Polymer Bulletin 1, 1-6 (1978)

Polymer Bulletin

Thermal and Photochemical Cationic Polymerisations Induced by $AgPF_6$ in the Presence of Free Radical Initiators

Firas A. M. Abdul-Rasoul, Anthony Ledwith and Yusuf Yağci

Department of Inorganic, Physical and Industrial Chemistry,
University of Liverpool, Liverpool L69 3BX, U. K.

Summary

Cationic polymerisations of n-butylvinylether, tetrahydrofuran and a typical bis-epoxide are readily induced in the presence of $AgPF_6$ by thermal and photochemically active sources of free radicals.

Introduction

Recently we have presented evidence for the oxidation of electron donor free radicals to corresponding carbocations (LEDWITH,1978; ABDUL-RASOUL ET AL.1978). The overall process may be represented simply as

$$R \xrightarrow{-e} R^+$$

and, when applied to polymerising systems, has the effect of converting initiating and early propagating free radicals into initiating or propagating species for cationic polymerisations. These transformations are of obvious importance in the design of photocurable cationic systems required for surface coatings and printing plate manufacture. Currently there is significant interest in the use of aryl diazonium salts ($ArN_2^+X^-$), diaryl iodonium salts ($Ar_2I^+X^-$), and triaryl sulphonium salts ($Ar_3S^+X^-$) as photochemical initiators for cationic polymerisations of epoxides, alkylvinylethers and related monomers (CRIVELLO and LAM, 1977). All three types of salt yield cationic species on U.V. irradiation and the simple aryl homologues have absorption maximum below 300 nm with little or no photoactivity at wavelengths above the glass cut off point. We have noted (ABDUL-RASOUL ET AL,1978) that electron transfer to these cations results in fragmentation with 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 polymerisable monomers are present, e.g. for polymerisation of alkyl vinylethers,

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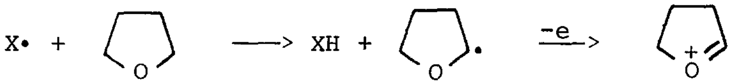
$$X\cdot + CH_2{=}CHOR \longrightarrow XCH_2\dot{C}HOR \quad \text{etc.}$$

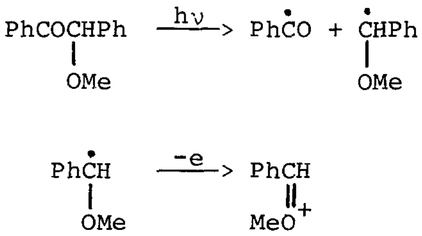
$$\sim\!\sim CH_2\dot{C}HOR + Ar_2I^+PF_6^- \longrightarrow \sim\!\sim CH_2CH{=}\overset{+}{O}RPF_6^- + ArI + Ar\cdot$$

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

For alkylvinylethers electron donor free radicals are obtained by radical addition to the monomer, as indicated above, whilst for polymerisation of THF and other cyclic ethers such as epoxides the important reducing species must be obtained by hydrogen abstraction, e.g.



In principle, it should not matter whether the initiating free radical (X•) is obtained by thermal or photochemical (or any other) means and both types of radical source have been shown to be effective. For many different reasons it is convenient to employ photochemical sources of free radicals, particularly those such as benzoinalkylethers and alkoxyacetophenones which find commercial application in U.V. curable coatings (LEDWITH,1976,1977). In these cases the initial photofragmentation (which may be readily separated from photodecomposition of the oxidising 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. $Ar\dot{C}O$) will react with monomer, e.g. for benzoin methylether;



$$PhCO\underset{\displaystyle OMe}{\underset{|}{C}}HPh \xrightarrow{h\nu} Ph\dot{C}O + \underset{\displaystyle OMe}{\underset{|}{\dot{C}}}HPh$$

$$Ph\underset{\displaystyle OMe}{\underset{|}{\dot{C}}}H \xrightarrow{-e} PhCH{=}\overset{+}{O}Me$$

Another convenient source of free radicals which may be used thermally or photochemically is phenylazotriphenylmethane which decomposes to give a triphenylmethyl radical (readily oxidised to the corresponding cation (LEDWITH,1978)) and a phenyl radical (reactive in hydrogen abstraction and addition).

$$PhN{=}NCPh_3 \xrightarrow[\text{or } \Delta]{h\nu} Ph\bullet + N_2 + \bullet CPh_3$$

$$Ph_3C\bullet \xrightarrow{-e} Ph_3C^+$$

For successful cationic polymerisations it is necessary to have essentially anhydrous reagents and to ultilise a counter-ion of low nucleophilicity to avoid termination by anion recombination with the propagating cationic centre. Complex anions such as PF_6^-, SbF_6^-, BF_4^- are most stable in this respect. Oxidation of organic radicals by metal salts is a well-established phenomenon (KOCHI,1973) and therefore it seemed appropriate to test the use of metal salts in converting free radicals to propagating carbocations. Of the common oxidising metal cations, the only readily available salts matching the criteria for successful cationic polymerisation are those of silver(I) such as $AgPF_6$, $AgAsF_6$, $AgClO_4$. We now report evidence that $AgPF_6$ in particular is effective in promoting cationic polymerisations from free radical initiator systems and thus demonstrate further the general value of electron transfer reactions of organic radicals.

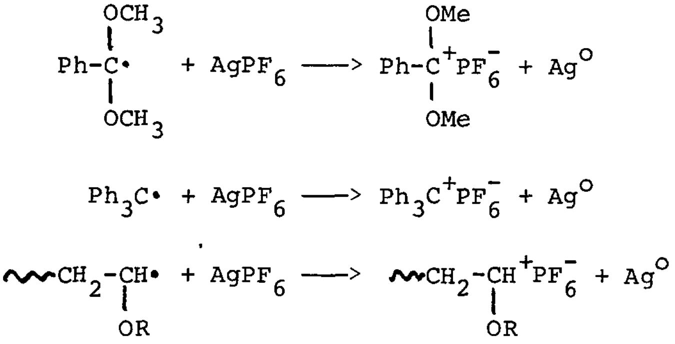
Experimental

The representative monomers used in this study were n-butylvinylether, tetrahydrofuran and 1,2-expoxyethyl-3,4-epoxycyclohexane and these were purified by the conventional drying and distillation procedures. All polymerisations were performed in vacuum outgassed systems and, where appropriate, the polymers were recovered by precipitation into ether methanol or water containing a little base. The results are not optimised in any way and conversions to polytetrahydrofuran were deliberately kept very low so as to permit easy handling of the very viscous solutions obtained.

Aromatic carbonyl compounds generally, and aliphatic azo compounds are readily selectively excited in the presence of the silver salts by the simple expedient of using glass vessels. Appropriate wavelength filters may also be used. Photochemically induced polymerisations were carried out as for the thermal reactions except that the reaction vessels (1.cm diameter glass tubes) were irradiated by means of a 250 watt medium pressure mercury lamp whilst maintained in a water bath at 25°C.

Results and Discussion

Typical data for the polymerisation of n-butylvinylether initiated by free radical sources is given in the Table and it is quite clear that $AgPF_6$ functions as a one electron oxidant for electron donor radicals in a manner similar to that previously established for organic cation salts. In all cases the polymerisations were accompanied by formation of a black precipitate or colloidal dispersion of silver metal. Presumably the reactions may be generalised as follows:



$$\mathrm{Ph{-}\overset{\displaystyle OCH_3}{\underset{\displaystyle OCH_3}{C}}\bullet + AgPF_6 \longrightarrow Ph{-}\overset{\displaystyle OMe}{\underset{\displaystyle OMe}{C}}{}^{+}PF_6^{-} + Ag^{0}}$$

$$\mathrm{Ph_3C\bullet + AgPF_6 \longrightarrow Ph_3C^{+}PF_6^{-} + Ag^{0}}$$

$$\mathrm{\sim\!\sim CH_2{-}\underset{\displaystyle OR}{CH}\bullet + AgPF_6 \longrightarrow \sim\!\sim CH_2{-}\underset{\displaystyle OR}{CH}{}^{+}PF_6^{-} + Ag^{0}}$$

A typical photochemically induced polymerisation of bulk THF at 25° with $[AgPF_6] = 10^{-2}M$, $[PhCOC(OCH_3)_2Ph] = 5 \times 10^{-3}M$ produced an 11% yield of polytetrahydrofuran after 55 mins irradiation time. A control experiment without the acetophenone derivative failed to produce any precipitable polymer after the same irradiation time although silver metal was produced in both experiments.

Even more convincing evidence for the promoting effect of free radical sources on cationic polymerisation induced by $AgPF_6$ was obtained from the cross-linking monomer 1,2-epoxyethyl-3,4-epoxycyclohexane. Bulk polymerisations of the bis-epoxide containing $10^{-2}M$ $AgPF_6$ were carried out. In the absence of a free radical source control experiments at 60° failed to produce a gel and photochemical irradiation gave evidence of some gel formation after 6-7 hours irradiation. In contrast addition of $5 \times 10^{-3}M$ $PhN{=}NCPh_3$ produced complete gelation after heating for 60 mins at 60° and after irradiation for 120 mins at 25°. Similarly photolysis in the presence of $5 \times 10^{-3}M$ $PhCOC(OCH_3)_2Ph$ produced complete gelation after about 30 mins at 25°.

TABLE

Polymerisation of n-butylvinylether[a] in the presence of 10^{-2}M $AgPF_6$

Method	Radical Source (M)	Reaction Time (Temp)	Conversion (%)
Photo	none	3 hrs (25°)	0
Photo	$PhCOC(OCH_3)_2Ph$	10 mins (25°)	95
Thermal	none	2 hrs (25°)	0
Thermal	$PhN{=}NCPh_3$	30 mins (60°)	98
Photo	$PhN{=}NCPh_3$	140 mins (25°)	95
Photo (366 nm)[b]	$PhN{=}NCPh_3$	4 hrs (25°)	90

[a] Bulk monomer containing 10 vol % CH_2Cl_2 to facilitate dissolution of $AgPF_6$

[b] Interference filter which greatly reduced the amount of light available at this wavelength

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A recent publication (WOODHOUSE ET AL,1978) provides evidence that photolysis of solution of $AgPF_6$ and similar salts in pure THF with light of 254 nm wavelength initiates cationic polymerisation with concomitant formation of silver metal. In the present work direct photoexcitation of a THF-silver salt complex is precluded by the use of glass vessels which exclude wavelengths below about 310 nm. However, it is extremely probable that oxidation of initially-formed THF-derived radicals is a common feature of both types of initiation. In our own work we have observed that whilst $AgPF_6$ dissolved in CH_2Cl_2 spontaneously initiates polymerisation of N-vinylcarbazole, a highly reactive, electron donor monomer, comparable polymerisations of the less reactive p-ethoxystyrene occurs only upon irradiation in glass vessels.

Conclusions

The role of one electron oxidants having non-nucleophilic anions as promoters for cationic polymerisations initiated by free radical sources is further confirmed and extended. Results presented may go someway to explaining the long debated (ELEY and RICHARDS, 1949; BURTON and PRAILL,1953) polymerisation of alkylvinylethers initiated by silver perchlorate since ethers generally contain peroxide impurities which could function as free radical sources. Detailed studies of these reactions are now in progress together with a search for suitable metal oxidants other than silver salts.

Acknowledgement

We are indebted to the Ministry of Education, Turkey, for financial support (Y.Y.).

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Received July 3, 1978.