Translated from *Uspekhi Khimii* **60** 205–237 (1991) U.D.C. 541.14:541.64

Electron phototransfer in the initiation of polymerisation

M N Usacheva, I I Dilung
Pisarzhevskii Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev

ABSTRACT. The results of studies on the participation of exciplexes and other products of electron phototransfer in the initiation of polymerisation are correlated in this review. The relationship between the nature of the primary radical species and the mechanism of formation of a polymerisation chain is discussed. Particular attention is given to the effect of the electronic structure of the photoinitiator, the chemical nature of the activator and monomer, and the polarity of the medium on the mechanism of photoinitiation and its efficiency.

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I. Introduction

Photopolymerisation processes have been widely applied in current practical methods.[1–4] They are carried out with the participation of active products that are generated in various photochemical reactions. These can be products of unimolecular photodissociation[5–9] or products of bimolecular reactions involving electron or hydrogen atom transfer.[10–19] Recently a large number of reports have been published on the participation in polymerisation photoinitiation processes of different intermediates of electron phototransfer, principally exciplexes,[20–26] which help to increase the efficiency of the process.

The role of photoinitiators in polymerisation processes is very important. They determine the region of spectroscopic sensitivity of the polymerising compositions,[2,25] and the kinetics and mechanism of not only the initiation process but also that of the overall polymerisation reaction.[20–29] To a certain extent they influence the physicochemical and mechanism properties of the polymer materials obtained.[2,28] Meanwhile the question of the mechanism of photoinitiation with the most effective binary systems that are susceptible to electron phototransfer has received virtually no study.

This review attempts to correlate the existing literature data on the participation of exciplexes and other electron phototransfer products in the initiation of polymerisation in order to establish the scientific principles for the choice of initiating systems that can achieve effective polymerisation over a wide spectroscopic range.

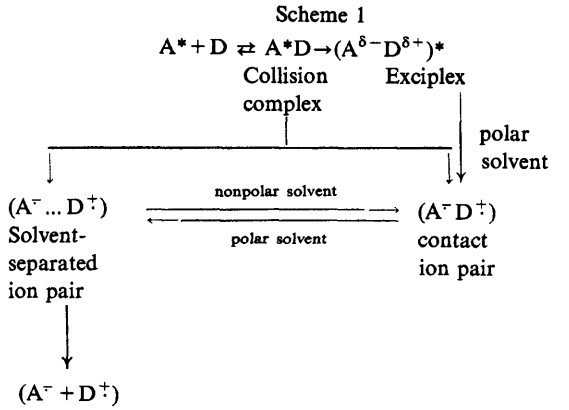
We shall consider the main questions relating to the phenomenon of electron phototransfer.

II. Main mechanisms of electron phototransfer

1. Classification of the intermediates of electron phototransfer

The formation of exciplexes and their photophysics have formed the subject of a number of reviews.[30–35] An exciplex is an excited molecular complex of a given stoichiometric composition which is stabilised in an excited state and unstable in its ground state.[31] It has a specific geometry that is characterised by a bond energy of the order of 5–200 kcal mol^{-1}, a significant dipole moment which is to a certain extent a measure of the charge transfer,[36] and a lifetime that is sufficient for emission of fluorescence or phosphorescence (depending on its multiplicity). An exciplex is one of the intermediates formed during electron phototransfer (EPT). According to the ideas put forward in one of the most recent reviews,[35] the scheme for electron transfer (ET) can be depicted as follows:

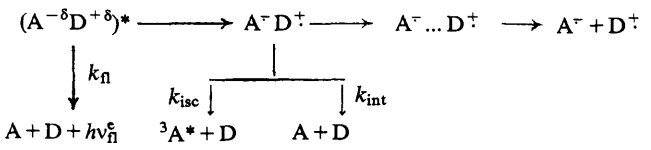
Scheme 1



In this case all the intermediate products are classified according to lifetime, distance between the partners, and number of solvent molecules inserted between them. The lifetime of the collision complex (of the order of 10^{-9}–10^{-10} s) is sufficient for "quenching" of the excited state of the photoactive component by an ET mechanism to occur.[35–37] In this case the collision complex is initially converted to a contact ion pair going via or avoiding the formation of an exciplex, depending on the conditions. It follows from Scheme 1 that the solvent, depending on its polarity, can stabilise contact or solvent-separated ion pairs, combined under the general title of geminate ion pairs. Solvent-separated radical ions that are situated at considerable distances from each other in solution are known as free solvated radical ions. They are completely independent of their partner and in a similar manner to free radicals can exist as independent species for a relatively long period.

If a strong interaction occurs between A* and D in the collision complex, it is converted to an exciplex. When stabilisation of the exciplex is determined to a considerable extent by a charge-transfer interaction, with an increase in polarity of the medium all the electron transfer processes described above can also occur via an exciplex in accordance with Schemes 1 and 2. Deactivation of an exciplex occurs through radiationless processes of internal conversion and intersystem crossing as well as through fluorescence (if a singlet exciplex is involved).[22]

Scheme 2



Fluorescence occurs when there is a transition from the equilibrium state of the exciplex to the dissociative ground state in accordance with the Franck–Condon principle. If the intramolecular transitions are accompanied by a considerable nuclear rearrangement of the components, emission is absent, namely, the exciplex does not fluoresce and its properties are similar to those of a contact ion pair.[35]

Triplet exciplexes exist in addition to singlet exciplexes, and these have been discussed in detail in reivews.[31,38,39] They are formed either through the interaction of a triplet-excited molecule with an electron donor or acceptor[40] or through the intersystem crossing of a singlet exciplex or weak charge-transfer complex occurring in the ground state.[39,41]

The wave function of the exciplex, whatever its multiplicity, can be represented as a combination of wave functions of states with the excitation localised on one of the components of the complex and a state with complete charge transfer:[42]

$$\psi_{ex} = c_1\psi(D^*A) + c_2\psi(DA^*) + c_3\psi(D^+A^-), \quad (1)$$

where c_1, c_2, and c_3 are coefficients denoting the contribution of each of the states of Ψ_{ex}.

If $c_3 \gg c_2$ and $c_3 \gg c_1$, the contribution of charge-transfer states to the stabilisation energy of the exciplex is very large.

The EP scheme involving a singlet exciplex considered above can be applied equally to a triplet exciplex with the distinction that in the latter case a triplet radical ion pair is formed instead of a singlet solvent-separated radical ion pair.

Singlet fluorescing exciplexes are readily identified from the appearance of a structureless emission band which is shifted to longer wavelength in the spectrum relative to the fluorescence band of the uncomplexed photoactive component. Similarly, formation of triplet exciplexes can be monitored (in extremely rare cases in the condensed state because of the very low quantum yields, it is true) from the formation of a structureless fluorescence band, which is shifted to the "red" region relative to phosphorescence from the initial molecule.[43]

Fast kinetic methods can now be used to study singlet and triplet exciplexes, making it possible to record short-lived intermediates with a lifetime of the order of 10^{-11} s or more and to follow the kinetics of their deactivation.[44–46]

2. Thermodynamic and kinetic aspects of electron phototransfer

Electron phototransfer takes place whenever the changes in free energy of the processes $\Delta G_{ET} \ll 0$. Whatever the pathway of electron transfer, the expression for ΔG_{ET} has the following form:[35]

$$\Delta G_{ET} = E_{D^+/D} - E_{A/A^-} - e^2/\varepsilon R - E_{00}, \quad (2)$$

where $E_{D^+/D}$ and E_{A/A^-} are the values of the half-wave potentials of polarographic oxidation of the donor and polarographic reduction of the acceptor, $e^2/\varepsilon R$ is the Coulombic interaction energy between components A and D, ε is the dielectric constant of the solvent, R is the distance between the centres of molecules A and D, E_{00} is the energy of the excited state of molecule A.

Expression (2) does not take into account the structural changes which occur in electron donor-acceptor (EDA) systems during electron phototransfer. However, in a number of cases it is these which determine the probability of electron transfer. In the theory of Marcus,[47–50] which describes a mechanism for outer-sphere electron transfer, the effect of configurational changes, including changes in bond angles and bond lengths of the reactants, their steric configuration and the reorientation of the solvent molecules around them, in the initial and final states is examined. According to this theory the expression for the rate constant of the electron transfer has the following form:[50]

$$k_{ET} = Zk\exp(-\Delta G^{\neq}/RT), \quad (3)$$

where Z is the number of collisions, equal to 10^{11} litre mol^{-1} s^{-1}, k is a constant that depends on the magnitude of the electronic reaction barrier, and $\Delta G^{\neq}$ is the free energy of activation, including the contribution of the nuclear reaction barrier.

The electronic reaction barrier depends on the degree of overlap of the filled orbital of donor with the vacant unoccupied orbital of acceptor, their symmetry and relative steric configuration.

The nuclear reaction barrier is taken to mean the energy needed to change the bond angles and bond lengths and to change the molecular orientation resulting from both intramolecular factors and solvation effects during electron transfer.

The expression for the free energy of activation of electron transfer for neutral organic molecules has the form

$$\Delta G^{\neq} = (\lambda/4)(1 + \Delta G_{ET}/\lambda)^2, \quad (4)$$

where λ is the internal reaction barrier. It is equal to

$$\lambda = \lambda_i + \lambda^0, \quad (5)$$

where λ_i is a component that takes into account the energy expended on the change in bond lengths and λ_0 is a component that takes into account the energy expended on the reorientation of solvent molecules.[47,48]

Eqn. (4) gives the parabolic dependence of $\Delta G^{\neq}$ on ΔG_{ET}. The region of highly exothermic values of ΔG, where the free energy of activation starts to increase and the rate constant of electron transfer correspondingly decreases is known in the literature as the "inverted" region.[49]

The efficiency of EPT is determined to a considerable extent by the lifetime of the excited state of the photoactive component. It must be sufficiently long for EPT to occur in preference to the other deactivation processes competing with it. The probability of the latter depends on the photophysical properties of the excited

molecules (electron configuration and multiplicity of the excited state of the photoactive molecules) and their photochemical activity.

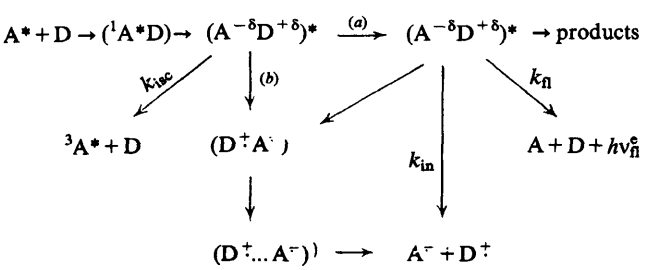
Electron transfer that involves an exciplex is the most rapid process, since in this case the maximum possible overlap of the orbitals of the electron donor and acceptor occurs.[35] Obvious examples of this are provided by exciplexes of the "sandwich" $\pi\pi$-type, formed between polynuclear aromatic amines, where favourable conditions for effective electronic interaction are created because of the similar symmetry of the overlapping orbitals.[51]

Together with this during electron transfer many systems involving an exciplex exhibit hindrances which increase the height of both the nuclear and electronic reaction barriers. In this case there are differences between the non-equilibrium Franck–Condon state $(A^{-\delta}D^{+\delta})^*$ and the equilibrium state of the exciplex $(A^{-\delta}D^{+\delta})^*$.[38,52,53] The first of these has a new electronic configuration as a result of charge transfer, distinct from the electronic configuration of the ground state and a nuclear configuration which corresponds to the electronic configuration of the initial state. In the non-equilibrium state the structure of the exciplex is flexible. During relaxation, which is accompanied by changes in bond lengths and bond angles in the molecules making up the complex and a reorientation of solvent molecules around them, the system changes to an equilibrium state from which the exciplex emits (if the probability of the radiative transition is sufficiently high). In such systems a significant Stokes shift of the fluorescence of the complex due to the molecular rearrangements which occur in them has been recorded.[54]

Non-equilibrium and equilibrium states of the exciplex were detected during emission of the system pyrene–tri(n-butyl)amine.[55] The nuclear electron transfer barrier in this system increased because of the unfavourable (tetrahedral) configuration of the amine molecule for formation of a complex relative to the pyrene molecule. The high values of the Franck–Condon energy of destabilisation of the exciplexes in the ground state (~90 kJ mol^{-1}) and the large Stokes shift of fluorescence of the exciplexes of aromatic azines with *N,N*-dimethylaniline (DMA) is also in all probability due to the two-stage nature of their formation.[56] In this case the geometric hindrance for formation of a complex is due to bending of the π-skeleton of molecules of the photoactive components during excitation. On the other hand, the exciplex of the "sandwich" $\pi\pi$-type structure between anthracene and DMA is formed in a single stage, as shown by the results of study over a picosecond timescale.[57]

The subsequent deactivation processes of exciplexes (internal conversion and intersystem crossing, dissociation in low-polarity or polar media, the formation of secondary products) can occur from both an equilibrium and a non-equilibrium state in accordance with Scheme 3.[58] As ε increases the probability of deactivation by route (*b*) increases.

Scheme 3



The probability of each of these will be determined by kinetic factors. Kuzmin et al.[53] have proposed a method for determining the probability of a Franck–Condon state participating in secondary reactions.

The kinetics of radiationless transition processes are governed by the energy gap principle but together with this principle the values of the rate constants of these processes show a significant dependence on characteristics of the electronic structure of the components of the exciplex. Thus a relatively slow relaxation of the Franck–Condon state of the exciplex to the equilibrium state caused by the unfavourable steric configuration of the components for electron transfer (perpendicular or inclined relative configuration of the planes of the partner molecules) is a prerequisite for the occurrence of a "rapid" intersystem crossing to a triplet state from the non-equilibrium state of the complex. The high rate constant for intersystem crossing ($k_{disc} \approx 10^9 - 10^{10}$ s^{-1}) is due, in the opinion of several authors,[58–61] to the considerable dependence of the matrix element of the spin-orbit interaction between the charge-transfer state of the singlet exciplex and the locally excited triplet state of the photoactive component on the geometry of the components in the exciplex. When the respective orbitals of the partner molecules of the complex are perpendicular to each other, the value of k_{isc} increases sharply.[59–61] In the case of a parallel orientation of the partner molecules, which is typical of exciplexes of polycondensed hydrocarbons with aromatic amines, intersystem crossing occurs relatively slowly ($k_{isc} \approx 10^8$ s^{-1}) from the equilibrium state of the exciplex.[62]

3. Relationship between the rate constant of fluorescence quenching and the efficiency of photodissociation with a change in free energy during electron transfer

One of the arguments in support of EPT is the existence of a correlation between the efficiency of quenching of the photoexcited state of the molecules being studied and the electron-donating (electron-acceptor) properties of the quencher. The efficiency of quenching in this case is determined by the expression[35]

$$\Phi_{ET} = \varphi_{S(T)} \frac{k_q[Q]}{k_q[Q] + k_d + k_q'[Q]}, \quad (6)$$

where $\varphi_{S(T)}$ is the quantum yield of formation of the respective excited state, k_q and k_q' are the bimolecular rate constants of quenching due to electron transfer and other reactions respectively, k_d is the rate constant of monomolecular deactivation processes, [Q] is the concentration of quencher.

If the quenching process is due to electron transfer, the expression for k_q has the following form:[63]

$$k_q = \frac{2 \cdot 10^{10}}{1 + 0.25[\exp(\Delta G^{\neq}/RT) + \exp(\Delta G_{ET}/RT)]} \quad (7)$$

According to this equation a linear dependence must occur between $\lg k_q$ and ΔG_{ET} with a plateau being reached at values of k_q close to the diffusion-controlled rate constant.[63,64] The slope of the linear section of this curve is equal to $1/RT$,[65] which can serve as evidence for the existence of electron transfer in a study of bimolecular quenching processes of excited states.

However, it should be remembered that the rate constant of quenching k_q is not always identical to the rate constant of electron transfer. When electron transfer is slow, $k_q = k_{ET}$. During rapid electron transfer ($k_{ET} \gg k_{diff}$) the rate constrant of quenching is

limited by the rate constant for diffusion. It was shown in two studies[66,67] that this is one of the reasons for the absence of an inverted region in the experimentally observed dependences of $\lg k_q$ on ΔG_{ET}.

In the diffusion-controlled region of the rate constants of quenching there is no systematic relationship between the quantum yield of photodissociation and the value of ΔG_{ET}.[52,68] Thus, the quantum yields of photodissociation for systems containing naphthalene derivatives as the electron donor are considerably higher than would be expected from their values of ΔG_{ET}. At the same time the efficiency of photodissociation for systems with electron donors containing a nitrogen, oxygen, and sulphur atom is considerably lower than the expected values.

However, there is a significant effect of the chemical nature of the reacting compounds and the multiplicity of their excited states on the quantum yield of photodissociation φ_D. In terms of the values of φ_D, the most frequently used quenchers of the excited state of photoactive compounds can be divided into 4 classes: amines, nitriles, esters, and anhydrides.[52] Within each class of quenchers it is already possible to establish some correlations between the values of φ_D and ΔG_{ET}. Thus, in a series of donors or acceptors of a single type φ_D decreases with an increase in oxidising potential of the electron donor or reducing capacity of the electron acceptor, in other words, with the shift of ΔG_{ET} to the exothermic region. The observed mechanism is quite obvious if account is taken of the fact that when $\Delta G_{ET} < 0$, in addition to the increase in probability of photodissociation processes, the probability of a competing process of radiationless transfer to the ground state also increases due to the decrease in the energy gap between it and the state with complete electron transfer.

4. Effect of solvent on the process of electron phototransfer

The solvent has a considerable effect on the mechanism of electron transfer. In this respect electrostatic (dipole-dipole and dipole-polarisation) interactions of the excited complex and its partners with the medium must be taken into consideration. These interactions are of a universal nature and are determined by such factors as the dielectric constant ε and refractive index n of the solvent. As a result of the solvating effect of the solvent a change in the electronic structure of the exciplex and its geometry is possible as is a change in the kinetics of electron transfer.[52] The polarity of the medium determines the dynamics and succession of stages in electron transfer (see Scheme 1). It is known that with an increase in the dielectric constant of the solvent, the probability of electron transfer in the collision complex increases, with the stage involving formation of an exciplex being absent.[52] With an increase in polarity of the medium ($\varepsilon > 7$) the final products of deactivation of the exciplex or contact ion pair are solvent-separated radical ions or geminal ion pairs possessing sufficient energy for subsequent conversions classified as secondary reactions of electron transfer.

It was noted earlier that the quantum yield of photodissociation (φ_D) depends strongly on the chemical properties of the partners that participate in electron transfer. Along with this there is a specific relationship between φ_D and the dielectric constant of the solvent[52]

$$\lg(1/\varphi_D) = A/\varepsilon + B, \qquad (8)$$

where A and B are constants that do not depend on ε. This equation is identical to the expression obtained from the Onsager model of ionic recombination.[69]

According to expression (8), an increase in φ_D is to be expected as ε increases, namely, with a shift of ΔG_{ET} towards the exothermic region. In fact, this type of dependence occurs in many cases.[69]

Donor-acceptor systems of a similar chemical nature having approximately the same values of ΔG_{ET} but which have φ_D values that differ considerably in polar solvents are known.[70] Recently it has been possible to account for these apparent contradictions by taking into account the nature of the solvating effect in vibrational relaxation processes during electron transfer.[70–73] The expression obtained by Mataga et al.[70–73] was used in an analysis of the magnitudes of the rate constants of charge separation v_S and recombination v_R at the following stages of electron transfer:

$$A^*...D \rightarrow A^{\cdot-}...D^{\cdot+} \rightarrow A...D.$$

As a result of this analysis the following conclusions were made. The rate constant of charge separation (dissociation constant) v_S is virtually independent of the magnitude of the energy gap between the initial ($A^*...D$) and final ($A^{\cdot-}...D^{\cdot+}$) states since the energy of activation of this process is extremely small. This conclusion is in complete agreement with the dependence of $\lg k_{eq}$ on ΔG_{ET} in the inverted region.[63] The rate constant of recombination v_R depends to a considerable extent on the energy gap between the initial ($A^{\cdot-}...D^{\cdot+}$) and final ($A...D$) states. Apart from this, the magnitude of v_R, in contrast to v_S, is determined to an appreciable extent by the individual properties of the participants in electron transfer (their donor-acceptor properties, steric configuration, relative orientation, etc.). It may be assumed that the ratio of the rate constants for charge separation and for recombination which depend on ΔG_{ET} will also determine the true value of the quantum yield of photodissociation.

One of the reasons for the existence of an inverted region may be related to secondary proton-transfer reactions.[67]

5. Secondary proton-transfer reactions

We shall only consider below those systems in which proton transfer follows electron transfer. Protonation can occur in one of the intermediates: in the collision complex,[74,75] exciplex,[76] contact radical ion,[77] or solvent-separated ion pair[78] in accordance with Scheme 4:

Scheme 4

$$^{1,3}A^* + DH \xrightarrow{k_q} {}^{1,3}(ADH)^* \xrightarrow{k_{PT}} (AH^{\cdot}...D^{\cdot}) \xrightarrow{k_{sep}} AH^{\cdot} + D^{\cdot}$$

$$^{1,3}(ADH)^* \xrightarrow{k_{int}} A + DH \qquad ^{1,3}(ADH)^* \xrightarrow{} A + DH + h\nu_{fl} \qquad (AH^{\cdot}...D^{\cdot}) \xrightarrow{k_{diss}} A^{\cdot-} + DH^{\cdot+}$$

where $^{1,3}(ADH)^*$ is any of the intermediates of EPT.

The formation of intermediates naturally reduces the potential barrier of proton transfer through the convergence of the partners and as a rule it produces a more favourable orientation for their interaction. Apart from this, the radical cations formed as a result of EPT are stronger acids and the radical anions are correspondingly stronger bases than their electron-neutral precursors.[78] Thus EPT assists an increase in not only kinetic but also thermodynamic acidity of proton donors, by increasing their reactivity. According to Marcus,[79] the expression for the rate constant of proton transfer is similar to expression (3) and has the form:

$$k_{PT} = Z \exp(-\Delta G^{\neq}_{PT}/RT), \qquad (9)$$

where $\Delta G_{PT}^{\neq}$ is the Gibbs free energy of activation

$$\Delta G_{PT}^{\neq} = W_R + (\lambda/4)(1 + \Delta G_{PT}/\lambda^2). \quad (10)$$

Here W_R is the change in free energy needed for convergence of the components and their rearrangement required for proton transfer. In turn

$$W_R = \omega^R - RT \ln S^r s^r, \quad (11)$$

where ω^R is the Coulombic interaction energy between the reaction partners expended on their convergence to a distance r, S^r and s^r are values representing steric and statistical factors.

During exothermic proton transfer (this occurs in all of the systems examined in this section), the rate-limiting stage of the overall process is proton transfer. Its rate constant depends on the relative orientation of donor and acceptor in the complex, the chemical nature of the reaction partners, and in particular on the type of hydrogen bond undergoing cleavage and the polarity of the medium.

If the resulting intermediate has a geometry which is favourable for proton transfer, the latter occurs freely with a rate constant exceeding the diffusion constant. Thus, in the system benzophenone–triethylamine in acetonitrile the formation of a ketyl radical occurs within 1.5×10^{-12} s after flash photolysis. Its precursor is an excited charge-transfer complex (CTC) ($\tau < 10^{-11}$ s), which comprises a superposition of radical ions[19]. Here the C–H bond of the α-carbon atom is positioned parallel to the half-filled orbital of the unshared electron pair of the nitrogen atom. In the system benzophenone–*N,N*-dimethyl(diethyl)aniline the corresponding process is slower. Formation of a ketyl radical occurs only 2×10^{-9} s after flash photolysis, and its generating contact pair is formed after $\tau = 3 \times 10^{-10}$ s.[77] The triplet exciplex of benzophenone with *N,N*-dimethylaniline is known to have two conformations of $n\pi$ and $\pi\pi$ type.[80] The second conformation corresponds to free proton transfer. In all probability the slight delay in the proton transfer time in this system is due to the need to transform the geometry of the contact ion pair. The rate constant of proton transfer in this case is equal to 2×10^{-9} s.

Proton transfer in the system anthracene–*N,N*-dimethylaniline, where a stable sandwich-type exciplex is formed, is considerably inhibited. On the basis of calculated data, the rate constant of proton transfer in this case is equal to $\sim 1-5 \times 10^6$ s^{-1}.[81]

The efficiency of proton transfer and the type of radical products formed depend to a considerable extent on the chemical nature of the proton donor. Thus, if tertiary amines are used as the donor, the proton of the α-C–H bond proves the most active. In this case an α-aminoalkyl radical is formed as a result of deprotonation. Radicals of this type have a low ionisation potential because of the formation of a three-electron bond (>N̈–Ċ<), and they are excellent reducing agents.[82] The rate constant of proton transfer by these amines depends on the size of the alkyl substituent (it increases in the series isopropyl < ethyl < methyl),[84] on the symmetry of their configuration relative to the nitrogen atom, and on the donor-acceptor properties of the substituents.

The most active proton in secondary amines is that of the N–H bond. In many cases it can participate in the formation of a hydrogen bond with the acceptor molecule, which gives additional stabilisation to the exciplex. Such a situation occurs in exciplexes of pyrene with primary and secondary amines.[84] The resulting hydrogen bond between the partners reduces the energy of cleavage of the N–H bond compared to the α-C–H bond and gives rise to a favourable geometry of the complex for proton transfer. As a result of deprotonation, radical cations of primary and secondary amines form mainly aminyl radicals.

Together with these, the formation of α-aminoalkyl radicals cannot be excluded. An increase in electron-accepting capacity of the partner[85] and an increase in polarity of the medium weakens the hydrogen bond and reduces the proton-donating activity of primary and secondary amines. It was established that as the polarity of the medium increases, the yield of aminyl radicals decreases relative to α-aminoalkyl radicals.[86]

The probability of proton transfer can vary according to the solvating properties of the solvent. With an increase in the dielectric constant of the solvent the exciplex becomes more polar and with complete electron transfer it is converted to a radical ion pair. As already mentioned, this results in a significant increase in the acidity of the proton donor and the basicity of the acceptor. It may be assumed that the type of EPT intermediate in which proton transfer occurs is determined by the thermodynamic condition $\Delta G_{PT} \leqslant 0$ for this process. The change in free energy of proton transfer ΔG_{PT} has the following form:[87]

$$\Delta G_{PT} = 2.3RT[pK_a(DH^{+\cdot}) - \pi K_a(AH^{\cdot})]. \quad (12)$$

If the acidity of the proton donor and the basicity of the acceptor are sufficient high, proton transfer is thermodynamically possible even in a collision complex which achieves a convergence of partners.[74,75] If the acidity of the donor is low, an initial complete electron transfer is necessary for proton transfer to occur. In this case the process only occurs in the radical ion pair.[77] For high values of ε, when the efficiency of the dissociation process competing with proton transfer (see Scheme 5) increases markedly, the rate of the latter decreases sharply. This is very clear in the case of the benzophenone–*N,N*-dimethylaniline system, in which the quantum yield of photodissociation of the complex increases from zero to unity with an increase in polarity of the medium while the quantum yield for formation of ketyl radicals correspondingly falls.[8] At high values of ε the molecules of the polar solvent stabilise the solvent-separated radical ions. This conteracts the convergence of the partners that is necessary for subsequent proton transfer. It follows from this that the role of a polar medium involves control of the kinetic and thermodynamic conditions for proton transfer.

III. Photoinitiation of polymerisation with organic redox systems

1. General ideas about the initiation of photopolymerisation with electron donor-acceptor systems

Thus, electron phototransfer between the components of a redox system can result in the formation of two types of active product that are energy-rich. These are radical ions or radical ion pairs which are formed as a result of complete electron transfer and free radicals that are the secondary products of proton transfer. Depending on the nature of the substrate that converts a monomer molecule to a lower-valence species, polymerisation is classified as being initiated by free radicals, ions, or radical ions (electron transfer).[147] In addition to this there is another classification, which does not take into account the nature of the initiated species. In this case the nature of the end of the growing chain (free radical or ionic) is the distinctive feature. Subsequently, in establishing the

mechanisms of polymerisation initiation and chain propagation we shall use the latter classification, which is based on the combination of features listed in Table 1, in each specific case. But at the same time we shall adhere to currently accepted principles. As a rule free radicals initiate radical polymerisation and ions initiate ionic polymerisation. Systems in which initiation is achieved using radical ions are conventionally grouped under ionic polymerisation in the majority of cases, since it is impossible to determine *a priori* which function—ionic or radical—generates the chain.[39,147]

Table 1. Distinctive features of free-radical and ionic polymerisation.

No.	Distinctive feature	Type of polymerisation		
		free-radical	ionic	
			cationic	anionic
1	Effect of polarity of the medium on polymerisation rate	Has almost no effect (with an increase it even decreases slightly)	Rate increases sharply with an increase in polarity of the medium	
2	Dependence of V on [M]	$V \approx k[M]^1$	$V \approx k[M]^n$ ($n \gtrsim 1-2$)	
3	Induction period in the presence of O_2	Occurs	None	
4	"Post-effect"	Occurs	None	
5	Value of k_p/k_t	$k_p^2/k_t \approx 10^{-2}-10^{-1}$	$k_p/k_t \geqslant 10^2$	
6	Effect of acceptors of primary active products	On introducing radical acceptors (eg., nitrobenzene, diphenylphosphate, 1,1-diphenyl-2-picrylhydrazyl, etc.) termination of polymerisation chain occurs	Polymerisation terminates in the presence of added amines or water	Polymerisation terminates in the presence of added oxygen
7	Temperature system	$T > 20$ °C	$T \ll 20$ °C	

Data on the most familiar redox systems that initiate polymerisation by light excitation at $\lambda > 300$ nm are given in Table 2. For the majority of them (systems 1–18) the primary photochemical stage is interaction of an excited molecule of photoinitiator (PI) with a molecule of monomer, resulting in the formation of primary active products of the monomer (free radicals or radical ions) which produce a polymerisation chain. In the absence of a PI, polymerisation does not occur on exposure to low-energy light quanta.

There are a number of systems (19–41) that consist of an initiator whose range of photosensitivity can vary from 300 to 700 nm and a so-called activator,[13,112] co-activator,[113] or promoter[90] between which electron transfer occurs. The activator is an electron donor or acceptor that is insensitive to light with $\lambda > 300$ nm and inert (as a polymerisation initiator) under these conditions. In contrast to this, the photoactive component of the redox system (PI) can independently initiate polymerisation which, however, takes place at a low rate. When it is used in combination with an activator it is possible to accelerate the process by a factor of 10^1-10^2 or more.

The fundamental processes for generation of radicals R$^\cdot$ that generate the polymerisation chain can be given in the form of Scheme 5;

Scheme 5

$$P \xrightarrow{h\nu} {}^{1,3}P^*, \quad {}^{1,3}P^* + A \xrightarrow{k_1} {}^{1,3}(PA)^*,$$

$${}^{1,3}(PA)^* \xrightarrow{k_2} R^\cdot, \quad {}^{1,3}(PA)^* \xrightarrow{k_3} P + A,$$

$$R^\cdot + M \xrightarrow{k_4} M^\cdot, \quad M^\cdot + M_{m-1} \xrightarrow{k_p} M_m^\cdot,$$

$$M_m^\cdot + M_n^\cdot \xrightarrow{k_o} M_{m+n},$$

where P and A are molecules of photoactive component and its partner in complexation (monomer or co-initiator) respectively.

It can readily be demonstrated that the solution of differential equations derived from a formal kinetic scheme such as Scheme 5 using the steady-state concentration method gives the following expression for the initial rate of polymerisation V:[133]

$$V = BI^{n_1}[P]^{n_2}[A]^{n_3}[M]^{n_4}, \tag{13}$$

where B is a proportionality constant that is dependent on the ratio k_p/k_o of the polymerising monomer and on the rate constants of the mono- and bi-molecular deactivation processes of the excited state of the PI; I is the intensity of incident light; [P], [A], and [M] are the concentrations of the PI, co-initiator, and monomer, n_1, n_2, n_3, and n_4 are exponents that are dependent on the polymerisation mechanism and the initiation mechanism. When the monomer is involved in the initiation process, $n_4 \geqslant 1$ and $n_3 = 0$.[93,119] Comparison of expression (13) for V obtained from treatment of the formal kinetic scheme with the experimentally observed value proves to be productive for study of the mechanism of polymerisation.

2. Photoinitiation of polymerisation with secondary products of proton transfer

In the photoinitiation systems (19–30 in Table 2) studied in this section, the thermodynamic condition for electron transfer is fulfilled. It is therefore to be expected that the probability of proton transfer between the components of these systems is high. In fact, in systems 20 and 22 the formation of an exciplex is detected while in systems 23–27 and 29 the quenching of fluorescence is established or bimolecular deactivation of the triplet state of the PI occurs, on which the mechanism of electron transfer is based. Since photopolymerisation initiated with these systems (see Table 2) corresponds to a free radical mechanism in accordance with the criteria indicated in Table 1, it may be assumed that the only possible active products are protonated and deprotonated free radicals that have left the solvent "cage". In accordance with the ideas put forward in Section II, it may be assumed that the initial formation of some form of intermediate involving electron transfer should be conducive to proton transfer.

It follows from Table 2 that amines, in particular tertiary amines †, are used as activators in the vast majority of cases in these redox systems. It was mentioned earlier (see Section II.5) that they

† We will not stop to analyse dye–activator photoinitiation systems in this review. These systems have been described in detail.[13] We shall merely point out that in addition to amines other classes of compounds, including sulphonates, carboxylates, organometallic compounds, etc., are used as activators in these systems.

Table 2. Systems that photoinitiate polymerisation.

No.	Initiating system	Monomer	Acceleration effect	Solvent	Evidence for ET or exciplex	Expression for initial rate of polymerisation	Polymerisation mechanism	Evidence for initiation mechanism	Refs.
1	2	3	4	5	6	7	8	9	10
1	^{3}Anthracene* + ^{3}Pyrene* + ^{3}Chyrsene	Styrene	×5	Benzene (no O_2)	Rate constant of deactivation of triplet states k_q^T varies in same way as the electron-donating properties of quenchers	$V \approx I^{0.5}[P]^1$	Free-radical		[11, 92]
2	^{1}Naphthalene* and its derivatives + ^{1}Anthracene* + ^{1}Pyrene* + ^{1}Fluorenone* + ^{1}Diphenyl*	Acrylonitrile	×2–6	Dimethyl formamide (no O_2)	k_q of fluorescence varies in the same way as the electron-donor properties of the photoinitiator, % conversion of monomer to polymer varies in the same way	$V \approx I^{0.57}[P]^{0.2-0.4} \times [M]^{1.1-1.5}$	"	Inhibition with oxygen	[93, 94]
3	^{3}Phenazine* + ^{3}Acridine* + ^{3}Anthracene* + monomer	Butylmethacrylate	×4–6	Toluene tetrahydrofuran (no O_2)	k_q^T of quenching varies in proportion to EA of photoinitiators ($k_q \approx 10^5-10^7$ litre mol^{-1} s^{-1})	$V = I^{0.5}[P]^{0.4-0.6}[M]^{1.0}$	"	"	[95, 138]
4	^{1,3}*N*-Vinylcarbazole* + triethylamine	*N*-Vinylcarbazole		Benzene (no O_2), acetone (in the presence of O_2)	k_q of fluorescence of *N*-vinylcarbazole with amines varies in the same way as their electron-donating capacity		Free-radical (α-aminoalkyl radical causes polymerisation)	1. Inhibition of polymerisation with O_2 2. Proton transfer from TEA to monomer takes place	[91, 96]
5	^{1}*N*-Vinylcarbazole* + CBr_4	"		Dichloroethane, nitrobenzene, benzene	Quenching of fluorescence of *N*-vinylcarbazole CCl_4 and CBr_4. Fluorescence band of exciplex appears		Free-radical and cationic	Bromine free radical and active cationic sites with C–Br bond occur	[97, 98, 140, 141]
6	^{3}*N*-Vinylcarbazole* + azobutyronitrile	"	more than 10 times	Dichloromethane, benzene	Excited triplet complex of *N*-vinylcarbazole with the solvent rate constant of quenching diffusion controlled	$V_p = \frac{k_p}{k_t^{0.5}} I^{0.5}[A]^{0.5}[M]^{1.5}$ $V_{cat} = \frac{k_p}{k_t} I[A]^{1.0}[M]^{1.0}$	Free-radical and cationic mechanism (at high concentrations of monomer)	Cationic polymerisation is terminated in the presence of dimethylformamide—a trap of cationic sites. Distribution of polymerisation products varies according to the polarity of the solvent	[27]
7	^{1}*N*-Vinylcarbazole* + fumaronitrile	"		Dichloromethane, benzene	Band of exciplex in fluorescence spectrum; rate constant of fluorescence quenching of the same order as the diffusion constant		Cationic and free-radical		[99, 123]
8	^{1}*N*-Vinylcarbazole* + diethyl fomarate	"		Acetone, acetonitrile, dimethyformamide	Fluorescence quenching, band of exciplex in fluorescence spectrum		Free-radical and cationic	Ratio of polymerisation products varies in solvents of different basicity	[100]
9	*N*-Vinylcarbazole* + benzoyl peroxide	*N*-vinylcarbazole		Benzene, dichloromethane	Cation radicals of *N*-vinylcarbazole detected using pulsed methods in dichloromethane but not in benzene		Free-radical and cationic	Agreement between effect of basicity on formation of radical cations and ocurrence of corresponding polymerisation products	[101]
10	*N*-Vinylcarbazole* + chloranil	"					Free-radical	Inhibition with oxygen	[102]
11	^{1}Thiobenzophenone* + *N*-vinylcarbazole	"		Benzene, toluene, acetonitrile (in a current of argon)	Forms singlet exciplex		Cationic	Polymerisation occurs in the presence of thiobenzophenone, which is a free radical trap	[90, 103]
12	^{3}α-Methylstyrene* + tetracyanobenzene	α-Methylstyrene		Dichloroethane (no O_2)	Singlet and triplet exciplex formed. Photoconductivity recorded		"	Water and amines inhibit polymerisation	[18, 104, 105]
13	^{3}α-Methylsytrene* + pyromellitic dianhydride	"		"	Exciplex formed		"	"	[106]
14	Styrene* + maleic anhydride	Styrene		Acetonitrile	Radical cation of styrene observed in absorption spectra (pulsed excitation)		"	Addition of tertiary amines terminates polymerisation	[107]
15	Styrene* + acrylonitrile	Styrene and acrylonitrile (copolymer)		Dichloromethane			"	Addition of water and amines inhibits polymerisation	

Table 2 (continued).

No.	Initiating system	Monomer	Acceleration effect	Solvent	Evidence for ET or exciplex	Expression for initial rate of polymerisation	Polymerisation mechanism	Evidence for initiation mechanism	Refs.
1	2	3	4	5	6	7	8	9	10
16	Nitroethylene* + cyclohexene oxide	Nitroethylene	more than 10 times	Tetrahydrofuran	Band of weak charge-transfer complex in absorption spectrum		Cationic and anionic simultaneously	Traces of HCl inhibit polymerisation by 20%. Polynitroethylene (0.73) and polycyclohexene (0.27) identified by fractional analysis	[109]
17	Maleic anhydride* + tetrahydrofuran	methyl methacrylate	×2–4	Tetrahydrofuran	Photocurrent recorded		Anionic and free-radical	Polymerisation occurs in the presence of free-radical traps—1,1-diphenyl-2-picrylhydrazyl. It slightly lowers the rate of polymerisation	[110]
18	^{1}Benzyl-1,4-dihydronicotinamide* + monomer	Styrene, methyl methacrylate	×10	Dichloromethane, acetonitrile, methanol	Fluoroescence quenching of photoinitiator varies in the same way as the donor-acceptor properties of partners	$V \approx [P]^{0.5}$	Free-radical	Polarity of medium has virtually no effect on rate of polymerisation. Linear dependence of reverse polymerisation stage on inhibitor concentration	[111]
19	^{3}Benzophenone* + triethylenetetramine	Methyl methacrylate		Benzene, toluene, acetone, methanol (in a current of nitrogen)		$V \approx [P]^{0.5}[A]^{0.5}$	"	With an increase in ε of the medium the rate of polymerisation decreases, $k_p^2/k_t = 1.06 \times 10^{-2}$ litre mol^{-1} s^{-1}	[22]
20	^{3}Benzophenone* + tertiary amines	Methyl methacrylate		t-Butyl alcohol (no O_2)	Deactivation of triplet state of benzophenone with amine, formation of a radical ion pair	$V = k[M]^{1-1.5}[A]^{0.5}$	Free-radical	Higher rate of proton transfer $k_{PT} \geqslant 10^9$ s^{-1}	[24, 75, 114]
21	^{3}Benzophenone* + triethylamine (tributylamine, di-n-butylamine, n-butylamine)	Acrylonitrile	×11	Benzene dimethylformamide (in a current of nitrogen)	Deactivation of triplet states of benzophenone by amines with $k_q^T = 2.3 \times 10^9$ litre mol^{-1} s^{-1}	$V \approx [P]^{0.3-0.4}[M]^{1.3}$		Rate of polymerisation remains almost the same on going from benzene to dimethylformamide	[115]
22	^{3}Benzophenone* + aliphatic amines (primary, secondary, tertiary)	Methyl methacrylate	×10	Benzene, carbon tetrachloride, dimethylformamide	Triplet exciplex formed	$V \approx [P]^{0.38}[A]^{0.5}[M]^{1.5}$	Free-radical	Induction period occurs in the presence of O_2. Hydroquinone inhibits polymerisation. $k_p^2/k_t = 1.54 \times 10^{-3}$ litre mol^{-1} s^{-1}	[116, 117]
23	^{3}Fluorenone* + triethylamine (*N,N*-dimethylethanolamine)	"	×7–10	Benzene	Quenching of singlet and triplet states of fluoroenone by amines with $k_q^T \geqslant 10^{10}$ litre mol^{-1} s^{-1}		"	With an increase in ε of the medium the rate of polymerisation decreases. $k_p^2/k_t = 1-4 \times 10^{-3}$ litre mol^{-1} s^{-1}	[20]
24	^{1}Anthracene* (Phenanthrene, naphthalene, acetonaphthone)* + (di- and tri-ethylamine, aniline, *N*-methyl- and *N,N*-dimethylaniline	Methyl methacrylate, acrylonitrile	×15 to 16	Dimethylformamide (in a current of nitrogen)	Fluorescence quenching of photoactive components by amines with $k_q > 10^9$ litre mol^{-1} s^{-1}	$V \approx [P]^{0.5}[A]^{0.5}[M]^{1.0}$	Free-radical or ionic		[15]
25	Fluorenone* (acetophenone, Michler Ketone) + aliphatic amines	Acrylonitrile	×5–10	Dimethylformamide, benzene (in a current of nitrogen)	Quenching of triplet states of photoactive components by amines with $k_q \geqslant 10^9$ litre mol^{-1} s^{-1}	$V \approx [P]^{0.35}[M]^{2.20}$	"	Polymerisation does not occur in a nonpolar solvent	
26	^{3}Thioxanthone* + aliphatic amines	Methyl methacrylate		Benzene, acetonitrile	Quenching of triplet state of photoactive component by amines with $k_q^T \geqslant 10^9$ litre mol^{-1} s^{-1}. Polarity of medium did not affect k_q^T		Free-radical	Formation of free radicals—partners of initiating mixture—detected. Lack of dependence on polarity	[118]
27	^{3}Benzophenone salts* + triethylamine (triethanolamine, methylethanolamine)	Acrylamide	×3–15	Water (in a current of nitrogen)	Quenching of triplet states of photoinitiator by amines with $k_q^T \geqslant 10^9$ litre mol^{-1} s^{-1}	$V \approx I^{0.5}[P]^{0.5}[A]^{0.5}[M]^{1.5}$	Free-radical, but anionic not excluded	Ketyl radical of benzophenone occurs	[119]
28	Iron tetraphenyl porphin* + aliphatic amines + carbon tetrachloride	Methyl methacrylate	×5–10	Methanol (no O_2)			Free-radical		[120]

Table 2 (continued).

No.	Initiating system	Monomer	Acceleration effect	Solvent	Evidence for ET or exciplex	Expression for initial rate of polymerisation	Polymerisation mechanism	Evidence for initiation mechanism	Refs.
1	2	3	4	5	6	7	8	9	10
29	Dyes* (thiazine, xanthine, acridinone) + activator (amines, enolates, organometallic compounds, thiols)	Acrylamide, vinyl alcohol, cellulose acetate, vinyl chloride	more than 10 timees	(no O_2)	Quenching of triplet states of photoactive component by activator with $k_q \geqslant 10^9$ litre mol^{-1} s^{-1}. Correlation between k_q and value of ΔG_{ET}		"		[13]
30	^{3}Fluorenone* (benzanthrone, acridine, 9-phenylacridine)* + hetero aromatic thiols	Methyl methacrylate derivatives	more than 10 times	In thin layers	Quenching of triplet states of photoinitiators with activators by electron and energy transfer mechanism		Free-radical		[121]
31	^{3}Phenazine and its derivatives* + benzophenone and its derivatives	Butyl methacrylate	more than 200 times	Toluene, acetonitrile (no O_2)	Quenching of triplet stages of phenazine with benzophenone derivatives. Correlation between k_q^T and Hammett σ-constants of substituents in benzophenone molecule. Photocondutivity in acetonitrile	$V_{exp} = I^{0.5}[P]^{0.3-0.5} \times [A]^{1.0}[M]^{1.8}$ $V_{calc} = k[P]^{1.0}[A]^{1.0} \times [M]^{\geqslant 1.5}$	Ionic (involving radical ion pairs)	Rate of polymerisation increases sharply with ε of medium. In a nonpolar solvent polymerisation does not occur, $k_p/k_t \approx 3-3.8 \times 10^2$ litre mol^{-1} s^{-1}. Solvent-separated radical ions detected in acetonitrile	[26, 122]
32	^{1}Acridine* (^{1}phenazine, 1anthracene)* + N,N-dimethylaniline	"	× 15 to 30	Toluene, acetonitrile (no O_2)	Formation of singlet fluorescing exciplexes between partners. Photodissociation in acetonitrile (photoconductivity occurs)	$V = I^{0.5}[P]^{0.5}[A]^{0.5}[M]^{2.0}$	Ionic (involving radical ion pairs and ionic triads)	Rate of polymerisation increases sharply with ε of medium. Free radicals are absent. Solvent-separated radical ions and ternary complexes detected in acetonitrile	[123]
33	^{1}Perylene* + dicyanobenzene	N-Vinyl carbazole	× 6	Acetone, dimethyl sulphoxide (in the presence of O_2)	Fluorescence quenching of perylene by dicyanobenzene with $k_q > 10^9$ litre mol^{-1} s^{-1}. It increases as ε increases			Sharp increse in rate of polymerisation with ε of medium	[23]
34	^{3}Benzophenone (benzaldehyde)* with acceptor substituents + 4,4-bis-N,N-diethylaminobenzophenone	Methyl methacrylate		In a current of nitrogen	Quenching of triplet-excited states of photoinitiator with activator		Free-radical	Induction period in the presence of O_2	[124]
35	^{3}Benzophenone* + benzaldehyde + triethylamine	"	more than 10 times				"		[125]
36	^{3}Benzophenone* + tri-, di-, and monoethylenediamine + maleic acid		× 10		Quenching of triplet states of benzophenone with amines			Induction period occurs	[126]
37	^{3}Benzophenone* + diethanolamine + O_2	Hexane diol acrylate					"	"	[159,127]
38	^{3}Benzophenone* + 2-ethylhexyl p-(N,N-dimethylamino)benzoate + O_2	Epoxy acrylate	× 10 to 20	Films (in the presence of O_2)	Quenching of triplet states of benzophenone with amines		"		[128]
39	^{3}Benzophenone* + N,N-dialkylaminoethyl methacrylate	N,N-dialkylaminoethyl acrylate		Benzene (in the absence of O_2, in its presence, and in a current of argon)	Formation of excited charge-transfer complex		"	Induction period occurs. Free radicals detected	[129]
40	Benzoin isobutyl ether* + tetramethyl-p-phenylenediamine + O_2								[130]
41	^{3}(Xanthene, triazene, anthracene, phenanthrene)* + onium compounds	Cyclic ethers, epoxy compounds		In the presence of O_2, acetonitrile, water			Cationic mechanhism	No induction period	[162,163, 131,132]

act as donors of a hydrogen atom detached from a CH group at the α-position relative to the nitrogen atom. The α-aminoalkyl radical formed as a result of deprotonation is responsible for generating the polymerisation chain. The presence of nitrogen atoms in the polymer provides proof of this.[134]

It should be noted that there is a dependence of the rate of polymerisation on the size of the alkyl substituents in the aminoalkyl group that is similar to the dependence of the rate constant of proton transfer on the same parameters, as discussed in Section II.[83] Thus the rate of polymerisation V for system 25 is higher when triethanolamine is used as the activator than when tributylamine is used, while for system 24 it is higher when dimethylaniline is used compared to the use of diethylaniline and it varies in the same way as the rate constant of proton transfer.[15] The experiments conducted in parallel with two activators—triphenyl- and triethylamine in combination with benzophenone—showed that only in the second case, in which proton transfer occurs, does the polymerisation of methyl methacrylate occur (systems 20–22).[114] Meanwhile, electron transfer in both systems occurs at a rate that is higher than the diffusion rate. All of these facts suggest that proton transfer between the components of the initiating mixture plays a role in the generation of active radicals.

The same reaction of proton transfer with the formation of semi-reduced radical products forms the basis of the interaction of the photoactive components of a number of aromatic, heteroaromatic, and carbonyl compounds with proton-donating solvents.[135,136] However, the rate of polymerisation in this case is low, in contrast to systems in which the same photoinitiators are used in combination with amines.[15,135,137] As in fact the polymerisation mechanism (free-radical) does not change, why is there a preference for the latter?

In actual fact the rate of initiation of polymerisation with primary active products depends on the efficiency factor of the initiator β and the concentration of the primary radicals [R$^{\cdot}$]:[24,90]

$$V_i = \beta[R^{\cdot}]. \qquad (14)$$

The efficiency factor of the initiator β is governed by the proportion of radicals formed that participate in initiation of polymerisation. It is usually considerably less than unity, as a result of radicals participating in side reactions, and it is determined by the nature of both the initiator and the monomer. The concentration of primary radicals, [R$^{\cdot}$] depends on the rate constant for their formation, in these particular cases—on the rate constant of proton transfer k_{PT}. In the presence of photoinitiation mixtures in which proton transfer occurs rapidly, such as in benzophenone–triethylamine systems (18–19), $k_{PT} = 10^{12}$ s^{-1};[77] even with a comparatively low value of β for the α-aminoalkyl radical equal to $1-5 \times 10^{-3}$,[24] the polymerisation of methyl methacrylate is very active. On the other hand, when polymerisation is initiated by a deprotonated tetrahydrofuran radical, which has a value of $\beta = 5 \times 10^{-2}$,[24] because of the low value of $k_{PT} = 4.2 \times 10^6$ mol^{-1} s^{-1} its rate is considerably lower.[115] The very slow polymerisation initiated by the system aromatic hydrocarbon–propanol is apparently related to this.[15] It is known that in this system $k_{PT} = 6 \times 10^5$ mol^{-1} s^{-1}.[178] As has already been mentioned in Section II, an unfavourable geometry for proton transfer of the components in exciplexes of aromatic or heteroaromatic compounds with *N,N*-dimethylaniline (DMA) is responsible for the low value of k_{PT} in benzene. As a result, a low rate of polymerisation of butyl methacrylate is recorded in it (system 32), although in this system in a non-polar solvent the α-aminoalkyl radical of DMA should be present with almost the same efficiency as the α-aminoalkyl radical of triethylamine.[15]

Aminyl radicals which are formed as a result of deprotonation of primary and secondary amines are less effective than the α-aminoalkyl radical because of their increased tendency to undergo a disproportionation reaction.[103]

The least effective were protonated radicals of the photoactive components of the initiation system (ketyl radicals of benzophenone, semi-reduced radicals of phenazine, acridine, anthracene, etc.). Generation of a polymerisation chain in their presence occurs either at a very low rate or not at all (systems 20 and 32). On the contrary, in a number of cases they have an inhibitory effect by participating in chain termination reactions.[140] This accounts for the appearance of a descending curve on graphs of the rate of polymerisation against the concentration of photoinitiator.[15,94,115] Moreover, the semi-reduced radicals are consumed to form final products of the destructive bleaching of the photoabsorbent compound accompanying polymerisation.

The adoption of a free-radical photopolymerisation mechanism for the systems examined above is consistent with the ideas about the effect of the polarity of the medium on these processes (Table 2). In fact, in systems 19, 21, 23, 29, and 36 polymerisation occurs more rapidly in benzene than in any polar solvent. Careful analysis of the active products initiating polymerisation, their precursors—exciplexes or other intermediates of electron transfer—and the kinetics of electron and proton transfer also support the idea of a free-radical mechanism of polymerisation in these systems.

Unfortunately, a detailed study of the mechanism of polymerisation with identification of the intermediate stages of initiation has only been carried out for a narrow range of reactions (systems 19, 20, 23, 26). For the remaining systems given in Table 2, a free-radical mechanism of polymerisation has only been established from its similarity with the above systems. Meanwhile, such similarities are not always consistent. Thus, although for a number of systems such as 24, 25 and 27 a free-radical mechanism is maintained by the authors, the experimental evidence for such conclusions is insufficient. The study of polymerisation was conducted with the use of a polar solvent—dimethylformamide, acetonitrile, or water. The nature of the radicals generating the polymerisation chain was not verified. The authors did not take into account the fact that the photoactive components of the initiating systems studied by them—aromatic compounds (24) or carbonyl compounds (25, 27) with a $^3\pi^*$ lowest excited state—on reacting with amines have a greater tendency to undergo complete electron transfer reactions than to undergo secondary proton transfer reactions, especially in polar media[77,80] (see Section II). It cannot be excluded that it is this fact which accounts for the acceleration by a factor of 3–5 of the polymerisation of acrylonitrile in systems 24 and 25 on going from benzene to acrylonitrile. In adhering to their view of a free-radical mechanism, Kubota and Ogiwara[15] cannot account for the effect of the polarity of the medium on the rate of polymerisation.

There is no doubt that many factors such as the nature of the photoinitiator (the type of electronic transition responsible for excitation, its multiplicity), the activator, and monomer can affect the mechanism of initiation of polymerisation. It is therefore interesting to consider the behaviour of two photoinitiators from the class of aromatic ketones—benzophenone and fluorenone. They differ according to the electronic nature of the lowest excited states. In benzophenone the $^1S^*$ and $^1T^*$ states have an $n\pi^*$ electronic configuration.[141] The majority of reactions, including electron and proton transfer, occur in the $^1T^*$ state. The polarity of the medium does not affect the quantum yields of formation of triplet states,

formation of ketyl radicals, or the quantum yield of the overall reduction process.[141,142] In contrast to benzophenone, the $^1S^*$ and $^1T^*$ states of fluorenone have a $\pi\pi^*$ electronic configuration.[143] However, in view of the proximity of the $^2S^*_{\pi\pi^*}$ and $^1S^*_{\pi\pi^*}$ state and also the $^2T^*_{\pi\pi^*}$ and $^1T^*_{\pi\pi^*}$ states, the contribution of the $n\pi^*$ electronic configuration to the lowest $^1S^*$ and $^1T^*$ states is quite evident. Therefore the polarity of the medium has a substantial effect on the kinetics of the photophysical processes. With an increase in ε the quantum yield and duration of fluorescence increase by a factor of almost 10^2 and the quantum yield of intersystem crossing is halved.[144] The quantum yields of formation of ketyl radicals and the overall reduction reaction decrease by the same order of magnitude.[145]

The lowest triplet state of benzophenone participates in electron and proton transfer from amines. The latter reaction, as has aleady been mentioned, occurs with a high rate constant ($k_{PT} \approx 10^9$ s^{-1}).[19,77] The resulting free radicals generate the polymerisation chain. The polarity of the medium has virtually no effect on the rate of polymerisation[15,22,24] (systems 19–21, 26 in Table 2).

Fluorenone behaves in a similar manner in the initiation of the polymerisation of MMA (system 23).[113] The maximum rate V of photopolymerisation has been recorded in benzene. In acetonitrile V decreases by a factor of almost 5,[114] which is an argument in favour of a free-radical mechanism of polymerisation. However, an alternative explanation for this phenomenon is also possible. With an increase in ε the quantum yield of intersystem crossing decreases and the quantum yield of formation of ketyl radicals of fluorenone and deprotonated amine radicals correspondingly decreases.[144]

Fluorenone behaves quite differently in the polymerisation of acrylonitrile (system 25). The rate of polymerisation of this monomer, initiated with system 25, increases by a factor of 4 on going from benzene to acetonitrile, although the yield of radical products in this case is halved,[144] as in the example considered above. It is known, however, that with an increase in ε the lifetime of the $^1S^*$ state increases. It is sufficiently long for fluorenone in the $^1S^*$ state to interact with amines by a charge-transfer mechanism.[146] The rate constants of quenching of the $^1S^*$ state of fluorenone with triethylamine in benzene and acetonitrile are equal to 1×10^9 and 7×10^9 litre mol^{-1} s^{-1} respectively, whereas the rate constants of deactivation of the $^1T^*$ state with the same amine is two orders lower ($1.7-2.3 \times 10^7$) litre mol^{-1} s^{-1}.[145] Apparently at concentrations of amine greater than 10^{-2} mol $litre^{-1}$, which is commonly used in polymerisation, the excited fluorenone molecules mainly in the $^1S^*$ state interact with amines. Since with an increase in ε the probability of proton transfer decreases sharply in the system fluorenone–amine because of electron transfer competing with it,[145] the quantum yield of formation of free radicals must decrease. It can be expected that in system 25, where $\varepsilon \approx 20$, the photoinitiating mixture will exist as radical ion pairs as a result of light absorption. It is possible that acrylonitrile, being a stronger electron acceptor than MMA, can interact with such an ion pair to form a "loose" ternary complex. This will generate the polymerisation chain. Such a possibility has also not been excluded for MMA.[10] Similar views about the initiation of polymerisation of acrylontrile by means of radical ions have also been expressed.[113]

3. Photoinitiation of polymerisation with the final products of electron phototransfer

In this section we shall examine the polymerisation processes that are initiated by the products of complete electron transfer in redox systems of radical ions. This applies to polymerisation initiated by EPT.[147,148] It has a specific nature which at the present time is still far from understood.

The possibility of initiation of polymerisation by radical ion species is influenced by a considerable effect from the polarity of the medium, its acidity or basicity. Thus, polymerisation initiated with radical anions occurs preferentially in more basic solvents while that initiated with radical cations is preferred in more acidic solvents.[91,149]

No less important a factor is the stability of solvent-separated radical ions. Depending on this, either the rapid combination of radical ions or the formation of a neutral radical producing a polymerisation chain by a free-radical mechanism is possible.

a) Photoinitiation systems of monomer–activator

Table 2 lists a number of binary systems (1–18), one component of which is the monomer. In the majority of cases the latter functions as the photoactive partner of the mixture. *N*-Vinylcarbazole (VC) and α-methylstyrene, which participate in cationic polymerisation, are good electron donors. Their ionisation potentials are equal to 7.42 and 8.35 eV respectively.[114] Systems with styrene,[110] *p*-methoxystyrene,[152] and phenyl vinyl ether[153] which as a result of electron phototransfer form radical cations that cause cyclodimerisation have not been included in Table 2. The latter may be regarded as a chain reaction that differs from polymerisation in the length of the chain.

Cyclohexene oxide is a weaker electron donor. As a result of interacting with strong electron acceptors it forms a radical cation and causes polymerisation by a cationic mechanism. Interestingly, in the presence of nitroethylene (system 16) polymerisation occurs simultaneously by cationic and anionic mechanisms.[109] Weak electron acceptors such as maleic anhydride and methyl methacrylate in the ternary system tetrahydrofuran–maleic anhydride–monomer (system 17) cause polymerisation by an anionic mechanism.

Indirect evidence for the ionic polymerisation route and the presence in these systems of the respective radicals ions is given in Table 2. Direct evidence has only been obtained for two monomers—α-methylstyrene (systems 7 and 8) and VC (systems 5–7, 12, 13). Singlet and triplet exciplexes of α-methylstyrene with tetracyanobenzene and pyromellitic dianhydride have been detected using pulsed spectroscopic methods.[104, 105] In methylene dichloride and n-amyl alcohol these exciplexes dissociate to radical ions that have been recorded using pulsed photoconductivity. However, the rate of recombination of the radical ions which are formed from singlet-excited molecules is so high that they can only be reliably observed at low temperatures (below −40 °C).[121] The lifetime of ion radicals formed in a triplet route is considerably longer (of the order of tens of microseconds). This time is sufficient for the resulting cation radicals to undergo a chain propagation reaction. The sequence of reactions of a monomeric radical cation of α-methylstyrene to dimeric and trimeric forms, etc. has been observed from the respective absorption spectra. Introduction of air caused an almost complete cessation of the photocurrent and termination of polymerisation. Since the generation of cation radicals of α-methylstyrene capable of initiating a polymerisation chain has been carried out using a triplet route, these systems are unfortunately also sensitive to oxygen, like the photoinitiating components for free-radical polymerisation.

VC behaves differently. On excitation with light at $\lambda \geqslant 350$ nm it forms fluorescing exciplexes with dimethyl terephthalate, diethyl fumarate (system 8),[9] and with thiobenzophenone (system 11) (in the latter case, however, the thiobenzophenone molecule is excited).[90,103]

The rate constant of formation of exciplexes is of the same order as the diffusion constant. Radical cations of VC that are formed by photodissociation of singlet exciplexes have been recorded by pulsed methods.[154] They are involved in the generation of a polymerisation chain in systems 6–11. Arguments in favour of a cationic mechanism of polymerisation are provided by the results when it is carried out in nitrobenzene, which serves as a free radical "trap" (see Table 1) and by its inertness towards oxygen. Furthermore, it was established that in a number of cases oxygen assists the cationic polymerisation of VC. It can act as a co-initiator, interacting with VC to form a stable radical anion, being a counterion for the radical cation of monomer. Moreover, it promotes chain transfer during cationic polymerisation.[91,155]

The ability of VC in the presence of electron acceptors to initiate polymerisation by a cationic mechanism was discovered in the 1970s.[99,102] Before then it was assumed that it could only cause polymerisation by a free-radical mechanism. However, polymerisation, as a rule, was carried out in solvents with a high basicity (acetone, tetrahydrofuran, dimethylformamide). The generation of free radicals in this case was achieved from a triplet-excited state of VC. By changing to solvents with a higher acidity it was possible to alter the mechanism of polymerisation when mixtures of VC and acceptor-type activators were used. It appeared that the charge-transfer complexes and exciplexes formed by these mixtures could generate charged primary active products. At the same time the efficiency of initiation of cationic polymerisation with exciplexes is higher than with charge-transfer complexes.[104] The reason for this is not clear. One of the explanations put forward by the authors is the more favourable geometry for electron transfer in an exciplex than in a charge-transfer complex.

b) Initiation systems of photoinitiator – activator

The advantage of these over the systems examined above is obvious. Firstly, with a wide series of photoinititors and activators being available, it is possible to select those systems which achieve a high probability of free electron transfer and the formation of active products. Secondly, by using suitable photosensitive compounds it is possible to extend the spectroscopic sensitivity and increase the total sensitivity of the polymerising system. Unfortunately, the mechanism of the action of most photoinitiating systems of initiator–activator is so far unclear. However, as was mentioned above, it is highly probable that these systems (24 and 25) can generate radical ions that are capable of initiating and producing a polymerisation chain.

More definite information indicating a change in mechanism of initiation from free-radical to radical-ion has been obtained for the binary systems 31 and 32. The photoactive components in these are heteroaromatic (phenazine, acridine, and their derivatives) or aromatic (anthracene and its derivatives) compounds. Depending on their partner they act as an electron donor (system 31) or electron acceptor (system 32). Redox systems that include them initiate the polymerisation of butyl methacrylate. The latter can participate in chain propagation by both a free-radical and an anionic mechanism.[90] However, in benzene photopolymerisation occurs at an extremely slow rate. When acetonitrile is added the rate of polymerisation increases by a factor of 10^1-10^3. The dependence of $\lg V$ on the Kirkwood polarity function is linear and has a positive gradient.[122,123] With an increase in ε, semi-reduced radicals of heteroaromatic or aromatic compounds were not detected in any of these systems, nor were ketyl radicals of benzophenone, which would suggest proton transfer. On the other hand in acetonitrile a photocurrent developed, that was induced by excitation of photoactive mixtures with a pulsed laser. It originates from the solvent-separated radical ions formed as a result of complete electron transfer between the partners of the mixture.

Interestingly, in system 31 the signal due to the photocurrent disappeared after the introduction of atmospheric oxygen while in system 32 it persisted under these conditions.

There are other arguments that suggest the electron donor-acceptor nature of the interactions in these mixtures. Thus for system 31 there was a correlation between the rate constant for deactivation of triplet-excited molecules of phenazine derivatives and the Hammett σ-constants of substituents in the benzophenone molecule acting as an electron acceptor. The reaction constant $\rho = 1.1$ (Fig. 1*a*). It is significant that a value of $\rho = 1.0$ (Fig. 1*b*), which is similar to it, was obtained for the correlation between the rate of polymerisation V and the same parameters.[122] This is one of the most serious arguments in favour of the electron donor-acceptor interactions of triplet-excited phenazine molecules with electron acceptors playing a decisive role in the overall photopolymerisation process.

It was established for system 32 that the partners of photoinitiating mixtures form singlet fluorescing exciplexes with a considerable degree of charge transfer.[156,157] It is these which take part in the subsequent chemical reactions that are responsible for the generation of primary active products. As well as binary exciplexes, ternary singlet photoinitiator–activator–monomer exciplexes were detected, having a characteristic fluorescence band that is shifted towards the "red" end of the spectrum relative to the fluorescence of the binary exciplex (Fig. 2). Since charge-transfer interactions also make a considerable contribution to the stabilisation energy of a ternary exciplex, it may be assumed that with an increase in polarity of the medium it will be converted to a "loose" ionic triad occurring in a solvent cage.[160]

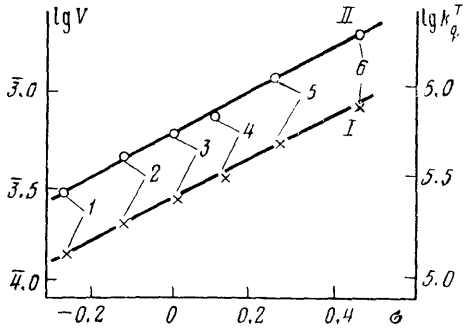


Figure 1. Dependence of the rate constant of deactivation of triplet states of 2-dimethylaminophenazine (line *I*) and the rate of polymerisation initiated with 2-dimethylaminophenazine in the presence of benzophenone (line *II*) on Hammett σ-constants of substituents in the acceptor molecule: *1*) 4-OCH_3; *2*) 4-CH_3; *3*) 4-H; *4*) 4-C_6H_5; *5*) 4-Cl; *6*) 4,4′-$(Cl)_2$.

From what has been stated it may be concluded that in systems 31 and 32 the primary active products in polar media are radical ion pairs, solvent-separated radical ions, and also "loose" ionic triads rather than neutral radicals which are mainly formed in a non-polar medium. They initiate polymerisation, which was taken into account in a kinetic scheme of initiation with systems 31 and 32. A whole

series of relationships confirming the experimental results follows from the expression for V obtained on the basis of this scheme. These are primarily the agreement between the values of the exponents in the equation for V (see Table 2) and the series of rate constants of the fundamental stages that are determined from this expression and by using independent experimental methods.[122] Consideration should be given to the value of the ratio k_p/k_t determined from this expression. It is equal $(3.1-3.8) \times 10^2$, which corresponds to values that are typical for the anionic polymerisation of vinyl monomers, in which generation of the chain involves radical ion pairs (see Table 1).[162] An argument in favour of the involvement of radical ion pairs rather than solvent-separated radical ions in initiation is the low reaction constant $\rho = 0.18$ for the correlation dependence of $\lg(k_p/k_t)$ on the Hammett σ-constants of substituents in the benzophenone molecule (system 31). In fact, by conducting the polymerisation in acetonitrile it is not possible to achieve a value of $\varepsilon > 20$. With such a value of ε it is doubtful whether the ionic "triads" can be converted to solvent-separated radical ions (we should note that the values of k_q are equal to 10^7-10^8 litre mol^{-1} s^{-1} for the quenching of fluorescence from the binary exciplexes with a monomer in this case).

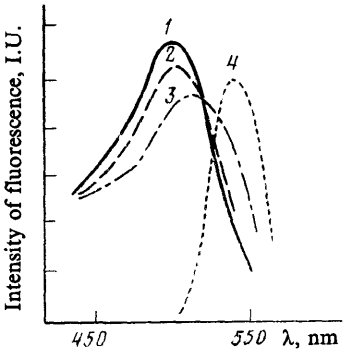


Figure 2. Effect of addition of butyl methacrylate (BMA) on the fluorescence intensity of the exciplex of anthracene with *N,N*-dimethylaniline. *1*) $C_{BMA} = 0$; *2*) $C_{BMA} = 1$ mol litre^{-1}; *3*) $C_{BMA} = 2.5$ mol litre^{-1}; *4*) differential fluorescence spectrum of ternary complex on a scale of 1:4.

From the expression obtained for V (Table 2) it is possible to account for the effect of the electronic structure of the photoactive components of system 32 on the rate of polymerisation. It results from the different thermodynamic and kinetic conditions of electron transfer between the components of the photoactive mixtures of system 32.[123]

The latter system is also of intereest in that for the first time the formation of a ternary excited complex involving a monomer has been detected in it. The possibility that it is formed followed logically from the results of more recent studies, including also those for system 31.[10,26,113] The advantage of agglomerates of this type is that polymerisation initiated and carried out with their participation is less sensitive to the effect of inhibitors.[89,147] Moreover, systems 31 and 32 demonstrate the real possibility of a change in the multiplicity of the excited state of the photoactive component participating in photoinitiation through a suitable choice of partners. This in turn suggests the possible ways of conducting polymerisation in the presence of oxygen during photogeneration of the primary active products in a singlet route and generation of the polymerisation chain by a cationic mechanism.

These conditions are met when photoinitiation system 33 is used, which is involved in polymerisation that occurs in the presence of oxygen. Perylene, which absorbs light with $\lambda \geqslant 436$ nm, serves as the photoactive component in it, dicyanobenzene is the activator, and VC is the monomer. As a result of light absorption the singlet-excited molecules of perylene donate an electron to dicyanobenzene. The rate constant of fluorescence quenching of perylene, which results from this process, is of the same order as the diffusion constant.[23] The resulting radical cation of perylene initiates polymerisation of vinylcarbazole through electron transfer from the latter. Photopolymerisation in acetonitrile in this case takes place under mild conditions—at room temperature in air. In strongly polar solvents with well-defined basic properties (dimethylformamide, dimethyl sulphoxide) it does not take place. A sixfold increase in the rate of photopoymerisation initiated with the binary mixture perylene–dicyanobenzene relative to initiation with perylene is recorded. It is likely that in the system perylene–activator–monomer an effective separation of charges is achieved, producing a marked acceleration of polymerisation.

IV. Conclusion

Thus photoinitiation systems whose action is based on electron phototransfer that occurs in an exciplex or another of its intermediates are highly effective. Neutral protonated and deprotonated radicals, radical ion pairs or solvent-separated radical ions can initiate polymerisation. In the first case the polymerisation chain is generated by a free radical mechanism while in the second case an ionic mechanism occurs. With all of the systems it is possible to carry out polymerisation by exposure to low-energy light quanta.

Radical polymerisation. The advantage of these initiating systems lies in the fact that by forming exciplexes or other electon transfer intermediates they create favourable conditions for the subsequent transfer of a proton between the partners. With a suitable choice of the components of photonitiating mixtures, based on an analysis of their thermodynamic and kinetic properties, it is possible to optimise their composition. Thus, for example, if tertiary aromatic amines that generate α-aminoalkyl radicals are used as activators, the latter can both initiate polymerisation and retard the inhibitory action of oxygen by reacting with it (see systems 37 and 38 in Table 2). In a number of cases systems that form a ternary complex with oxygen are used. The oxygen in them acts as an intermediate agent in electron transfer. Here, as in the previous case, peroxide radicals are formed, which also take part in the generation of the polymerisation chain (system 40).[130] The use of a monomer containing an amino group as the activator has future potential. The undesirable effect of oxygen can be inhibited in this way (system 40).[129]

Polymerisation initiated by electron phototransfer. In this case the choice of partners of the initiating mixture must guarantee a high probability of complete electron transfer followed by charge separation. An important condition for this to be fulfilled is $k_{ET} \gg k_{PT}$. It is necessary to bear in mind, however, that if anionic polymerisation occurs, whatever the multiplicity of the excited state of the photoinitiator it is not possible to exclude the inhibitory effect of oxygen.

If polymerisation occurs by a cationic mechanism and the photoinitiator "operates" in a singlet-excited state, oxygen does not

as a rule suppress it. The rate of polymerisation will depend to a large extent on the polarity of the medium and its acid-base properties. The latter influence the effectiveness of anionic polymerisation to the same extent.

Special requirements should be imposed on the choice of photoinitiator dictated by the mechanism of polymerisation. In this case it is mainly necessary to take into account the electronic configuration of the lowest excited states that take part in reaction and their multiplicity. Thus, if the formation of active primary radicals is based on secondary proton transfer reactions, the use of photoinitiators that have a considerable contribution of the $n\pi^*$ electronic configuration to the lowest excited state is preferred. This assists rapid proton transfer. When the secondary reaction is complete electron transfer with a passage of radical ions into the surroundings, systems with a significant or complete contribution of the $\pi\pi^*$ electronic configuration to the lowest excited state are more advantageous.

Finally, in order to improve the efficiency of initiation of polymerisation with radical ions it is necessary to ensure a more complete separation of charges. This can be achieved as a result of the formation of ternary initiating systems of photoinitiation–activator–monomer. In these one of the components acts as an electron transfer agent (mediator) between the second partner and the monomer (systems 31, 32, 35, 36). The second method involves the use of photoinitiators that have quaternary ammonium salts as a secondary substituent[164] or the use of activators connected to the π-electron skeleton of the molecule by a methine bridge.[165] Finally, very effective systems in which onium compounds are used as the partners of the photoinitiator (system 41) [131,132] have recently been developed.

References

1. D Phillips *J. Oil Chem. Assoc.*, 1976, **59** 202
2. R E Jacobson *J. Photogr. Sci.*, 1983, **31** 1
3. H J Hageman *Prog. Org. Coat.*, 1985, **13** 123
4. A V Vannikov, A D Grishina *Usp. Khim.*, 1989, **58**(12) 2056 [English translation in *Russ. Chem. Rev.*, 1989(12)]
5. A N Terenin *Fotonika Molekul Krasitelei i Rodstvennykh Organicheskikh Soedinenii* (The Photonics of Dye Molecules and Related Organic Compounds), Izd. Nauka, Leningrad, 1976, 616 pp
6. J Capek, J Barton *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13** 2691
7. C L Osborn *J. Radiat. Cur.*, 1976, **3** 2
8. C P Haz, J Eichler *Farbe Lack.*, 1979, **85** 37
9. Zh B Bednar, A V El'tsov, Ya Zakhoval, et al. *Svetochuvstvitel'nye Polimernye Materialy* (Light-sensitive Polymer Materials), Izd. Khimiya, Leningrad, 1985, p. 297
10. A Ledwith *J. Oil. Chem. Assoc.*, 1976, **59** 157
11. V S Anderson, R G W Horrish *Proc. R. Soc. London, A*, 1959, **251** 1
12. A Ledwith, G Ndaalio, A R Tailor *Macromolecules*, 1975, **8** 1
13. D F Eaton *Adv. Photochem.*, 1986, **13** 427
14. K Kameska, M Asai, I Takeda, S Tazuke *J. Polym. Sci., Polym. Lett.*, 1971, **9** 247
15. H Kubota, J Ogiwara *J. Appl. Polym. Sci.*, 1983, **28** 2425
16. M R Sander, C L Osborn, D J Trecker *J. Polym. Sci., Polym. Chem. Ed.*, 1972, **10** 3173
17. A Ohno, H Kito, N Kawase *J. Polymer Sci., Polym. Lett.*, 1972, **10** 133
18. V Iria, S Tomimoto, K Hayashi *J. Polym. Sci., Polym. Chem. Ed.*, 1970, **8** 585
19. C G Shaefer, R S Peters *J. Am. Chem. Soc.*, 1980, **102** 7566
20. A Ledwith, A Bosley, M D Parbrick *J. Radiat. Cur.*, 1979, **6** 2
21. D J T Hill, J J O'Donnell, O Sullivan *Progr. Polym. Sci.*, 1982, **8** 215
22. P Ghosh, A R Bandyopadhyaya *Eur. Polym. J.*, 1984, **20** 1117
23. N Kitamura, S Tazuke *Bull. Chem. Soc. Jpn.*, 1980, **53** 2594
24. A Merlin, D-J Lougnot, J-P Fouassier *Polym. Bull.*, 1980, **3** 1
25. USSR P. 741 227; *Byull. Izobret.*, 1980, (22)
26. T I Viktorova, V M Granchak, M N Usacheva, I I Dilung *Vysokomol. Soedin., Ser. A*, 1983, **25** 1025
27. R G Jones, N Khalid *Eur. Polym. J.*, 1982, **18** 285
28. Li B Gluseppe *J. Radiat. Cur.*, 1987, **14** 18
29. P Ghosh, R Ghosh *Eur. Polym. J.*, 1981, **17** 545
30. B Stevens *Adv. Photochem.*, 1971, **8** 161
31. T Forster *The Exciplex*, Academic Press, New York, 1975, p. 7
32. M G Kuz'min *Zh. Vses. Obshch. im D I Mendeleeva*, 1974, **19** 362
33. C Lewis, W R Ware *Mol. Photochem.*, 1973, **5** 261
34. S L Matter, S Farid *Science*, 1984, **226** 917
35. G J Kavarnos, N Turro *Chem. Rev.*, 1986, **86** 401
36. H Beens, H Knibbe, A Weller *J. Chem. Phys.*, 1967, **47** 1183
37. A Weller *Pure Appl. Chem.*, 1982, **54** 1855
38. A K Chibisov *Usp. Khim.*, 1981, **50**(7) 1169 [English translation in *Russ. Chem. Rev.*, 1981(7)]
39. P P Levin, V A Kuz'min *Usp. Khim.*, 1987, **56**(3) 527 [English translation in *Russ. Chem. Rev.*, 1987(3)]
40. E I Kapinus, I I Dilung *Usp. Khim.*, 1988, **57**(7) 1087 [English translation in *Russ. Chem. Rev.*, 1988(7)]
41. N Mataga, N Nakashima *Spectrosc. Lett.*, 1975, **8** 275
42. H Beens, A Weller *Organic Molecular Photophysics*, Wiley, London, 1975, Vol. 2, p. 159
43. H Masuhara, Y Maeda, H Nakajo, et al. *J. Am. Chem. Soc.*, 1981, **103** 643
44. M G Kuz'min, N A Sadovskii *Khim. Vys. Energ.*, 1975, **9** 291
45. T J Chuang, K B Eisenthal *J. Chem. Phys.*, 1973, **59** 2140
46. T Okeda, M Migita, H Magata, et al. *J. Am. Chem. Soc.*, 1981, **103** 4715
47. R A Marcus *J. Chem. Phys.*, 1956, **24** 966
48. R A Marcus *J. Chem. Phys.*, 1957, **26** 867
49. R A Marcus *Faraday Discuss. Chem. Soc.*, 1960, **29** 22
50. R A Marcus *J. Chem. Phys.*, 1965, **43** 2654
51. D Rehm, A Weller *Z. Phys. Chem. (N.F.)*, 1970, **69** 183
52. N Mataga *Molecular Interactions* (Translated into Russian), Izd. Mir, Moscow, 1984, p. 598
53. M G Kuz'min, N A Sadowski, I V Soboleva *J. Photochem.*, 1983, **23** 27
54. N Mataga, G Murata *J. Am. Chem. Soc.*, 1969, **91** 3144
55. N Nakashima, N Mataga *Z. Phys. Chem. (N.F.)*, 1972, **79** 150
56. M N Usacheva, V V Osipov, I V Drozdenko, I I Dilung *Dokl. Akad. Nauk SSSR*, 1985, **283** 168
57. N A Lysak, S V Mel'nichuk, S A Tikhomirov, G B Tolstorozhev *Zh. Prikl. Spektrosk.*, 1987, **47** 267
58. H Masuhara, T Saito, Y Maeda, N Mataga *J. Mol. Struct.*, 1978, **47** 243
59. T Okada, I Karaki, E Matzuzawa, et al. *J. Phys. Chem.*, 1981, **85** 3957

60. Y Hatano, N Yamamoto, Y Nishijima *Chem. Phys. Lett.*, 1981, **77** 299
61. D Webster, J H Baegher, B T Lim, E C Lim *Chem. Phys. Lett.*, 1981, **77** 294
62. T Nishimura, N Nakashima, N Mataga *Chem. Phys. Lett.*, 1977, **46** 334
63. D Rehm, A Weller *Ber. Bunsenges. Phys. Chem.*, 1969, **73** 834
64. E Vogelmann, W Roluscher, R Traber, H E A Kramer *Z. Phys. Chem. (Munich)*, 1981, **124** 13
65. P G Gassman, K D Olson, L Walter, R Yamaguchi *J. Am. Chem. Soc.*, 1981, **103** 4977
66. R A Marcus, P Siders *J. Phys. Chem.*, 1982, **86** 622
67. A Weller, K Zachariasse *Chem. Phys. Lett.*, 1971, **10** 590
68. H Masuhara, N Mataga *Acc. Chem. Res.*, 1984, **14** 312
69. H Masuhara, T Hino, N Mataga *J. Phys. Chem.*, 1975, **79** 994
70. T Kakitani, N Mataga *J. Phys. Chem.*, 1985, **89** 4752
71. T Kakitani, N Mataga *J. Phys. Chem.*, 1985, **89** 1
72. N Mataga *J. Mol. Struct. Theochem.*, 1986, **136** 279
73. J J Jortner *Chem. Phys.*, 1976, **64** 4860
74. H Kobashi, M Funabashi, T Kondo, et al. *Bull. Chem. Soc. Jpn.*, 1984, **57** 3557
75. N A Borisevich, N A Lysak, S V Mel'nichuk, et al. *Dokl. Akad. Nauk SSSR*, 1987, **295** 900
76. F D Lewis, P J De Voe *Tetrahedron*, 1982, **38** 1069
77. J D Simons, K S Peters *J. Am. Chem. Soc.*, 1981, **103** 6403
78. F D Lewis *Acc. Chem. Res.*, 1986, **19** 401
79. R A Marcus *J. Phys. Chem.*, 1968, **72** 891
80. M W Wolf, R E Brown, L A Singer *J. Am. Chem. Soc.*, 1977, **99** 526
81. N C Yang, D B Shold, B Kim *J. Am. Chem. Soc.*, 1976, **98** 6587
82. G D Griller, F P Lossing *J. Am. Chem. Soc.*, 1981, **103** 748
83. F D Lewis T-Y Ho *J. Am. Chem. Soc.*, 1980, **102** 1751
84. T Okada, J Karaki, N Mataga *J. Am. Chem. Soc.*, 1982, **104** 7191
85. W Hub, S Schneider, F Dörr, et al. *J. Am. Chem. Soc.*, 1984, **106** 708
86. F D Lewis, P E Correa *J. Am. Chem. Soc.*, 1984, **106** 194
87. A Warshel, R Weiss *J. Am. Chem. Soc.*, 1980, **102** 6218
88. S Arimitsu, H Masuhara, N Mataga, H Tsubomura *J. Phys. Chem.*, 1975, **79** 1255
89. E G Rozantsev, M D Gol'dfein, A V Trubnikov *Usp. Khim.*, 1986, **55**(11) 1881
90. J Audian *Basic Principles of the Chemistry of Polymers* (Translated into Russian), 1986, **55** 1881
91. Y Shirota, H Mikawa *J. Makromol. Sci., Chem.*, 1978, **16** 129
92. R G W Norrish, J P Simons *Proc. R. Soc. London, A*, 1959, **251** 4
93. J Barton, J Capek, P Hhdbolic *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13** 2671
94. J Capek, J Barton *J. Polym. Sci., Polym. Lett.*, 1974, **12** 305
95. I V Drozdenko, I A Dolidze, M N Usacheva, I I Dilung *Vysokomol. Soedin., Ser. A*, 1984, **26** 694
96. H Masuhara, G Tohgo, N Mataga *Chem. Lett.*, 1975, 59
97. M Asai, K Kameoka, Y Takeda, S Tazuke *J. Polym. Sci., Polym. Lett.*, 1971, **9** 247
98. O F Olaj, J W Breitenbach, H F Kaufman *J. Polym. Sci., Polym. Chem. Ed.*, 1971, **9** 877
99. K Tada, Y Shirota, H Mikawa *J. Polym. Sci., Polym. Lett.*, 1972, **10** 691
100. Y Shirota, A Matsumoto, H Mikawa *Polym. J.*, 1972, **3** 643
101. M L Kusai, Al-Abidin, R G Jones *J. Chem. Soc., Faraday Trans. 1*, 1982, **78** 513
102. Y Shirota, K Kawai, N Yamamoto, et al. *Chem. Lett.*, 1972, 145
103. G Tsuchihashi, M Yamauchi, A Ohno *Bull. Chem. Soc. Jpn.*, 1970, **43** 968
104. M Irie, S Tomimoto, K Hayashi *J. Phys. Chem.*, 1972, **72** 1419
105. M Irie, S H Masuhara, K Hayashi, N Mataga *J. Phys. Chem.*, 1974, **72** 341
106. M Irie, S Tomimoto, K Hayashi *J. Polym. Sci., Polym. Chem. Ed.*, 1972, **10** 3243
107. M Rätzsch, G Schient *Acta Polym.*, 1982, **33** 441
108. J Gaylord, N G Dixid *J. Polym. Sci., Polym. Lett.*, 1971, **9** 359
109. M Irie, S Tomimoto, K Hayashi *J. Polym. Sci., Polym. Chem.*, 1973, **11** 1859
110. J Becker, M Lasar *J. Polym. Sci. A1*, 1968, **6** 3109
111. K Tabuchi, N Sakota *Polym. J.*, 1985, **17** 537
112. G M Brauer, H Argentar *Initiation of Polymerisation. 83rd ACS Nat. Meet. Las Vegas, 1982*, Washington, D.C., 1983, p. 359
113. J Hatchinson, A Ledwith *Adv. Polym. Sci.*, 1974, **14** 49
114. A Ledwith *The Exciplex*, Academic Press, New York, 1975, p. 209
115. K Hubota, U Oguwara *J. Appl. Polym. Sci.*, 1982, **27** 2683
116. P K Sengupta, S K Modak *J. Macromol. Sci.*, 1983, **A20** 789
117. P K Sengupta, S K Modak *Makromol. Chem.*, 1985, **186** 1593
118. S F Gates, C B Schuster *J. Org. Chem.*, 1984, **49** 3349
119. H-J Timpe, K P Kronfield, U Müller *J. Photochem.*, 1987, **36** 347
120. T Okimoto, M Takahashi, J Phaki, K Takemoto *J. Polym. Sci., Polym. Lett.*, 1974, **12** 121
121. A Umebara, S Kondo, K Tamoto, A Matsufuji *J. Chem. Soc. Jpn. Chem. Ind. Chem.*, 1984, 192
122. M N Usacheva, T I Viktorova, V M Granchak, I I Dilung *Teor. Eksp. Khim.*, 1987, **24** 433
123. I V Drozdenko, Abstract of Candidate's Thesis in Chemical Sciences, Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, 1986
124. V D McGuiness, T Provder, G Kuo, A Gallopo *Macromolecules*, 1978, **11** 405
125. E Wang, M Li, Z Chang, H Feng *Kexue Tongbau*, 1984, **29** 201
126. R Premamoy, D Kummar, B A Ratan *J. Makromol. Sci.*, 1983, A20 549
127. C R Morgan, D R Kyle *J. Radiat. Cur.*, 1983, **10** 4
128. J E Christensen, W L Wooten, P J Whitman *J. Radiat. Cur.*, 1987, **14** 35
129. G-J Jiang, Y Shirota, H Mikawa *Polym. Photochem.*, 1986, **7** 311
130. E S Klimov, F Kim, K A Trufanova, et al. *Vysokomol. Soedin., Ser. B*, 1986, **28** 119
131. H-J Timpe, H Baumann, Z Wiss *Hochn. Hochsch. Leuna-Merseburg*, 1984, **26** 439
132. P Pappas *New Trends in Photochemistry. Polymers*, 1985, 99
133. Kh S Bagdasaryan *Teoriya Radikal'noi Polimerizatsii* (Theory of Radical Polymerisation), Izd. Nauka, Moscow, 1966, p. 300
134. M R Sander, C L Osborn, D J Trecker *J. Polym. Sci., Polym. Chem. Ed.*, 1972, **10** 3173
135. M N Usacheva, I V Drozdenko, I A Dolidze, I I Dilung *Teor. Eksp. Khim.*, 1983, **19** 572

136. V M Granchak, V P Sherstyuk, I I Dilung *Teor. Eksp. Khim.*, 1977, **14** 257
137. M N Usacheva, I V Drozdenko, I I Dilung *Teor. Eksp. Khim.*, 1989, **26** 40
138. H Levanon, P Neta, A M Trozzolo *Am. Chem. Soc. Symp. Ser.*, 1978, **69** 23
139. S Inhar, H Linschitz, S G Cohen *J. Am. Chem. Soc.*, 1981, **103** 1048
140. H Block, A Ledwith, A R Tailor *Polymer*, 1971, **12** 271
141. S G Cohen, A Parola, G H Parsons *Chem. Rev.*, 1973, **73** 141
142. S G Cohen, M D Salitzman, J B Guttenplan *Tetrahedron Lett.*, 1969, 4321
143. L A Singer *Tetrahedron Lett.*, 1969, 923
144. L Andrews, A Deroulede, H Linschitz *J. Phys. Chem.*, 1978, **82** 2304
145. P G Stone, S G Cohen *J. Am. Chem. Soc.*, 1982, **104** 3435
146. G A Davis, P A Carapellucci, K Sgoc, J D Gresser *J. Am. Chem. Soc.*, 1969, **91** 2264
147. N J Gaylord *Usp. Khim.*, 1972, **41**(6) 1067 [English translation in *Russ. Chem. Rev.*, 1972(6)]
148. M Szwaro *Pure Appl. Chem.*, 1984, **56** 447
149. T Kagiya, Y Sumida *Bull. Chem. Soc. Jpn.*, 1968, **41** 767
150. T Asanuma, M Yamamoto, Y Nishijima *J. Chem. Soc., Chem. Commun.*, 1975, 608
151. M Yamamoto, Y Asanuma, Y Nishijima *J. Chem. Soc., Chem. Commun.*, 1975, 53
152. T Asanuma, M Yamamoto, Y Nishijima *J. Chem. Soc., Chem. Commun.*, 1975, 56
153. S Ku, T R Evans, R W Ware, O Jacnicke *The Exciplex*, Academic Press, New York, 1975
154. M Yamamoto, M Ohoka, K Kitagawa, et al. *Chem. Lett.*, 1973, 745
155. Y Shirota, T Tomikawa, T Nogami, et al. *Bull. Chem. Soc. Jpn.*, 1974, **47** 2099
156. M N Usacheva, V V Osipov, I V Drozdenko, I I Dilung *Teor. Eksp. Khim.*, 1985, **21** 484
157. V V Osipov, M N Usacheva, I I Dilung *Dokl. Akad. Nauk SSSR*, 1980, **254** 407
158. Y Taniguchi, N Mataga *Chem. Phys. Lett.*, 1972, **8** 596
159. M G Kuz'min, N A Sadovskii, I V Soboleva *Khim. Vys. Energ.*, 1980, **14** 38
160. M Schwarz *Ions and Ion Pairs in Organic Reactions* (Tranlsated into Russian), Izd. Mir, Moscow, 1975, 423 pp
161. M Schwarz *Anionic Polymerisation* (Translated into Russian), Izd. Mir, Moscow, 1971, 670 pp
162. B L Erusalimskii *Ionnaya Polimerizatsiya Polyarnykh Monomerov* (Ionic Polymerisation of Polar Monomers), Izd. Nauka, Leningrad, 1970, 288 pp
163. K Bamford, W Barb, A Jenkins *Kinetics of Radical Polymerisation* (Translated into Russian from English), Izd. Inostr. Lit., Moscow, 1961, 345 pp
164. N Kitamura, S Imabayashi, S Tazuke *Chem. Lett.*, 1983, 455
165. S Takuze, N Kitamura *Chem. Lett.*, 1983, 136