Notes to the Editor

Possibilities for promoting cationic polymerization by common sources of free radicals

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It is now fairly well established[1,2] that organic cations, anions and free radicals participate in electron transfer equilibria which may be represented generally as in equation (1)

One example of such an overall transformation, important in polymer chemistry, is the inhibition[3,4,5] of free radical polymerization by iron (III) and copper (II) salts (equation (2). In this case, the growing free radical is effectively oxidized to the corresponding carbocation with simultaneous ligand transfer from the metal. Metal-promoted oxidations of free radicals have been extensively characterized by Kochi[6,7] who showed that, for appropriate metal oxidants, ligands and solvents, the free carbocation may be produced (equation 3).

In these transformations it may be assumed that electron-releasing substituents attached to the carbon-centred radical will favour electron transfer processes by stabilizing the product carbocation and hence lowering both the ionization potential and oxidation potential of the free radical.

Previously[8,9,10] we have given conclusive evidence for the efficiency of electron oxidation of hydroxyalkyl radicals by paraquat (PQ^{2+}) cation (equation 4).

Similarly the propagating radical derived by AIBN-initiated polymerization of 9-vinyl carbazole (NVC), which has good electron donor properties, is readily scavenged by methylene blue (MB^+) in methanol solution[11]. Inhibition of polymerization involves electron transfer to the coloured dye molecule and, because methanol is a precipitant for poly(9-vinyl carbazole), the onset of polymerization is denoted by the simultaneous decolourization of dye and formation of precipitated polymer. Presumably the inhibition arises because the cation formed in rapidly destroyed by methanolysis. Upon opening the reaction vessels to the air, the reduced dye component is immediately reoxidized to methylene blue (equations 5).

In complete contrast it is known[12] that addition of CBr_4 to AIBN-initiated polymerization of NVC in aprotic solvents produces an acceleration in the rate of reaction due, probably, to oxidation of growing free radical to propagating cation by CBr_4 (equation 6). In this case the solvent (e.g. CH_2Cl_2) is not reactive towards the cation produced and both free radical and cationic polymerization may occur simultaneously. Other cationic polymerizations arising from free radical sources include the thermal, photochemical, and radiation-induced polymerizations of tetrahydrofuran in the presence of maleic anhydride[13].

Aryl diazonium salts, which initiate cationic polymerization by thermal[14] and photochemical[15] processes under appropriate conditions, are known to participate[16] in a variety of redox reactions with electron-donor free radicals (equation 7).

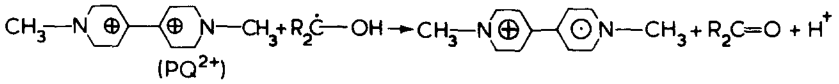
For these systems there is the added advantage that each electron transfer to a diazonium cation produces an aryl radical which may then generate a reducing radical (e.g. $\cdot CH_2OH$) by hydrogen abstraction, and hence create a chain process.

The previous discussion serves to illustrate the range of combinations of organic radicals and oxidants which are known to participate in redox processes. It seemed reasonable therefore to determine whether any of these, or related reactions, might conveniently be employed to initiate cationic polymerization of olefins and cyclic ethers under appropriate conditions. For successful cationic polymerizations it is necessary to ensure that the systems are essentially free from protic agents, nucleophiles or nucleophilic anions[17]. Fortunately, all monomers participating in cationic polymerizations (alkyl vinyl ethers, NVC, cyclic ethers, substituted styrenes, etc.) readily yield corresponding electron donor radicals either by addition of a free radical to the olefinic group, or by abstraction of a hydrogen atom by a free radical. Reactions of AIBN in solutions containing alkyl vinyl ethers and tetrahydrofuran exemplify the

$$R^+ \underset{-e}{\overset{+e}{\rightleftharpoons}} R\cdot \underset{-e}{\overset{+e}{\rightleftharpoons}} R^- \qquad (1)$$

$$P_n^{\cdot} + FeCl_3 \longrightarrow P_nCl + FeCl_2 \qquad (2)$$

$$R-\underset{CH_3}{\overset{CH_3}{C}}\cdot + Cu^{II} \longrightarrow R-\underset{CH_3}{\overset{CH_3}{C^+}} + Cu^{I} \qquad (3)$$



(4)

$$AIBN \xrightarrow{50°C} R\cdot$$
$$R\cdot + NVC \longrightarrow R{-}NVC\cdot \xrightarrow{MB^+} R{-}NVC^+ + (MB\cdot) \qquad (5)$$
$$R{-}NVC^+ + MeOH \longrightarrow R{-}NVC{-}OMe + H^+$$

$$R{-}NVC + CBr_4 \longrightarrow R{-}NVC^+ + {}^{\cdot}CBr_3 + Br^- \qquad (6)$$

$$\cdot CH_2OH + ArN_2^+ \longrightarrow CH_2O + H^+ + Ar\cdot + N_2 \qquad (7)$$

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possibilities (equations 8).

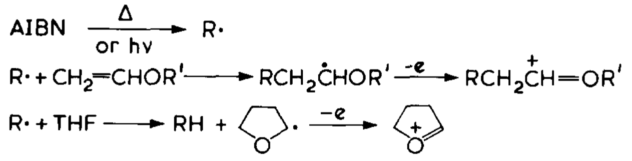
It remains only to devise suitable oxidants which simultaneously supply the necessary counterion for successful propagation to ensue.

Recently there has been a growth of interest in the use of aryl diazonium salts[15,18] ($ArN_2^+X^-$), diaryl iodonium salts[19] ($Ar_2I^+X^-$), and triaryl sulphonium salts[20] ($Ar_3S^+X^-$) as photochemical initiators for cationic polymerizations. Of these, only the aryl diazonium salts are useful as thermal initiators[14] and for all three types of salt (X^- = PF_6^-, SbF_6^-, AsF_6^-, etc.) detailed mechanisms of photochemically-induced decomposition are varied and may change from monomer to monomer. However, all three types of salt may fragment on electron transfer reduction (equations 9).

It seemed possible therefore that electron donor free radicals such as those obtained from cationically polymerizable monomers might be capable of inducing similar homolytic fragmentation. Taking diaryl iodonium salts as a typical case, the overall reduction sequence would be represented by equation (10).

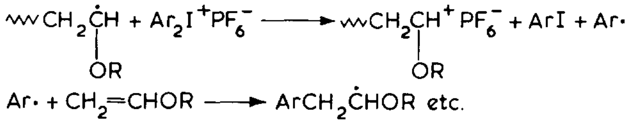
Thus, in principle at least, any method generating electron donor free radicals in the presence of monomers such as alkyl vinyl ethers, THF etc. would then yield, in the presence of fragmentable salts $Ar_2I^+PF_6^-$, etc., a *chain reaction* leading to initiation of cationic polymerization. Clearly there will be certain thermodynamic constraints on these possiblities according to the solvents employed and the redox potentials of the free radicals and organic salts involved. Nevertheless, as indicated in the accompanying communication[21], the usual range of cationically polymerizable monomers give rise to free radicals active in the manner indicated above.

For many different reasons it is convenient to employ photochemical sources of free radicals, particularly those such as bonzoin alkyl ethers and alkoxyacetophenones which find commercial application in u.v. curable coatings[22]. In these cases the initial photofragmentation (which may be readily separated from photodecomposition of the oxidizing salt by use of glass vessels or other appropriate filters) yields two radicals, one of which (e.g. $Ar\dot{C}H{-}OR$) must be expected to undergo immediate oxidation to the corresponding cation, whilst the other (e.g. $Ar\dot{C}O$) must be expected to react with monomer, e.g. for benzoin methyl ether (equation 11).

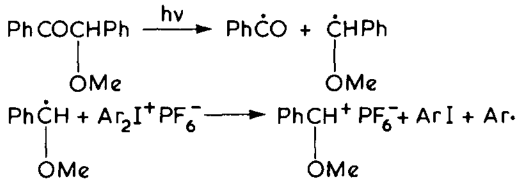


(8)

$$\begin{aligned} &ArN_2^+ \xrightarrow{e} Ar\dot{N}_2 \longrightarrow Ar\cdot + N_2 \\ &Ar_2I^+ \xrightarrow{e} Ar_2I^\cdot \longrightarrow ArI + Ar\cdot \\ &Ar_3S^+ \xrightarrow{e} Ar_3\dot{S} \longrightarrow Ar_2S + Ar\cdot \end{aligned} \qquad (9)$$



$$\begin{aligned} &\sim\!\sim CH_2\dot{C}H(OR) + Ar_2I^+PF_6^- \longrightarrow \sim\!\sim CH_2CH^+(OR)\,PF_6^- + ArI + Ar\cdot \\ &Ar\cdot + CH_2{=}CHOR \longrightarrow ArCH_2\dot{C}HOR \text{ etc.} \end{aligned} \qquad (10)$$



$$\begin{aligned} &PhCOCH(OMe)Ph \xrightarrow{h\nu} Ph\dot{C}O + \dot{C}H(OMe)Ph \\ &Ph\dot{C}H(OMe) + Ar_2I^+PF_6^- \longrightarrow PhCH^+(OMe)\,PF_6^- + ArI + Ar\cdot \end{aligned} \qquad (11)$$

$$\begin{aligned} &PhN{=}NCPh_3 \xrightarrow[\text{or}\,\Delta]{h\nu} Ph\cdot + N_2 + \cdot CPh_3 \\ &Ph_3C\cdot + Ph_3S^+PF_6^- \longrightarrow Ph_3C^+PF_6^- + Ph_2S + Ph\cdot \end{aligned} \qquad (12)$$

As in the case of diazonium salt decompositions, there will be a chain reaction leading to formation of propagating cationic centres which would provide a further significant quantum amplification factor for the design of light sensitive systems for all applications of photoinitiated polymerizations.

Support for the proposed electron transfer oxidation of organic radicals of the types described was readily obtained by studies of the decomposition of phenylazotriphenyl methane in CH_2Cl_2 containing the various cation salts. The azo compound[23] (λ_{max} 420 nm; ϵ_{max} 204 M^{-1} cm^{-1}) may be conveniently decomposed by u.v. irradiation, or by heating, to yield two radicals (equations 12).

Whilst the fate of the Ph· (or $PhN_2\cdot$) radical is as yet unknown, in a typical reaction, u.v. irradiation (2 h, 25°C) of a CH_2Cl_2 solution containing 9×10^{-4} M (PhN_2CPh_3) and 10^{-3} M ($Ph_3S^+PF_6^-$) produced the characteristic absorption spectrum of the Ph_3C^+ cation[24] (λ_{max} 410 and 438 nm; ϵ_{max} 39 000) with an absorbance corresponding to approximately 95% conversion of triphenyl methyl groups.

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Photochemical and thermal cationic polymerizations promoted by free radical initiators

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In the accompanying communication[1] we have indicated the supporting evidence for a proposed oxidation of electron donor free radicals to corresponding carbocations. The overall process envisaged may be represented as:

$$R\cdot \xrightarrow{-e} R^+ \qquad (1)$$

and, if applicable to initiating and early propagating intermediates in free radical polymerization, would result in the formation of initiating or propagating species for cationic polymerizations. Such processes would have considerable value in the design of photocurable cationic systems required for surface coatings, printing plate manufacture, etc., and we now report preliminary results which provide experimental support.

Recently there has been a significant growth of interest in the use of aryl diazonium salts[2] ($ArN_2^+X^-$), diaryl iodonium salts[3] ($Ar_2I^+X^-$) and triaryl sulphonium salts[4] ($Ar_3S^+X^-$) as photochemical initiators for cationic polymerizations of epoxides, alkyl vinyl ethers and other related monomers. With the exception of aryl diazonium salts, which are known to decompose thermally at moderately elevated temperatures[5], the other types of cationic salt ($X^- = PF_6^-, SbF_6^-, AsF_6^-$, etc.) are essentially thermally stable and unreactive to many cationically polymerizable monomers. In contrast all three types of salt yield cationic species on u.v. irradiation and the simple aryl homologues have absorption maxima below 300 nm with little or no photoactivity at wavelengths above the glass cut-off point. We have noted[1] that electron transfer to these cations results in fragmentation with the formation of aryl radicals and, if the reducing species is a suitable initiating or propagating free radical, a *chain reaction* for formation of cations will ensue provided that cationically polymerizable monomers are present, e.g. for polymerization of alkyl vinyl ethers (equations 2).

In principle, it should not matter whether the initiating free radical (X·) is obtained by thermal or photochemical (or any other) means. Both types of radical source have been studied in order to support the mechanistic ideas (thermal initiation) and to outline the scope for practical u.v. curing systems.

It is probable that atmospheric oxygen will interfere with radical promoted cationic polymerization by the usual peroxide forming processes – preliminary results suggest that the effect is greatest for alkyl vinyl ethers – and each system will need to be considered individually.

THERMAL PROMOTION OF CATIONIC POLYMERIZATION BY FREE RADICAL INITIATORS

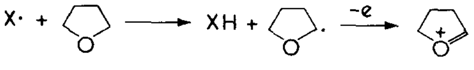
Monomers chosen for study were tetrahydrofuran and n-butyl vinyl ether. Polymerizations were performed in vacuum, outgassed systems and purification procedures were those conventionally used for cationic polymerizations[6]. Representative results are given in *Tables 1* and *2* and it must be stressed that the data are not optimized in any way and conversions to polytetrahydrofuran were deliberately kept very low so as to permit easy handling of the very viscous solutions obtained.

For n-butyl vinyl ether electron donor, free radicals are obtained by

$$X\cdot + CH_2{=}CHOR \longrightarrow XCH_2\dot{C}HOR \text{ etc.}$$

$$\sim\!\sim CH_2\dot{C}HOR + Ar_2I^+PF_6^- \longrightarrow \sim\!\sim CH_2CH{=}\overset{+}{O}R\ PF_6^- + ArI + Ar\cdot \qquad (2)$$

$$Ar\cdot + CH_2{=}CHOR \longrightarrow ArCH_2\dot{C}HOR \text{ etc.}$$



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