Organic Polymer Photochemistry

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ABSTRACT: Some fundamental characteristics of polymer photochemical reactions are shown and their differences with reactions of their model compounds are underlined. Successively are considered: i) photodegradation of methacrylic copolymers carrying photolabile acyl-*O*- α ketooxime side groups and degradation of polyethylenimines by H-abstraction by photoexcited benzophenone; ii) photoinitiation of block polymerization by photolysis of methylbenzoin ether incorporated in a condensation polymer and by selective photolysis of a heterofunctional initiator, *e.g.*, oligoazoperoxides, and azo-di-*t*-butyl peresters. The advantages of the photochemical initiation with respect to corresponding thermal processes reside in its high selectivity and low reaction temperature; iii) photochemical electron donor-acceptor (EDA) interactions in copolymers of vinylbenzophenone (VB) and *p*-dimethylaminostyrene (DAS), and in terpolymers VB-DAS and methacrylic esters. The influence of crossed dyad concentration on absorption and emission spectra is underlined. Electron paramagnetic resonance (EPR)-measurements of radical concentration indicate a strong effect of the physical state of the matrix.

KEY WORDS Photochemical Reactions / Degradation / Block Polymerization / EDA-Complexation /

It is the purpose of the present paper to illustrate on the basis of recent experimental data some fundamental characteristics of polymer photochemical reactions and their differences with respect to the reactions of their low molecular model compounds. Successively we will consider:

1. photodegradation of polymers carrying photolabile side groups, and photodegradation of polymers in presence of photosensitive compounds
2. photoinitiation of block polymerization using functionalized prepolymers
3. photochemical interactions and photocross-linking of copolymers of electron donor and electron acceptor monomers.

1. POLYMER PHOTODEGRADATION

Two systems will be considered which differ fundamentally by their respective reaction mechanism. The first is based on the photolysis of acyl-*O*- α -keto-oxime side groups in a methacrylic copolymer, the second involves H-abstraction by photoexcited benzophenone of polyethylenimines.

a) Photochemical initiation of chain degradation has gained interest for microlithography purposes and ultraviolet resist materials. Degradation may be continued with depolymerization if the formation of active centra occurs above the ceiling temperature of the system. High quantum yield of degradation requires the incorporation of photolabile groups, which accelerate the main chain scission. Such requirement is fully realized by α -keto-*O*-acyl oximes of which the quantum yield of photolysis ϕ_s is equal to 0.84 in benzene and 1.4 in carbon tetrachloride as shown by Delzenne *et al.*¹ The reaction scheme is

It is assumed that the $n-\pi^*$ absorption of the $\text{C}=\text{N}$ -group is followed by scission of the $\text{N}-\text{O}$ band of the oxime, generating two radicals. Delzenne *et al.* showed also that copolymers of methyl methacrylate

and 2,3-butanedione-2-oximino methacrylate can act as photochemical macroinitiator for the graft polymerization of styrene and acrylamides, and that in absence of monomer, they degrade progressively as shown by the decrease of their solution viscosity. On the other hand, Chandross *et al.*² have shown the use of copolymers of methyl methacrylate and acyloximino methacrylate ester as deep UV resists and found it about 5 times faster than poly(methyl

methacrylate) (PMMA) at $\lambda > 240$ nm. Thus 1-phenyl-1,2-propanedione-2-*O*-methacroyloxime (OMA-Ph; $R' = C_6H_5$, λ_{max} : 338 nm, $\epsilon = 90$) and 2,3-butanedione-2-*O*-methacroyloxime (OMA-Me; $R' = CH_3$, λ_{max} : 320 nm, $\epsilon = 20$) have been prepared and copolymerized with methyl methacrylate (1 to 20 mol% oxime).³ The photoinitiated degradation was carried out in benzene solution (5 g dl⁻¹) using an irradiation wavelength of 367 nm.

Acetonitrile and the endgroup $-\text{CH}_2-\text{C}=\text{CH}_2$ were easily identified by ¹H NMR and carbon

dioxide by infrared spectrometry.

Eventually the radical $\text{R}'\text{CO}\cdot$ or $\text{R}'\cdot$ may abstract a H-atom and originate another chain scission

or may induce the decomposition of another *O*-oximino-ester, increasing the quantum yield ϕ_s

Degradation was followed by gel-permeation chromatography (Figure 1) and the number of chain scissions per molecule calculated from the equation $N_s = (M_{n0}/M_n) - 1$, M_{n0} and M_n being the number-average molecular weight before and after irradiation at time t . The quantum yield of chain scission ϕ_s is expressed by $\phi_s = N_s/I_a t N_A$; on the average it is equal to 0.8 when R' is phenyl and only 0.2 when R' is methyl. As can be seen from Table I the chain degradation of OMA-Ph copolymers is rapid and practically independent of the irradiation temperature (Figure 2). On the contrary, with

Figure 1. GP-chromatograms of Co(MMA80-OMA-Ph20). λ_{irr} , 367 nm. 0, before irradiation; 1, 15 min irradiation; 2, 35 min irradiation; 3, 75 min irradiation; B, PMMA before and after 75 min irradiation (unchanged).

OMA-Me copolymers the reaction is slow (Table II). In both cases however it is impossible to detect chain scission in solid films at 25 or 60°C, M_n

Table I. Photodegradation of co(MMA-OMA-Ph) polymer (λ_{irr} , 367 nm)

Solution ^a	mol% OMA-Ph	Irradiation		I_a E cm ⁻² s ⁻¹	M_n^b	N_s^c	ϕ_s^d
		time/min	$t/^\circ\text{C}$				
Film + 30 wt% T_g 32° DBP	20	—	25	4.7×10^{-9}	28,000		
		15			9,900	1.83	0.77
		35			6,100	3.60	0.65
		75			3,000	8.3	0.63
	5.4	—	25	4.3×10^{-9}	29,100		
		15			10,500	1.77	0.79
		30			6,600	3.42	0.76
		60			4,760	5.11	0.57
	5.4	—	60	4.2×10^{-9}	29,100		
		15			10,200	1.85	0.84
		60			4,100	6.14	0.70
		—	25	3.5×10^{-9}	31,200	—	
	3	15			13,300	1.34	0.68
		30			8,600	2.63	0.67
		60			7,300	3.24	0.41
	3.5	—	60	1.75×10^{-9}	20,900		
		15			17,500	0.19	
		30			6,700	2.12	

^a In benzene (5 g dl⁻¹). ^b Determined by GPC.^c $N_s = (M_{no}/M_{ni}) - 1$. ^d ϕ_s , quantum yield of chain scission.**Table II.** Photodegradation of co(MMA-OMA-Me) polymer (λ_{irr} , 367 nm)

C ₆ H ₆ solution	mol% OMA-Me	Irradiation		I_a E cm ⁻² s ⁻¹	M_n	N_s	ϕ_s
		time/min	$t/^\circ\text{C}$				
	2	—	25	1.6×10^{-9}	22,500		
		15			22,500		
		30			19,700	0.14	0.21
		60			15,400	0.46	
Film 30 wt% DBP	2	—	60	0.77×10^{-9}	28,000		
		5			29,300		
		15			22,000	0.27	
		30			21,300	0.32	

remaining practically unchanged. It is assumed that free radical recombination in cage prevails on account of lack of diffusion possibilities below T_g . Indeed if the films are plasticized by addition of di-*n*-butyl phthalate (DBP) in order to lower their T_g , degradation again occurs.

This example stresses again the rate determining role of the physical state of the glassy matrix on the chemical degradation phenomena. Usually that influence was investigated in the case of the reversible

cis-trans isomerization of photochromic groups (azo- and spirobenzopyran groups)⁴; evidently chain segment mobility, *i.e.*, the distribution of the free volume in the polymer matrix must affect the course of most reactions, including degradation phenomena.⁵

b) The second photodegradation example is that of polyethylenimine (PEI) in the presence of benzophenone as photoinitiator. It is generally admitted that photoinduced α -hydrogen transfer from

Figure 2. Number of chain scissions. Influence of time of irradiation. Co(MMA-OMA-Ph) mol%: ○, 3; ×, 5.4; ●, 20 in benzene solution □, 3.5 in film + 30% DBP. Co(MMA-OMA-Me) mol%: ■, 2 in benzene solution; ○, 2 in film + 30% DBP.

the amine to the triplet excited benzophenone occurs with intermediate formation of a pair of ion radicals.⁶ Semipinacol radicals $\text{Ar}_2\dot{\text{C}}\text{OH}$ are formed, which mainly dimerize to benzpinacol, while the polymeric radicals undergo β -scission with chain degradation.

Cross-termination processes by disproportionation or addition between the primary radicals as well as reaction of a macro-radical with benzophenone also involve photoreduction of benzophenone however without chain degradation. Therefore from the reaction scheme given below it must be expected that the rate of benzophenone photoreduction will exceed the rate of chain scission.

termination

H-transfer

In the present experiments all irradiations were carried out in a Rayonet photochemical reactor at constant temperature under inert atmosphere. Both reactions, photoreduction of benzophenone and chain degradation have been followed respectively by ultraviolet spectrophotometry and solution viscosimetry.⁷ By following the decrease of absorbance at 336 nm with the time of irradiation, the rate of photoreduction of benzophenone can easily be mea-

sured; it is proportional to the concentration of PEI and the phenone concentration (Figure 3). Noteworthy is that this rate is almost equivalent for linear $\text{-NH-CH}_2\text{-CH}_2\text{-}$ and branched PEI, which contains only 40% secondary amino groups (of which 25 belong to the main chain and 15% in side chains), besides 30% primary and 30% tertiary groups according to the following structure.⁷⁻⁹

Table III. Photoreduction of benzophenone with aliphatic amines^a

Amine	$-\Delta(\text{Ar}_2\text{CO})/\Delta t$	Rate per $\alpha\text{-H-atom/min}$ $\times 10^4$	Relative rate
	$\text{mol l}^{-1} \text{ min}^{-1} \times 10^3$		
$\text{N}(\text{CH}_2\text{CH}_3)_3$	5.8	9.7	1
$\text{NH}(\text{CH}_2\text{CH}_3)_2$	3.2	8	0.83
$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.9	4.5	0.44

^a [amine] = 0.107 mol l⁻¹. [Ar₂CO] = 4.39 × 10⁻³ mol l⁻¹. *t*, 30°C. Solvent dimethyl sulfoxide–water (99:1, vol%).

Structure of b-PEI

Photoreduction experiments in the same experimental conditions as for PEI with propylamine, di- and tri-ethylamine as model compounds, give the results given in Table III; they show the decreasing order tertiary > secondary > primary amine.

At a same amine concentration, the photoreduction of benzophenone was found ten times faster with diethylamine than with the linear PEI. So far this difference is not explained satisfactorily.

Chain degradation after hydrogen transfer was followed by measuring the change of inherent viscosity of the PEI solution with the time of irradiation. (The irradiation was carried out in a Rayonet photochemical reactor at constant temperature under nitrogen atmosphere.) The concentration of benzophenone was 2.14 or 4.28 × 10⁻³ mol l⁻¹, that of PEI ranged from 0.1 to 0.5 molar. By plotting the number of chain scissions per molecule ($N_s = \eta_0/\eta - 1$) against the time, η_0 and η being the inherent viscosity before and after irradiation at time *t*, one obtains the rate of degradation *S*, i.e., the number of chain scission per time unit (Figure 4). As can be seen from Figure 5 *S* depends linearly on the polymer concentration; by extrapolating at infinite dilution (Figure 5) *S*₀ values are obtained. The data are summarized in Table IV. Though the values are difficult to compare with those of benzophenone reduction, nevertheless Table IV shows that the number of chain scission

Figure 3. Rate of benzophenone (BzPh) photoreduction. Influence of the concentrations of b-PEI ($M_n = 40,000$) and benzophenone. *t*, 40°C; [BzPh] in mol l⁻¹: (a) 4.28 × 10⁻³; (b) 2.14 × 10⁻³; solvent, dimethyl sulfoxide (DMSO).

per minute is about one-third for linear PEI compared to the branched one, while the photoreduction rate is equivalent. This difference becomes even more pronounced if one considers that only the amino group in the main chain can contribute to chain scission, i.e., 45% of the total amount.

This second example shows that a comparison polymer/model compound can only be significant if the detailed internal structure of the polymer is known.

II. PHOTOINITIATION OF BLOCK POLYMERIZATION

Block polymers can be prepared photochemically

Figure 4. Variation of number of scissions per molecule with time of irradiation: solvent, DMSO/40°C; [BzPh], $2.14 \times 10^{-3} \text{ mol l}^{-1}$; [PEI] in mol l^{-1} : branched (1) 0.116; (2) 0.166; (3) 0.299; (4) 0.399; linear (1') 0.235; (2') 0.353; (3') 0.465; (4') 0.577.

Figure 5. Rate of chain scission. Dependence on b-PEI concentration. [BzPh], $4.28 \times 10^{-3} \text{ mol l}^{-1}$. $t/^\circ\text{C}$, (a) 50; (b) 40; (c) 30.

Table IV. Rate of degradation $S_0 \times 10^2$ (Influence of the temperature and structure of the polymer)

$T/^\circ\text{C}$	Linear PEI	Branched PEI
30	1.2	4.0
40	2	5.7
50	2.2	6.2
E_a in kJ mol^{-1}	24	15.5 ± 1

by photolysis of light sensitive groups incorporated in a condensation polymer in the presence of a vinyl monomer; their formation results from the second step by free radical polymerization of the monomer. Depending on the mode of termination by disproportionation and/or by addition, their general structure will be PC-PV and/or PC-PV-PC (where PC indicates a condensation polymer sequence and PV—a polyvinyl sequence) as far as the polymer contains one photolabile group per macromolecule. If the number of these groups exceeds the unity, the block polymers will also contain PV-PC-PV triblocks, and multiblocks of the $\text{PV}(\text{PC-PV})_x$ and $(\text{PC-PV})_x$ type, as resulting from the middle sequences. This procedure was already applied earlier by Smets *et al.*¹¹ for the synthesis of block copolymers of polytetrachlorobisphenol-A-adipate and polystyrene by incorporating 5 to 15 mol% of 1 (*p*-hydroxyphenyl) 1,2-propanedione-2-oxime into the polyester. The yield of block polymers was very high, only 5–10% polystyrene being extractable by boiling cyclohexane.

In the present paper the same reaction principle is applied to the incorporation of *p,p'*-dihydroxybenzoin methylether (BME) in poly(bisphenol-A carbonate).¹² BEM itself was prepared by a four step synthesis, of which the two first steps were recently published¹³: 1) 1-methoxymethylation of *p*-hydroxy benzaldehyde, 2) benzoin condensation of the protected *p*-hydroxyaldehyde, 3) methylation of the benzoin secondary alcohol, 4) deprotection of the phenolic group (reaction scheme 9). In

Table V. Photolysis of BME poly(bisphenol-A carbonate)^a

$[\eta]_{20^\circ\text{C}}$ in CHCl_3		M_n		N_s	BME in PC	
dl g^{-1}		M_o	M_i		BME/Bis A molar ratio	Number per macromol.
$[\eta]_o$	$[\eta]_i$					
0.73	0.39	33,600	14,800	1.27	1/104	1.26
0.90	0.57	50,600	28,600	0.77	1/235	0.84

^a 1 g polymer/30 ml CH_2Cl_2 .

order to assure the incorporation of the BME within the polycarbonate chain, it must be first transformed *via* its bis-chloroformate into bis-(bisphenol-A) dicarbonic ester by reaction with a large excess of bisphenol-A; it is assumed that the

reactivity of the dicarbonic ester is equal to that of bisphenol-A itself. Polycondensation of the reaction with phosgene produces a polycarbonate with incorporated BEM-groups designated as BME-PC polymers (reaction scheme 10). Preliminary experi-

ments had shown that the photolysis of the BME-groups was completed after one-half hr irradiation, while homopolycarbonate remains unchanged in the same conditions (Figure 6a).

Table V summarizes the photodecomposition data of two BEM-PC's different in their BEM-content after irradiation at room temperature (λ_{irr} 300 nm). (η)₀ and (η)_i indicate the intrinsic viscosity of the polymers before and after irradiation; similarly M_0 and M_i are the number average molecular weights before and after irradiation, as determined by gel permeation chromatography. The molar BME-content of the polymers was determined by proton-NMR analysis. The agreement between the number of chain scissions per macromolecule, ($N_s = M_0/M - 1$) and the BME-content is very remarkable.

When such BME-PC is photolyzed in the same irradiation conditions but in presence of methyl methacrylate, it gives rise to the formation of polycarbonate-PMMA block polymers. The PMA-weight fraction remains constant after 1 h irradiation (Figure 6b); it increases proportionally with the monomer concentration in the dichloromethane solution (Figure 7). Table VI summarizes the experimental data.

The reaction products were almost pure block polymers. Indeed starting from a 33 mol% PC-reaction product, extraction with boiling acetone (30 h) gives only 10 to 11% weight soluble fraction, which contained 5 mol% PC. The composition of the acetone insoluble product was almost unchanged. As expected these block polymers show on differential scanning calorimetry two distinct glass

Table VI. Polymerization of MMA photoinitiated with BME-PC

Feed					Product					
BME-PC	BME concn	MMA	CH ₂ Cl ₂	Total amount	PMMA ^a content	MMA conversion	$[\eta]_{20^\circ\text{C}}$ in CHCl ₃	M_n^b	Calcd ^c	
g	mol l ⁻¹	mol	ml	g	mol%	%	dl g ⁻¹		MW	
1.0	0.0013	0.094	10	20	1.51	57	6	0.45	27,200	22,500
1.0	0.0013	0.14	15	15	1.88	67	6	0.52	32,000	26,600

Polymerization condition: H.P.-Hg Lamp > 300 nm for 1 h at 25°C.

^a Calculated from NMR.

^b By GPC calibrated for polystyrene.

^c Calculated from NMR results, assuming a diblock PC-PV structure.

Figure 6. Photolysis of BME-polycarbonate. a) in absence of monomer. Curve PC represents the blank exp. without BEM group. b) in the presence of methyl methacrylate.

methacrylate.

Figure 7. Polymerization of methyl methacrylate photoinitiated with BME-PC. Dependence on monomer concentration. *t*, 25°C. solvent, dichloromethane.

transition domains corresponding to PMMA and to partially crystalline PC at 90 and 176°C, respectively. The high efficiency of this photochemical block polymerization was confirmed with many other vinyl monomers and will be reported later. This photochemical method permits a regulation of block lengths, the poly(bisphenol-A carbonate) ones by the BME-content, and the polyvinyl block by the polymerization conditions. Its high efficiency makes this method preferable to the thermal decomposition of incorporated azogroups, as was recently described by Ueda and Nagai in the case of polyamide, where the original chain lengths are modified by recombination of radicals and the initiation efficiency towards styrene was as low as 15%.¹⁴

In this first example of block polymerization, the basic principle of the synthesis was the incorporation of a photolabile group within a condensation polymer. If however two different polyvinyl sequences are desired, the photochemical method has to be adapted to this new problem by using an heterofunctional initiator, *i.e.*, an initiator containing two different thermo- or photolabile groups which differ sufficiently in their decomposition activation energy or selective light absorption to permit a two step synthesis.

In our knowledge Ivanchev and coworkers¹⁵⁻¹⁹ were the first to use oligoperoxides with peroxidic linkages of different stability, *e.g.*, diacylperoxide, α -substituted diacylperoxides, peresters etc. Thus by reaction of nonanedioic peracid with 2-bromo-nonanedioyl dichloride, they obtain following oligoperoxide:

Considering that the α -bromoperoxide has a decomposition activation energy of 95.7 kJ mol^{-1} and the unsubstituted one of 123.3 kJ , it is assumed that the difference of 27.6 kJ mol^{-1} is sufficient to enable the 2-step synthesis of styrene-methyl methacrylate block polymers. The higher the degree of polymerization x of the oligoperoxide, the higher the yield of block polymer.

An alternative method which does not require this difference of activation energies is based on the selective photochemical decomposition of one of the groups of the heterofunctional initiation, *e.g.*, azo-nitrile groups incorporated in an azo-oligo-peroxide.²⁰ Such compound can easily be prepared by reaction of hydrogen peroxide with 4,4'-azobis(4-cyanopentanoic acid chloride):

The difference of thermal stability between the azo- and peroxidic groups is low; their activation energies of decomposition is 113 kJ (27 kcal) and 130 kJ mol^{-1} (31 kcal) respectively, and at 70°C the azo group decomposes about four times slower than the peroxides. However selective photolysis of the azo groups at 350 or 371 nm in the presence of styrene permits to obtain a styrene prepolymer containing acyl peroxidic groups. The number of these groups per molecule was evaluated from the ratio $(M_{no}/M_n) - 1$ where M_{no} and M_n designate the number average molecular weights before and after thermal decomposition in boiling chlorobenzene; it amounts to 0.64 to 0.87. This peroxidic polystyrene prepolymer was dissolved in tetrahydrofuran or in trichlorobenzene and used for the free radical polymerization of vinylchloride at 75°C . After reaction the product mixture was extracted for polystyrene and separated by preparative GPC. Some results are summarized in the following Table VII.

As expected on the basis of the low peroxide content (0.61–0.64) the reaction product contains inert polystyrene. On the other hand homopoly(vinyl chloride) is always formed mainly by chain transfer with the monomer, while the relative importance of transfer with solvent appears from the comparison THF/TCB. Figure 8 shows the GP-chromatograms with infrared detector equip-

Table VII. Block polymerization of peroxidic styrene prepolymer with vinyl chloride^a

	Tetrahydrofuran	Trichlorobenzene
M_{no}	102,500	50,000
$(M_{no}/M_n) - 1$	0.64	0.61
VC/ml	80	50
Solvent/ml	20	35
React. Product		
VC %	40	54
Polystyrene	45 (66,700) ^c	31 (36,900)
PVC + block polymer ^b	55 (42,200)	69 (39,700)
PVC	18	20
Block	37	49
Prepolym. in block	25	33

^a t , 70°C , 4 h with 3 g prepolymer.

^b The separation of PVC and block polymer by preparative GPC is uncomplete and reflects also differences in molecular weight instead of chemical composition.

^c The values between parentheses indicate number average molecular weight of the polystyrene or of the PVC + block polymer mixture.

ment of the PVC block polymer mixture (after extraction of homopolystyrene with cyclohexane). It can be seen that the polystyrene blocks are more concentrated in the high molecular fractions, while the lowest fractions are homopoly(vinyl chloride),

Figure 8. Gel permeation chromatograms with infrared detector of PVC-block polymer mixture prepared in tetrahydrofuran (A) and in trichlorobenzene (B).

and that the polystyrene is more homogeneously distributed in the reaction product obtained in trichlorobenzene.

Similar photochemical essays have been carried out with di-*t*-butyl 4,4'-azobis(4-cyanoperoxy-pentanoate) instead of an oligoazoperoxide initiator. This initiator, prepared by reaction of the corresponding bisacid chloride with *t*-butyl hydroperoxide,

is easily soluble in styrene monomer and can be obtained with a high degree of purity (>99%). Photolysis at 367 nm in the presence of styrene monomers gives a telechelic polystyrene with two perester end groups; its composition determined by ^{13}C NMR corresponds to 2 perester for 242 styrene units, which is in fair agreement with the number average molecular weight 25,600 (246 units) as determined by GPC. This photochemical method for the synthesis of the ω,ω' -bisperoxy-polystyrene has to be preferred to the thermal and redox methods described by Piirma and Chou²¹ because it offers a well defined and pure polymeric initiator. On heating at 95°C in the presence of methyl methacrylate

block polymers are obtained in high yield without residual homopolystyrene. In this context mention should be made of the similar bifunctional initiator prepared by Simionescu *et al.*²² carrying two acyl peroxides, *e.g.*, *m*-chlorobenzoylperoxidic groups instead of peresters. So far however no block polymers were described.

III. PHOTOCHEMICAL INTERACTIONS AND CROSS-LINKING OF EDA-COPOLYMERS

Interactions between electron donor (D) and electron acceptor (A) groups along a copolymer chain give on photoexcitation excited EDA-complexes, with ion-radicals pair formation.

p-Vinylbenzophenone (VB) and *p*-dimethylaminostyrene (DAS) can easily copolymerize and form EDA-copolymers where the phenone is the electron acceptor (A) and the tertiary amine the electron donor (D). In principle the reaction mechanism is similar to that described above for the photodegradation reaction of polyethyleneimine in the presence of benzophenone. In the present case however excited EDA complexation involves an intramolecular instead of a bimolecular process; moreover the tertiary aryl dimethylamino group is a much better donor group on account of its aromatic substitution. Finally combination of the radicals after H-exchange results in cross-linking.^{23,24}

Absorption (at room temperature) and emission (at 77 K) spectra of copolymers show a pronounced tendency on complex formation. Mixtures of the two homopolymers PVB and PDAS and mixtures of the model compounds, 4-methylbenzophenone (MBP) and *N,N*-dimethyltoluidine (DMT) do not show intermolecular complex formation. At MBP concentration 10^{-3} molar, a high amine concentration (1.5 molar) is needed for observing some red absorption shift. On the contrary copolymers show the existence of a new absorption band, even in high diluted benzene solution (10^{-4} molar of both D and A groups); its optical density increases with increasing DAS-content. On the other hand the intensity of the emission spectra in methyltetrahydrofuran of a co(VB79-DAS21) polymer is much higher than that of PVB in the presence of 10 vol% dimethylaniline, though the concentration of amines in the copolymers is 1,000 to 10,000 times lower than that of the dimethylaniline (Figure 9).

Figure 9. Emission spectra of copolymer (VB79-DAS21): b_3 and difference spectrum: c_3 and of polyvinylbenzophenone: a , and of polyvinylbenzophenone (PVB) in 1 volume dimethylaniline/9 volume methyltetrahydrofuran. [VB], 4.8×10^{-3} ; t , 77 K; λ_{exc} , 365 nm.

Figure 10. Emission spectra of PVB (4.8×10^{-3}), methylbenzophenone (1.7×10^{-3}) and copolymer (VB53-DAMS47) at [VB]: 5.4×10^{-3} , t , 77 K; λ_{exc} , 335 nm; solvent, methyltetrahydrofuran.

It can be shown that the emission spectrum of the copolymer results mainly from the emission of the photoexcited complex. This tremendous difference in phosphorescence intensity between the two systems must be attributed to the high local concentration of both D and A groups and particularly the high crossed dyad concentration in the copolymer. In this context it may be interesting to mention that copolymers of VB and *p*-dimethylaminomethylstyrene ($((CH_3)_2NCH_2-C_6H_4-CH=CH_2)$) show no clear evidence of complexation between D and A units; the emission spectrum of a co(VB53-DAMS47) polymer is similar to

Figure 11. Plot according to dyad complexation equilibrium equation.

Figure 12. Benesi-Hildebrand plot for 4-methylbenzophenone and *N,N*-dimethyltoluidine.

that of PVB (Figure 10).

These absorption and emission spectra observations justify the use of crossed dyad concentration for calculating the complexation equilibrium constant instead of the overall D and A concentrations.

Assuming the equilibrium $Dy \xrightleftharpoons{K} complex$ one obtains the equation $K = [C]/([Dy]_0 - [C])$ where $[Dy]_0$ is the initial dyad concentration and $[C]$ the concentration of complex at equilibrium. The equilibrium constant is in this case dimensionless. Since $[C] = [OD]_c/\epsilon_c$, $[OD]_c$ and ϵ_c being the optical density and extinction coefficient of the complex, by substitution one obtains the final equation $[OD]_c = \{\epsilon_c / (1 + (1/K))\} [Dy]_0$. $[Dy]_0$ is the product of the crossed dyad probability $P_{(1,2)}$ ²⁵ and the mean average

concentrations of both D and A components, *i.e.*,

$$([Dy]_0 = ([A]_0 + [D]_0)/2)P_{(1,2)}$$

Plotting $[OD]_e$ against $[Dy]_0$, a slope equal to $\epsilon_c/(1+(1/K))=350$ is obtained (Figure 11). Assuming $K=1$, $\epsilon_c=700$ (at 340 nm). For the model compounds MBP and DMT, on the basis of the classical Benesi-Hildebrand²⁶ equation $\epsilon_c=400 \pm 100$ and $K_c=0.07$ (in mol^{-1}) at 367 nm (Figure 12).

If one considers terpolymers VB, DAS, and methyl acrylate locally excited state benzophenone emission is clearly observed; difference spectra show nevertheless always the presence of excited state complexes as well. Even in a terpolymer co(VB8, DAS5, MA87) polymer, where the D and A groups are practically isolated from each other by the high MA content, and where the structural dyad probability is negligible, phosphorescence emission is still observed. The participation of remoted A and D groups to complex formation has therefore to be taken into account.

As pointed out above excited state complexation should be followed up by H-exchange within the radical-ions pair, and formation of free radicals. It is their combination that results in crosslinking. It was therefore interesting to study the formation of radicals in a film of terpolymer (VB47, DAS14, BuA39) in function of the time of irradiation, and their subsequent decay. EPR measurements have been carried out at 20°C and 79°C, *i.e.*, below and above the glass transition temperature of the terpolymer (T_g 64°C). The plots of the radical concentration according to a simple second order kinetics show two successive phases (Figure 13). The use of the integrated equation of Waite for diffusion controlled reaction,²⁷⁻³⁰ namely

$$\frac{1}{C} - \frac{1}{C_0} = 4\pi r_0 D + 8r_0^2 \sqrt{\frac{D}{t}}$$

by plotting the left hand term against $1/t^{1/2}$ permits to evaluate the characteristic parameters of the system, namely the radius of the kinetic cage r , the diffusion constant D and the lifetime of the radicals in the cage. In this expression C_0 and C are the concentration of the radical at time 0 and after decay time t (Figure 14). The results are given in Table VIII.

Experiments carried out by incorporating 4-hydroxy-2,2,6,6-tetramethylpiperidinoxy radicals

Figure 13. Radical decay with time. Second order kinetic plot.

Figure 14. Radical decay with time following Waite's equation.

Table VIII. Kinetic parameters of radical decay in terpolymer (VB41, DAS14, BuA39) film^a ($T_g=64^\circ\text{C}$)

	20°C	79°C
k_D in $\text{mol M}^{-1} \text{s}^{-1}$	0.03	0.13
D in $\text{cm}^2 \text{molecule}^{-1} \text{s}^{-1}$	8×10^{-18}	4.1×10^{-12}
r_0 in Å	55	43
τ in s^{-1}	120	14

^a k_D , rate constant of diffusion.

(nitroxyl $1.2 \times 10^{-3} \text{ M}$) in the film permitted also to follow the rate of formation of radicals and their diffusion out of the cage by measuring the decrease of total radical concentration with the time of irradiation. Figure 15 represents the change above and below T_g at high intensity of irradiation. Again the importance of the physical state of the matrix is evident. Cage recombination of radicals produced in the film must be very important; it explains that the rate of cross-linking is apparently insensitive to

Figure 15. Change of total radical concentration in terpolymer in the presence of nitroxyl free radicals (1.2×10^{-3} molar) at 20 and 79°C.

air oxygen, and in large limits independent of the film composition.

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