



New Trends in UV Curing

Marc J.M. Abadie* and Vanda Yu Voytekunas

Laboratoire d'Etude des Matériaux Polymères/Matériaux Organiques Avancés
LEMP/MAO – CC 021, Université Montpellier 2, Sciences et Techniques du Languedoc, Place Eugène
Bataillon, 34095 Montpellier Cedex 05, France

Abstract

We present an overview of the use of photochemistry applied to polymerization and crosslinking reactions by radical or cationic process used for thin film technologies and more generally for coatings. Industrially, most of the formulations used are initiated by radical mechanism. Since the discovery by J. Crivello of iodonium and sulfonium salts, the market has been oriented to use cationic systems to crosslink monomers/oligomers. One of the main advantage of such a system is that it is not sensitive to the presence of oxygen as it is for radical mechanisms. An overview of a photosensitive formulation is presented *i.e.* photoinitiators, photosensitisers, monomers and/or oligomers mainly used by formulators and additives.

A new technique which has been developed to study and optimise any photosensitive formulation – differential photo calorimetry DPC – and which permits to determine kinetic parameters such as enthalpy, degree of conversion, rate constant, Arrhenius parameters, *etc.* is also describe.

Some of the main characteristics and properties of UV cured polymers like acrylates, epoxides, vinyl ethers and others are correlated with their structures and the photocuring conditions. Applications to thin film technologies based on acrylates, epoxides and silicones is presented.

A promising area of research which opens a new route for the obtention of new structure of alternating copolymers for coatings without the use of photoinitiator and based on charge transfer complex CTC is also presented.

Introduction

Over the last thirty years there has been a constant development in the use of photochemistry [1,2] (UV and visible, and more recently E-Beam) in various sectors of application, mainly in the coating industry, graphic arts, micro and nano electronics, dental composites and composites. These developments, based on the use of energy of photons (or electrons for E-Beam) is possible because the technology, is simple, quick in process and allows the formation of thin films (thickness from a few Angströms to a few microns or tens of microns or a few centimeters in the case of E-Beam). However the optimisation of photosensitive formulations are often of concern by an empirical approach based essentially on experience and closely guarded know-how of the formulator, rather than on a rational and scientific basis.

Radiation curing of polymer coatings using UV light has in the past been dominated by photoinitiated

*corresponding author. E-mail: abadie@univ-montp2.fr

radical polymerization process. More recently [3], as a result of the replacement of the thermally unstable aryldiazonium salts with more stable alternatives such as the onium salts as photoinitiators, cationic polymerization processes have become increasingly important. Cationic polymerization has several significant advantages. The main advantage is that, in contrast to radical polymerization, cationic polymerization is not inhibited by the presence of oxygen, thereby allowing the cure process to occur in air to provide a significant advantage in costs. The other advantage for cationic polymerization is that the process also generate reactive electrophiles (acids) which help to sustain the polymerization even after UV exposure has been completed in the case of epoxy curing, giving the characteristics of what has been termed a "living" polymerization. As such, the cure process requires only a relatively short UV exposure limited to just that amount of time required for photolysis of the photoinitiator. Once initiated, curing continues spontaneously long after exposure

to UV radiation has been stopped.

An overview of a photosensitive formulation will be presented *i.e.* photoinitiators, photosensitisers, monomers and/or oligomers mainly used by formulators and additives. We will also describe a new technique which has been developed to study and optimise any photosensitive formulation – differential photo calorimetry DPC – and which permits to determine kinetic parameters such as enthalpy, degree of conversion, rate constant, Arrhenius parameters, *etc.*

Some of the main characteristics and properties of UV cured polymers like acrylates, epoxides, vinyl ethers and others are correlated with their structures and the photocuring conditions. Applications to thin film technologies based on acrylates, epoxides and silicones will be presented.

Recently, systems composed of donor/acceptor molecules and working via a charge transfer complexes (CTC) [4], have raised considerable interest, generating new structure of polymers such as alternating copolymer types without the use of any photoinitiator. An example of such a new system will be discussed.

Photosensitive Formulation

A photosensitive formulation is somewhat complex and composed of apart from mono and multi-functional monomers and/or oligomers, photoinitiator, photosensitiser and some additives such as inhibitors (thermal and oxidative), pigments, dyes, stabilisers, plasticisers, *etc.* Thus it is essential to be able to control each of the components of the formulation and particularly to know the nature of their

response to a photochemical event, with respect to their reactivities in presence of other additives, as well as to the overall property-requirement of the end-product. Very often, the photoreactive formulations used are made using empirical approach, based essentially on experience and closely guarded know-how than a rational and scientific procedure.

Photoinitiators

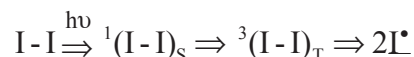
These are at the heart of any photosensitive formulation, which upon exposure to UV radiation, produce active species (radical or protons). In presence of monomers/oligomers (M), initiation and propagation take place to form either a linear chain or a three dimensional network, depending on the average functionality of the monomer used.



Depending on the chemical structure of the photoinitiator, the active species could be divided into two categories: those which produce radicals and those producing protons.

Radical photoinitiators (RPI)

Absorption of energy through chromophore groups leads to the formation of radicals by photocleavage of fascile chemical bonds through the singlet and triplet states, according to the equation:



Most of the photoinitiators of this class are acetophenone derivatives producing acyloxy radicals which rearrange to produce simpler radicals like H^\bullet and CH_3^\bullet – Fig. 1, and an inactive species.

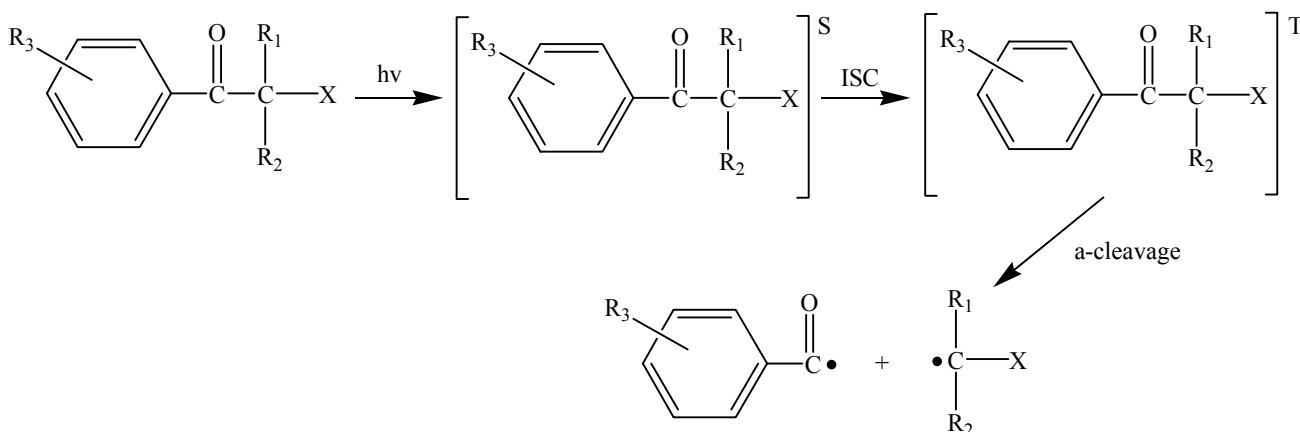


Fig. 1. Norrish type I photocleavage of alkylaryl ketones. R_1, R_2 = alkyl, aryl; $X = O, NR_2$; S = Singlet; T = Triplet; ISC = Intersystem crossing.

It may be mentioned here that newer versions of radical photoinitiators based on phosphine deriva-

tives are available (Lucirin™ from BASF – Fig. 2; BAPO® from Ciba-Geigy – Fig. 3).

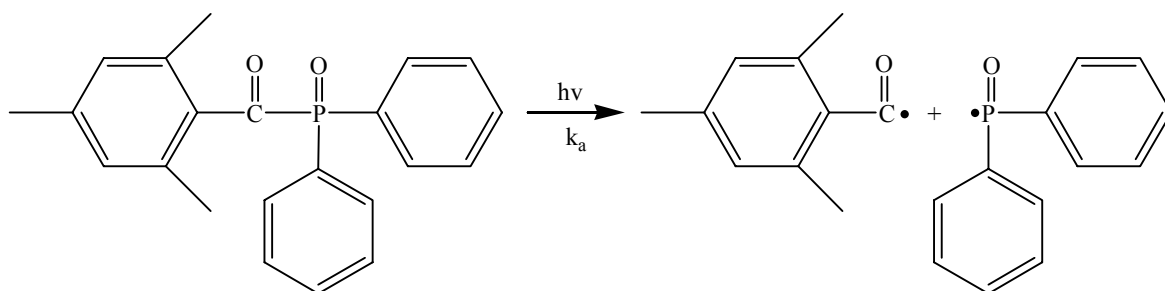


Fig. 2. Photocleavage of triphenylphosphine oxide TPO Lucirin™ from BASF.

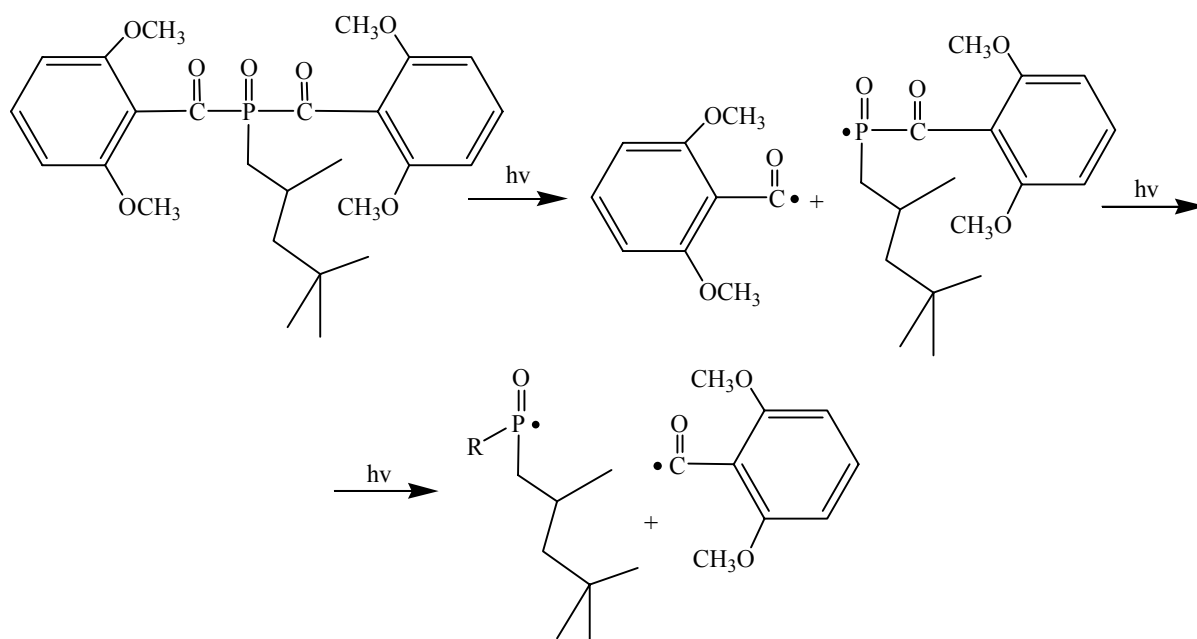
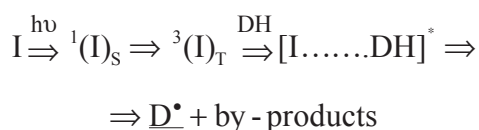


Fig. 3. Photocleavage of bis(2,4,6-trimethylbenzoyl)phosphine oxide BAPO® from Ciba-Geigy.

Another class of radical photoinitiators are based on amine derivatives of benzophenone or xanthone, which produce free radicals by intermolecular hydrogen abstraction. The radical producing mechanism of such a reaction goes via an excimer, which decomposes with amine (DH) to generate the radical and a by-product obtained by radical combination (usually a pinacol), according to the equation:



Cationic photoinitiators (CPI)

Cationic photoinitiation represents the second

method of initiating a photopolymerisation reaction [5] and is generally based on the ring opening of the oxirane group or polymerisation of vinyl ethers. However, despite detailed studies reported using this method of initiation, it has been less frequently used compared to the radical method of initiation.

The best known and most widely used compounds to be used as cationic photoinitiators are based on diaryl iodonium and triaryl sulfonium salts and were developed by James Crivello – Fig. 4 [3,6].

The decomposition of these types of salts have been thoroughly studied by Dektar & Hacker [7] and it has been reported that besides the formation of protons (H^+), there is also production of free radicals – Fig. 5.

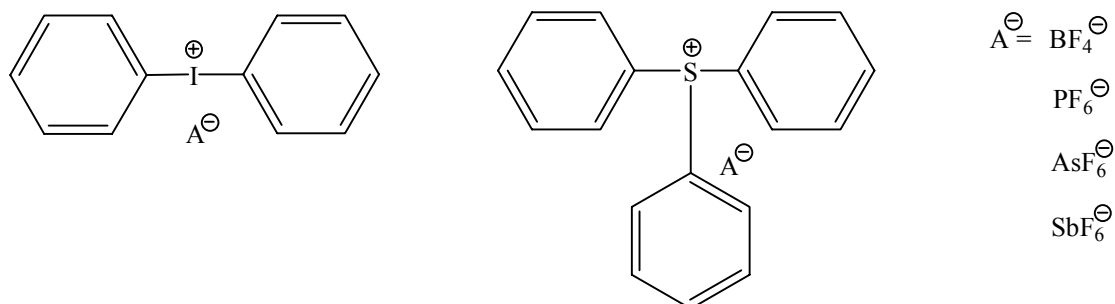


Fig. 4. Iodonium and sulfonium salts as cationic photoinitiators.

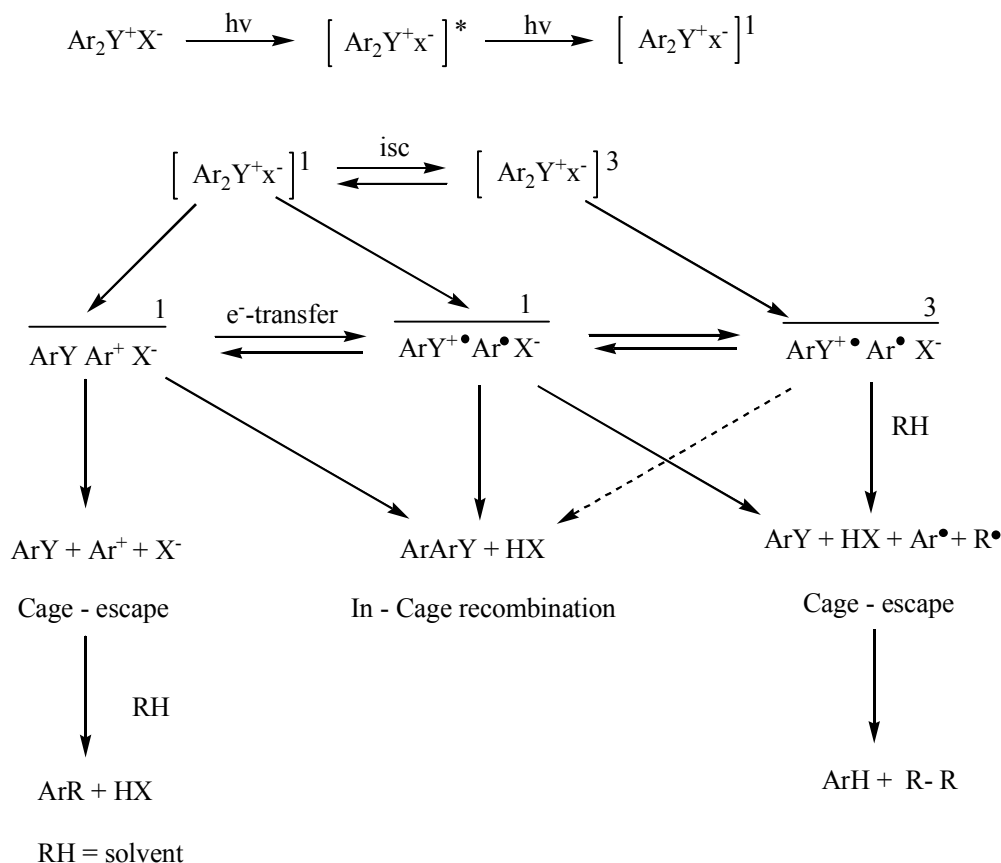


Fig. 5. General scheme of decomposition of iodonium or sulfonium salts upon UV irradiation

Union Carbide is one of the commercial producers of cationic photoinitiators, selling Cyracure® UVI 6974/6976 and Cyracure® UVI 6990/6992 which differ by in the counter anion, SbF_6^- for Cyracure® UVI 6974/6976 and PF_6^- for Cyracure® UVI 6990/6992 – Fig. 6. Recently, Rhodia (a subsidiary of Rhône-Poulenc) has developed (tolylcumyl) iodonium tetrakis (pentafluorophenyl) borate (Silcolease UV 200 or Rhodorsil® Photoinitiator 2074), a highly soluble cationic photoinitiator [8] for silicone [9] applications – Fig. 7. As opposed to hexafluorophosphate or antimonate, this photoinitiator based on borate is not hydrolysable, non-hygroscopic and has higher thermal stability, which are some of the cov-

eted advantages to qualify for applications involving protective coatings.

Photosensitisers (PS)

The role of the photosensitiser, PS, in a photosensitive formulation, is to extend the spectral sensitivity of the photoinitiator, whose absorption does not match with the main bands of the radiation source. One possibility is to use a photosensitiser which directly accepts the energy from the source and subsequently, the excited molecules transfers the excess energy to the photoinitiator molecule, which acts as the acceptor. The process of radical formation which

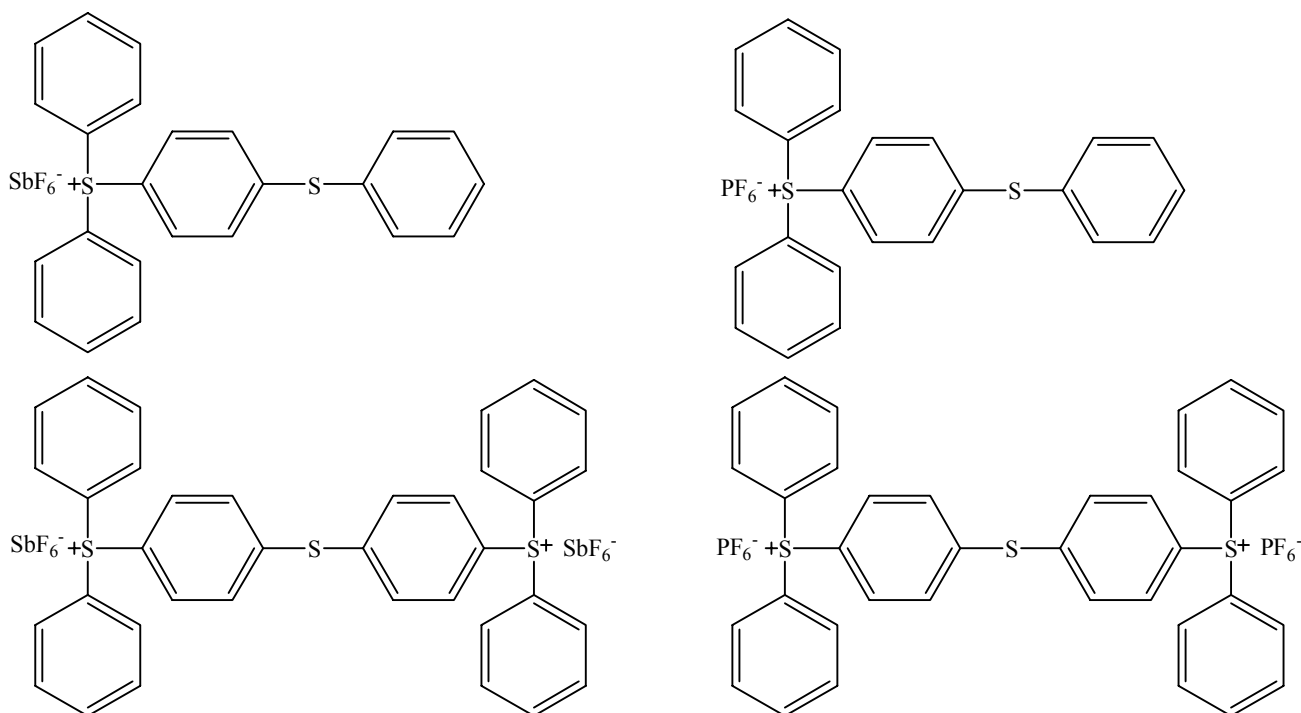


Fig. 6. Commercial cationic CYRACURE® photoinitiators from Union Carbide. UVI-6976 = mixed triarylsulfonium hexafluoroantimonate salts; UVI-6992 = mixed triarylsulfonium hexafluorophosphate salts.

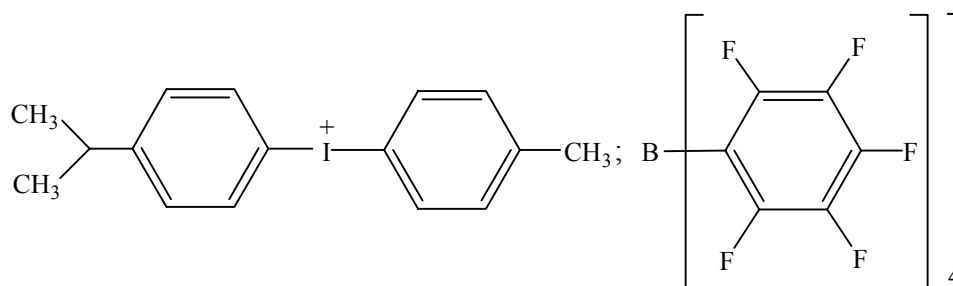
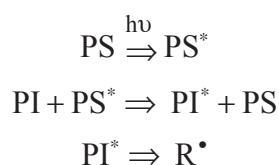


Fig. 7. Commercial cationic RHODORSIL® photoinitiator 2074 from Rhodia; (tolylcumyl) iodonium tetrakis (pentafluorophenyl)borate.

follows, is exactly the same as the unsensitised one:



Examples of the development of a new range of products based on thioxanthone (TX) derivatives as sensitisers and morpholino ketones (MoK) as acceptors, is summarised in Table 1.

Monomers or Oligomers

The functionality of the monomer or oligomer used plays a great role on the properties of the final product obtained. Thus, a monofunctional monomer leads to the formation of a linear structure (thermo-

plastic), whereas a multifunctional system permits the achievement of a three dimensional network structure (thermoset).

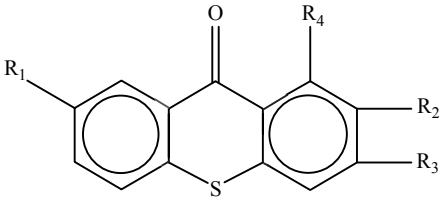
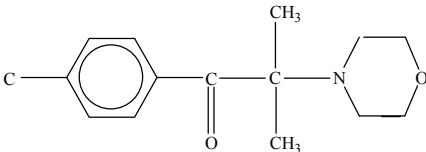
In the process of UV curing, most of the monomers used are difunctional or trifunctional, mixtures with monofunctional monomers being used sometimes.

Radical polymerisation

There are available in the market, quite a large numbers of monomers or oligomers bearing acrylate functions (mono and multifunctional acrylates like polyester acrylates, polyether acrylates, polybutadiene acrylate, epoxy acrylate, polyurethane acrylate). All these acrylates are prone to the radical process of polymerisation and are strongly reactive under con-

Table 1

New range of products based on thioxanthone (TX) derivatives as sensitizers and morpholino ketones (MoK) as acceptors

TX's	R ₁	R ₂	R ₃	R ₄	Abbreviation	Triplet-state energy level (kcal/mol)	
	H	Cl	H	H	CTX	62	
	H	CH(CH ₃) ₂	H	H	ITX	61	
	CH ₃	H	COOET	H	ETX	58.5	
	H	H	H	COOET	TXI	63	
Mok's					R		
					H	HMK	65
					SCH ₃	TPMK	61
					OCH ₃	OMK	65
					N(CH ₃) ₂	NMK	63

ditions of UV curing as compared to vinyl or allyl groups.

Besides the classical multifunctional acrylates mostly used in applications involving UV curing, there are two other categories of monomers based on:

- Unsaturated polyester resins: the unsaturation located on the polyester backbone undergoes chain addition copolymerisation with a vinyl monomer, usually styrene and more recently, dicyclopentadiene;
- Thiol-polyene systems: the photoinitiated addition of tetrathiol onto a diene or polyene leads to the formation of a cross-linked polythioether.

Cationic polymerisation

Protonic acids produced by UV radiation of onium salts or the Lewis acid coming from radiolysis of ferrocenium salts, initiate the ring opening polymerisation of epoxy monomer. Some other functions such as vinyl ether or exotic monomers like vinyl carbazole, vinyl pyrrolidone, isobutene, aziridine and indene derivatives only polymerise through a cationic process.

Difunctional cyclohexane oxide and vinyl ether monomers are quite useful for the formulator and could be mixed with high molecular weight epoxy, thanks to their low viscosity and high photoreactivity, leading to insoluble cross-linked materials – Fig. 8.

Kinetics of Photopolymerisation

In most photocuring reactions, cross-linked polymer networks are formed by irradiation of monomers

and/or functional oligomers that contain at least two reactive functionalities in their structural unit. Since these monomers do not produce initiating species with a sufficiently high yield upon UV exposure, it is necessary to introduce a photoinitiator that will absorb the incident radiation effectively and generate free radicals or ions with a high quantum yield. The rate of initiation, r_i , is directly related to the intrinsic absorbance A of the photoinitiator, to the quantum yield for the primary active species (protons, Lewis acids) production ΦR , and to the efficiency e of the active species in starting polymer chains:

$$r_i = \Phi R \times e \times I_0 [1 - \exp(-A)]$$

where, I_0 , is the fluence rate (light intensity) of the incident radiation. Compared to thermal polymerisation, photoinitiation allows the attainment of very high values of r_i , which in addition, can be varied throughout a large range by simply controlling the fluence rate.

The resins are usually exposed as thin film, typically between 1 and 100 μm thickness, to the UV radiation of high pressure mercury lamp for different durations. In order to determine the degree of curing, the irradiated coatings are submitted to various empirical tests (tack-free, scratch-free) or other methods based on the evaluation of the coating properties (hardness, dynamic modulus, solvent rub resistance). Beside these empirical techniques, a number of analytical methods have been developed to determine the degree of curing more accurately, particularly using real-time methods.

These novel analytical methods – real-time tech-

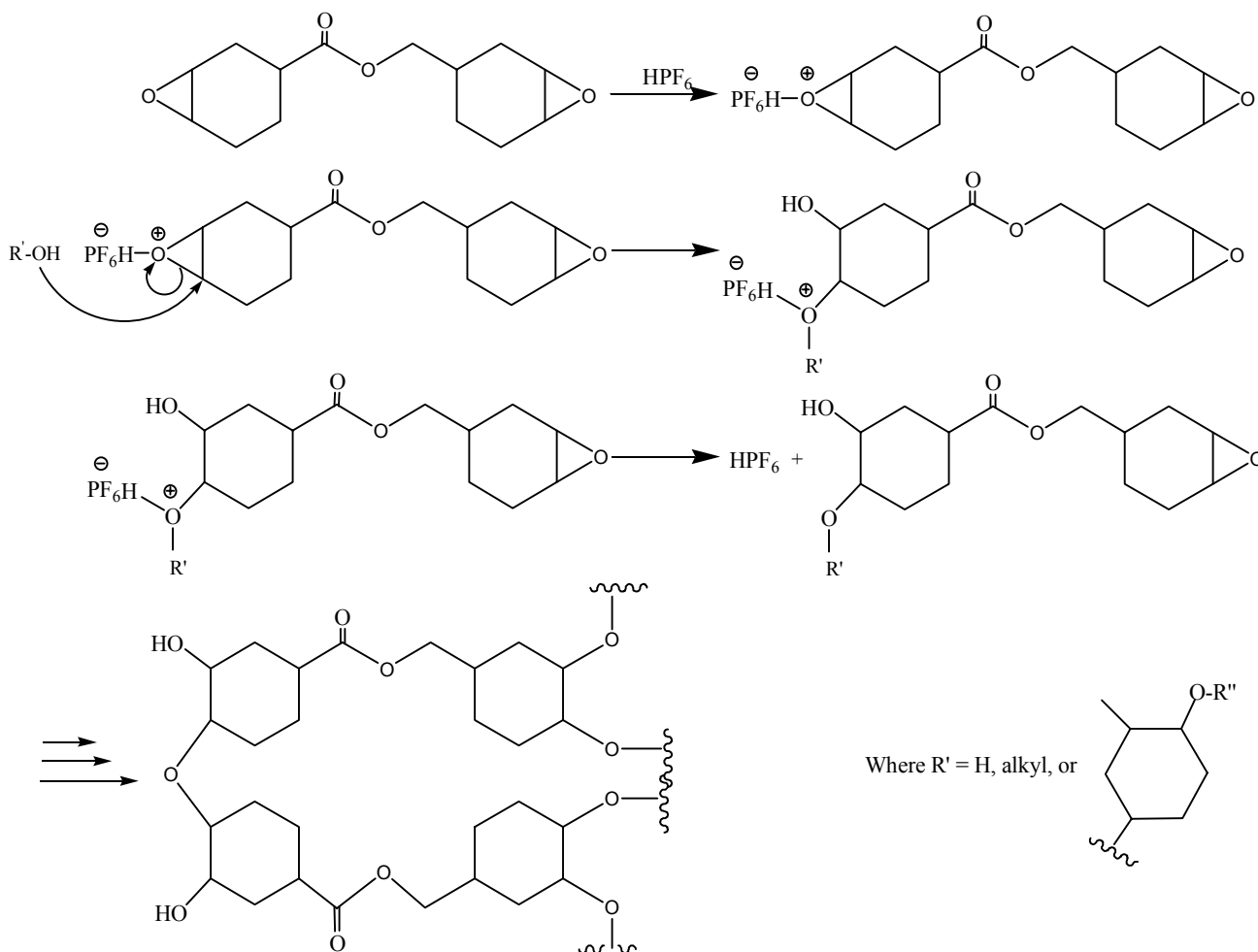


Fig. 8. Cationic polymerization of diepoxides.

niques (IR spectroscopy) based either on the variation of the absorbance of reactive functions [10,11] (e.g. acrylates in the 800 cm^{-1} region before and after UV exposure) or measuring the quantity of heat involved using a differential scanning calorimeter equipped with an UV lamp, are most commonly used for investigating photopolymerisation reactions. The latter method is known as photocalorimetry [12,13] or Differential PhotoCalorimetry (DPC). The advantage of these two techniques is to permit one to monitor the kinetics of ultrafast photopolymerisation reactions, *in situ*, and to follow UV curing reactions directly and on a real-time basis.

Differential Photocalorimetry [14,15], DPC

Calorimetry is the method of choice for monitoring the UV curing reactions, which are highly exothermic processes, in real time. The sample and reference cells of the DSC head are simultaneously exposed to UV radiation and the exotherm due to the polymerisation reaction is directly recorded as a func-

tion of time – Fig. 9.

The rate of polymerisation R_p (mol/L/s) can be derived at any moment from the heat flow value dH/dt (J/mol/s), provided that the standard heat of polymerisation ΔH_0 (J/mol) is known for the mono-

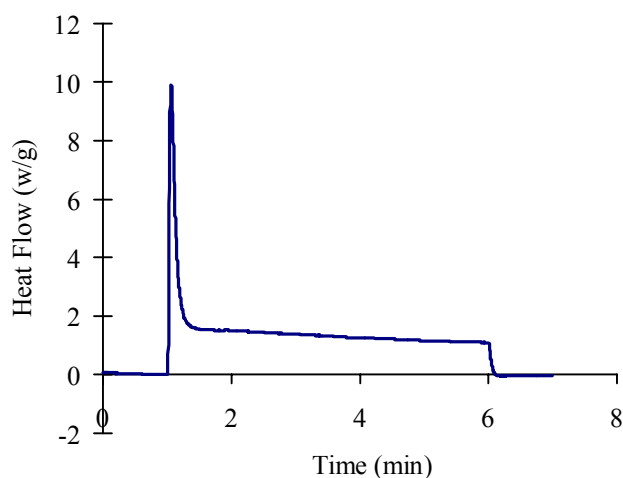


Fig. 9. DPC photogramme of TMPTA initiated by IRGACURE® 651.

mer considered.

$$Rp = (dH/dt) \times [M_0] / \Delta H_0$$

The total area under exotherm gives a measure of enthalpy of the polymerisation, ΔH , which compared to ΔH_0 , allows the degree of conversion of the cured polymer to be evaluated.

The rate constant k of the photopolymerisation can be evaluated according to the equation [16]:

$$Rp_{(T)} = d\alpha_{(t,T)}/dt = k_{(T)} \alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^p$$

where: α – degree of conversion; k – rate constant; m, n, p – orders of the reaction, respectively initiation, propagation and termination.

Assuming that one is very far away from the termination reaction at the beginning of exposure to radiation, we can consider $p = 0$, which leads to the simplified expression:

$$Rp_{(T)} = d\alpha_{(t,T)}/dt = k_{(T)} \alpha^m (1-\alpha)^n$$

Besides the rate constant, another parameter important in terms of photoreactivity is the *induction time*, which is the time required for the consumption of 1% of the monomer. Thus, lower the induction time, higher is the reactivity of the system.

Kinetic Results

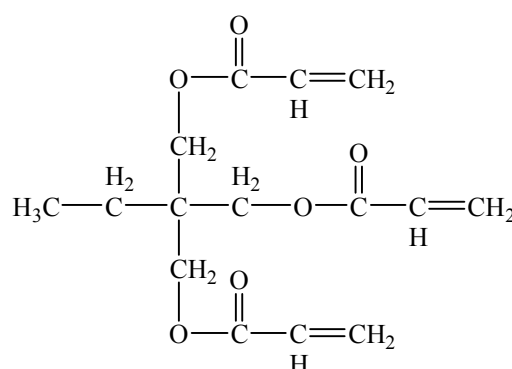
Radical Polymerisation - Acrylates

Monomers of functionalised oligomers bearing acrylate groups are very reactive [17,18]. Whatever the radical photoinitiator used, the exotherm will be high with a narrow peak, assuming that its absorbance matches with principal bands emitted by the lamp. A comparison of the photoreactivity of different monomers follows – Table 2.

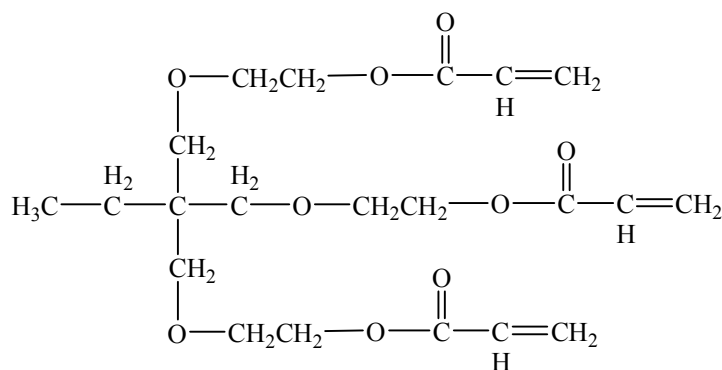
The influence of the chemical structure has an important role to play in the reactivity of a chemical function. How the spacer between the acrylate functions will affect the reactivity of the oligomer. Let us consider the example of trimethylol propane tri-

acrylate (TMPTA) and trimethylol propane triethylene oxide acrylate TMPT(EO)A, a similar monomer where an ethylene oxide unit has been introduced before the terminal acrylate, in order to appreciate the importance of the spacer length, between the acrylate functions – Fig. 10 and Table 3.

We observe that the photoreactivity of a chemical function, here acrylate, is directly related to the flexibility of the chain to which the function is linked, ethylene oxide unit furthering the mobility of the chain due to the presence of oxygen and carbon atoms. For TMPTA, we have one methylene carbon and one oxygen whereas for TMPT(EO)A three methylene carbons and two oxygen atoms are present



TMPTA



TMPT(EO)A

Fig. 10. Chemical structures of trimethylolpropane triacrylate TMPTA and trimethylolpropane tri(ethylene oxide)acrylate TMPT(EO)A

Table 2

Rate constant k (1/min.) of different acrylates,
 $I = 5 \text{ mW/cm}^2$, $[PI] = 4\% \text{ w/w}$

	Acrylate	Methacrylate
Tetrahydrofurfuryl	1.94	0.54
Glycidyl	4.64	0.86
Trimethylol Propane Tri	6.41	1.55

Table 3

Rate constant and induction time of acrylates,
 $I = 5 \text{ mW/cm}^2$, $[RPI] = 4\% \text{ w/w}$

	k (1/min)	Induction time (s)
TMPTA	6.41	10.7
TMPT(EO)A	12.40	3.2

between the acrylate and the tertiary carbon of the molecule. In other words, more flexible the spacer between functions, higher is the photoreactivity.

The viscosity of the medium is also a parameter that affects the reactivity. Comparing TMPTA (liquid) and a mixture of 25 and 75% by weight of TMPTA and PMMA respectively, we observe – Fig. 11a & 11b, that the viscosity of the medium (liquid or pasty) plays a great role in the reactivity of the function and affects the degree of conversion. This degree of conversion may be increased by elevation of temperature – Fig. 12.

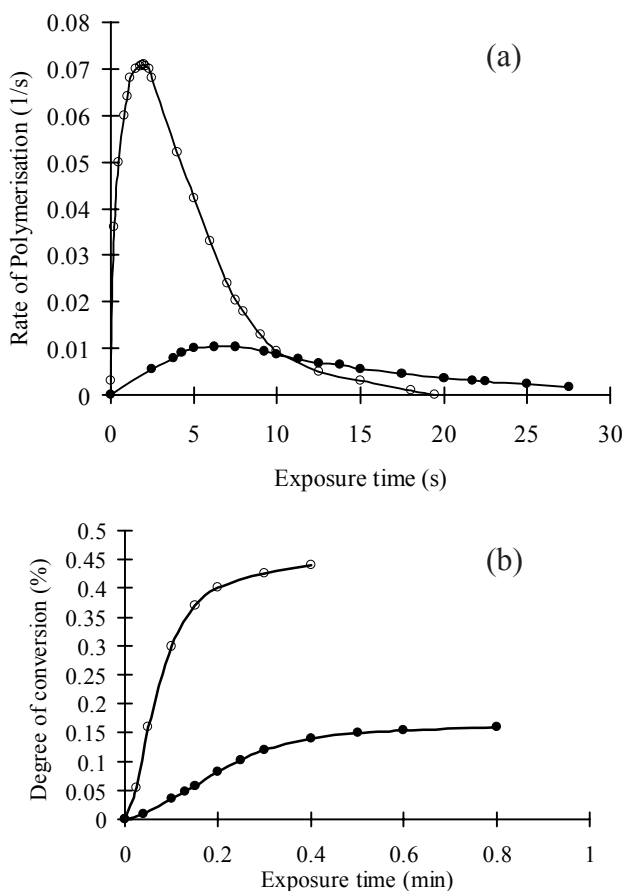


Fig. 11. Rate of polymerization (a) and conversion (b) at 25°C versus duration of UV exposure – o TMPTA (100%); • PMMA (75%)/TMPTA (25%).

Cationic Polymerisation

• Epoxides

Epoxides show a very high reactivity under UV curing and particularly classical glycidyl epoxy [19,20] structure has been shown to be more reactive than cyclohexane oxide structure – Table 4.

We observe that the classical glycidyl epoxy function is much less reactive than epoxide linked directly

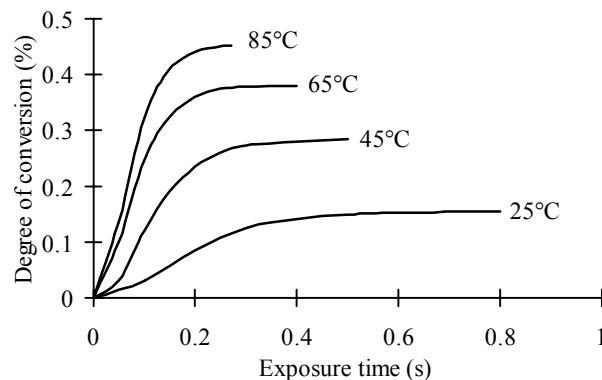


Fig. 12. Degree of conversion versus duration of UV exposure for a mixture PMMA (75%)/TMPTA (25%) at different temperatures.

Table 4

Rate constant and induction time for different mono and difunctional epoxydes, $I = 5 \text{ mW/cm}^2$, $[CPI] = 4\% \text{ w/w}$

	Rate constant k (1/min)	Induction time (s)
Epichlorhydrin	1.66	30.60
Cyclopentane oxide	12.43	4.30
Epoxy-pinane	16.60	2.07
Cyclohexane oxide	19.66	2.25
Monoepoxy limonene	37.60	2.12
DGEBA	1.78	16.67
Dicyclohexane oxide carboxylate	10.22	4.10
Diepoxy limonene	26.73	2.20

to cyclopentane or hexane cycle *i.e.* cyclo-aliphatic epoxy resin. The induction time varies in inverse manner as compared to k , demonstrating the high photoreactivity of epoxy limonene.

• Vinylethers

Vinyl ethers are reactive under radiation curing conditions and have shown the ability to enhance formulation performance especially with epoxides due to their low viscosity and high reactivity.

The reactivity of the vinyl ether is also related to the chemical structure of the molecule – Fig. 13 and Table 5.

Rapi-Cure® CHVE, *i.e.* 1,4-cyclohexane dimethanol divinyl ether is less reactive than Rapi-Cure® DVE-3, *i.e.* triethylene glycol divinyl ether – Fig. 13, due to the presence of cyclohexane structure, compared to two oxygens and six methylene groups,

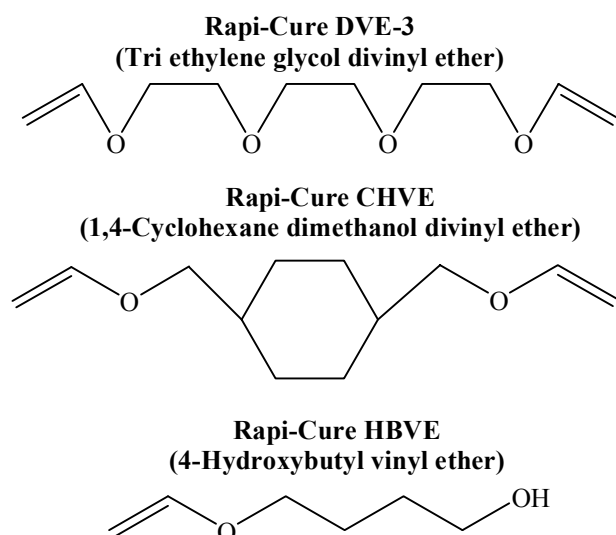


Fig. 13. Chemical structures of mono and difunctional vinyl ethers from GAF ISP.

Table 5

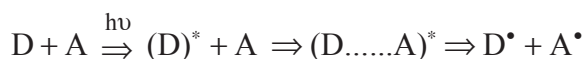
Rate constant and induction time of two vinyl ethers,
I = 5 mW/cm², [CPI] = 4% w/w

	Rate constant <i>k</i> (1/min)	Induction time (s)
Rapi-Cure® CHVE	23.87	4.53
Rapi-Cure® DVE-3	44.34	3.00

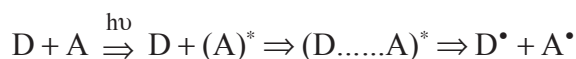
which give more flexibility to the main chain, *i.e.* more reactivity to the vinyl ether function.

Charge Transfer Reactions

Free radical or radical reactions are often rendered more likely when there is a large disparity of charge between two molecules, *i.e.* an electron rich molecule donates an electron to an electron deficient molecule. Such mechanisms are termed donor/acceptor or charge transfer reactions.



or



Examples of these reactions occur in photoinitiator transformations between donor like vinyl ethers and such electron deficient molecules as maleic anhydride or maleimide derivatives to produce vinyl ether/maleate or maleimide copolymers.

Recently, we have studied [21] the copolymerisation of hydroxybutylvinyl ether (HBVE) and male-

imide (MI) and demonstrated the formation of alternating copolymers. We have also proposed the mechanism of formation of rotaxane structure via bi-radicals. The polymer obtained was insoluble but swelled up to 600%.

Conclusions

Thanks to the advantages of photocalorimetry we have been able to evaluate the reactivity of different monomers or oligomers bearing either functions sensitive to radical process like acrylates or to cationic mechanism like epoxides or vinyl ethers. We have also demonstrated the structure-property relationships between the flexibility of a chain and the reactivity of the terminal functions.

Besides, this technique helps the formulator to optimize the formulations and have a better control of the different components of the formulation.

Photosensitive formulations based on the concept of donor/acceptor property is a promising area of research which opens a new route for the design of polymers with novel structure and property combination, for applications in coatings without the use of photoinitiators.

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