

Research Signpost
37/661 (2), Fort P.O., Trivandrum-695 023, Kerala, India



Photochemistry and UV Curing: New Trends, 2006: ISBN: 81-308-0014-4
Editor : J.P. Fouassier

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Wavelength tunability in photoinitiated cationic polymerization

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Abstract

Onium salts, widely used cationic photoinitiators, have absorption in the short wavelength of the UV spectrum. However, their spectral sensitivity can be tuned up to the visible region by using several methods. Photosensitization of onium salts, their charge transfer complex formation and their free radical promotion are some techniques that are used to provide wavelength flexibility. This chapter summarizes these methods. Upon irradiation photosensitizers such as anthracene, perylene and phenothiazine form exciplexes with onium salts generating reactive species via electron transfer. Furthermore, ground state charge transfer formation

between alkoxy pyridinium salts and aromatic electron donor compounds is another way to initiate cationic polymerization in wavelength range between 350-650 nm. In this case, the radical cations of the electron donor compounds formed by electron transfer reaction are responsible for the initiation. Bisacylphosphine oxides, dimanganese decacarbonyl in conjunction with alkyl halides and titanocene type photoinitiators such as Irgacure 784 were shown to be useful free radical promoters providing the possibility of performing cationic polymerization in the long wavelength and visible region.

1. Introduction

Photoinitiated cationic polymerization is an important industrial process widely used in different applications. For instance, coatings, inks, adhesives and photolithography can be performed without the use of solvents, so a potential source of air and water pollution is eliminated^{1,2}. UV initiated cationic polymerization holds considerable promises in the future, particularly as a means of overcoming volatile emission, toxicity and molecular oxygen inhibition limitations. The types of general monomers which may undergo photoinitiated cationic polymerization, are vinyl and alkoxy vinyl monomers, heterocyclic monomers involving sulphur, oxygen, nitrogen atoms as summarized in Chart 1. Most importantly, these monomers do not decomposed nor give any side reactions at the wavelength of irradiation.

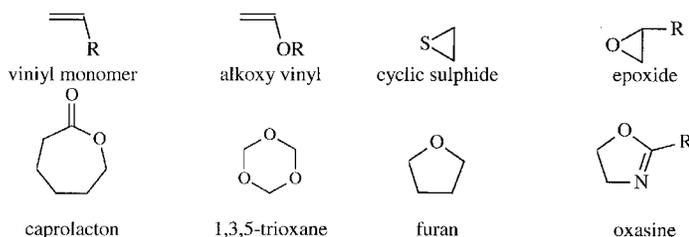
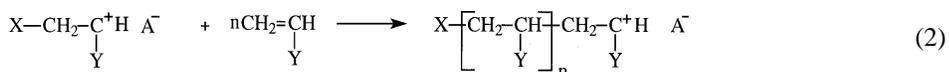
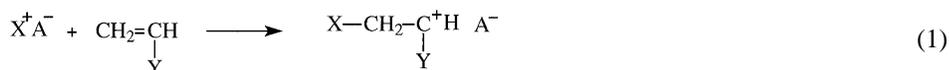


Chart 1. Monomers used in photoinitiated cationic polymerization.

Onium salts such as diaryliodonium^{3,4} triarylsulphonium⁵ and alkoxy pyridinium⁶⁻⁸ are the most used initiators that mainly absorb the light in the region between 225 and 350 nm^{4, 9-11} in photoinitiated cationic polymerization. Upon UV irradiation, reactive cations or Brønsted acids are produced by means of homolytic and heterolytic bond cleavages of these salts respectively (Scheme 1).



Scheme 1. General mechanism for cationic photopolymerization.

This reaction scheme holds for all types of cationic photoinitiators. Notably, the counter anion has to be nonnucleophilic in order to prevent the termination of a growing chain. Generally, molecular weights and percentage conversion increase in the order of $\text{BF}_4^- < \text{PF}_6^- < \text{AsF}_6^- < \text{SbF}_6^-$.

The chemical construction of the system used determines the photoinitiator which is suitable for the generation of the cations. In the case of onium salt, there are two acting systems, direct and indirect photolysis. In direct initiating systems, the energy is absorbed by the onium salt leading to decomposition. On the other hand, an additional component absorbs the energy in indirect systems. After absorbing energy, either the additives themselves or the species formed from additives can react with the onium salt thus producing initiating cations. Various wavelengths for specific applications can be tuned by altering the additional component. Photoinitiated cationic polymerization by direct irradiation of simple onium salts can be performed usually below 300 nm, so some limitations occur on the potential uses of cationic polymerization at high wavelength. Moreover, conventional light sources emit the light at a significant proportion at higher wavelengths. Therefore, limited absorption of the initiating system in a broad range causes a waste of energy. One way to broaden the spectral sensitivity of the onium salts is a substitution of the chromophores onto the aromatic groups of the salts. However, this method has some disadvantages such as multistep synthetic procedures, a high cost and the failure in desired shift in the absorption characteristics of the salts. Several indirect ways to overcome this problem have been described¹¹. All of these pathways involve electron transfer reactions either with photoexcited sensitizer¹²⁻¹⁶, the electron donor compounds in the excited charge transfer complexes^{17,18} or with free radicals¹⁹⁻²².

This chapter concentrates on the recent aspects in the expansion of a short wavelength region of the UV spectrum to longer wavelengths by using indirect ways for providing working conditions for photoinitiated cationic polymerization. Special emphasis will be placed on the use of organic and organic-inorganic hydride-free radical sources such as bisacylphosphine oxides, and manganese decacarbonyl and titanocene type photoinitiators, respectively.

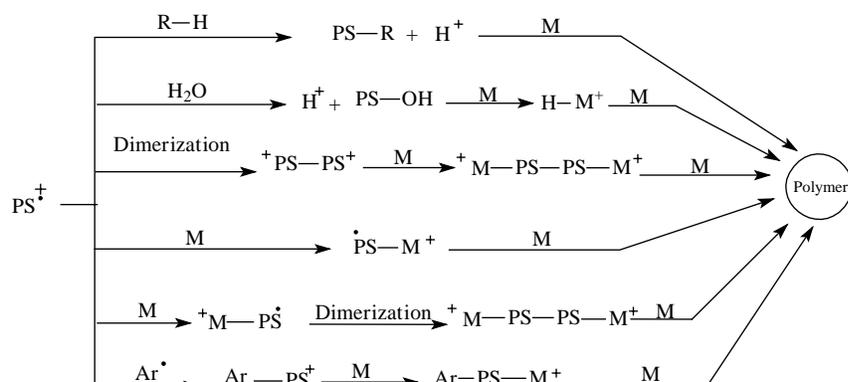
2. Photosensitized cationic polymerization

The absorption characteristics of the onium salts based photoinitiating systems can be adapted for particular applications requiring activation at wavelengths between 330-650 nm by the use of various photosensitizers. The photosensitizers enhance the sensitivity of the light source that used and accelerate the rate of polymerization by inducing onium salt decomposition with electron transfer reaction (3).

Notably, aromatic carbonyl photosensitizers that undergo electron transfer via a radical route are not included¹⁷⁻²².



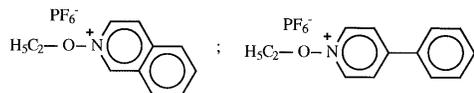
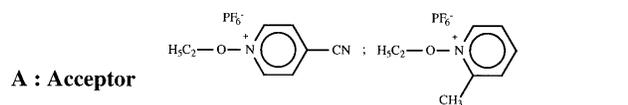
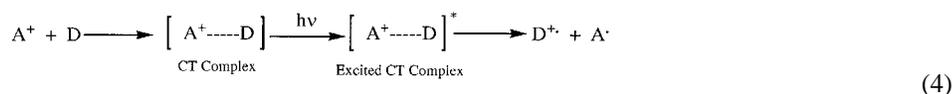
The photosensitizer radical cations initiate the cationic polymerization with the various mechanisms, which are depicted in Scheme 2²³.



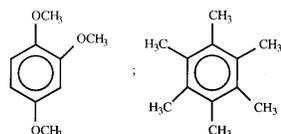
Scheme 2. Photosensitized cationic polymerization.

3. Photoinitiated cationic polymerization by charge transfer complexes

It has been reported^{17,18} that charge transfer complexes formed by mixing certain pyridinium ions with aromatic electron donors act as photoinitiators for cationic polymerization. It was suggested that radical cations of donors, formed by excitation of CT complex according to the following mechanism, are responsible for the polymerization.



D : Donor



The radical cations formed initiate the cationic polymerization directly or they undergo hydrogen abstraction yielding Brønsted acid capable of initiating cationic polymerization. The absorption bands of the charge transfer complexes lie in the range

between 350-650 nm depending on the structure of the electron donor compound and the acceptor pyridinium salt. Interestingly, CT initiation can be realized only with alkoxy pyridinium salts. The iodonium and sulphonium salts either do not form such complexes or their complexes absorb at lower wavelengths. Notably, the CT complexes described above are applicable for the photoinitiation of epoxide monomers but not for the photoinitiation of vinyl ethers and N-vinyl carbazol. The latter monomers are already polymerized in a dark reaction upon addition of these complexes due to the strong electron donating power of the monomers.

4. Free radical promoted cationic polymerization

Onium salts may be used to oxidize free radicals according to the reaction (5). The cations thus generated are used as initiating species for cationic polymerization. This process is usually termed as free radical promoted cationic polymerization.



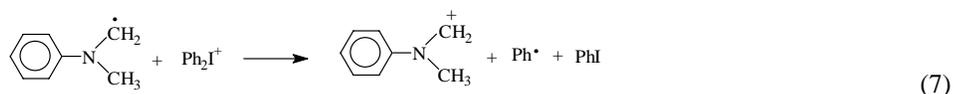
The efficiency of onium salts as oxidizing agents depends on their electron affinity. The higher the oxidation power of the onium salt, the higher is the reduction potential. Whether a radical can be oxidized by an onium salt or not is determined by using the Rehm-Weller Eqn. (6) providing that the oxidation and reduction potentials of the free radical and the onium ion are known.

$$\Delta G = F [E_{\text{ox}}^{1/2}(R^{\cdot}) - E_{\text{red}}^{1/2}(\text{On}^+)] \quad (6)$$

However, the exact oxidation potentials of most radicals in radical polymerizations are unknown. Therefore, the calculation of ΔG in most cases is not feasible.

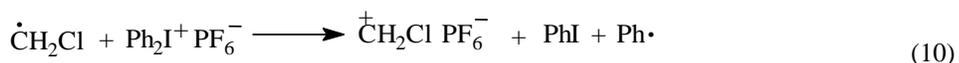
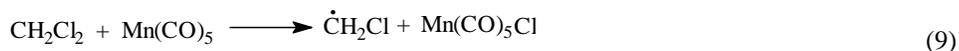
4.1. The use of visible light free radical photoinitiators

Although the use of many photoinitiators in free radical promoted cationic polymerization has been described, the sensitivity of the initiating system could be only rarely extended to the region of visible light. In a recent study²⁴, the developed system consists in xanthene dye functions as a photon acceptor and, together with the aromatic amine produces radicals from visible light; the wavelengths of incident light is between 500 and 650 nm. The diaryliodonium salts are responsible for oxidizing α -amino radicals formed after hydrogen abstraction to the respective cations, and the latter are responsible for the initiation of cationic polymerization. This initiating system has been successfully applied to block copolymerization²⁵.

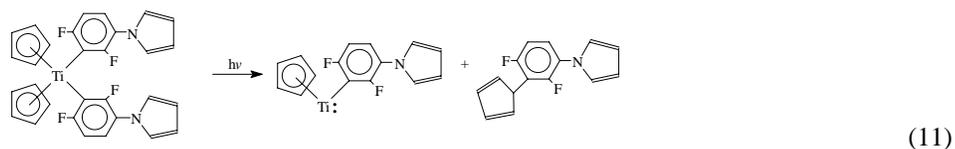


In another study, a novel visible light initiating system for the cationic polymerization of cyclic ethers such as cyclohexene oxide (CHO) and alkyl vinyl ethers such as butyl vinyl

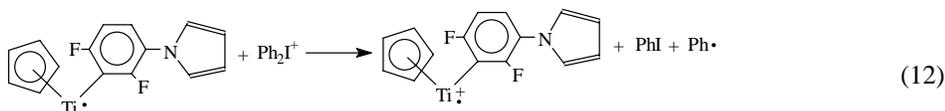
ether (BVE) was described²⁶. This system consists of an organic halide, namely halogen containing solvents, dimanganese decacarbonyl, $\text{Mn}_2(\text{CO})_{10}$, and an onium salt such as diphenyliodonium salt, $\text{Ph}_2\text{I}^+\text{PF}_6^-$. Carbon-centered radicals were formed upon irradiation ($\lambda = 436$) of organic halides in the presence of dimanganese decacarbonyl, $\text{Mn}_2(\text{CO})_{10}$. Since the diphenyliodonium ion does not absorb at the irradiation wavelength, $\lambda = 436$ nm, all the light is absorbed by $\text{Mn}_2(\text{CO})_{10}$. Upon absorption of light, $\text{Mn}_2(\text{CO})_{10}$ decomposes to $\text{Mn}(\text{CO})_5$. The latter reacts with the terminal halide group yielding carbon-centered radicals oxidized by suitable onium salts.



Both systems consisted of three components for the generation of reactive cations, and the initiation mechanisms are rather complex. However, titanocene derivatives represent one of the few examples of the one component systems directly activated upon photolysis to initiate free radical polymerization²⁷. A commercial titanocene type photoinitiator, namely Irgacure 784, was also tested for its suitability as a visible light free radical source in free radical promoted cationic polymerization. For this purpose, cyclohexene oxide (CHO) was polymerized with a combination of Irgacure 784 and an onium salt²⁸. Polymerizations were performed at $\lambda = 460$ nm where all onium salts are transparent and all the light emitted is absorbed by the titanocene initiator. CHO was polymerized effectively with iodonium and N-alkoxy pyridinium salts. Simple triaryl sulphonium salts do not undergo radical induced decomposition due to the unfavorable redox potentials. Notably, the two components of the initiating system are indispensable for the polymerization to occur; no polymer is formed in the absence of one of the compounds under our reaction conditions. When a proton scavenger, 2,6-di-tert-butyl-4-methylpyridine, was present in the reaction mixture, no polymer was formed during irradiation indicating that the protons act as initiators. The photodecomposition behavior of titanocene derivatives is related to their structure. Radical trapping experiments revealed that non-fluorinated diaryl titanocenes photodecompose via homolytic cleavage of the metal-aryl-ligand bond to generate aryl and titanocene radicals. It is known that fluorinated titanocene derivatives such as Irgacure 784 yield no primary organic radicals but rather titanium centered diradicals according to the following reaction.



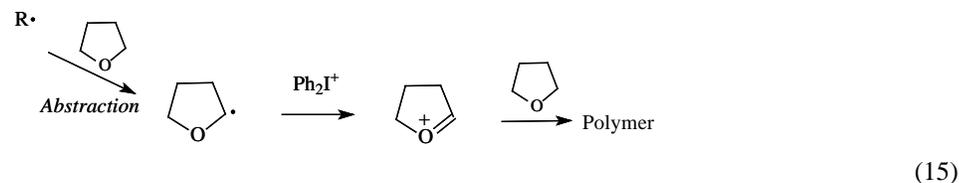
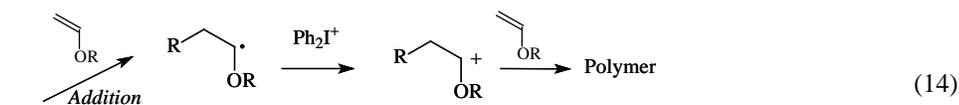
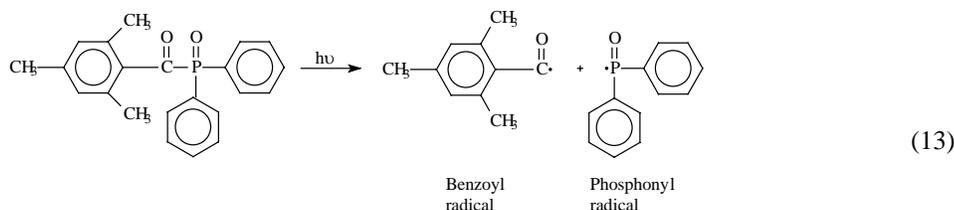
In the presence of suitable oxidants such as onium salts, these biradicals may undergo electron transfer reaction to yield radical cations.



The possibility of a direct initiation by the radical cations thus formed is precluded by the spectroscopic investigations and the absence of polymerization in the presence of a proton scavenger. Although how the protons are generated is not known at present, these results suggest that they played an important role in the initiation.

4.2 The use of bisacylphosphine oxides

Acylphosphineoxides absorb UV light (≈ 380 nm) at longer wavelengths with a high extinction coefficient²⁹. However, in spite of their high performances, these photoinitiators are only active when the photochemically generated (through α -cleavage) benzoyl and phosphonyl radicals undergo addition or abstraction reactions³⁰ with the monomer. The resulting carbon centered radicals are converted to carbocations by reaction with Ph_2I^+ ions which initiate the cationic polymerization.



This leads to some limitation about their use in technical applications requiring monomers which are unreactive towards photochemically generated radicals. In order to overcome these limitations, the use of bisacylphosphine oxides that are especially appropriate in free radical promoted cationic polymerization was reported³¹. The absorption of bisacylphosphine oxides is shifted to longer wavelengths due to conjugative carbonyl-phosphinoyl-carbonyl interactions. In general, radicals with electron donating groups undergo oxidation more favorably and are therefore more efficient in free radical promoted cationic polymerization. In contrast to acylphosphine oxides, the radical formed from bisacylphosphine oxides were shown to be directly oxidizable without the need of a reaction with the monomer.

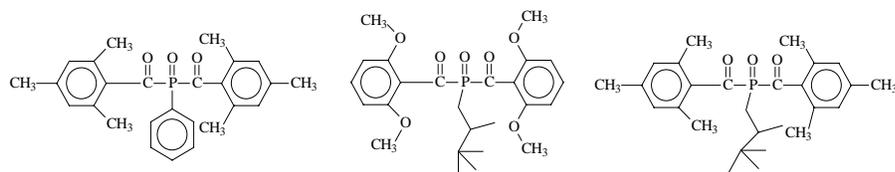
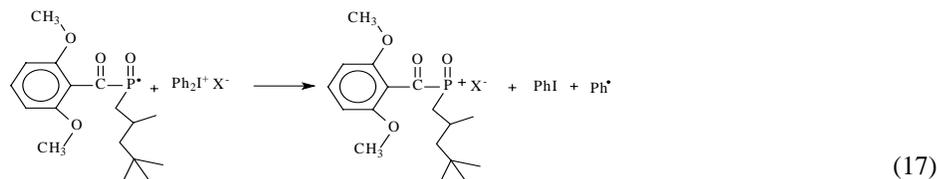
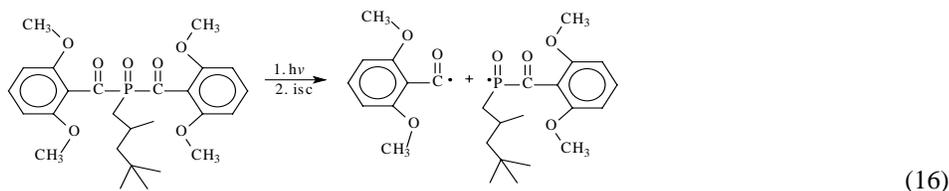
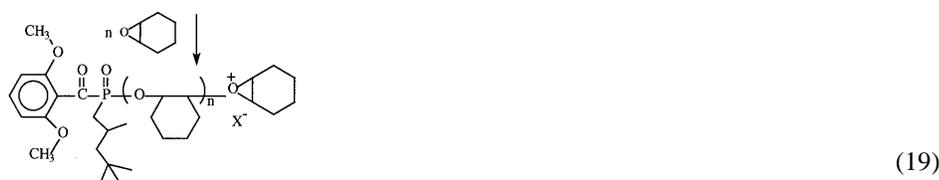
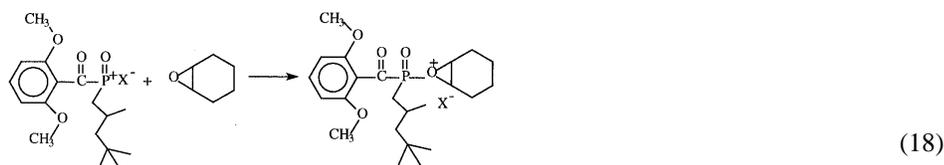


Chart 2. The structure of bisacylphosphine oxides used in free radical promoted cationic polymerization.

Contradictorily, the bisacylphosphine oxides (Chart 2) perform significantly better than the monoacylphosphine oxides. This better performance was correlated with the *p*-character on the phosphorous atom, which improves the reactivity of the radicals in the redox process, as reflected by the ^{31}P hyperfine coupling constant.

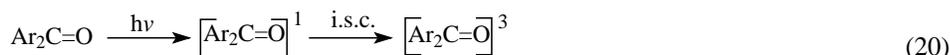


The resulting phosphonium ions must be capable of initiating the cationic polymerization, as illustrated in following reaction. As an example, monomer CHO was chosen because it is not inclined to undergo a hydrogen abstraction nor to be polymerized by a radical mechanism. $^1\text{H-NMR}$ measurements show that the benzoylphosphinoyl groups are attached to the poly(cyclohexene oxide) chains.



4.3 Free radicals generated by hydrogen abstraction

The most practically used free radical initiating system is the reduction of aromatic carbonyls, usually ketones, by an electron donor molecule. Benzophenone, thioxanthone, camphorquinone, benzyl, anthraquinone derivatives and some dyes are the most used sensitizers for this type of initiating system. Irradiation of the sensitizer results in the formation of its singlet state, which is rapidly converted to its triplet state by intersystem crossing. Subsequently, a hydrogen is abstracted from an electron donor molecule and electron transfer reaction yields Brønsted acid which is capable of initiation.



5. Conclusion

It has been shown that the indirect activation of onium salts based on electron transfer with various additives can be used to initiate cationic polymerization with the decisive advantage of a photosensitivity range extending up to the visible range. The systems mentioned throughout this chapter are collected in Figure 1. Also the photoinitiators, photoinitiation types, initiating species, and incident wavelengths of all these systems are listed in Table 1. Moreover, the addition-fragmentation reaction - which is another type of the indirect initiating systems - has been excluded since these systems have been discussed in a separate chapter.

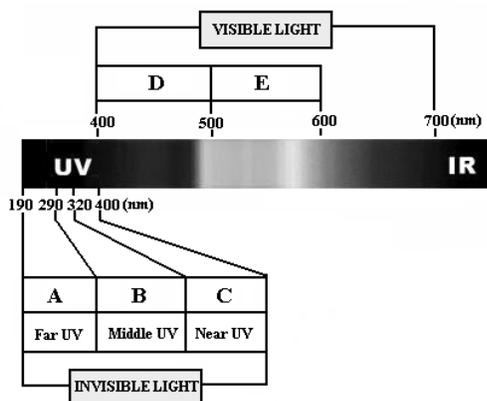


Figure 1. Summary of suitable wavelengths for photoinitiated cationic polymerization systems (see Table 1 for the details).

Table 1. Photoinitiating compounds acting in UV and visible light.

	Photoinitiators ^d	Initiating Species ^a	Activation Wavelength ^b	Photoinitiation Type	Ref.
A		H ⁺	< 300	Direct	5,32
A		H ⁺	< 300	Direct	5,32
A		H ⁺	< 300	Direct	5,32
C		H ⁺	366	Direct	33
A		H ⁺	< 300	Direct	4
B		H ⁺	300	Direct	4
B		⁺ CH ₂ -C ₆ H ₅	315	Direct	34
B		H ⁺	315	Direct	35
A		H ⁺	< 300	Direct	36
C		⁺ CH ₂ -C ₆ H ₅	352	Direct	37
C		⁺ CH ₂ -C ₆ H ₅	352	Direct	10,37
A			< 300	Direct	6
A		$\overset{\cdot}{\text{C}}\text{H}_2-\overset{\cdot}{\text{C}}\text{H}-\text{R}$	< 300	Direct	11

Table 1. Continued

B			310	Direct	6
C			>350	Direct	6,38
A			< 300	Direct	39
C			> 300	Direct	40
C			>350	Direct	38
C		H ⁺	> 340	Indirect ^c	13
C			> 340	Indirect ^c	41
C			342	Indirect ^c	42
C			340	Indirect ^c	7

Table 1. Continued

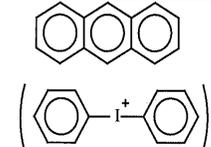
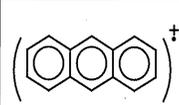
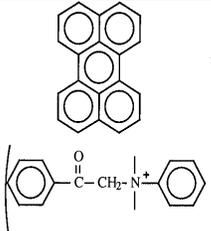
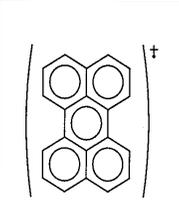
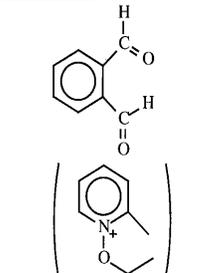
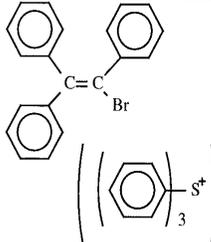
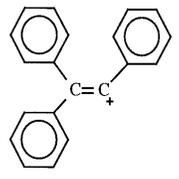
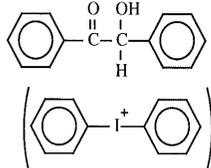
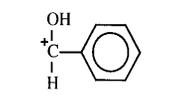
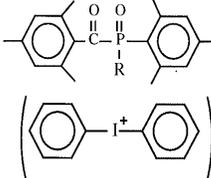
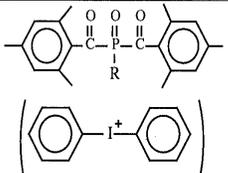
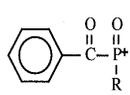
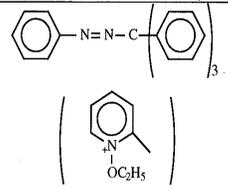
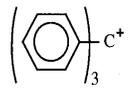
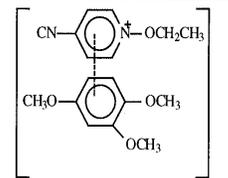
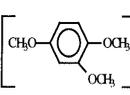
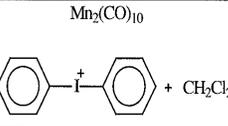
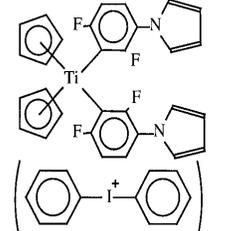
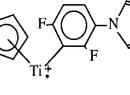
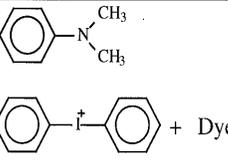
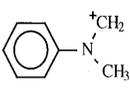
C			>340	Indirect ^c	12-14, 43-45
C			>350	Indirect ^c	35,46, 47
C		H ⁺	350	Indirect ^d	48,49
C			350	Indirect ^d	50,51
C			350	Indirect ^d	52
C		R-M ⁺	380	Indirect ^g	29,30

Table 1. Continued

D			420	Indirect ^d	31
D			420	Indirect ^d	53
D			425	Indirect ^f	17,18
D		⁺ CH ₂ Cl	436	Indirect ^e	26
D			460	Indirect ^e	27,28
E			500-600	Indirect ^e	25, 54-56

^a counter anions are omitted for the related salts and initiating species^b absorption maxima or activation wavelength^c sensitisation via exciplexes^d oxidation of free radicals^e electron transfer reactions^f ground state charge transfer complexes^g addition or abstraction reactions

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