

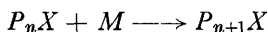
NEW METHODS OF POLYMERIZATION

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Every addition polymerization process involves two fundamental steps: initiation and propagation. Termination is also an important step but in some processes termination may be avoided by a judicious choice of experimental conditions. In the exploration of either new methods of polymerization or the development of existing methods attention may be concentrated on either the initiation process or on the propagation reaction. Sometimes both of the steps may be involved together. This paper will be largely concerned with recent progress in the study and development of new initiators and initiating processes.

The propagation process of a conventional addition polymerization of a monomer M consists of a series of reactions described by



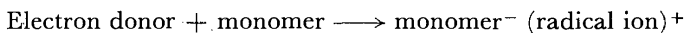
The reactive moiety X attached to the chain—which may be part of the initiator—is responsible for the onset of the reaction and the monomer does not require any further activation. In such processes the initiator participates only in the step creating the growing centre and not usually in the subsequent propagation.

Three types of reactive centre may be identified: radicals, ions and coordination complexes. The ionic species may be further divided into cationic and anionic, depending on whether the growing species carries a positive charge or forms the positive end of a dipole or is negatively charged or forms the negative end of a dipole.

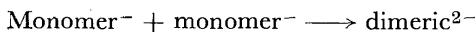
The most striking developments in ionic polymerization in recent years have been made in anionic polymerization and have resulted largely from the discovery of two important features of the reaction:

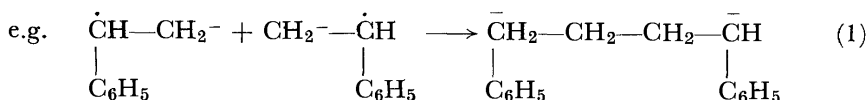
- (1) the initiation of polymerization through an electron transfer process;
- (2) the possibility of avoiding termination and transfer and therefore the feasibility of producing living polymers.

In the electron transfer initiation reaction the first step is an electron transfer from a suitable electron donor to the monomer with the formation of a radical ion

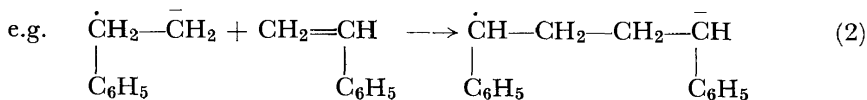


The radical ion may undergo two types of reaction, namely





or Monomer⁻ + monomer \longrightarrow dimeric radical ion

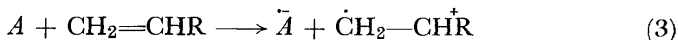


The dimeric species initiates the conventional chain of the polymerization growth taking place essentially on the carbanion ends since the radical end if formed in (2) disappears either by mutual termination or through another electron transfer. The concepts have been firmly established and their application to ionic polymerization has been admirably reviewed by Szwarc¹.

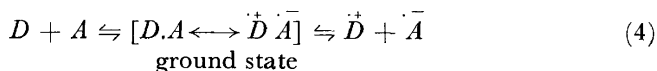
While anionic polymerization may be induced by transferring an electron from a suitable donor to monomer, the transfer of an electron from an electron rich monomer (donor) to a suitable acceptor may lead to cationic polymerization. For example, transfer to a cation will produce a radical and a radical cation:



The process may be generalized as follows:



where A the acceptor may be a neutral molecule or an ion. The process may be, and usually is, much more complex than represented by (3) and the donor D and acceptor molecule A interact to form a complex which may often be sufficiently stable to be characterized.



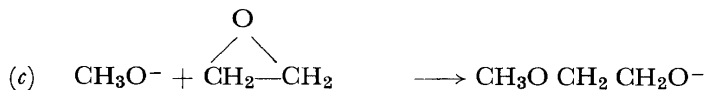
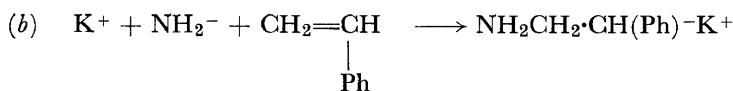
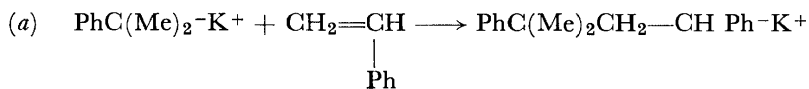
In this paper we shall review the development of the general reactions (3) and (4) for the formation of cation radicals and their application as polymer-initiating reactions. Unlike the corresponding anionic reactions, cationic polymerizations are subject to monomer transfer reactions. This follows since olefinic reactivity in cationic polymerization requires the presence of strongly electron-releasing substituents. These substituents are usually polar groups or conjugated electron systems and provide in the polymer an electron-rich site of considerable reactivity. These active sites easily take part in transfer or branching reactions and the control of the propagation and molecular weight is a much more difficult operation. Isobutene, $(\text{CH}_3)_2\text{C}=\text{CH}_2$, is an exception to this rule and readily give much higher molecular polymers than the other commonly cationically susceptible monomers. Because of these difficulties it has not so far been

possible to demonstrate the existence of the propagating dimeric cationic species as in the comparable anionic polymerization.

A further complication which arises in cationic polymerization is the ready oxidation of any free radical centre by the reagent used initially for the one electron oxidation of the olefin. This reaction is important in systems employing charge-transfer complexes as initiating agents (q.v.).

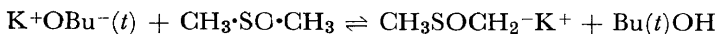
ANIONIC POLYMERIZATION IN DIMETHYL SULPHOXIDE

Before proceeding to the main topic of cationic initiation, reference will be made to some recent developments in anionic polymerization. In addition to the process of electron transfer already mentioned anionic polymerization may be initiated by the addition of a negative ion or ion pair to a suitable monomer. This mode of initiation is illustrated by the following examples:



In (a) the polymerization is initiated by an ion pair; in (b) reaction in liquid ammonia initiation is by the free NH_2^- ion. Example (c) seems to be a case where free ions initiate and propagate the reaction. A catalyst in this group of very wide applicability is the potassium derivative of dimethyl sulphoxide².

In recent years there has been a widespread development in the use of dimethyl sulphoxide (DMSO) as a solvent for promoting base-catalysed reaction. The most common systems involve the use of potassium *tert*-butoxide in DMSO where enhanced basic characteristics result, in part, from the equilibrium



The most striking feature of DMSO as solvent is its high solvating power for cations and low solvating power for anions and this leaves the dimethyl ion $\text{CH}_3\text{SOCH}_2^-$ free to take part in polymerization initiating reactions. Thus ethylene oxide, propylene oxide, acrylonitrile and methyl methacrylate are polymerized rapidly at 25°C. Molecular weights, at high conversion, were in reasonable agreement with those calculated on the basis of one polymer chain per catalyst molecule and this was confirmed by end-group analysis. With ethylene oxide and methyl methacrylate the reaction kinetics

Table 1. Polymerization in DMSO catalysed by potassium *t*-butoxide at 25.0°C

Monomer	Concentration (mole/litre)		$10^3 \times \text{Rate}$ (mole litre ⁻¹ sec ⁻¹)	$10^3 \times k_p^{(a)}$ (litre mole ⁻¹ sec ⁻¹)	Degree of Poly ⁿ (b)	
	[Monomer]	$10^3 \times [\text{Initiator}]$			Calculated	Found
Ethylene oxide	3.22	11.6	2.32	6.2	198	139
	4.25	12.2	8.35	12.4	174	193
	4.31	2.19	1.22	12.8	985	750
	5.50	12.2	8.35	12.4	226	261
Propylene oxide	1.81	6.83	0.25	1.92		Oily liquid
Methyl methacrylate	1.30	5.30	3.40	49	123	281
	1.28	0.26	0.04	13	2430	1862
	1.32	1.18	0.52	33	550	355
	1.30	2.73	2.78	78	250	260
	1.58	7.70	7.60	63	100	140
	2.21	7.70	9.60	56	150	132
	1.28	7.64	6.00	61	90	135

^a Calculated from the expression: Rate = k_p [Monomer] [Initiator]

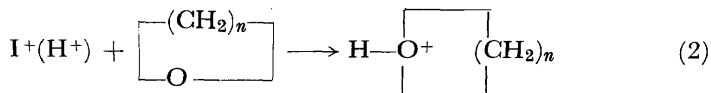
^b For ethylene oxide, polymerization was taken to completion and yields of polymer recovered were in excess of 80%.

For methyl methacrylate, polymerization was stopped at 50% conversion.

Estimation of DP was from measurements of intrinsic viscosity using the following relationships:

Polyethylene oxide $[\eta] = 1.25 \times 10^{-4} M^{0.74}$ in water at 30°C

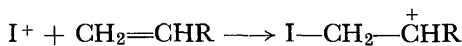
Polymethylmethacrylate $[\eta] = 0.75 \times 10^{-4} M^{0.76}$ in benzene at 25°C.



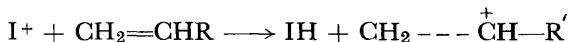
Strong acids, especially sulphuric and perchloric, readily polymerize monomers such as styrene and it was thought until recently that initiation was due to carbonium intermediates formed according to (1). Recent work has established that the propagating species in this reaction is not a carbonium ion—either free or paired—but an ester formed from the monomer and the catalyst⁸. Friedal-Crafts halides which form the most important group of catalysts do not usually initiate alone but catalyse the initiation of some other substance—the cocatalyst—which provides the actual initiating fragments. The cocatalyst is usually water but acids, alcohols and other polar substances cause initiation. The species formed may have only a transitory existence and there are obvious difficulties in defining the precise initiator. Furthermore, kinetic studies of cationic polymerization are difficult to evaluate because the cocatalyst can act as a transfer agent or even as a reaction terminator. True termination processes are not often encountered in these cationic processes and the chain activity is usually destroyed by some side process.

It seems therefore clearly desirable that, in order to overcome some of the difficulties mentioned above, the catalyst and cocatalyst components should be completely utilized in the form of a well-defined, stable and easily characterizable material. The most useful substances for this purpose are stable carbonium-ion salts. They are well known and the particular salts which have been used extensively in our work are those of the triphenyl methyl and tropylium cation. These salts with the general formulae $Ph_3C^+X^-$ and $C_7H_7^+X^-$, where X is a stable anion, ClO_4^- , $SbCl_6^-$, BF_4^- , PF_6^- , etc., are easily prepared as stable crystalline materials and readily and reproducibly polymerize tetrahydrofuran, vinyl alkyl ethers, n -vinyl carbazole, acenaphthalene, styrene and other vinyl monomers⁹.

Stable carbonium ions may initiate vinyl polymerization by several possible mechanisms: (1) Direct addition to the unsaturated system to give a carbonium or oxonium ion



(2) Hydride extraction

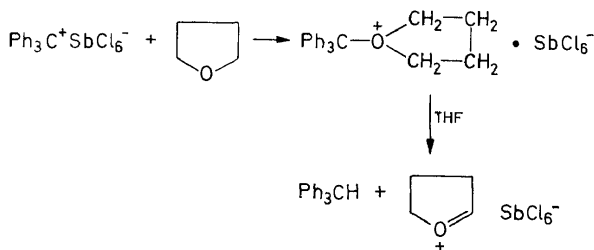


(3) The formation of cation-radical, by electron transfer or other mechanism

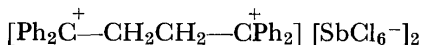


The relative significance of these alternative initiating reactions will be considered in detail and in particular their relation to the initiation of the polymerization of monomers known to be readily susceptible to cationic initiation, viz. tetrahydrofuran, n -alkyl vinyl ether and n -vinyl carbazole.

The trityl hexachloroantimonate—a bright-yellow-coloured stable solid—with tetrahydrofuran gave instant discoloration of the catalyst and homogeneous polymerization of the monomer¹⁰. Although the initial discoloration of Ph_3C^+ cation is due to oxonium ion formation it has now been established that a subsequent reaction produces triphenyl methane before polymerization occurs, viz.

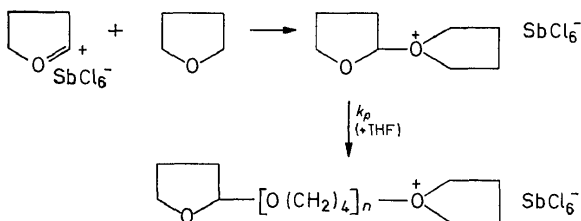


Evidence for the formation of triphenylmethane was provided initially by attempts to produce di-cations in the polymerization of tetrahydrofuran. Kuntz¹¹ showed that the stable dicarbonium salt



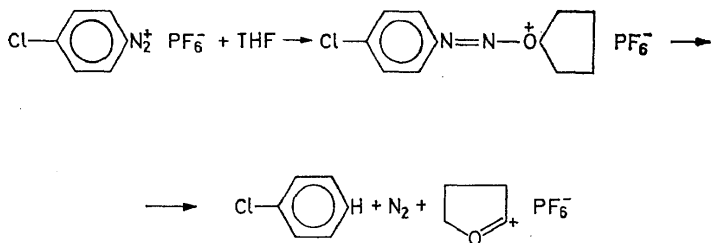
produced polytetrahydrofuran having the same molecular weight as that produced by corresponding concentrations of the mono-salt $\text{Ph}_3\text{C}^+\text{SbCl}_6^-$. Later work by Kuntz¹² using n.m.r. techniques showed that triphenylmethane was rapidly formed during initiation. Independent work by Ledwith and Fitzsimmons in this laboratory has shown that triphenylmethane can be detected by gas chromatography during the polymerization initiated by $\text{Ph}_3\text{C}^+\text{SbCl}_6^-$ and can actually be isolated from the reaction mixture by chromatography on neutral alumina.

The subsequent steps in the propagation reactions are

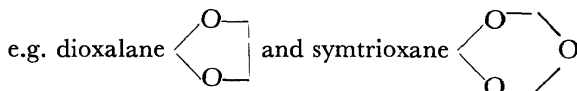


At room temperature and below, there was little termination and reaction proceeded to equilibrium conversion. Later work¹³ with different anions—especially PF_6^- —showed that termination could be completely eliminated and a truly “living” polymer system established.

It was also first shown by P. Dreyfuss and Mrs Dreyfuss¹⁴ working in this laboratory that *p*-chlorophenyl diazonium hexafluorophosphate was a very effective initiator for tetrahydrofuran polymerization. Extremely high molecular weight polymers were obtained and the system was free from termination reactions. The initiation was thought to be hydride abstraction, viz.



Since the publication of the use of triphenylmethane cation salts for tetrahydrofuran polymerization, many different laboratories have used these catalysts for the polymerization of other cyclic ethers,



The effect of the anions differs for each monomer but non-terminating systems have been developed in each case. Thus for trioxane polymerization, SbF_6^- appears to be the preferred anion, whereas PF_6^- and AsF_6^- are better for dioxalane. The subject has been recently reviewed by Dreyfuss and Dreyfuss¹⁵ and by Ledwith¹⁶.

Parallel with the studies of the polymerization of tetrahydrofuran, it was shown that reactive olefins such as alkyl vinyl ethers, *n*-vinylcarbazole and alkoxy-styrenes were also readily polymerized using triphenylmethyl cation salts as catalysts. These reactions are easily carried out in a variety of non-protic solvents such as CH_2Cl_2 , CH_3CN , CH_3NO_2 , $\text{ClCH}_2\text{CH}_2\text{Cl}$ —in which the catalyst is soluble. Many of these polymerizations are much faster than tetrahydrofuran and catalyst concentrations as low as 10^{-5} M are necessary to give measurable rates. For example, with isobutyl vinyl ether (*Table 2*) the overall rate of polymerization, k_p , estimated from the rate equation $-\text{d}M/\text{d}t = k_p(M)$ (Catalyst) or $k_p(M)^2$ (Catalyst) was of the order of 10^4 l. mole⁻¹ sec⁻¹. At temperatures below 0°C, little termination occurred but the molecular weights of the polymer were less than 5000 even

Table 2. Polymerization of vinyl isobutyl ether in CH_2Cl_2 at 0°C

[CH ₂ =CHOBu ¹] M	Initiator		Overall rate coefficient ^a 10 ⁻³ k_p (l.m ⁻¹ sec ⁻¹)	Polymer viscosity ^{b,c} [η] dl/g
	[Ph ₃ C ⁺ SbCl ₆ ⁻] 10 ⁶ M	[C ₇ H ₇ ⁺ SbCl ₆ ⁻] 10 ⁶ M		
0.079	5.64		3.0	0.071
0.19	1.93		3.6	0.087
0.19	3.75		3.7	0.083
0.19	5.57		3.6	0.084
0.19	7.42		3.4	0.084
0.19		7.1	4.1	0.085
0.08		5.32	5.0	0.072

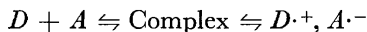
^a Reaction rates were followed *in vacuo* in an adiabatic calorimeter essentially as described by Biddulph and Plesch. The rate coefficient was estimated from the expression:

$$-\frac{\text{d}[\text{Monomer}]}{\text{d}t} = k_p [\text{Monomer}] [\text{Catalyst}]$$

^b Measured in benzene at 25°C.

^c The yield of polymer was always quantitative.

can occur to a significant extent even in the ground state of the complex. That is, mutual oxidation and reduction will occur according to



and it is therefore possible to use the three common propagating intermediates for initiation of polymerization—cation, anion and radical in the form of radical ions.

Kosower¹⁸ has discussed in detail the conditions under which radical-ion formation from charge transfer will be significant. In polymerization reactions the most favourable situation occurs when, by suitable choice of reactants and solvent, it is possible to have a thermal equilibrium between complex and ion pairs (see *Figure 1*). Certain olefinic substances with

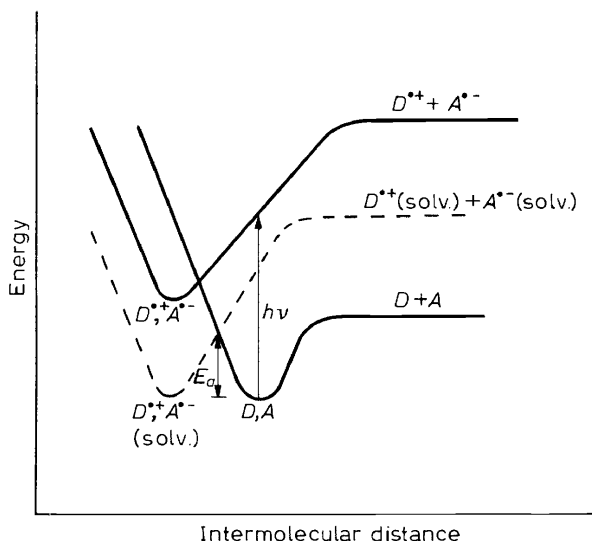
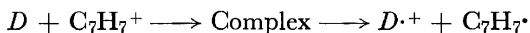
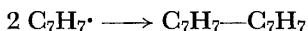


Figure 1

relatively low ionization potentials (7–9 eV) function as donors and common electron acceptors include (a) neutral molecules, such as quinones, anhydrides, nitrocompounds, etc., and (b) ionic intermediates, such as metal ions, ionic acids and carbonium ions. Both classes of acceptor are important to the polymer chemist and, by careful choice of reaction (monomer, acceptor and solvent), conditions may be attained which facilitate the radical-ion formation and the initiation of the polymerization reaction. An extremely favourable case is that when the acceptor is a cation, for example the tropylium cation^{9, 19}:



The cycloheptatrienyl radical formed may dimerize to give ditropyl

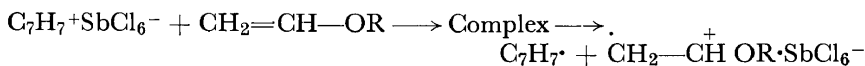


and thus shift the equilibrium to the right in the above equation.

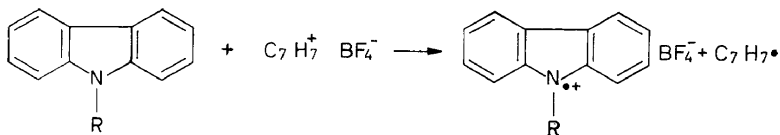
Using methylene chloride and acetonitrile as solvents, it has been found that tropylium chloroantimonate ($C_7H_7^+SbCl_6^-$) and tropylium tetrafluoroborate ($C_7H_7^+BF_4^-$) initiate the polymerization of *n*-vinylcarbazole, acenaphthylene, 1- and 2-vinylnaphthalene, vinylmesitylene and styrene. Tropylium salts are known to form stable charge-transfer complexes with aromatic molecules, and with olefinic monomers significant initiation of polymerization occurs after initial formation of coloured charge-transfer complexes between monomer and the $C_7H_7^+$ ion. The monomers used are those known to be susceptible to cationic polymerization and it seems highly probable that the $C_7H_7^+$ initiated polymerization follows a carbonium-ion mechanism. Support for this conclusion was obtained from a detailed study of the polymerization of isobutyl vinyl ether (IBVE) and vinylcarbazole (VC).

Both the catalysts $Ph_3C^+SbCl_6^-$ and $C_7H_7^+SbCl_6^-$ gave rapid and complete initiation of IBVE. Using $Ph_3C^+SbCl_6^-$ as initiator, it is certain that a classical carbonium ion is involved and the very close agreement between rate and molecular-weight data obtained with this and $C_7H_7^+SbCl_6^-$ as initiator (*Table 2*) confirms the cationic nature of the polymerizations initiated by the tropylium salt.

The tropylium-ion initiation reaction may therefore be represented as occurring *via* a radical cation:



The cation radical may dimerize directly or, after reaction with further monomer, give a di-cation as the propagating entity. Experimental confirmation of the formation of di-cations has not been achieved because of the occurrence of monomer transfer reactions. However, the proof of the occurrence of the oxidizing properties of the tropylium cation and the formation of radical-cation intermediates has been established by the use of non-polymerizable model compounds. Thus $C_7H_7^+BF_4^-$ in acetonitrile forms charge-transfer band spectra in the visible region with a large number of aromatic donors; for example, *n*-phenylcarbazole, carbazole, *n*-methylcarbazole, triphenylamine, phenothiazine and tetramethylphenylene diamine. The reaction of carbazole with the tropylium salts leads to the formation of the stable red crystalline solid:

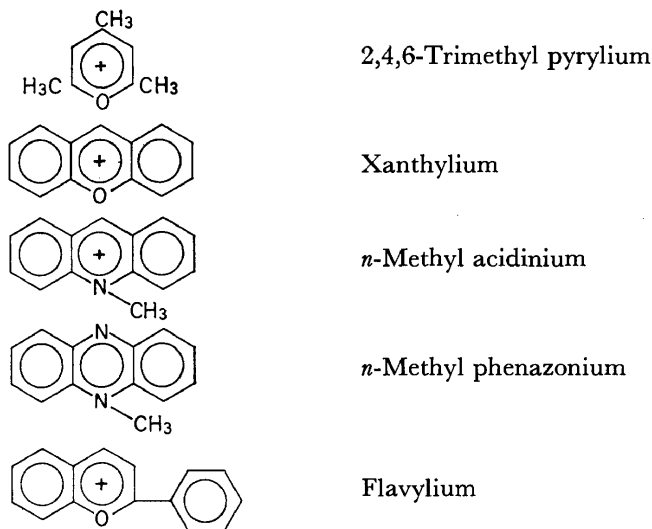


The ion-radical character has been characterized by e.s.r. and spectral measurements. The equilibrium constant for the reaction K at 25°C ($D + A \xrightleftharpoons{K} DA$) was measured spectroscopically to be 3.18 l. mole⁻¹.

Other planar organic cations have also been used with equal success for the polymerization of electron-rich olefins. All of these form stable crystalline

salts with many different anions and also show evidence of charge-transfer complex formation with the monomers.

There is now considerable literature information which indicates that a



wide variety of neutral acceptor molecules may also be used to polymerize very reactive olefins such as *n*-vinylcarbazole²¹. The reactions are not so efficient as when using ionic acceptor species and each system has its own specific complications. As an example we have studied in detail the initiation of the polymerization of *n*-vinylcarbazole by tetracyanoethylene in methylene chloride solution. *Figure 2* shows the reactions occurring in this system and all the products shown have been confirmed and isolated.

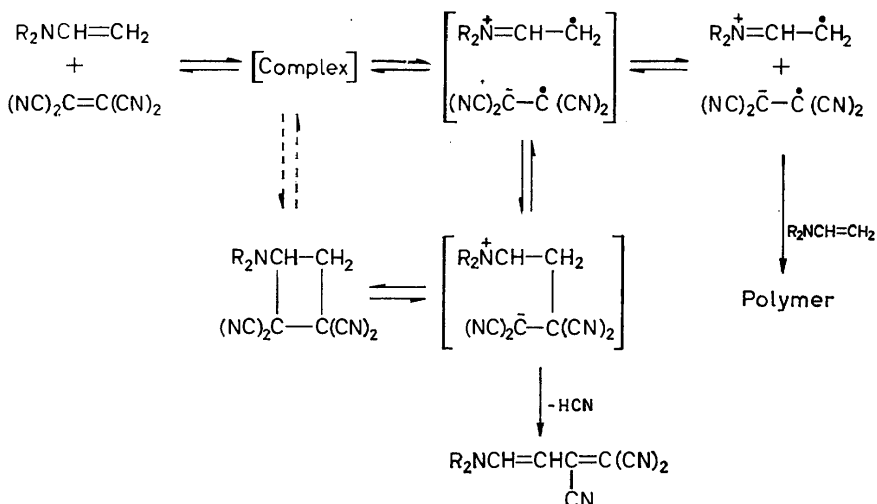


Figure 2

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High yields of polymer may be obtained under suitable conditions and kinetic investigations *Figures 3 and 4* show that the rate of polymerization was proportional to the catalyst and monomer concentrations. The molecular weight of the polymer varied between 80 000 to 100 000 over a ten-line

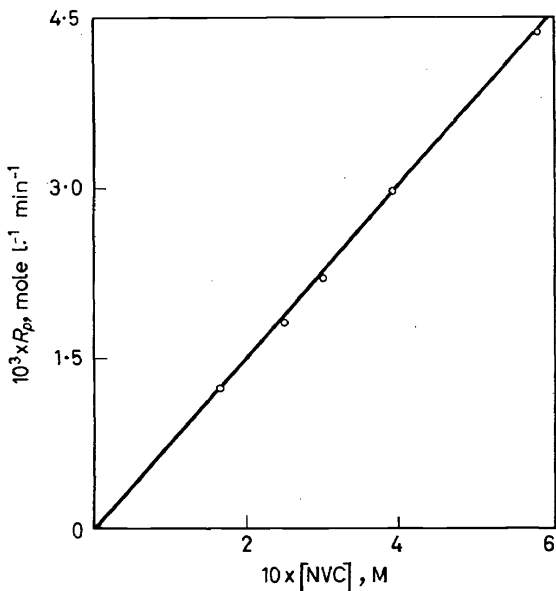


Figure 3. A plot of initial rate of polymerization (R_p) against initial [NVC]

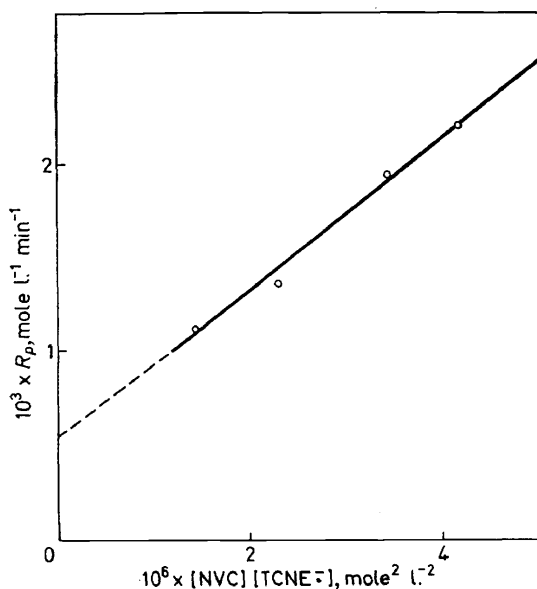
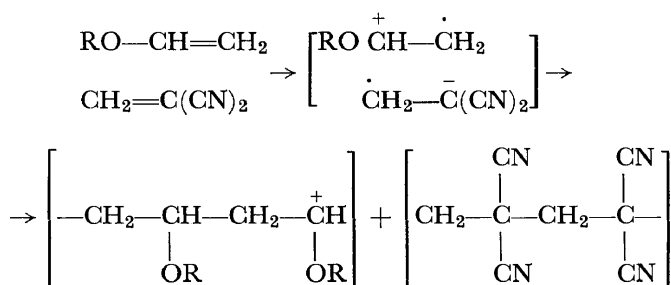


Figure 4. A plot of R_p versus [NVC] [TCNE⁻]

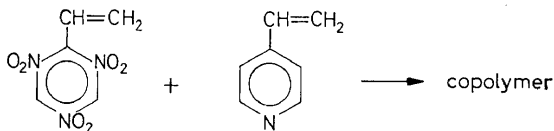
range of monomer concentration. The formation of the TCNE \cdot^- anion-radical during the polymerization was confirmed by e.s.r. measurements. The polymerizing solution gave an eleven-line e.s.r. spectrum with a spacing of 1.60 g identical to that reported in the literature for this anion-radical. The concentration of TCNE \cdot^- obtained from the area under the e.s.r. spectrum (calibrated against picrylhydrazyl) was determined during the course of the polymerization and showed that the rate of polymerization R_p was given by

$$R_p = k [\text{NVC}] [\text{TCNE}\cdot^-]$$

A particularly interesting situation arises when both donor and acceptor are polymerizable olefins. Gilbert reported²² the spontaneous polymerization of vinyl isobutyl ether and vinylidene cyanide on mixing to give homopolymer of the two reacting monomers. A possible reaction scheme is



Similarly Yang and Gaoni have reported²³ the spontaneous copolymerization of trinitrostyrene and vinylpyridine on mixing



These interactants probably form charge-transfer intermediates but before generalization as to the exact mechanism of polymerization can be proposed a detailed study of the products of these and similar reactions is clearly advisable.

Formation of cation radicals by chemical oxidation

Lewis acids commonly employed for initiation of cationic polymerization can act as oxidizing agents by themselves or in conjunction with easily reducible molecules²⁴. Particularly useful combinations are $\text{SbCl}_5/\text{CH}_2\text{Cl}_2$ ^{14,25}, $\text{SbCl}_5/\text{SbCl}_3$ ²⁶, SbCl_3/O_2 ²⁶, $\text{AlCl}_3/\text{CH}_3\text{NO}_2$ ¹⁷, and $\text{BF}_3/\text{Pb}(\text{OAc})_4$ ²⁸. All these reagents have been used to prepare stable cation radicals from condensed hydrocarbons (Figure 5). It is evident from these observations that

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many common Lewis acids (SnCl_4 , SbCl_3 , TiCl_4 , AuCl_3 , CuCl_2 and FeCl_3) could function as primary oxidizing agents in their reactions with olefins. Protonic acid cocatalysts would not necessarily inhibit oxidation with Lewis acids and it has been shown conclusively by Ledwith and Woods²⁹ that SbCl_6^- is a good electron acceptor and can be used to oxidize a wide range of substrates, for example ferrocene, arylamines and phenoxide anions. These

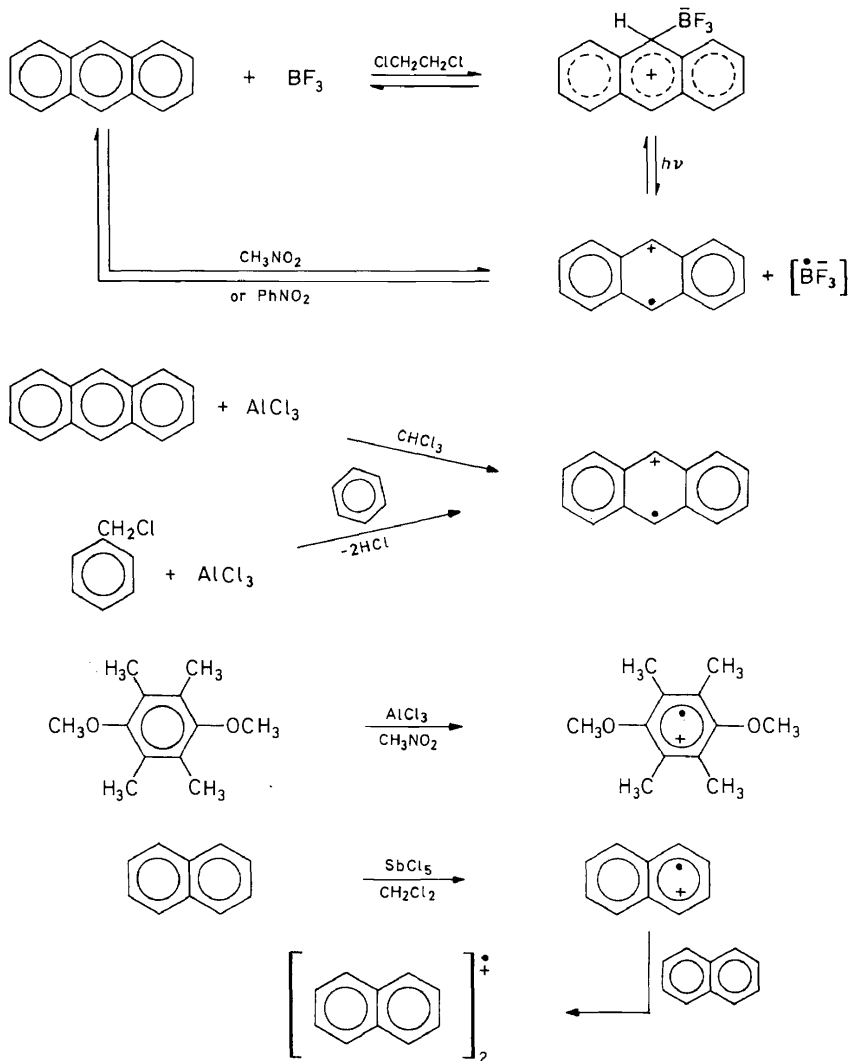


Figure 5

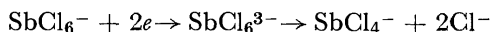
authors also showed that SbCl_6^- used in the form of the stable quaternary salt $\text{R}_4\text{N}^+\text{SbCl}_6^-$ is an initiating agent for the polymerization of *n*-vinylcarbazole and *p*-methoxystyrene in methylene chloride or acetonitrile solvent.

Typical polymerization measurements are shown in *Table 3*. Most of the initiator remains unused and it is thought that the polymerization is cationic but with a slow rate of initiation. The SbCl_6^- anion will not initiate the polymerization of alkyl vinyl ethers and it therefore follows that dissociation of the anion into its components (SbCl_5 and Cl^-) is not the mechanism

Table 3. Polymerization of *n*-vinylcarbazole with dimethyl benzyl phenyl ammonium hexachloroantimonate in CH_2Cl_2 at 20°C

[Monomer] mole/litre	$10^3 \times$ [Initiator] mole/litre	Yield %	Molecular Weight
0.24	—	—	—
0.24	9.61	78.5	5040
0.24	4.81	71.6	4270
0.24	0.96	68.8	5200
0.66	4.42	91.5	8710
0.46	4.61	87.3	5980
0.12	4.90	66.3	6490

whereby initiation occurs since SbCl_5 is a powerful initiator for vinyl ether polymerization. The overall oxidation reaction corresponds to



and the primary initiation step



followed by a rearrangement leading to a cationic propagation, e.g.

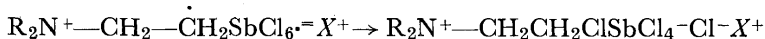
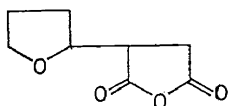


Photo-induced formation of ion radicals

The initiating reaction discussed in the foregoing section take place in a manner which may be rationalized according to equation (4) by complex formation and electron transfer. The electron transfer is induced by thermal means as illustrated by the potential energy curves shown in *Figure 1*. The transfer process is assisted and accelerated by solvation. In non-polar solvents and even with some systems in polar solvents strong charge-transfer complexes may be formed with little or no ion-pair formation in the ground state. In such cases it is often possible to effect oxidation and reduction (initiation) by using visible or ultraviolet light. For example, tetrahydrofuran forms a donor-acceptor complex with maleic anhydride and on irradiation of a mixture of these two substances in solution a quantitative yield of the 1:1 adduct³⁰ may be isolated by vacuum distillation. The addition of vinyl monomers, susceptible to free-radical polymerization to the mixture of tetrahydrofuran and maleic anhydride suppresses the photochemical synthesis of (I) and results in the polymerization of the added vinyl monomer. An increase in the concentration of the maleic anhydride-THF complex

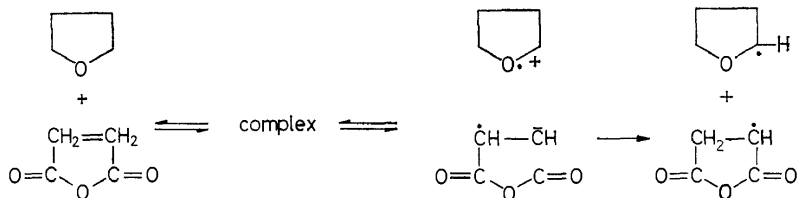
functions in a manner similar to more conventional free-radical initiators in that it increases the rate of polymerization and decreases the molecular weight. In support of this view it was observed that copolymerization of the maleic anhydride occurred according to the well-known relative monomer reactivities in free radical polymerization. Thus there was no



(I)

incorporation of maleic anhydride when methyl acrylate was used as monomer but with vinyl acetate and isobutyl vinyl ether rapid and quantitative formation of 1:1 alternating copolymers occurred. In the latter reactions polymerization stopped as soon as all the initiator was copolymerized.

Closely-related observations have recently been reported by Okamura and his coworkers³¹ who describe the cationic polymerization of cyclic ethers and vinyl ethers by a species derived from the γ -ray and ultraviolet irradiation of ethereal solutions of maleic anhydride. Trioxane or 3,3-bis-chloromethyloxetane in the presence of maleic anhydride and oxygen polymerized completely when irradiated and benzoyl peroxide may be used instead of oxygen. The maleic anhydride was practically unchanged at the end of the reaction and the polymerization was inhibited by hydroquinone which indicates that free radicals are involved. Addition of a small amount of the irradiated mixture to isobutyl vinyl ether caused immediate and extreme polymerization of the ether. These authors postulate that a free radical is formed from the ether by hydride extraction of an α -hydrogen atom. This is followed by a one-electron transfer from the radical to the maleic anhydride to yield the ether cation and the maleic anhydride radical anion. Cationic polymerization of the ether proceeds in the normal way. It seems reasonable to assume therefore that in our system the initial donor-acceptor complex when photoactivated gives rise to a radical ion, e.g. THF



may be replaced with other ethers and from a study of a wide series of ethers it appears that rate of polymerization of MMA parallels the ability of ethers to act as donors in complex formation. Maleic anhydrides may also be replaced by other anhydrides with considerable variation in the rates of polymerization. Clearly the nature of the donor-acceptor complexes offers a very wide scope for similar photochemical initiation reactions and other systems are being investigated.

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