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FORMATION AND REACTIVITIES OF FREE IONS IN CATIONIC POLYMERISATION

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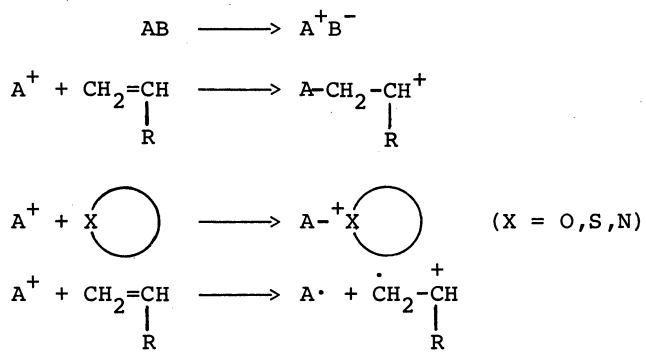
Abstract - Stable salts of carbocations such as triphenyl methyl and especially tropylium ion are useful initiators for cationic polymerisation of reactive olefins such as alkyl vinyl ethers and vinyl carbazoles. Although it is now clear that reaction kinetics are more complex than was originally assumed, use of tropylium hexachloroantimonate as initiator gives a useful estimate of the order of magnitude for free ion propagation rate coefficients in the systems studied. Polymerisation of carefully purified N-ethyl-3-vinylcarbazole by $C_7H_7^+SbCl_6^-$ in CH_2Cl_2 at 0°C yields an estimate for $k_p^+ = 2 \times 10^{+4}\ M^{-1}\ sec^{-1}$ which is some twenty times smaller than that for the closely related monomer N-vinylcarbazole. Distinguishing aspects of the cationic polymerisation of N-ethyl-3-vinylcarbazole are the very high molecular weights obtained and the linear dependence of $\overline{M}_n$ on the monomer/catalyst mole ratio, indicating that transfer and termination are comparatively unimportant.

Polymerisation of trimethylvinyloxysilane, (-)menthylvinylether and (S)-(1-methylpropyl)vinyl ether using tropylium hexachloroantimonate as cationic initiator under conditions in which free carbocations are the important propagating intermediates provides both support and qualification for current theories of stereoregulation in polymerisation of alkyl vinyl ethers.

The organic cation components of comparatively stable molecules such as aryldiazonium, arylsulphonium, and aryliodonium salts undergo electron transfer-induced fragmentation with the donor free radicals obtained from alkyl vinyl ethers and cyclic ethers. This affords a new method for promoting cationic polymerisation with the assistance of conventional thermal and photochemical sources of free radicals.

INTRODUCTION

Initiation of cationic polymerisation (ref.1) involves generation of a positively charged species with an attendant counter-ion. The charged electrophile can then either add to a susceptible monomer molecule, producing a positively charged active centre, or it can accept an electron again yielding a propagating cation, e.g.



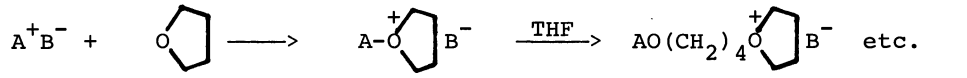
The process of charge generation takes place in situ with Lewis Acid initiators ($TiCl_4$, BF_3, AlR_3 etc) and often requires a bimolecular reaction involving neutral components, e.g.

$$2AlBr_3 \rightleftharpoons AlBr_2^+ \; AlBr_4^-$$

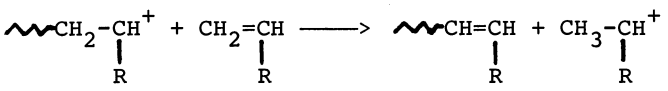
$$BF_3 + H_2O \rightleftharpoons H^+BF_3OH^-$$

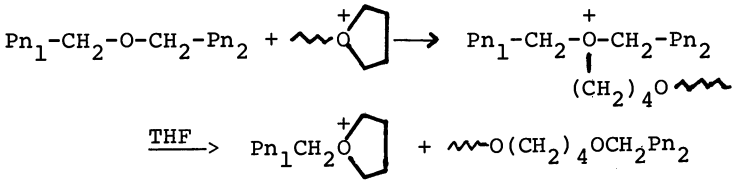
Pre-initiation equilibria of these types have the effect of complicating kinetic analysis of cationic polymerisations which must, in any case, take account of ion-pair dissociation equilibria of the propagating species (Ref.2).

Propagating intermediates in the common types of cationic polymerisation include a range of carbocations (R_3C^+) together with carboxonium ($R\overset{+}{O}{=}CR'_2$), oxonium (R_3O^+), strained sulphonium (R_3S^+), immonium ($R_2\overset{+}{N}{=}CR'_2$), and strained quaternary ammonium (R_4N^+) ions. Monomers susceptible to cationic polymerisation include olefins ($RCH{=}CH_2$) where R is electron releasing (e.g. Ar-, R'O-, R'_2N- etc), and strained heterocyclic compounds for which the propagating entity is the corresponding cyclic 'onium' ion, as exemplified by the ring opening polymerisation of tetrahydrofuran.



Cationic polymerisations differ markedly from anionic and free radical polymerisations in that the very substituents which help to stabilise the growing centre simultaneously afford basic sites in the polymer, or activate monomer, to participate in transfer reactions (Ref.2). For olefins, monomer transfer predominates whereas transfer to polymer is more important in ring opening polymerisation, e.g.





It follows therefore that few, if any, cationic polymerisations are living in the sense of the description as applied to anionic polymerisations, although under certain experimental conditions cationic polymerisations of strained heterocyclic monomers fit the description reasonably well. A further problem is that cations are usually highly reactive towards many common laboratory solvents and this remains a major obstacle to full characterisation of reacting species.

A full discussion of all aspects of cationic polymerisation has recently been published (Ref.2) and this survey will outline our original simple approach to overcoming the problems noted above, giving recent results which modify or support any assumptions made, and will conclude with a brief introduction to a completely new and convenient method for promoting cationic polymerisation with the help of the usual free radical initiators.

INITIATION VIA CARBOCATION SALTS

There are a number of carbocationic salts sufficiently stable to be isolated and characterised in the crystalline state of which triphenyl methyl (Ph_3C^+) and tropylium ($C_7H_7^+$) salts have been the most useful. In the form of salts with comparatively non-nucleophilic anions such as $SbCl_6^-$, PF_6^-, SbF_6^- etc. these cations afford highly convenient initiators for polymerisation of alkyl vinyl ethers and heterocyclic monomers such as tetrahydrofuran. Furthermore, ion-pair dissociation equilibria in solvents such as CH_2Cl_2 are amenable to analysis by the Fuoss treatment (Ref.2) and typical values for ion-pair dissociation constants K_d(mole/litre at 0^oC) are $Ph_3C^+SbCl_6^-$

(3.1×10^{-4})(Ref.4), $Ph_3C^+SbF_6^-$ (2.4×10^{-4})(Ref.5), $Ph_3C^+AsF_6^-$ (1.9×10^{-4}) (Ref.5), $C_7H_7^+SbCl_6^-$ (0.3×10^{-4})(Ref.4).

For polymerisation of tetrahydrofuran, initiation involves hydride ion abstraction by the stable carbocation (Refs. 6,7) and living systems result (Refs. 8,9) when the anion is PF_6^- or SbF_6^- but not for $SbCl_6^-$. Hexachloroantimonate anion is apparently unstable in the presence of growing oxonium ions and some termination occurs, presumably by back-donation of chloride ions (Ref.6).

As a simplified model for cationic polymerisation of olefins, it was assumed (Refs. 10,11) that the very rapid reactions which occur when triphenyl methyl and tropylium salts interact with alkyl vinyl ethers and N-vinyl carbazole arose via rapid and complete addition of the cation to the olefin followed by propagation without termination, although transfer to monomer was indicated by the polymer molecular weights. A further assumption, important to the following discussion, was that, for given conditions of solvent and temperature, ion-pair dissociation constants of the initiating carbocation salts would not differ significantly from those of the appropriate propagating cations. Thus by working with initiator concentrations equal to or less than the ion-pair dissociation constant of the initiating salt, propagation would occur almost exclusively via free ions.

With these assumptions it was possible to estimate values of k_p^+, an apparent free cation propagation rate coefficient. Of the original values obtained (Refs.10,11) those for isobutyl vinyl ether ($k_p^+ = 6.8 \times 10^{+3}$ M^{-1} sec^{-1} in CH_2Cl_2, 0^oC, $C_7H_7^+SbCl_6^-$) and N-vinyl carbazole ($k_p^+ = 4.6 \times 10^{+5}$ M^{-1} sec^{-1} in CH_2Cl_2, 0^oC, $C_7H_7^+SbCl_6^-$) were important in establishing an order of magnitude for values of free ion propagation rate coefficients in chemically initiated cationic polymerisation of olefins. The assumptions made appear to have been completely justified for the case of N-vinylcarbazole polymerisations because independent workers subsequently reported (Ref.12) similar data using different initiating cations and counter-ions. For isobutyl vinyl ether, more recent work (Refs.13,14) has illustrated the invalid nature of some of the assumptions made but even after more refined kinetic analysis (Ref. 13), the order of magnitude established for k_p^+ remains, and best values (Ref. 14) appear to be about two times higher than the value originally quoted (Ref. 10) for initiation by $C_7H_7^+SbCl_6^-$. A particular problem arises with the assumption that ion-pair dissociation constants for growing polymer chains are essentially the same as those of the initiating carbocations. Recent work by Stannett (Ref.15) suggests that this is unlikely - especially for initiation by triphenyl methyl cation salts - and that propagating species may be more associated, with a consequent overestimate of the number of free propagating species and hence artifically low values of k_p^+. It must be noted, however, that in the few cases (Refs. 12,16) where it has been possible to make assessments of the relative values of k_p^+ and corresponding coefficients for ion-pair propagation ($k_p^{\pm}$), it appears that k_p^+ and $k_p^{\pm}$ differ in value by only one order of magnitude. For propagation in polymerisation of certain cyclic ethers it is suggested (Ref.17) that monomer solvation of ion pairs and free ions is essentially equivalent so that values of k_p^+ and $k_p^{\pm}$ become virtually identical. In this respect also, cationic polymerisations differ markedly from their anionic counterparts. A most useful and critical survey of the significance of reported values of rate constants for cationic polymerisations has recently been published by Dunn (Ref.18).

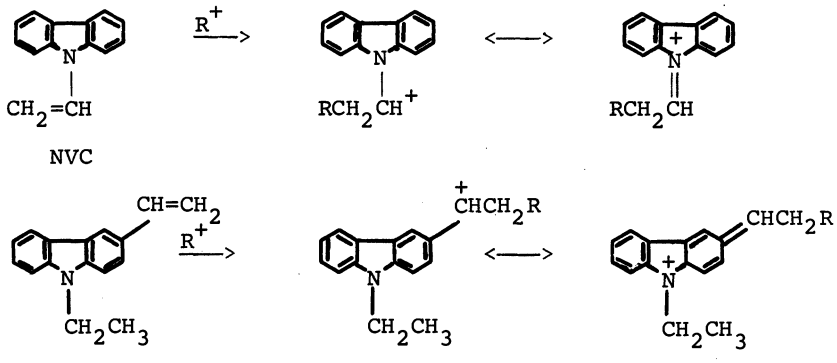
CATIONIC POLYMERISATION OF N-ETHYL-3-VINYLCARBAZOLE

Cationic polymerisation of olefins is, as we have already noted, greatly affected by monomer transfer processes such that every active site generated will ultimately be responsible for the formation of many (10-50) polymer chains. The problem appears to be maximised in polymerisation of alkyl vinyl ethers and styrene and becomes progressively less, though still significant, in polymerisation of p-methoxystyrene and N-vinylcarbazole (NVC). Apparently the propensity to monomer transfer decreases with increasing stabilisation of the propagating cation.

In an attempt to design an olefinic cationic polymerisation having living character, we have collaborated with the group led by J.M. Pearson at Xerox Corporation in the synthesis, purification and polymerisation of vinyl derivatives of carbazole. Other than NVC, polymerisable carbazole-

containing compounds include the isomeric N-ethyl-2-vinyl carbazole (NE2VC) (Refs. 19,20) and N-ethyl-3-vinyl carbazole (NE3VC)(Ref.21). The latter has been known for some years and would be expected to exhibit activity in cationic polymerisation since it would yield a comparatively stable p-aminobenzylic type cation as propagating species. Recently it has been shown (Ref. 20) that NE3VC may be polymerised by anionic processes but only at low temperatures (-80°C), due to the instability of the propagating (p-aminobenzylic) anion. In contrast, NE2VC may be most conveniently polymerised by anionic processes but will also undergo cationic and free radical homopolymerisation (Ref.19).

Although NVC and NE3VC have carbazole constituents attached to the polymerising vinyl groups, they differ significantly in that the vinyl group of NVC is part of an enamine system whereas NE3VC possesses a vinyl group with styrene-like conjugation which is further activated by an alkylamino group in the para position.



As indicated above, the positions of the vinyl groups in the two olefins imply that the propagating species in cationic polymerisation of NVC will be a substituted immonium ion, whereas for NE3VC the propagating species will be a substituted p-aminobenzyl type cation, likely to exhibit higher stability. It was decided therefore to study the polymerisation employing tropylium hexachloroantimonate ($C_7H_7^+SbCl_6^-$) as initiator in dichloromethane solvent, under conditions previously established (Ref. 11) for the polymerisation of NVC, such that free cations are the dominant propagating species.

N-ethyl-3-vinyl carbazole (NE3VC) is readily polymerised by cationic initiators and appears to undergo a spurious polymerisation in the crystalline state. The latter process makes for great difficulties and frustration in accomplishing reproducible quantitative rate and molecule weight data for catalytically induced polymerisations. Nevertheless, in contrast to many olefinic monomers which undergo cationic polymerisation, NE3VC invariably gives products of very high molecular weight. Under the best conditions available, number average molecular weights of poly-NE3VC initiated by tropylium hexachloroantimonate, were directly proportional to the initial molar ratio [monomer]/[catalyst] and were approximately 70% of the theoretical value assuming rapid and complete initiation (Figure 1). This is a particularly significant result in the area of cationic polymerisation of olefins and it may be concluded that cationic polymerisation of NE3VC proceeds essentially without the usual monomer transfer and termination processes. Reasons for this probably lie in the anticipated thermodynamic stability of the propagating cation which has a para-aminobenzylic structure, similar to that of many stable cationic dye molecules. Polymerisations of NE3VC initiated by tropylium hexachloroantimonate exhibit a characteristic absorption band at 468 nm, tentatively assigned to the propagating cation, which undergoes rapid changes after all the monomer has been consumed. (Ref. 50)

It is interesting to note that whereas styrene gives products of mainly low molecular weight in cationic polymerisations (Ref.22), paramethoxystyrene (Refs. 16,23) gives much higher molecular weight polymers when polymerised under conditions similar to those used in the present work. p-Methoxystyrene would, of course, yield a propagating cation intermediate in stability between those from styrene and NE3VC. Previous work (Refs. 6,11) has shown that NVC, polymerised with $C_7H_7^+SbCl_6^-$, gives polymers with molecular weights clearly influenced by transfer or termination, even under the best reaction conditions. We have already noted that the propagating cation derived from NVC would be less stable than that from NE3VC.

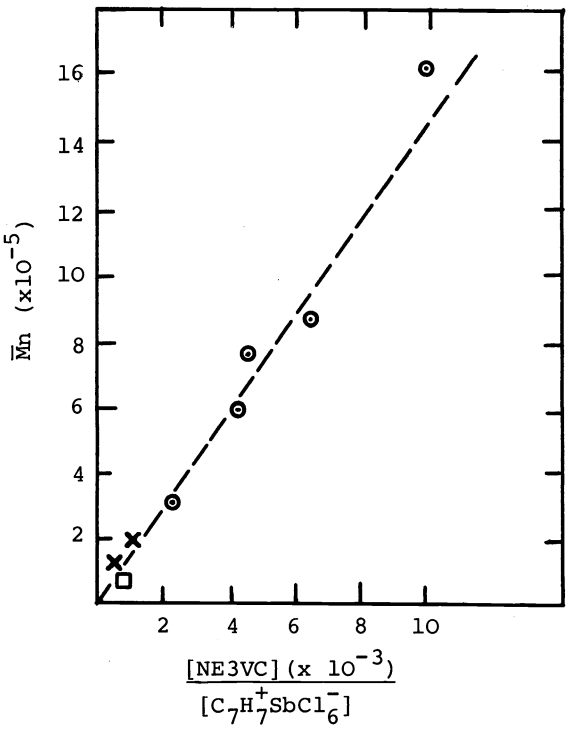


Figure 1. Variation in $\bar{M}_n$ of poly-N-ethyl-3-vinyl carbazoles initiated by $C_7H_7^+SbCl_6^-$ in CH_2Cl_2 at 0°C, with monomer/catalyst ratios.

○ $C_7H_7^+SbCl_6^-$ = 1 x 10^{-5} M; □ $C_7H_7^+SbCl_6^-$ = 1.5 x 10^{-5}M;
x $C_7H_7^+SbCl_6^-$ = 2 x 10^{-5} M

Additional differences between NE3VC and NVC are to be seen in the respective rate coefficients for propagation by free cations in CH_2Cl_2 at 0°C. Under identical experimental conditions (Ref. 11) values of k_p^+(M^{-1} sec^{-1}) were 4.5 x 10^5 (NVC) and 2 x 10^4 (NE3VC). Here again the apparent lower activity of NE3VC can be ascribed to the increased stabilization of the propagating cation compared with that from NVC. NE3VC is, of course, a substituted styrene and it is worthwhile to note that the value of k_p^+ for NE3VC is very similar to those recently estimated for related chemically initiated polymerisations of styrene (Ref. 22) and p-methoxystyrene (Refs. 16,23). The measured enthalpy of polymerisation (17 kcal $mole^{-1}$) is also very similar to those for other styrene monomers.

It seems reasonable to assume that polymerisation of NE3VC with $C_7H_7^+SbCl_6^-$ in CH_2Cl_2 at 0°C approaches the kinetic characteristics of typical anionic living systems. In view of the influence of more stable anions (e.g. PF_6^-, SbF_6^-) and lower reaction temperatures on transfer processes in the cationic polymerisation of NVC (Ref. 12), it may yet be possible to change the reaction conditions so as to confer an even longer lifetime on the carbocation responsible for propagation in polymerisation of NE3VC and related olefins.

STEREOREGULATION IN THE POLYMERISATION OF ALKYL VINYL ETHERS

It is now well established that in free radical propagation, syndiotactic placements are slightly favoured over isotactic placements with the difference becoming progressively more important as the polymerisation temperature is lowered (Ref. 24). In contrast, propagation by ionic species is complicated by effects of medium and temperature on ion-pair dissociation equilibria and the inevitable stereochemical control resulting from association of counterion with the growing chain end (Ref. 25).

Studies of the polymerisation of optically active monomers have been useful in helping to understand details of the stereospecific polymerisation of several types of vinyl monomers (Refs. 26,27). Alkyl vinyl ethers constitute

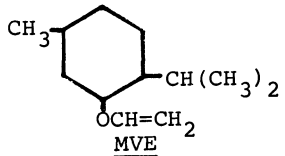
one such class of vinyl monomers known to give rise to stereoregular polymers under the influence of a large variety of catalyst types and reaction conditions (Ref. 28). For example, it has been shown that isotactic polymers from several optically active alkyl vinyl ethers are readily produced by polymerisation with catalysts such as $EtAlCl_2$ in hydrocarbon solvents at low temperatures (Ref. 29) and also, at ambient temperature, by heterogeneous catalysts derived from aluminium alkyls (or alkoxides) and sulphuric acid (Ref. 30) and by aluminium based catalysts (Ref.31).

In a general sense, both optically active 1-methylpropyl vinyl ether and (-)menthyl vinyl ether have been useful in helping to correlate main chain regularity with polymerisation mechanism on account of the substantial enhancement of optical rotation (compared with low molecular weight model compounds) exhibited by the polymers shown to be highly isotactic by independent spectroscopic techniques (X-ray and I.R.)(Refs. 32,33). It is now quite common and convenient to associate enhancement of optical rotation for isotactic poly(α-olefins) and poly(alkylvinylethers) with the existence of an helical conformation of the main chain with a prevailing screw sense (Refs. 34,35).

Examination of all the published data suggests generally that formation of isotactic polymers from alkyl vinyl ethers requires the use of either incompletely characterised initiation and propagation systems or the presence of some separated phase (solid or liquid).

As we have already seen, polymerisation of alkyl vinyl ethers is readily accomplished by initiation with carbocation salts such that free ions are the important propagating species. This technique affords the possibility to investigate homogeneous cationic polymerisation of optically active vinyl ethers with propagation by freely dissociated cationic species. The optical activity of polymers produced under these conditions facilitates immediate conclusions, at least qualitatively, concerning the stereoregulating influence of such freely propagating species and therefore to evaluate the influence of a chiral centre, with a prevailing configuration, present in the monomer.

In collaboration with E. Chiellini and R. Solaro at the University of Pisa, polymerisation of (S)-(1-methylpropyl)vinyl ether (BVE) and (-)menthylvinyl ether (MVE) initiated by tropylium hexachloroantimonate in CH_2Cl_2 was studied at several temperatures. (Ref. 51)



MVE

$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HOCH{=}CH_2$

BVE

$(CH_3)_3SiOCH{=}CH_2$

TVOS

Typical data for MVE are given in Table 1 and it is apparent that for poly-(MVE) both conversion and number average degree of polymerisation ($\overline{DP}$) depend very much on experimental conditions. Even though the experimental data are limited, it seems clear that lowering monomer concentration and raising polymerisation temperature have the effects of lowering both conversion and $\overline{DP}$. On the other hand, for polymerisation of BVE (Table 2) both yields of methanol insoluble polymer (always larger than 80%) and $\overline{DP}$ (∿ 60) are fairly independent of polymerisation conditions.

Table 1. Polymerisation of (-)menthylvinylether (MVE) by tropylium hexachloroantimonate ($C_7H_7SbCl_6$) in dichloromethane.

[MVE] (M)	$10^5[C_7H_7SbCl_6]$ (M)	Temp. (°C)	Conv. (%)	$[\alpha]_D^{25}$ (toluene)	$\overline{DP}_n$
1.1	110	0	93.1	-206	121
1.1	11	0	72.5	-199	129
0.18	1.8	0	63.1	-206	85
0.18	1.8	-30	40.1	-209	66
0.18	1.8	+30	30.0	-202	30

Table 2. Polymerisation of (S)-(1-methylpropyl)vinylether (BVE) by tropylium hexachloroantimonate ($C_7H_7SbCl_6$) in dichloromethane.

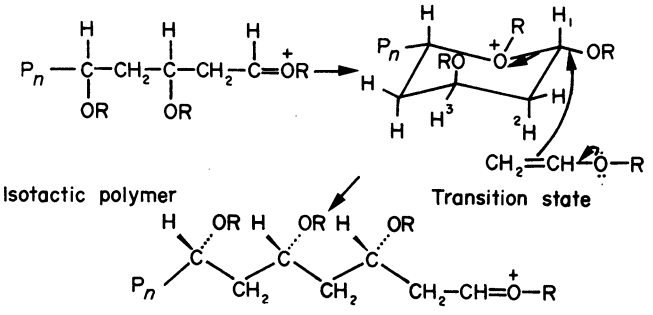
[BVE] (M)	$10^5[C_7H_7SbCl_6]$ (M)	Temp. (°C)	Conv. (%)	$[\alpha]_D^{25}$ (benzene)	$\overline{DP}_n$
1.0	100	0	82.0	+146	72
1.0	10	0	94.5	+147	77
0.2	1	0	92.6	+143	58
0.2	1	-30	83.1	+158	61
0.2	1	+30	80.2	+124	52

From Table 1 it can be seen that, under conditions favouring propagation by free cationic species, MVE gives rise to polymers (unfractionated) having values of $[\alpha]_D^{25}$ very similar to the maximum value (∿ 220°) reported in the literature for the most stereoregular (isotactic) sample obtained by low temperature polymerisation with $BF_3.OEt_2$ (Ref. 36) or $EtAlCl_2$ (Ref. 37). The values of $[\alpha]_D^{25}$ now reported are essentially independent of temperature at least in the range examined -30 - +30°C and the conclusion must be that isotactic poly(MVE) is produced with only the stereoregulating control exerted by freely growing solvated cationic chain ends and the incoming monomer. It follows therefore that use of complex catalysts and/or heterophase systems are not essential requirements at least for the formation of isotactic poly(MVE). It is conceivable that propagating systems under the influence of counterions or heterophase surfaces could enhance or even oppose stereoregulating effects apparently arising only from steric interactions between solvated growing chains and monomeric MVE.

By comparison with MVE, the data of Table 2 show that polymerisation of (S)-(1-methylpropyl)vinyl ether (BVE) carried out in the same experimental conditions reported for MVE gives polymeric products having optical rotations which are approximately one half of the average value (+ 300°) reported for a fractionated, highly isotactic sample (Refs. 33,38) and approximately five times that of the appropriate low molecular weight model compound (Ref.33). This indicates a significant degree of steric control in the propagation reaction and illustrates the substantially greater asymmetric inductive influence of the (-)menthyl groups over that of the sec-butyl group during insertion of the monomer onto the growing chain end. Therefore, it must be concluded that the much more stereoregular fraction of poly(BVE), obtained by polymerisation with the heterogeneous catalysts, arises from a propagation process assisted (in a stereochemical sense) by either a complex counterion and/or, more probably, by the catalyst surface.

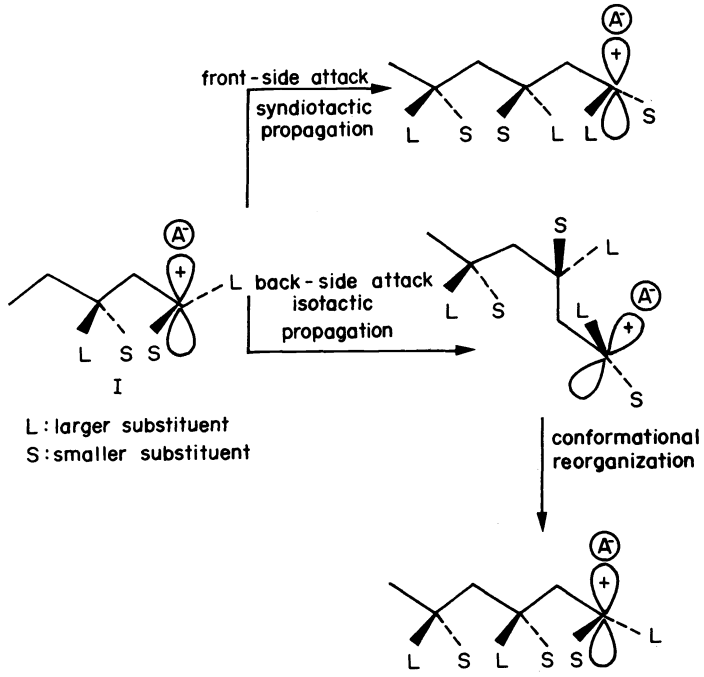
Under the same experimental conditions reported for MVE and BVE, trimethylvinyloxysilane (Table 3) gives rise to an almost completely syndiotactic polymeric product, as evidenced by NMR spectra performed on dimethylsulfoxide solutions of the poly(vinyl alcohol) recovered from the precipitated polymeric products (Ref. 37).

The earliest attempts (Refs. 25,39) to explain stereoregulation in cationic polymerisation of alkyl vinyl ethers assumed that stereocontrol originated via a transition state involving internal ring formation by alkoxy substituents in the polymer chain and the growing carbocation. Entry of new monomer (CH_2=CHOR) into the growing polymer chain was thought to arise with the substituents (R) maintained at maximum separation as indicated below.



The mechanism predicts that isotactic polymers will result in all cases, in agreement with experimental results for methyl-, isopropyl-, and isobutyl vinyl ethers (Refs. 25,28). However, it later became apparent that alkyl vinyl ethers having bulky constituents such as ter-butyl vinyl ether (Ref.40) ($(CH_3)_3COCH{=}CH_2$) and trimethylvinyloxysilane (Ref.41) ($Me_3SiOCH{=}CH_2$) yielded syndiotactic polymer when polymerised in relatively polar solvents, and isotactic polymer when polymerised with the same catalysts and reaction conditions in toluene. Although bulky groups such as tert-butyl and trimethylsilyl would be expected to exhibit the most pronounced degrees of stereoregulation in the growth process, the change from isotactic to syndiotactic placements, according to solvent, cannot be accounted for on steric grounds and indicates steric control by factors other than those represented above.

Kunitake and Aso (Ref. 42) proposed that the really important factor in controlling stereochemistry of chain growth in alkyl vinyl ether polymerisation is the degree of association of growing cation and counterion. The physical size of the counterion would also be important but in a less dramatic way. Thus, as illustrated below, steric hindrance of bulky substituents of terminal and penultimate monomer units may be minimised and, assuming a planar carbocation, attack of monomer on the same side as the counterion (front side attack) leads to mainly syndiotactic placements. With the same polymer chain configuration, attack of monomer on the side opposite to the counterion (back side attack) leads to mainly isotactic placements.



This sample model explains why polymerisations in toluene (which would favour tight ion-pairing) would promote formation of mainly isotactic polymers by backside attack of monomer on the growing ion-pair. More polar solvents would stabilise separated ion-pairs and favour frontside attack (thus minimising steric repulsion between bulky groups present in monomer and the growing polymer chain) with formation of syndiotactic polymer.

These general predictions are both supported and qualified by the present results which, in essence, involve polymerisation of alkyl vinyl ethers with bulky substituents under conditions where the counterion can not exercise any influence on the growth reaction.

Considering first the polymerisation of trimethyl vinyloxysilane (TVOS), propagation via free ions would be predicted to involve the equivalent of exclusively frontside attack, so as to minimise steric interactions and lead to syndiotactic polymer, as observed experimentally.

Putting aside effects of chirality, menthyl vinyl ether (MVE) might be regarded as having an even bulkier substituent than TVOS and hence would be expected to yield mainly syndiotactic polymer by free ion propagation. In

reality the product of free ion polymerisation of (-)MVE is a highly isotactic polymer whose stereoregularity does not vary as the temperature of polymerisation is varied in the range $-30^{o} \rightarrow +30^{o}C$. Thus it is clear that the chiral influence present in (-)menthyl vinyl ether is more important in controlling main chain stereoregularity than the more general bulkiness of the monomer substituent. It is not absolutely clear why isotactic polymer should be favoured in this way but it must be presumed that the chiral influence of one or more monomer units in the growing chain supplies a powerful asymmetric influence in the transition state leading to incorporation of an additional chiral monomer.

The polymerisation of (S)-(1-methylpropyl)vinyl ether (BVE) presents an intermediate case in terms of the bulky nature of the monomer substituent. Here the polymeric product has an apparent isotacticity approximately one half of that which may be obtained with the best heterogeneous stereoregular catalysts and it would appear that, as expected, the chiral influence of the (S)-1-methylpropyl substituent is significantly less than that of the corresponding (-)menthyl group. These results, although limited in scope, suggest that the influence of chiral substituents might be significant in other types of polymerisation and related studies could be useful in understanding details of the chain propagation processes.

PROMOTION OF CATIONIC POLYMERISATION WITH FREE RADICAL INITIATORS

Recently there has been a significant growth of interest in the use of aryl diazonium salts (Ref. 43) ($ArN_2^+X^-$), diaryl iodonium salts (Ref. 44)($Ar_2I^+X^-$), and triaryl sulphonium salts (Ref. 45) ($Ar_3S^+X^-$) as photochemical initiators for cationic polymerisations 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 (Ref.19), the other types of cationic salt ($X^- = PF_6^-$, SbF_6^-, AsF_6^- etc) are essentially thermally stable and unreactive to many cationically polymerisable monomers. In contrast 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 (Ref. 46) 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 vinyl ethers,

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

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

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

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 polymerisation by the usual peroxide-forming processes - preliminary results suggest that the effect is greatest for alkyl vinyl ethers - and every system will need to be considered individually.

Monomers chosen for study were tetrahydrofuran and n-butyl vinyl ether. Polymerisations were performed in vacuum outgassed systems and purification procedures were those conventionally used for cationic polymerisations (Ref.6). Representative results are given in Tables 3, 4 and it must be stressed that the data 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.

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

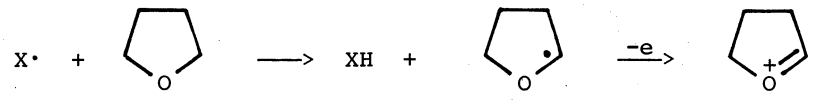


Table 3. Thermal Polymerisation[a] of Tetrahydrofuran (bulk)

Free Radical Source (M)	Cation Salt (M)	Heating Time (mins)	Conversion(%)
AIBN (10^{-2})	$(pCH_3C_6H_4)_2I^+PF_6^-$ (5.10^{-3})	110	5.3
Benzoyl Peroxide (10^{-2})	"	60	3.7[b]
none	"	110	0
$PhN{=}NCPh_3$ (5.10^{-3})	"	110	10.0
Benz pinacol (10^{-3})	"	60	16.7

[a] Reactions were initiated by heating the reaction mixtures at 70° for the time indicated, polymer was obtained by precipitation into water containing a little base.

[b] $\bar{M}_n$ = 119,7300 this is a typical molecular weight for the polytetrahydrofuran samples obtained.

Table 4. Thermal Polymerisation of n-butyl vinyl ether in bulk at 50°C.

Free Radical Source (M)	Cation Salt (M)	Reaction Time (hrs.)	Converstion (%)
none	$(pCH_3C_6H_4)_2I^+PF_6^-$ (5.10^{-3})	3.0	0
AIBN (5.10^{-3})	none	3.0	0
AIBN (5.10^{-3})	$(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$ (5.10^{-3})	3.0	75

The data of Tables 3 and 4 clearly provide experimental substantiation of these ideas and illustrate the range of common free radical sources which may be used to promote cationic polymerisations. Phenylazotriphenyl methane is an interesting case since the expected product of thermolysis ($Ph_3C\cdot$) has been shown (Ref. 46) to undergo oxidation to Ph_3C^+ and we have shown that the latter is a useful initiator for cationic polymerisation (Ref. 6).

In recent years there has been a dramatic increase in the utilisation of photo-active initiators for U.V. curing of surface coatings and many related applications (Refs. 47,48). Of the photo-initiator systems widely employed, benzoin and its alkyl ethers and alkoxyacetophenones are especially useful since they absorb light up to approximately 380 nm and fragment with high quantum efficiencies (Ref. 48). Azo compounds are also photochemically active initiators but with rather low extinction coefficients in the regions above the glass cut-off point. As we have already noted, aromatic carbonyl compounds generally, and aliphatic azo compounds are readily selectively excited in the presence of simple aryl-diazonium, -iodonium, and -sulphonium salts by the simple expedient of using glass vessels. Appropriate wavelength filters may also be used.

Table 5 gives data for a series of polymerisations of THF utilising p-chlorphenyldiazonium PF_6^- as cationic salt and 2,2-dimethoxy-2-phenyl-acetophenone (a commercial U.V. curing agent) as source of free radicals. These preliminary data are interesting in illustrating a possible rate saturation effect for the diazonium salt (identical behaviour was observed using $(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$) and the expected rate and molecular weight dependencies on both the time of polymerisation and the concentration of free radical initiator. A particular advantage in the use of alkoxyacetophenones and benzoin alkyl ethers is that of the two primary photo-fragments, one is a

Table 5. Photochemical Polymerisation of Tetrahydrofuran(bulk) at 25°C (Pyrex Glass Vessels)

$PhCOC(OCH_3)_2Ph$ [M]	$p\text{-}ClC_6H_4N_2^+PF_6^-$ [M]	Irradiation Time (mins)	Conversion (%)	$10^{-3}\overline{M}_n$
5.10^{-3}	5.10^{-3}	30	7.5	38.9
5.10^{-3}	5.10^{-3}	45	10.5	46.1
5.10^{-3}	5.10^{-3}	60	17.9	79.9
0	5.10^{-3}	45	1	51.8
10^{-3}	5.10^{-3}	45	4.3	50.9
5.10^{-3}	5.10^{-3}	45	10.5	46.1
10^{-2}	5.10^{-3}	45	15.0	24.2
5.10^{-3}	10^{-3}	45	3.7	33.4
5.10^{-3}	5.10^{-3}	45	10.5	46.1
5.10^{-3}	10^{-2}	45	11.9	52.7

powerful electron donor radical which should oxidise to the corresponding cation even more easily than similar radicals derived from the monomers, e.g.

$$PhC(=O)-CH(OR)Ph \xrightarrow{h\nu} PhC(=O)\cdot + \cdot CH(OR)Ph$$

$$PhCH(OR)\cdot + \text{e.g. } ArN_2^+PF_6^- \longrightarrow PhCH(=RO^+)\ PF_6^- + Ar\cdot + N_2$$

This assures formation of an initiating cation without the requirement for hydrogen abstraction or addition to monomer.

Table 6. Photochemical Polymerisation of Tetrahydrofuran (bulk) at 25°C (Pyrex Glass Vessels)

Photoactivator(M)	Cation Salt(M)	Irradiation Time (mins)	Conversion (%)	$10^{-3}\overline{M}_n$
$PhCOC(OCH_3)_2Ph$ 5.10^{-3}	$p\text{-}ClC_6H_4N_2^+PF_6^-$ 5.10^{-3}	45	10.5	46.1
none	$p\text{-}ClC_6H_4N_2^+PF_6^-$ 5.10^{-3}	45	∿1	51.8
$PhCOC(OCH_3)_2Ph$ 5.10^{-3}	$(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$ 5.10^{-3}	50	13.4	
none	$(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$ 5.10^{-3}	50	∿1	
$PhCOC(OCH_3)_2Ph$ 5.10^{-3}	$(C_6H_5)_3S^+PF_6^-$ 10^{-3}	150	5.7	54.6
none	$(C_6H_5)_3S^+PF_6^-$ 10^{-3}	150	∿1[b]	
Benzoin ethyl ether 5.10^{-3}	$p\text{-}ClC_6H_4N_2^+PF_6^-$ 5.10^{-3}	60	4.4	
$PhCOCH(OEt)_2$ 5.10^{-3}	$p\text{-}ClC_6H_4N_2^+PF_6^-$ 5.10^{-3}	60	4.4	
$PhN{=}NCPh_3$ 5.10^{-3}	$(pCH_3C_4H_4)_2I^+PF_6^-$ 5.10^{-3}	56	3.1	177.5
2-tert-butyl-anthraquinone 5.10^{-3}	$(pCH_3C_6H_4)_2I^+PF_6^-$ 5.10^{-3}	60	2.0	
2-chlorothioxanthone 5.10^{-3}	$(pCH_3C_6H_4)_2I^+PF_6^-$ 5.10^{-3}	60	4.2	
Benzophenone 5.10^{-3}	$pClC_6H_4N_2^+PF_6^-$ 5.10^{-3}	45	3.1	

Table 6 gives representative data for promoted photopolymerisation of THF with a range of photoactive radical sources and it is interesting to note the activity of benzophenone, 2-tert-butylanthraquinone, and 2-chlorothioxanthone. These molecules are well known(ref.49) to undergo photo-induced hydrogen ab-

straction reactions with THF and cation formation would then follow as described previously, e.g.

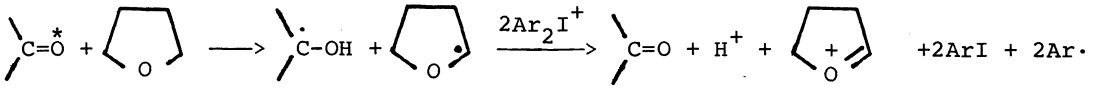


Table 7. Photochemical Polymerisation of n-butyl vinyl ether (bulk) at 25°C (λ = 366 nm).

$PhCOC(OCH_3)Ph$ [M]	$(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$ [M]	Irradiation Time (mins)	Conversion (%)
5.10^{-3}	0	10	0
0	5.10^{-3}	10	0.8
5.10^{-3}	5.10^{-3}	10	98

Table 7 gives perhaps the most convincing data for free radically promoted cationic polymerisation and points the way to other related promoter-systems for photochemically induced processes.

As a very simple but crude demonstration of the possible value of free radical promotion of cationic polymerisation, several experiments were performed using 1,2-epoxyethyl-3,4-epoxycyclohexane as the polymerisable monomer. Because of the presence of two epoxide groups, this monomer readily cross-links and ultimately forms gelled systems. In a typical experiment, photolysis through glass of bulk monomer containing 5 x 10^{-3} M $(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$ formed a gel after several hours irradiation. The same system containing 5 x 10^{-3} M $PhCOC(OMe)_2Ph$ or an equivalent concentration of 2-chlorothioxanthone formed a gel after about 10 minutes - clear evidence for the promoting effect of the free radical source.

These preliminary experimental results fully support the idea that suitable free radical sources in combination with oxidising cations may be used to promote cationic polymerisation of alkyl vinyl ethers and cyclic ethers. Mechanistic details remain to be evaluated but for all systems studied, an important feature is the generation of a chain reaction leading to formation of cationic initiators with obvious implications to quantum amplification in photoinduced phenomena.

TRIBUTE TO MICHAEL SZWARC

It is a privilege to have been involved in the Symposium honouring the retirement of Professor M. Szwarc, F.R.S., who has done so much to stimulate interest in ionic polymerisation by his insight and originality. Those of us in the British Isles who have maintained a practical interest in cationic polymerisation have derived invaluable benefits from his frequent visits to our Countries. It is a pleasure, therefore, to record the gratitude and warmest personal regards from Cecil Bawn, now happily retired in Devon, from David Pepper in Dublin, from Peter Plesch in Keele, from Rick Richards in Waltham Abbey, and, not least, from Clement Bamford and myself representing the polymer group in Liverpool with whom Michael has maintained a long and continuous interaction.

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