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INTRODUCTION

Photo-induced polymerization¹⁻⁶ is concerned with absorption of ultraviolet radiation to produce an unstable excited species. Subsequent formation of a free radical by rearrangement, fragmentation or energy transfer, followed by attack upon a monomer, leads to polymerization. Yamamoto and Oster⁷ have indicated that photo-induced polymerization resembles polymerization initiated by ionizing radiation (γ -rays).

PHOTOINITIATION BY ENERGY TRANSFER

The general scheme for photopolymerization, by energy transfer, may be represented as

$S + hv \longrightarrow S^*$ (excited state)	(1)
$S^* + M \longrightarrow S + M^* \Rightarrow M^*$ (initiation)	(2)
$\mathbf{M} \cdot + n\mathbf{M} \longrightarrow (\mathbf{M})_{n}\mathbf{M} \cdot \text{(propagation)}$	(3)
$(M)_n M^{\bullet} + {}^{\bullet}R \longrightarrow (M)_n MR$ (chain-transfer and termination)	(4)

where S = photosensitizer; M = monomer; $R \cdot = free radical or polymer fragment.$

Since a free-radical mechanism is involved in photo-induced polymerization, to the typical conditions governing thermal polymerization must be added the many factors (e.g., irradiation source, wavelength screening, distance of source from reaction cell, catalyst, photosensitizer, temperature, solvent, presence of oxygen, etc.) associated with ultraviolet-induced polymerization. The excited species (step 1) is formed by subjecting the initiator or photosensitizer to ultraviolet radiation (200 to 700 m μ). S*, the excited molecule, possesses more energy than the ground state and is, therefore, capable of transferring energy to another substance such as a monomer which then undergoes bond cleavage to give a free-radical initiation site. S* is then returned to the ground-state energy level and is no longer available to transfer energy to form active sites. Disappearance of S* may also occur without initiation; it may take the form of thermal energy, fluorescence, or energy transfer. Thermal energy results when molecular collisions of the excited species take place and when the absorbed energy in S* is dissipated through rotational and vibrational modes in non-rigid molecules. If S* emits energy at a higher wavelength than its original energy excitation, fluorescence will be observed. Unfruitful energy transfer may occur through deactivation of the sensitizer (S*) by collision with an

unexcited sensitizer molecule. In general, if the excited state of the photosensitizer has a long life, the greater will be the opportunity for transfer of energy and subsequent polymer initiation.

The metastable-excited photosensitizer has been considered as an ultraviolet-excited molecule capable of converting another substance (e.g., monomer) to a monoradical or biradical. Monoradical initiation is produced by a direct transfer of energy from the S* to form an intermediate-excited monomer (M*) to a monomer radical (M•). Monoradical formation is supported by Johnson and Tobolsky⁸; Baysal and Tobolsky⁹ in the polymerization of methyl methacrylate by photoinitiation at 290 m μ and 60 °C. Medvedev¹⁰, in preparing poly(methyl methacrylate), refers to the photoinitiating process as a transformation of excited molecules to biradicals which are promptly converted to monoradicals.

The excited photosensitizer S* may react with itself or a monomer to yield a diradical (\cdot S• or \cdot SM•) and in direct photopolymerization of a monomer via the formation of a diradical (\cdot M•). For example, diradicals are produced when anthracene in the presence of a monomer is excited by ultraviolet radiation. Melville¹¹ postulated that the initial step in ultraviolet irradiation of monomers is the formation of a diradical which is due to considerable electron excitation of the double bond and unpairing of the electrons.

Organic compounds which absorb ultraviolet radiation to form an excited species and by energy transfer, initiate polymerization have been used in photo-induced polymerizations. Mochel et al.18 studied benzoin derivatives as photosensitizers in the diradical polymerization of methyl methacrylate. The carbonyl group is the active moiety in benzoin and derivatives involving the hydroxyl do not appreciably alter the efficiency of photoinitiation. By radioactive-tagged carbon on the methyl group in benzoin methyl ether, it was determined that the poly(methyl methacrylate) contained 12 to 15 initiator fragments per polymer molecule on the average. This may suggest a polymerization mechanism by diradical initiation including termination by mutual combination or copolymerization of methyl methacrylate with the ultraviolet excited species of benzoin methyl ether. Thermal polymerization of methyl methacrylate with a peroxide catalyst in the presence of benzoin methyl ether yielded only homo polymer. Aromatic compounds (e.g., anthracene²¹, when ultraviolet excited, induce polymerization of styrene and the anthracene reacts as a comonomer in the photopolymerization.

PHOTOINITIATION BY DECOMPOSITION

Light-induced polymerization has also been studied in the presence of free-radical catalysts such as benzoyl peroxide and azobisisobutyronitrile. The energy required to decompose the catalysts to free radicals is supplied by the ultraviolet source and the mechanism for the initiation process is similar to free-radical initiation by application of thermal energy. Freeradical initiators in photo-induced polymerization involve competition between thermal and ultraviolet energy for the creation of the free radical; and heat produced in thermal polymerization has a pronounced effect on the molecular weight and the degree of polymerization. Nickerson¹² reported

the photopolymerization of chlorotrifluoroethylene with a peroxy catalyst in an aqueous system and an ultraviolet source 300 W high pressure mercury arc lamp. In the absence of light, no significant initiation was noted. Richards¹³ synthesized polystyrene (62 per cent yield) in nitrogen by ultraviolet irradiation (100 W Hg lamp) for 39 h at 25 °C of a styrene-benzoyl disulphide (1%) composition. Benzoyl peroxide activated at 350-380 m μ has been used to initiate polymerization of allyl methacrylate¹⁴. Similar results were obtained by Cohen *et al.*¹⁴ when the acetyl radical, produced by photolysis (400-600 m μ) of biacetyl, was used as the initiating free radical for the synthesis of polyallyl methacrylate. Photo-induced polymerization of allyl methacrylate below 25°C is preferred over thermal polymerization, because gelation may be postponed until a 39 per cent vield of polymer is obtained. Bianchi¹⁵ reported that azoisobutyramide is an excellent photoinitiator for the polymerization (275 W G.E. sun lamp) of styrene in an aqueous system. Burnett¹⁶ compared the role of 2,2'-azoisobutyronitrile with 1,1'-azo-1-cyclohexane in the polymerization of vinyl chloride below 2800 Å. The former catalyst decomposes at moderate temperatures and causes thermal polymerization at high rates. The azocyclohexane derivative also initiates at a similar wave length but its rate of thermal breakdown is very much less than the isobutyronitrile. The photopolymerization (irradiation at 3660 Å) of styrene initiated by 2,2'-azo-bispropane was studied by Miyama¹⁷. The results indicate that the rate of photopolymerization is proportional to the square root of the light intensity and the square root of the sensitizer concentration. Miyama also determined that the activation energy rate for thermal polymerization in this system was 23.3 kcal, while that for the photopolymerization was 5.8 kcal.

Benzoin¹⁹ sensitized at 3600 Å was effective in the photopolymerization of styrene, butyl acrylate, methyl acrylate, and methyl methacrylate. By ultraviolet radiation, benzoin fragments into the

$$\begin{array}{ccc} O & O \\ \parallel & \parallel \\ \varphi C \cdot \text{ and } \varphi - CH \cdot \end{array}$$

radicals with the latter being the more efficient initiator. Xanthate esters such as carboxymethylene bis(ethylxanthate)²⁰ are equivalent to or better than benzoin in photoinitiation.

Organic compounds containing dithiocarbamate groups²² [e.g., $\varphi(CH_2)_n SCSN(Et)_2$] considerably accelerate the photopolymerization of styrene and methyl methacrylate. The polymerization is initiated by the $\varphi(CH_2)_n SCS \cdot radical$ which is produced by ultraviolet $(250-300 \, \mu\mu)$ cleavage of the bonds in the dithiocarbamate. Additional sulphur-containing compounds²³ such as tetramethylthiuram monosulphide, thiophenol, *p*-thiocresol, and *o*-aminobenzenethiol have been reported as effective photopolymerization catalysts in the synthesis of poly(methyl methacrylate) (68 per cent yield). In the absence of the sulphur-containing photoinitiator, a 3 per cent yield of poly(methyl methacrylate) was obtained. The photopolymerization of methyl methacrylate, acrylonitrile, and acrylic acid may be accelerated by photoinitiators containing *N*-nitroso groups²⁴ (e.g.

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N-nitrosocaprolactam, N-nitrosoacetoacetanilide). Azoxybenzene²⁵ is also an effective initiator for the photopolymerization of acrylonitrile. Larilon²⁶ discovered that hydrazones are efficient initiators for the photopolymerization of acrylamide if R₃ or R₄ in the structure R₁R₂C=N-NR₃R₄ is hydrogen. The initiation sites are formed during the autoxidation of the hydrazone or by photolysis of the resulting a-azoperoxide. If R₁ and/or R₂ contain aromatic groups, the hydrazone becomes a poor photosensitizer.

DYE-SENSITIZED PHOTOPOLYMERIZATION

Dye-sensitized photopolymerization is a rapid process and can be considered as a free-radical initiated polymerization which can be readily controlled. Oster²⁷ proposed the following scheme for dye-sensitized photopolymerization.

M +	$- \mathbf{D} \xrightarrow{h\nu}$	$\mathbf{R} \cdot \mathbf{r}$ (rad	ical initiation)	(1)
R• +	M→	RM• (c	hain initiation)	(2)
$RM \cdot +$	$M \longrightarrow$	RM ₂ .	(propagation steps each with the same	(3)
•	•	•	rate constant)	
•	•	•		
$\mathrm{RM}_n \cdot +$	$M \longrightarrow$	RM_{n+1}		
$RM_n \cdot + RM$	$\Lambda_n \cdot \longrightarrow$	RMMR	(bimolecular termination)	(4)
	$R \cdot \longrightarrow$	S ("Cas	ge" recombination of primary radicals)	(5)

This scheme postulates that the monomer participates in the formation of the initiating free radical $(\mathbf{R} \cdot)$ (step 1) and some of $\mathbf{R} \cdot$ becomes inactive by a unimolecular process (step 5).

The rate of monomer consumption is proportional to the second power of the initial monomer concentration and to the square root of the visible light intensity. The molecular weight is independent of the monomer concentration and the smaller the light intensity the greater the molecular weight. This is explained by the unimolecular disappearance of part of the initiating free radicals and the diffusion-controlled bimolecular termination of the growing chain radicals.

Based on this proposed mechanism, $Oster^{30}$ prepared poly(methyl methacrylate) (mol. wt = 100 000) by irradiating with visible light (W lamp, green filter) a methanol solution of methyl methacrylate, Rose Bengal and phenyl hydrazine in the presence of oxygen. This method was also used for the polymerization of styrene, calcium acrylate, acrylonitrile, and acrylamide.

Dyes subjected to visible light and a mild reducing agent in an oxidationreduction system containing a monomer have also been effective in polymerization²⁷⁻²⁹. For example, Oster²⁷ reported that the photopolymerization of acrylamide in an aqueous solution of riboflavin-5'-phosphate in the presence of oxygen produced free radicals. The free radicals responsible for initiating polymerization result from the reaction between the leuco dye (reduced form) and oxygen to yield the semiquinone form of the dye and hydroxyl radicals. Mild reducing agents used in dye-sensitized photopolymerization studies include primary and secondary amines, amino acids,

thiourea and its derivatives, ascorbic acid, thiocyanates, dicarbonyl compounds such as 2,4-pentanedione and derivatives of malonic acid. Typical dyes used in this type of photopolymerization include the acridines, thiazines, fluoresceins, riboflavins, and chlorophyllins. Dye-sensitized photopolymerization generally leads to high molecular weight polymers and copolymers. As an example, allyl alcohol, a chain-transfer agent, does not normally yield high molecular weight copolymers. However, in a dye-sensitized photopolymerization, Oster²⁷ prepared copolymers of allyl alcohol and acrylonitrile in high molecular weight. Oxygen plays an important rôle in dye-sensitized photopolymerization. If oxygen is excluded from the system, the visible light will still reduce the dye to a colourless form but polymerization will not take place. Polymerization may be induced by the addition of oxygen even after photoreduction has been accomplished.

Delzenne, Toppet, and Smets³¹ reported the formation of H_2O_2 during photoreduction of dye-reducing systems in the presence of oxygen. This was determined by polarographic analysis of the irradiated solutions. The hydrogen peroxide is formed by the action of oxygen on the *leuco* form of the dye or on the intermediate semiquinone produced during photoreduction. These investigators explained the mechanism of formation of the initiating species in photopolymerization by considering the ultraviolet excited dye in its metastable triplet diradical form which is reduced to the intermediate semiquinone and *leuco* form of the dye. The oxygen or the already formed OOH• radical on these two reduced forms produced hydrogen peroxide which regenerates the oxidized form of the dye.

Dyes sensitized by ultraviolet irradiation and in the absence of oxygen may also interact directly by energy transfer with a monomer to initiate polymerization³². Koizumi³³ obtained polystyrene by subjecting the monomer and zinc tetraphenylchlorin to visible light (about 620 m μ) in vacuo at 40°C. Thermal polymerization is almost negligible at this temperature. The dye is not decomposed by irradiation and monomer radical formation is induced by energy transfer from the triplet state of the dye to the styrene molecule. Yoshida *et al.*³⁴ prepared poly(methyl methacrylate) in the absence of oxygen by carrying out the polymerization in the presence of an excited dye molecule (e.g., methylene blue). Here, too, the active radicals produced by photochemical decomposition of the dye initiated the polymerization reaction. Dye-sensitized photopolymerizations involving reducing agents have also been reported in the absence of oxygen, by reducing lightexcited thionine with β -diketones especially 2,4-pentanedione. The dicarbonyl compound is capable of undergoing keto-enol tautomerism and the enol form is responsible for the reactivity. The photopolymerization in the absence of oxygen of methyl methacrylate³⁶ by dyes (e.g., erythrosine, thionine blue) in the presence of amines (e.g., triethanolamine) was also reported.

PHOTOINITIATION BY INORGANIC COMPOUNDS

Inorganic metallic compounds [e.g., $Fe(OH)_3$ or $FeCl_3$] are also effective initiators in photopolymerization. Metallic ions³⁷ of the compound act as an ion pair complex. The light absorption by the ion pair results in electron

transfer to reduce the cation (e.g., to Fe^{2+}) and oxidize the anion to an atom or a free radical. The free radical initiates polymerization with the available monomer. For example, Simionescu et al.38 prepared polyacrylonitrile in stannic chloride solution at 20°C using a 300 W Thelta lamp as the ultraviolet radiation source. By a different mechanism, Hiltz and Lendrat³⁹ polymerized acrylamide in water, as well as in polar organic solvents (e.g., methanol, acetone, dioxane, and dimethylformamide), at room temperature in the presence of stannous chloride as the photoinitiator. Ferrous and nickelous compounds were also used in this study and were effective in photoinitiation. Other monomers such as styrene, vinyl acetate, and acrylonitrile were photopolymerized in this system. Zinc oxide has been used extensively in photoinitiated polymerization. Kuriacose⁴⁰ studied zinc oxide surfaces in oxygen-free solutions and concluded that surface-adsorbed oxygen is essential to chain initiation. If the zinc oxide is reduced under hydrogen or heated in vacuo to remove adsorbed surface oxygen, polymerization will be greatly reduced. The ultraviolet radiation of zinc oxide in water is most effective at 365 m μ and at this wave length, in the presence of a monomer, hydrogen peroxide is formed. Kuriacose postulates that the polymerization may be anion initiated although propagation may proceed by a free-radical mechanism. Kuriacose⁴⁰ also reported that zinc sulphide is an effective initiator. Oster⁷ reported that the zinc oxide under ultraviolet excitation causes polymerization of vinyl monomers if water and oxygen are present. Hydrogen peroxide is produced in addition to the excited zinc oxide and the peroxide is then decomposed by the reducing action of the light-excited zinc oxide. The hydroxyl radical thus obtained is responsible for chain initiation. Other oxides⁴¹ of importance in photo-induced polymerization include magnesium oxide, titanium dioxide, aluminium trioxide and chromium trioxide.

BLOCK AND GRAFT COPOLYMERS BY PHOTOPOLYMERIZATION

Photo-induced polymerization has also been used for the preparation of block and graft copolymers. Funt and Collins⁴⁴ applied the techniques of focusing a beam of intense ultraviolet radiation on a stream of monomer containing a free-radical initiator. The polymer chain grows to a certain block length which still possesses active end groups and this block is permitted to fall into a second monomer reservoir. The interval between the initial irradiation of the first monomer and contact with the second monomer controls the composition of the final block copolymer. Block copolymers⁴⁴ containing *n*-butyl acrylate and styrene or vinyl pyridine were prepared by this method. Similar block copolymer systems were studied by Hicks and Melville⁴⁵.

Ultraviolet-induced grafting to high polymers in the presence of a monomer provides a method of yielding a system relatively free of homopolymer. Oster⁴⁶ noted that benzophenone, under the action of far ultraviolet, is a poor photoinitiator but an excellent sensitizer for abstracting a hydrogen from adjacent polymer chains to produce a site for grafting. The benzophenone under these conditions is converted to benzhydrol. Benzoin⁴⁷, on the other hand, is a good photoinitiator of polymerization but is not effective for producing graft copolymers. It does not sensitize cross-linking and generally favours the formation of homopolymer.

Ultraviolet-excited dye molecules such as anthraquinone 2,7-disulphonic acid have also been used in the grafting of monomers (e.g., acrylonitrile) to cellulose⁴⁸. In the absence of oxygen, the photoexcited dye molecule abstracts a hydrogen atom from the cellulose molecule. The cellulose radical, thus produced, then reacts with the available monomer to initiate graft copolymerization. In the presence of oxygen, the photoexcited dye molecule also abstracts a hydrogen atom to form a cellulose radical. However, the oxygen interacts with the cellulose radical and thus retards the grafting reaction in the initial stages. When the oxygen is consumed, the grafting process is accelerated and additional grafting sites are then formed under anaerobic conditions. The simultaneous action of a photosensitized dye and a mild reducing agent was also extended to grafting reactions by photopolymerization⁴⁹. For example, by means of visible light, acrylamide was grafted to polyvinyl amine in the presence of eosin, ascorbic acid, and oxygen.

Polymers containing functional groups susceptible to photolysis also provide initiation sites for the synthesis of block and graft copolymers. A photosensitive sulphide such as tetraethylthiuram disulphide was used as an initiator for the polymerization of styrene⁵⁰. The polystyrene blocks contain $SC(S)N(C_2H_5)_2$ end groups and by photolysis yield initiation sites for the synthesis of blocks of methyl methacrylate and acrylonitrile blocks. Okawara *et al.*⁵¹ polymerized styrene containing the $SC(S)N(C_2H_5)_2$ in the phenyl ring and then by ultraviolet irradiation cleaved the photosensitive sulphide to produce active sites for grafting poly(methyl methacrylate) branches. Polyketones [e.g., poly(methyl vinyl ketone)]⁵² degrade to form an acyl radical such as acetyl and a polymer radical containing initiation sites for the polymerization of monomers (e.g., methyl methacrylate and vinyl acetate) to yield graft copolymers. The rate of grafting in this free-radical system is dependent on the potential initiation sites which are based on the ketone concentration in the backbone polymer.

PHOTOINITIATION BY TRIPHENYLPHOSPHINE

In this laboratory, Mao and Eldred⁴² discovered that the triphenyl derivatives of phosphorus, arsenic, antimony, and bismuth are capable of initiating photopolymerization. A comparison of the relative effectiveness of these compounds in photopolymerization of methyl methacrylate is $\varphi_3 P$, $\varphi_3 Bi$, $\varphi_3 Sb$, $\varphi_3 As$. Triphenyl bismuthine, triphenyl arsine and triphenyl stibine initiated photopolymerization of monomers which normally could be polymerized by a free-radical mechanism induced by peroxide or azo-type catalysts. For example, triphenyl bismuthine in ultraviolet decomposed to phenyl radicals and bismuth. The phenyl radical thus was the initiating species for the subsequent free-radical polymerization, and very selective, in that it initiated the photopolymerization of only acrylic-type monomers; styrene could not be photopolymerized when ultraviolet light-excited triphenylphosphine was used as the photoinitiator.

Experimentally, the bulk polymerizations were carried out in Vycor tubes and the source of ultraviolet was a 350 W Hanovia high pressure

mercury lamp; for solution polymerization, the source was a 450 W Hanovia high pressure lamp. For kinetic studies, the polymerizations were carried out at 20, 40, and $60^{\circ}C \pm 0.1^{\circ}C$. For the polymerizations in the absence of oxygen, the reaction mixtures were purged of oxygen by the freeze-melt method using nitrogen which was purified through chrymyl chloride solution and a copper furnace. The polymer [e.g., poly(methyl methacrylate)], was precipitated with *n*-heptane and the values for the kinetic rates were corrected for that portion of polymerization caused by the action of ultraviolet on the monomer.



Figure 1. Effect of irradiation on (C6H5)3P in heptane

The effect of ultraviolet irradiation on triphenylphosphine in hexane was determined spectrophotometrically (*Figure 1*). In the presence of dissolved oxygen, triphenylphosphine (λ_{\max} 262 m μ) was quantitatively converted to the oxide. In fact, this is an effective method for the synthesis of triphenylphosphine oxide. In the absence of oxygen, irradiation at low concentrations used in these studies, had no discernible effect on the triphenylphosphine.[†] In control experiments, triphenylphosphine oxide did not initiate polymerization.

The effect of temperature on the rate of polymerization (*Figure 2*) indicated a positive temperature coefficient and the energy of activation was 4.5 kcal/mole. This is in agreement with the value of 4.9 kcal/mole for the photopolymerization of methyl methacrylate when biacetyl is used as the photoinitiator⁴³. The triphenylphosphine-initiated copolymerization of methyl

[†] Although the photolysis of triarylphosphines was reported by Kaufman et al. [Tetrahedron Letters No. 12, 769 (1965)] their results were obtained under significantly different conditions. methacrylate and styrene yielded 1:1 copolymers and this further emphasized a free-radical mechanism for the propagation step; it also excluded the possibility of propagation by an ionic reaction.

The kinetic study of the triphenylphosphine-initiated photopolymerization resulted in a linear rate curve up to at least 10 per cent conversion. The



Figure 2. Arrhenius plot for triphenylphosphine-initiated photopolymerization of methyl methacrylate

effect of triphenylphosphine concentration on the rate of polymerization (*Figure 3*) indicates that the rate of polymerization increases up to a concentration of about 10^{-3} moles/litre of photoinitiator. This break in the curve



Figure 3. Effect of triphenylphosphine concentration on rate of polymerization of methyl methacrylate

is probably due to self-quenching of the excited state, similar to that observed with anthracene. In the presence of air, initiation did not occur until the triphenylphosphine concentration exceeded about 3×10^{-3} moles/litre and

then the rate was similar to the photopolymerization in a nitrogen atmosphere. The dissolved oxygen converted some of the phosphine to the oxide and when the available oxygen was consumed, initiation then proceeded via ultraviolet irradiation of triphenylphosphine.

The nature of solvent employed in the triphenylphosphine-initiated photopolymerization of methyl methacrylate has a decided effect on the rate of polymerization. In the absence of the phosphine initiator, the rate of polymerization was greater in ethyl acetate than in benzene (*Table 1*).

Table 1. Effect of solvent in triphenylphosphine-initiated photopolymerization

Solvent	Without Initiator (mole 1. ⁻¹ sec ⁻¹)	$\begin{array}{c} With\\ Initiator\\ (mole \ l.^{-1}sec^{-1}) \end{array}$	M (mole 1. ⁻¹)
Benzene Ethyl acetate	$rac{1\cdot 11 imes10^{-5}}{2\cdot 22 imes10^{-5}}$	$\begin{array}{c} 6.44 \times 10^{-5} \\ 5.81 \times 10^{-5} \end{array}$	5.66 5.66

In the presence of the initiator, triphenylphosphine, the rate of polymerization was greater in benzene than ethyl acetate. Probably there is an interaction between triphenylphosphine and ethyl acetate so that the phosphine is not readily available to initiate polymerization.



Figure 4. Ultraviolet spectra

Figure 4 is a plot of the ultraviolet spectra of triphenylphosphine in heptane, methyl methacrylate in heptane, and the reaction mixture containing photoinitiated triphenylphosphine and methyl methacrylate. The existence of a new peak at 292 m μ appears to be due to the formation of a weak complex between the photoinitiator and the monomer. To substantiate this point the following experiments were performed. Using a constant triphenylphosphine concentration, the ultraviolet spectra (Figure 5) of successive dilutions with heptane of the catalyst-monomer mixture were obtained. The λ_{max} and ϵ_{max} were determined after each dilution. As the

monomer concentration approached 0.1 per cent, the ultraviolet spectra value approached the value (262 m μ) for triphenylphosphine in heptane. At this point, the system contains essentially pure triphenylphosphine in the solvent. This behaviour is quite typical of weak complexes.



Figure 5. Change in wave length of complex peak of methyl methacrylate and triphenylphosphine upon dilution with heptane

In order to relate the complex formation to photo-induced polymerization, another experiment was performed in which methyl acrylate was used as the monomer because it polymerizes more rapidly than methyl methacrylate. The photopolymerization of methyl acrylate was monitored spectrophotometrically. The reaction mixture, containing methyl acrylate and triphenylphosphine in the absence of oxygen, was irradiated for short intervals and the ultraviolet spectra was determined after each exposure to ultravoilet light. The complex peak at 292 m μ decreased in intensity linearly with time of ultraviolet irradiation (*Figure 6*). This decrease in intensity was not caused by reaction of a polymer radical with the phosphine since no decrease was observed when the reaction mixture was allowed to stand in the dark for prolonged periods while polymerization continued. These results support the concept that complex formation was responsible for polymer initiation.

The selectivity of triphenylphosphine in initiating photopolymerization was demonstrated by the complex peak formation at 292 m μ . A complex peak was observed in all those monomers which could be initiated by the phosphine. Conversely, in no instance was a complex peak observed in a monomer which was not initiated by triphenylphosphine. The structural requirement differentiating the two types of monomers is the presence of an α,β unsaturated carbonyl group in those monomers responsive to triphenylphosphine initiation. For example, complex peaks were observed in the spectra of acrylate and methacrylate monomers. When polymerization was not effected (e.g., styrene or vinyl acetate) complex peak formation did not occur.



Figure 6. Decay of complex peak of methyl acrylate and triphenylphosphine with ultraviolet radiation

NATURE OF COMPLEX

The first choice for the site of complex formation in methyl methacrylate would be the double bond. However, failure of other vinyl compounds such as styrene to be initiated by the phosphine rules out this possibility. Alternatively, it is proposed that there is a dipole interaction between the carbonyl oxygen and the phosphorus. Upon irradiation, phosphorus donates one of its unpaired electrons to the oxygen, resulting in an inter-molecular chargetransfer complex. Rearrangement of electrons throughout the system, as shown in the following scheme, produces a methyl methacrylate radical which can proceed to propagate the reaction.



Similar complexes can be formed between the monomer and other triphenyl derivatives except triphenylamine. This can be explained by the fact that the nitrogen atom, unlike phosphorus or other members of the same family, does not have any d orbital, and, therefore, it is difficult to participate in this type of complex formation.

Although there are still many unanswered questions in the field of photoinduced polymerization, it has been demonstrated that this is a very effective method for the preparation of well-defined high molecular weight polymers. It permits the initiation of polymerization to occur at low temperatures and, therefore, yields well controlled rapid polymerizations.

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