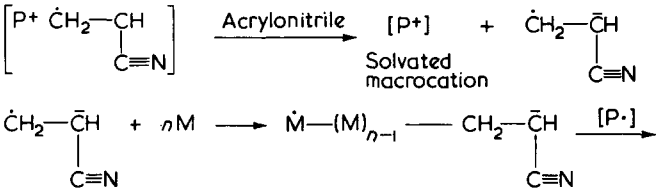


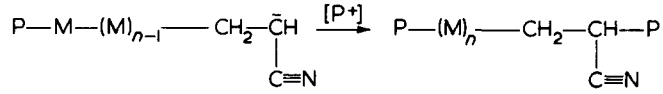
Figure 8 Conversion–time plots of sensitized polymerization of VA in benzene: A, AIBN alone; B, 5 X 10^{-4} mol DMA; C, complex-II; D, chloranil alone

which tend to cross combination with the relatively electron-rich VA growing chains leading to their termination. This is illustrated by the following equations in which P• represents the VA growing radical:



At higher concentrations of AN, solvation of the VA macrocations becomes possible so that the AN radical anion can be found as kinetically independent species capable for the initiation of the polymerization of either or both of AN and VA. The lower reactivity of the AN radicals relative to the corresponding VA analogues together with the lower concentration of AN monomer relative to VA, make the overall rate of growth lower than that for the normal polymerization in absence of AN which accounts for the retardation observed in this case. The reactions involved may be represented by the following equations in which M represents the monomer of AN or VA:





This implies that the inhibition reactions should be considered as oxidation–reduction processes in which the growing chains act as the electron donors.

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