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The Charge-Transfer Complexes as Polymerization Inhibitors. IV. Studies of the Mechanism of Inhibition of Vinyl Acetate Polymerization Using *N,N*-Dimethylaniline and Triphenylphosphine—Chloranil Complexes

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ABSTRACTS: The elucidation of the mechanism of inhibition and retardation of polymerization reactions of quinones has been investigated using the charge-transfer complexes of *N,N*-dimethylaniline (DMA) and triphenylphosphine (TPP) with chloranil as inhibitors for the bulk and solution polymerizations of vinyl acetate (VA) in benzene and in acetonitrile. The complexes have proved to be very efficient inhibitors. The efficiency of inhibition was found to depend on the stability of the complexes, the nature of the electron donor, and its ratio relative to chloranil, as well as on the polarity of the solvent. The greater efficiency (1) in the polar solvent and (2) of the complexes of TPP compared with that of the amine support the idea that inhibition reactions involve electron transfer from the growing radicals to the quinone, with the formation of molecular complexes of macrocations and semiquinone anions. The latter are the actual inhibiting species, so that the inhibiting efficiency is determined by the feasibility of their formation in the polymerizing system. The nature of the inhibition products depends on the extent to which the semiquinones are found as kinetically independent species in the medium. The inhibition reactions should accordingly be considered as oxidation—reduction processes in which the growing chains are the electron donors.

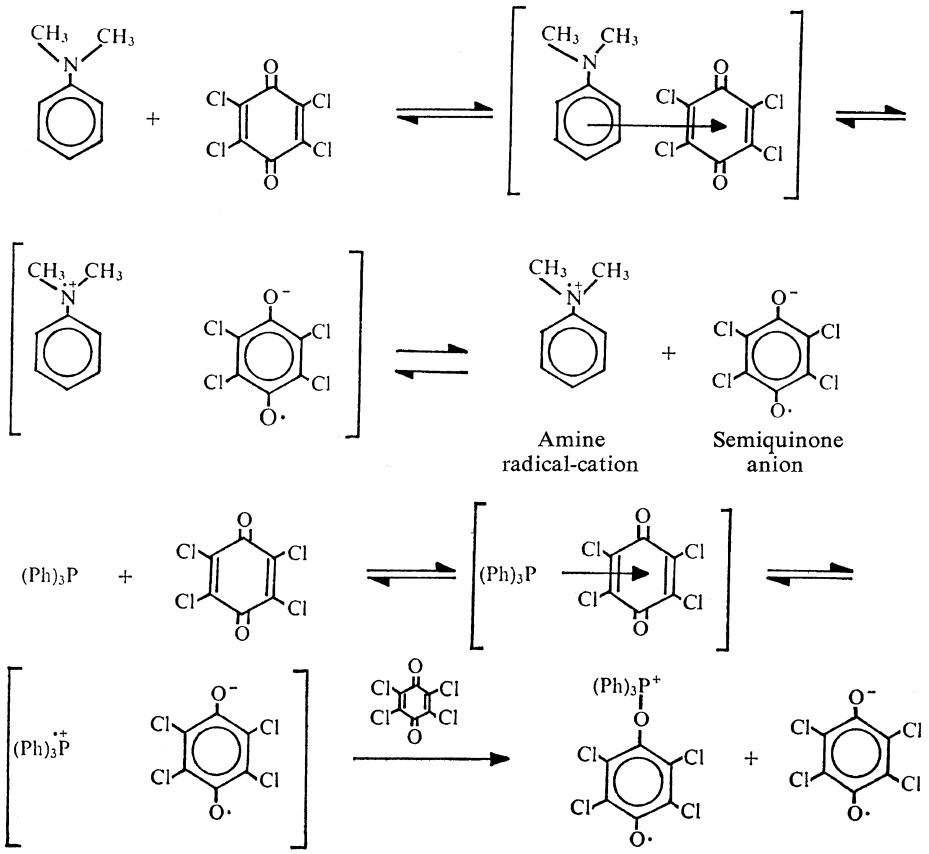
KEY WORDS Inhibition / Vinyl Acetate / Dilatometry / Charge-Transfer Complexes / *N,N*-Dimethylaniline / Triphenylphosphine / Chloranil /

Although quinones have been extensively studied as polymerization inhibitors, the mechanism of their action is not yet clear-cut. Both quinonoid and ether derivatives of the parent quinones have been suggested as products of the inhibition reactions.[1-5] The complexity of the problem is due to the fact that the inhibiting efficiency of a particular quinone is determined not only by its structure and its redox potential, but equally by the nature of polymeric radical and its electron-donating power.

It has already been shown that the formation of quinonoid products is the preferred mechanism during the inhibition of various polymerizations whenever the stabilization of the growing radical—quinone adduct, formed as an intermediate, becomes possible. The stabilization is effected through enolization followed by oxidation for parent quinones having hydrogen atoms in their nuclei, or through the abstraction of a halogen atom in the case of fully halogenated quinones such as chloranil.[6] The ease of enolization and oxidation, relative to halogen abstraction, not only accounts for the greater stability of the reaction intermediates (and consequently the formation of only quinoid products in the cases of benzoquinone and dichlorobenzoquinones) but also for their higher inhibiting powers relative to chloranil, irrespective of the higher

redox potential of the latter. Moreover, it has been recently shown[7] that the inhibiting efficiency of quinones as well as the nature of the inhibition products are also influenced by the polarity of the reaction medium. Thus an ether—styrene—chloranil copolymer is formed as an inhibition product. But when the polymerization is effected in bulk or in benzene solution, a quinonoid copolymer is formed in polar solvents such as acetonitrile.

The dependence of the efficiency of inhibition on the electron-donating power of the growing radical, the redox potential of the quinone, and the polarity of the reaction medium, has led to the idea that the inhibition process involves electron transfer from the growing radicals to the quinone, with the formation of molecular complexes of macrocations and semiquinone anions. The latter species are the actual inhibitors, so that the inhibiting power will be determined by the feasibility of their formation in the polymerizing system. Experimental evidence supporting this idea would be afforded if the inhibiting efficiency of a particular quinone is profoundly increased under conditions which would favor the formation of semiquinones at concentrations higher than those present in the normal inhibition processes. In other words, the inhibiting efficiency should be greatly increased if it were possible to introduce the quinone into the polymerizing system, at least partially, in the semiquinone anion form. For the realization of this idea, use was made of the fact that chloranil forms charge-transfer complexes with a variety of strong electron donors, such as DMA[8] and TPP.[9] The complexes are in equilibrium with their radical ions of semiquinone anions and radical cations.



The position of the equilibrium will be determined by the stability of the complexes formed and the polarity of the medium.

DMA and TPP belong to different classes of electron donors. While the former is, at least partially, a π-donor, the latter is known to be of the *n*-type.[10] The two donors might therefore correspond to different types of polymeric radicals, as regards the nature of the orbitals involved in the complex formation with the inhibitor. DMA corresponds to the styryl radicals and TPP to those of VA. Moreover, the π-complexes of DMA with an electron acceptor such as chloranil will be of lower stability as compared with the σ-complexes of the TPP.[11] This provides the possibility of investigating the influence of the structure of the polymeric radical and the stability of its complexes with the inhibitor on the mechanism and efficiency of inhibition. The inhibiting efficiency of some of these complexes for the polymerization of methyl methacrylate,[12] acrylonitrile,[13] and styrene[14] has been already investigated.

VA is one of the few monomers for which both benzoquinone and chloranil are true polymerization inhibitors, so that the elucidation of the mechanism of inhibition would afford a better understanding for the inhibition reactions in general.

EXPERIMENTAL

Materials

The monomer, amine, and solvents were distilled under nitrogen at low pressure. Azobisisobutyronitrile (AIBN), TPP, and chloranil were purified by crystallization from benzene and ethyl alcohol, respectively.

Reactions

2×10^{-3}-mol AIBN and 5×10^{-4}-mol chloranil were used per mole monomer. The amine was taken in amounts of 0.5, 1.0, and 5.0-mol/mol chloranil, while TPP was taken only in the first two ratios. On mixing the amine and chloranil solutions in the monomer, a blue color was developed, the intensity of which is greatest at the highest amine ratio. On the other hand, no change in the color was observed in case of TPP. The complexes of the three ratios are designated as complexes I, II, and III, respectively. The solution polymerizations were carried out in solutions of 1 : 2 monomer—solvent ratio by volume. The kinetics of the polymerizations was followed dilatometrically at 60 ± 1°C. On heating, the color gradually disappeared, so that by the end of the induction periods the polymerizing system became almost colorless. Only in acetonitrile was the disappearance of the blue color followed by the development of a deep violet color. At 15-% conversion the polymerizations were stopped and the polymers were precipitated by ice-cold petroleum ether at 60—80°C, followed by washing, and filtering. The filtrates and washings were distilled under nitrogen at low pressure and the viscous residues were examined with respect to their quinonoid nature by the Craven test.[15] This color test is extremely sensitive and permits the differentiation between the parent quinone and its derived quinonoid products, since different colors are formed in each case. Moreover, the residues of DMA were analyzed for the presence of nitrogen and chlorine, while those of TPP were redissolved in benzene and reprecipitated in cold petroleum ether to remove any free TPP. The resulting residues were similarly analyzed for phosphorous and the halogen.

RESULTS AND DISCUSSION

The conversion—time plots of the bulk polymerizations of VA in the presence of DMA, TPP, and chloranil separately, as well as in the presence of their various complexes, are shown in Figures 1 and 2. The results reveal that while the amine or TPP alone have a slight retarding effect, chloranil leads to complete suppression of the polymerization, followed by a marked retardation until the normal rate of growth is achieved. On the other hand, in the presence of the charge-transfer complexes the inhibition efficiency is greatly increased and the length of the induction period is determined by the nature of the donor as well as by its ratio relative to chloranil.

The inhibition reaction products were found to be nonquinonoid and free from combined nitrogen or phosphorous under all sets of reaction conditions. This implies that, though the donating partners of the complexes are

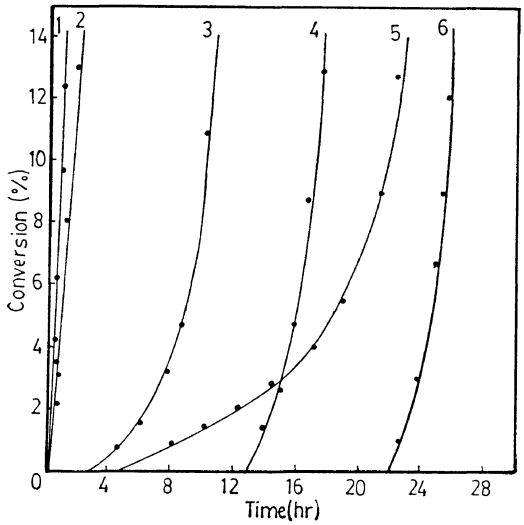


Figure 1. Conversion—time plots of bulk polymerization of VA: 1, AIBN alone; 2, DMA 5×10^{-4} mol; 3, chloranil alone; 4, complex I; 5, complex III; 6, complex II.

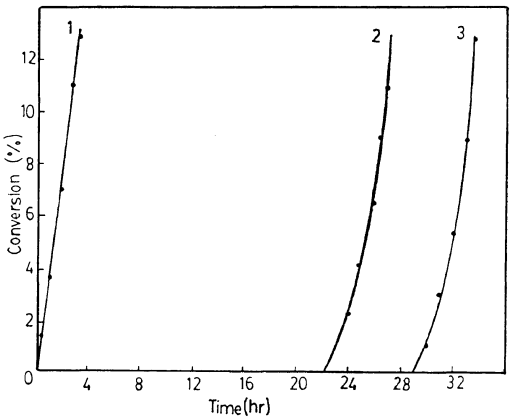
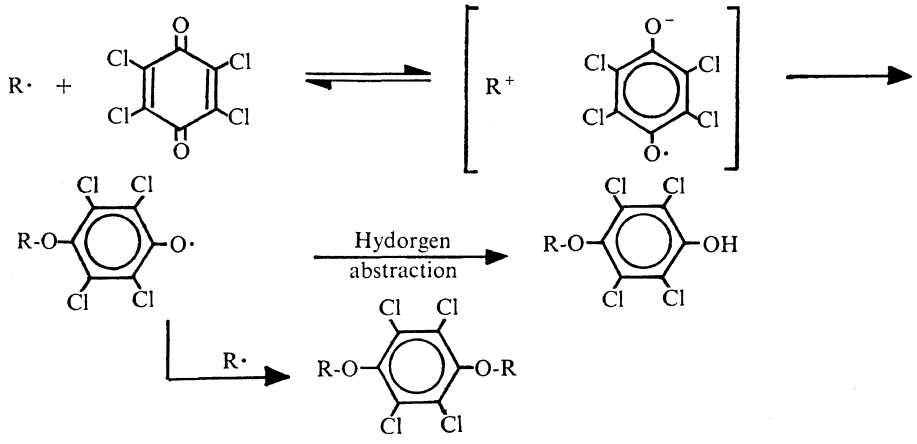


Figure 2. Conversion—time plots of bulk polymerization of VA: 1, TPP alone; 2, complex II; 3, complex I.

involved in the inhibition processes, they are not incorporated into the polymeric structure. On the other hand, chlorine was detected in the residues from the reactions with either chloranil alone or its complexes with both donors. This indicates that the mechanism of inhibition by chloranil alone or by its complexes is the same. The difference in efficiency is due to the difference in the extent to which chloranil is transformed into the active species responsible for inhibition.

The most acceptable mechanism which can account for these facts is one based on electron transfer from the growing radicals to chloranil, with the formation of molecular complexes involving macrocations and semiquinone anions; this can be represented by the following equations, in which R· represents a growing chain.

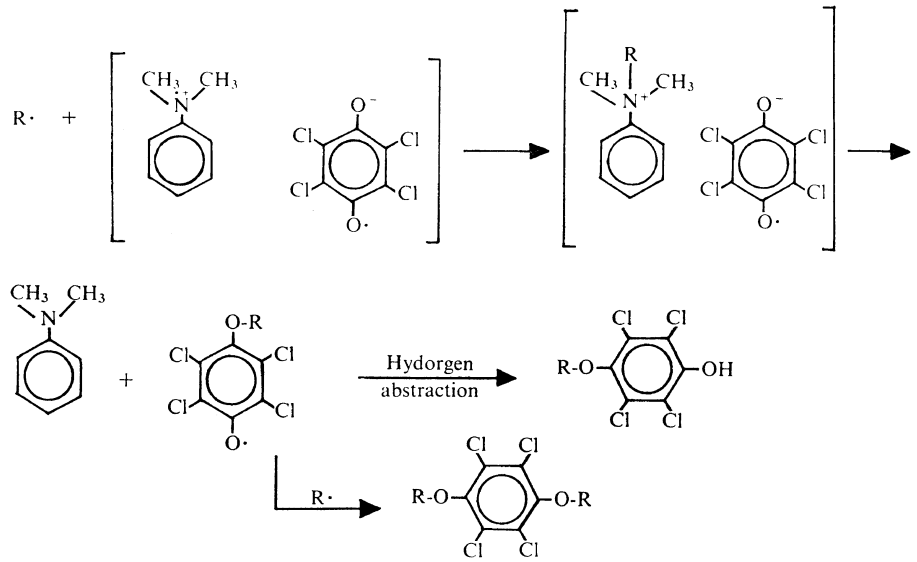


The rapid interaction between the macrocations and the semiquinone anions is responsible for the complete suppression of the growth reactions during the induction period. Since the resulting oxygen radical is insufficiently reactive to initiate the polymerization of the unreactive VA monomer, it will be terminated either by hydrogen abstraction or by combination with a

growing chain. This accounts not only for the retardation which follows the induction period, but also for the difference in the inhibiting power of chloranil for the polymerizations of styrene and VA. Although the polystyryl radical is relatively more electron-rich and highly stabilized, which greatly facilitates the electron-transfer process, the ease with which the oxygen radical initiates the polymerization of the more reactive styrene monomer accounts for the fact that chloranil acts as a retarder for the polymerization of styrene and as a true inhibitor for VA.[1]

The formation of nonquinonoid products in the polymerization of styrene and VA in the presence of chloranil, in contrast to the quinonoid derivatives formed in the cases of methyl methacrylate[12] and acrylonitrile,[13] indicates the greater stability of the molecular complexes of the styryl and VA radicals with chloranil. In these cases the complexes form intimate ion-pairs, in which 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 radicals.

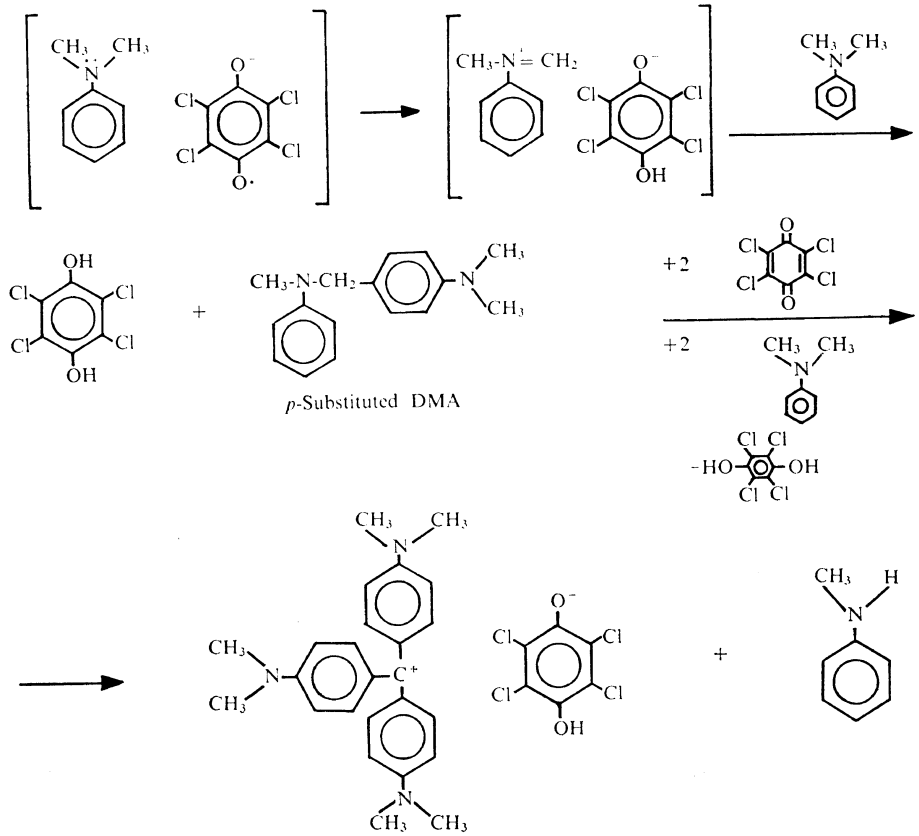
If the VA macroradicals are replaced by much stronger electron-donors, such as DMA or TPP, the semiquinone anion formation would be greatly facilitated. The resulting effect is manifested not only by much higher inhibiting efficiencies, but also by the increasing tendency towards the behavior of ideal inhibitors, whose effect is not followed by retardation. The mechanism of inhibition in the case of the amine may be represented by



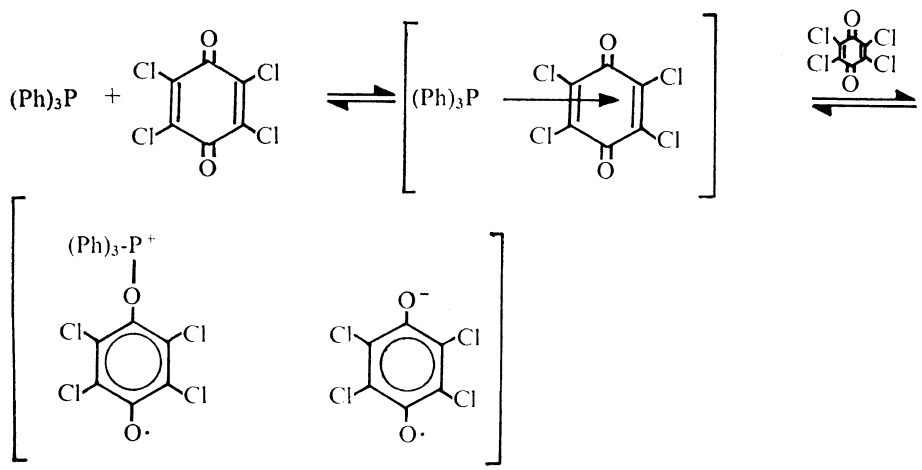
Both types of radical ions are sufficiently stabilized to be able to act as radical traps. In this respect the growing radicals, due to their nucleophilic nature, will be preferentially directed towards combination with the more reactive radical cations. The subsequent reaction of the charged species leads to the liberation of the free amine and the formation of the oxygen radical, which is terminated either by combination or by disproportionation with a growing chain. This implies that although both partners of the molecular 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. Further evidence to support this mechanism can be obtained by comparing the inhibiting efficiency of the various complexes formed at different amine ratios. At equimolar ratios of the amine and chloranil, the complex formation is greatly favored, so that a maximum

concentration of the radical ions becomes possible; this will account for the maximum inhibiting power observed (curve 6 in Figure 1). In this case, the efficiency of inhibition is more than seven times as great as the efficiency of chloranil alone and nearly twice as great as that of the complexes formed at lower amine ratios.

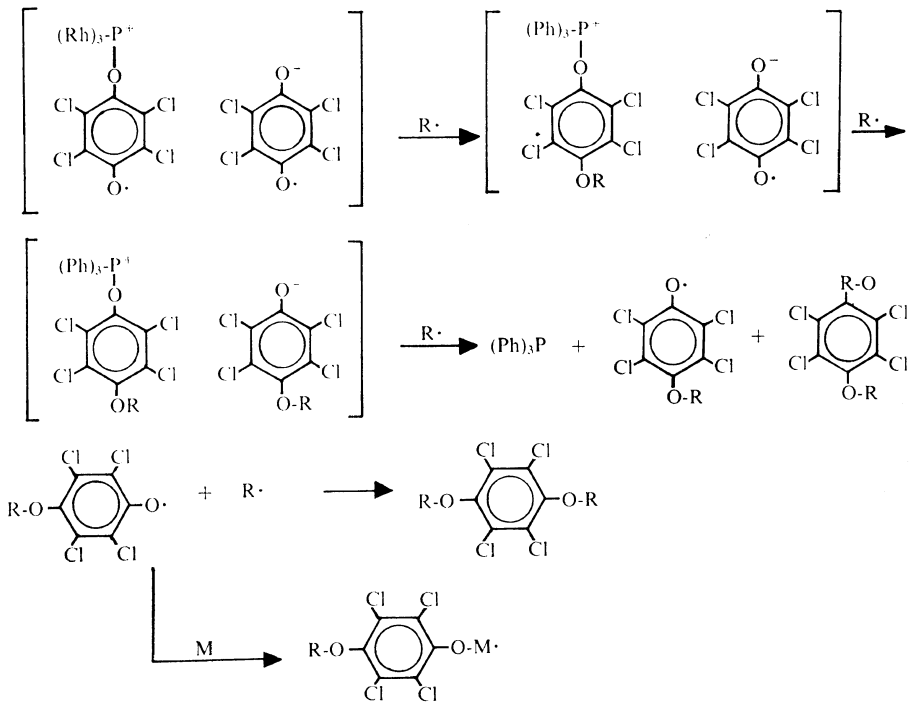
If the amine ratio is greatly increased, a sharp decrease in the inhibiting power is observed, followed by appreciable retardation (curve 5 in Figure 1). Although the complex formation is similarly favored in this case, the excess amine provides the possibility for the mutual interaction of the radical ions, with the eventual formation of tetrachlorohydroquinone and a *p*-substituted DMA. The latter is involved in a series of subsequent reactions, in which chloranil is transformed gradually into tetrachlorohydroquinone and the amine into crystal violet cation.[8]



The involvement of the semiquinone anions in these side reactions accounts for the sharp decrease of the inhibiting efficiency. The appreciable retardation observed can be attributed to the tetrachlorohydroquinone acting as a hydrogen donor for the growing chains. The greater inhibiting power of the TPP relative to their DMA analogues is obviously due to the greater stability of the TPP σ-complexes, which shifts the reaction towards the formation of a higher concentration of semiquinone anions, especially when chloranil is taken at higher ratios relative to TPP.[9]



The maximum inhibiting efficiency of complex I of TPP relative to complex II provides strong evidence that the semiquinone anions are the actual inhibiting species. The formation of nonquinonoid products in this case reveals that the semiquinone anions are not found as kinetically independent species, so that the inhibition reaction might be represented by the following equations.



The capacity of the growing chains for electron donation and stabilization of the resulting macrocation seems to facilitate the libration of TPP.

The aforementioned mechanism suggested for the inhibition process receives additional support

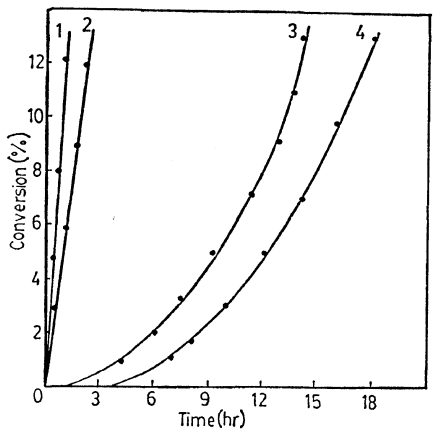


Figure 3. Conversion—time plots of sensitized polymerization of VA in acetonitrile: 1, AIBN alone; 2, DMA 5×10^{-4} mol; 3, chloranil alone; 4, complex II.

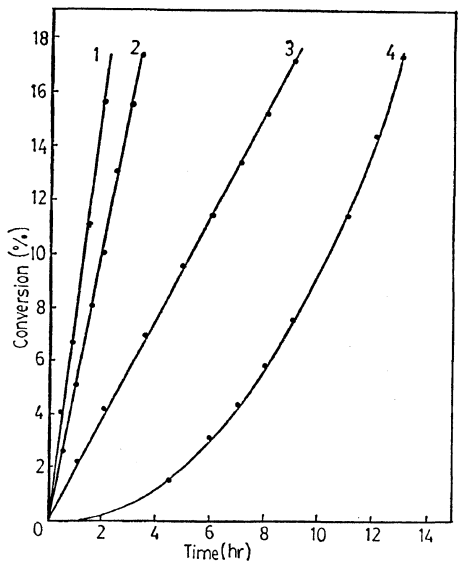
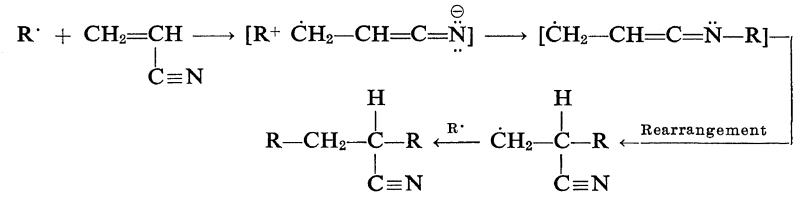


Figure 4. Conversion—time plots of sensitized polymerization of VA in benzene: 1, AIBN alone; 2, DMA 5×10^{-4} mol; 3, complex II; 4, chloranil alone.

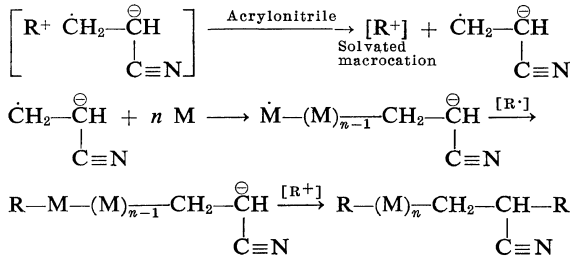
from the polymerizations carried out in benzene and in acetonitrile. Although nearly identical behavior is observed for the action of chloranil alone in both solvents, the inhibiting efficiency of its complexes with both donors was found to be greatly influenced by the polarity of the solvent. The effect of the solvent seems to be general, irrespective of the nature of the complex, so that only the results of DMA are given in Figures 3 and 4 for illustration. Generally, the complexes are only weak retarders in benzene, but are strong inhibitors in acetonitrile. The nonstabilizing effect of nonpolar solvents for the radical cations leads to their mutual interaction with the semiquinone-anion partners, and the eventual consumption of the latter in side reactions other than with the growing chains. The decomposition products of the complexes in the case of DMA are tetrachlorohydroquinone and substituted amine derivatives. The hydroquinone seems to be responsible for the retardation observed.

On the other hand, in acetonitrile, radical-ion formation is greatly facilitated and the equilibrium is shifted towards the formation of higher concentrations of such species, although side reactions involving their mutual interaction are known to occur to a minor extent.[8,9]

According to the mechanism suggested in this paper, it is now possible to offer a plausible explanation for the earlier observation that acrylonitrile in low concentration completely suppresses the emulsion polymerization of VA, while at higher concentrations it merely retards the growth reactions.[16] In this case, acrylonitrile fulfils the role of the electron acceptor, so that electron transfer from the VA growing chains to the nitrile will result in the formation of molecular complexes of VA macrocations and acrylonitrile radical-anions. The transformation of the macroradicals into macrocations is responsible for the full suppression of the growth reactions. Moreover, the mutual interaction of the complex partners probably leads to the formation of electron-deficient nitrile radicals, which tend to combine with the relatively electron-rich VA growing chains and lead to their termination. This is illustrated by the following equations, in which R· represents the VA growing radical.



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



In conclusion, it may be said that the use of the charge-transfer complexes of DMA and TPP with chloranil offers the possibility of investigating the elementary steps involved in the inhibition of the polymerization reactions by quinones.

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