PHOTOCHEMICAL REACTIONS ON POLYMERS

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Abstract – Between the several polymer photocross-linking processes, free radical
reactions remain very important. Two main cases are considered successively. In the
first process, photocross-linking results from the photoinitiated free radical poly-
merization of methacrylic side groups attached to copolymers of butyl-methacrylate
and glycidylmethacrylate after reaction with methacrylic acid. The kinetics of photo-
cross-linking in the solid state of copolymers with different content of unsaturated
groups (from 11 to 51 molar %) were followed by differential scanning calorimetry,
infrared spectrometry and by gravimetry, and the results of these methods compared to
each other. In the second case, photocross-linking results from the formation of photo-
excited electron-donor -acceptor complexes, in which hydrogen exchange may occur with
formation of free radical. Several copolymers of vinylbenzophenone and p.dimethyl-
aminostyrene were used and their solution behavior on irradiation considered by ultra-
violet absorption, phosphorescence emission spectrometry, and by gel permeation chroma-
tography. The influence of the copolymer composition on chain degradation and branching
during irradiation was taken in evidence. Similarly the rate of insolubilization in
solid state was studied in function of the copolymer composition and irradiation con-
ditions.

INTRODUCTION

Several processes of photocross-linking of polymers are based on the photodimerization of unsa-
turated groups (e.g. cinnamic esters and homologs) giving rise to cyclobutane cross-links (1,2)
and on the photodissociation of light labile groups as diazoketones and azides giving rise to
highly reactive carbene and nitrene species (3,4).

In the present lecture attention will be focussed mainly on photoinitiated free radical pro-
cesses. In such cases photocross-linking may result from the free radical polymerization of
unsaturated side groups attached to the polymer molecule in the presence of a suitable photo-
labile initiator; e.g. side acrylic (methacrylic) groups, eventually in combination with
plurifunctional monomers, in the presence of a benzoin ether (5). Such processes can be
compared with the photoinitiated cationic polymerizations of side oxirane groups, possibly
in combination with bis-epoxides in the presence of photolabile onium salts, which on photolysis
produce Brönsted or Lewis acids as cationic initiator as reported previously (6,7).

Special attention will also be devoted to photocross-linking reactions resulting from the inter-
action of electron donor and electron acceptor side groups attached to a copolymer backbone.
On irradiation photoexcited electron donor-acceptor (EDA) complexes are formed, in which
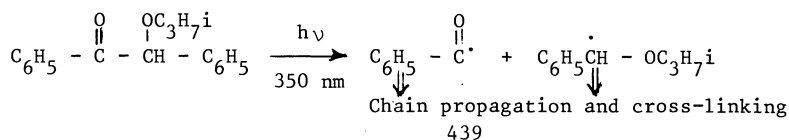hydrogen exchange proceeds and results in cross-linking by free radical combination.

Both reaction principles will be considered successively.

1. PHOTOCROSS-LINKING BY FREE RADICAL CHAIN POLYMERIZATION

Unsaturated polymethacrylic esters were synthesized by free radical copolymerization of n-butyl-
methacrylate and glycidyl methacrylate, followed by reaction of the epoxide groups with metha-
crylic acid. This synthesis is represented in following reaction scheme, as expressed in
Fig.1.

Thus four copolymers containing 11, 22, 40 and 51 mole percent pendant methacrylic groups
were obtained.

Their photoinitiated polymerization was studied in solid state in the presence of benzoin
isopropyl ether (3 wt.%) as photolabile initiator ($\lambda_{irr.}$ 350 nm).

$$C_6H_5 - \overset{\overset{O}{\|}}{C} - \overset{\overset{OC_3H_7i}{|}}{CH} - C_6H_5 \xrightarrow[350 \text{ nm}]{h\nu} C_6H_5 - \overset{\overset{O}{\|}}{C}{\cdot} + C_6H_5\overset{\cdot}{C}H - OC_3H_7i$$

Chain propagation and cross-linking

Kinetics of polymerization were followed by three different methods of which the data will be compared to each other, namely differential scanning calorimetry (DSC)   , infrared spectrometry (IR) and gravimetry.(8)
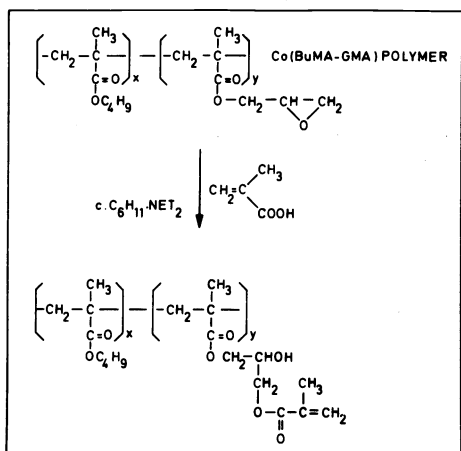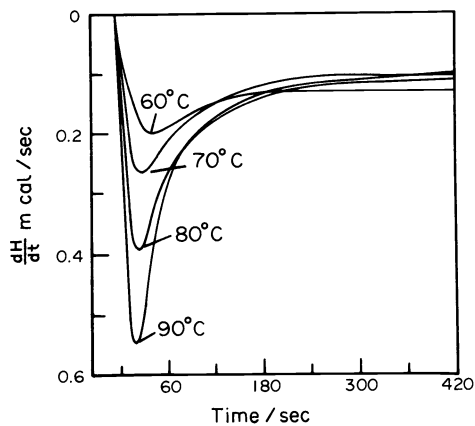

Fig. 1

Fig. 2

Fig. 1. Synthesis of unsaturated polymethacrylic esters.

Fig. 2. DSC-exotherms of copolymer IV_{51} at different temperatures.

a. Differential scanning calorimetry (9)

In this technique irradiation is carried out inside the sample holder covered with a quartz window. It was observed experimentally that a linear relationship exists between the content of methacrylic side groups and the initial rate by which the exotherm peak is reached, i.e. peak height divided by the time; these exothermic peaks can thus be considered as a measure of the relative rate of polymerization. Such measurements can be examplified by Fig.2 which refers to the cross-linking of copolymer IV_{51} at different temperatures, under nitrogen atmosphere.

This DSC-method presents the considerable advantage of its great simplicity; it lacks however accuracy at low degree of unsaturation of the copolymers. Moreover it must be noticed that the rate values have only a relative significance. The method has been used for the determination of the activation energy of polymerization by plotting the logarithms of the exotherm peak rates against ($\frac{1}{T} - \frac{1}{T_g}$) using the glass temperature T_g as reference temperature, as shown in Fig. 3.
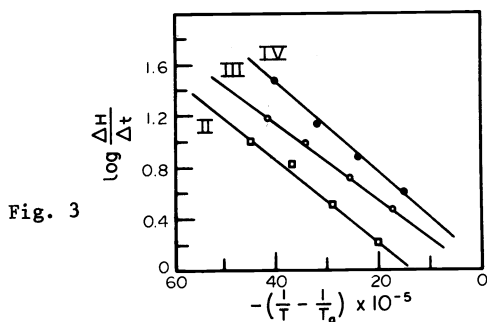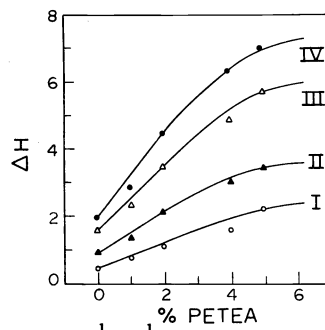
Fig. 3

Fig. 4

Fig. 3. Arrhenius-plot of DSC-exotherms against ($\frac{1}{T} - \frac{1}{T_g}$)

Fig. 4. Variation of DSC-peaks for copolymers I_{11}, II_{22}, III_{40} and IV_{51} in function of pentaerythritol triacrylate concentration.

For the three copolymers II_{22}, III_{40} and IV_{51} E_a varies between 14 to 15.5 Kcal/mol; consequently it is apparently unsensitive to the degree of unsaturation of the copolymers.

The great facility of this DSC-technique was also appreciated for measuring relative rates of cross-linking of films containing increasing concentrations of pentaerythritol triacrylate (PETEA) as represented in Fig. 4.

As expected the exotherms peaks are reached very rapidly; at constant PETEA content their ratio is nearly equal to the ratio's of the degree of unsaturation of the copolymers.

b. Infrared spectrometry

On the contrary to the previous method, infrared spectrometry permits the evaluation of overall rate constants of polymerization. It is based on the decrease of optical density at 1640 cm^{-1} (C=C stretching) in function of the time of irradiation, the carbonyl (C=O) band at 1735 cm^{-1} being choosen as internal reference. For conveniency, films (10 μm thickness) were casted directly onto the NaCl-plate.

Second order rate constants of polymerization were obtained by plotting the reciprocal of the molar concentration of double bond against the time. The data are summarized in table 1.

TABLE 1. Second order rate constant of polymerization[*]
       Influence of the degree of unsaturation

Copolymer % mole unsat.	k_2 $mole^{-1}$ 1 sec^{-1} x 10^5		
	30°C	60°C	
	air [a]	air [a]	N_2-atm. [b]
51	2.1	4.0	34.4
40	2.15	5	33.3
22	2.36	4.6	37.2
11	not determ.	5.8	45

[*] $1_{irrad.}$: a) 0.56 x 10^5 w.cm^2 b) 0.7 x 10^5 w.cm^{-2}

It must be observed that the rate constants vary only slightly with the degree of unsaturation. Their values are 7.5 to 8 times higher for the reactions carried out under inert nitrogen atmosphere than for air experiments. An apparent energy of activation of polymerization equal to 7.5 Kcal/mole was determined for copolymer II_{22} in air conditions by plotting log k_2 against ($\frac{1}{T_5} - \frac{1}{T_g}$). Noteworthy is the strong decrease of k_2 below T_g, e.g. 0.55 x 10^{-5} $mole^{-1}$1 sec^{-1} at 20° C; it results from the lack of mobility of the unsaturated side group.
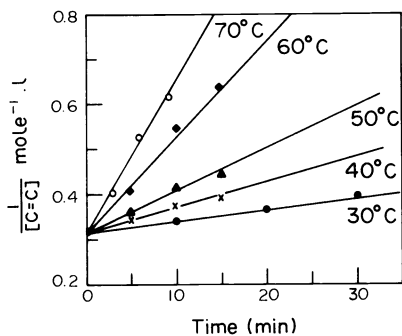

Fig. 5
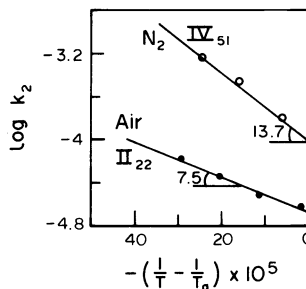

Fig. 6

Fig. 5. Second order plots of (C=C)$^{-1}$ unsaturation against time for copolymer IV_{51} at different temperatures. Film thickness : 10 μm . Nitrogen atmosphere.

Fig. 6. Influence of the temperature on the rate constant of polymerization of side groups of copolymers II_{22} and IV_{51} in solid state in air (●) and under nitrogen (o)

For irradiations under nitrogen,(Fig. 5) E_a equals 13.7 Kcal/mole in the case of copolymer IV_{51} (Fig. 6).

Considering however (as mentioned previously) that the rate constants are approximately independent of the degree of unsaturation, it must be concluded that the activation energy of cross-linking is higher under inert atmosphere than in air as a consequence of the easier diffusion of oxygen within the film than the diffusion of the side unsaturated groups.

c. Gravimetry

The gravimetric method is based on the determination of the increasing insoluble fraction of copolymer in function of the time of irradiation. While infrared spectrometry measures the residual unsaturation of the total irradiated copolymer (soluble and insoluble), insolubility already occurs when only few cross-links are formed. It must therefore be expected that rate constants of insolubilization should largely exceed those of photoinitiated polymerization.

This statement has been verified experimentally on films of copolymers containing 7, 11 and 22 mole % unsaturation. Here again second order plots were obtained; the rate constants are respectively 0.09, 0.07 and 0.063 $mole^{-1}$ l sec^{-1} (I_{irr} : 8.5 x 10^{-3} cm^{-2}) they decrease apparently with increasing unsaturation of the copolymer.

Taking account of the differences of irradiation intensities the rate constant of insolubilization has been estimated to be 10 to 15 times larger than the rate constant of polymerization.

From the comparison of these three experimental methods, it results that the gravimetric method is not only the most tedious one but gives also higher rate values compared to the IR-method. For evaluation of relative rate effects, the DSC-technique is particularly convenient.

2. PHOTOCROSS-LINKING THROUGH EDA-COMPLEXATION

The second photochemical cross-linking process to be considered is based on the interaction between electron donor (D) and electron acceptor (A) groups implanted along a polymeric chain. In these cases hydrogen atom exchange occurs within the photoexcited EDA-complex, giving rise to the production of two radicals, of which the combination results in cross-linking; no unsaturated side groups are required. The principle of the reaction is schematized in Fig. 7 for the case of benzophenone (A) and dimethylaminobenzene (D) as model compounds (10) for vinyl-benzophenone (VB) and dimethylaminostyrene (DAS) polymers and copolymers.

In order to understand this method more fundamentally, it is of great interest to examine the informations available from ultra-violet absorption and emission spectrometries as well as from gel permeation chromatography concerning the changes of molecular weight distribution in the course of the irradiation.
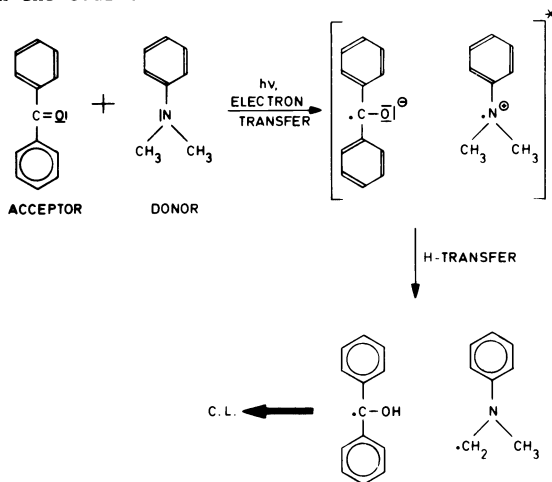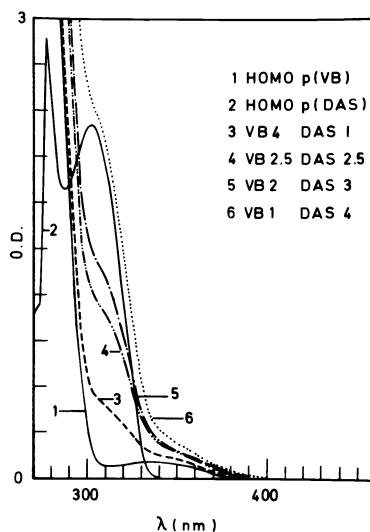

Fig. 7

Fig. 8

Fig. 7. EDA-complexation and hydrogen exchange reactions on irradiation.

Fig. 8. U.V. absorption spectra of vinylbenzophenone-dimethylaminostyrene copolymers. Influence of [DAS] concentration   [VB] = 6 x 10^{-4} mole 1^{-1}

a. Ultraviolet absorption spectrometry

Absorption spectra of mixtures of two homopolymers, polyvinylbenzophenone (PVB) and polydimethylaminostyrene (PDAS) in benzene solution do not show intermolecular complex formation at 10^{-5} concentration. At higher concentration polymer incompatibility causes precipitation. Mixtures of model compounds, 4-methylbenzophenone and dimethylaminotoluene behave similarly; only at high amine concentration (1.5 molar) broadening of the spectrum towards higher wavelength can be observed. On the contrary VB-DAS copolymers show a new absorption band around 340 nm even in dilute solution ([VB] = 10^{-4} mole 1^{-1}); its optical density increases with increasing DAS-content. (Fig. 8, curve 6). Formation of intramolecular EDA-complex in the ground state is evidently enhanced by the high crossed diad concentration. Using the equation

of Rose and Drago (11) and assuming that the product of donor and acceptor concentration $C_A C_D$ in this equation can be expressed in the present case by the structural diad concentration, a complexation constant equal to 29-30 $mole^{-1}$ 1. was evaluated with an EDA-complex extinction coefficient of 175 $mole^{-1}$.

b. Emission spectrometry

Exciplex emission of solution of PVB (4.8 x 10^{-3} molar) and dimethyl aniline (DMA) can be observed in methyl tetrahydrofuran at 77°K only at high amine concentration e.g. in MeTH containing 10 volume % DMA. Similar exciplex emission spectrum is observed in the case of a co(VB 79-DAS 21)polymer at the same VB concentration while (DAS) only equals 1.2 x 10^{-3}.

Incorporation of both groups in the same macromolecule favors intramolecular exciplex formation. Normalized emission spectra of PVB and of the copolymer are represented in Fig. 9. It shows that the contribution of the locally excited state benzophenone to the total emission of the
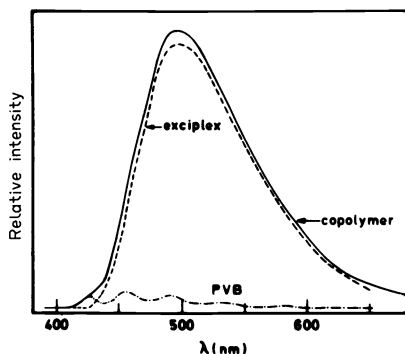

Fig. 9. Exciplex emission spectra of PVB and of Co(VB 79-DAS 22)polymer
at 77°K in methyl tetrahydrofuran. VB : 4.4 x 10^{-3} molar.

copolymer is very small, and consequently that the emission spectrum of the copolymer results essentially from excited state complexes.

In the case of terpolymers in which the VB and DAS units are diluted with methyl acrylate as a third monomer, intermediate cases are obtained. The presence of free locally excited state benzophenone is clearly observed in the total emission spectra, while the intensity of the excited state complex decreases, as expected, by increasing content of methyl acrylate. Even in the case of terpolymer II (Fig. 10) for which the crossed diad probability is almost negligible, remoted group participation in excited state complex formation must be admitted.
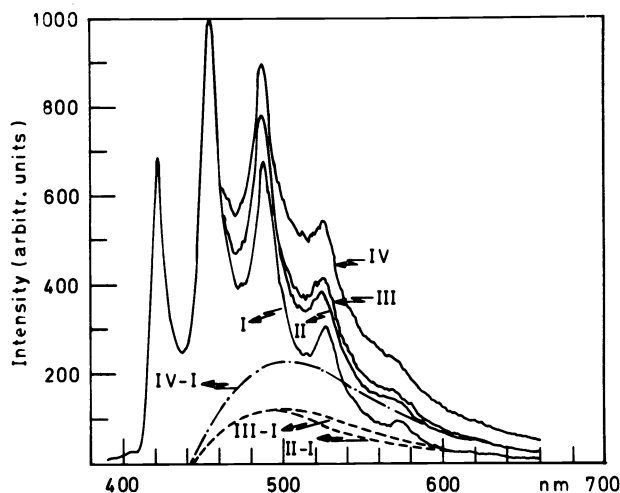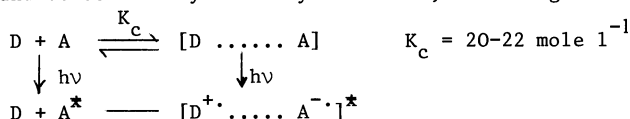

Fig. 10. Emission spectra of PVB and (methyl acrylate-VB-DAS) terpolymers.
$\lambda_{exc.}$: 350 nm   constant [VB] = 4.8 x 10^{-3} molar

Terpolymer composition :	VB	DAS	MA
II	8	5	87
III	13	8	79
IV	27	14	59

It must be however pointed out that formation of exciplexes may originate from the excitation of EDA-complexes preexisting in the ground state and (or) from excited triplet benzophenone with ground state dimethylaminostyrene units, following the reaction scheme :

$$D + A \xrightleftharpoons{K_c} [D \ldots\ldots A] \qquad K_c = 20\text{-}22 \text{ mole l}^{-1}$$

$$\downarrow h\nu \qquad\qquad \downarrow h\nu$$

$$D + A^* \longrightarrow [D^{+\cdot} \ldots\ldots A^{-\cdot}]^*$$

c. Gelpermeation chromatography

Exciplex formation is the first step in the photochemical cross-linking through EDA-complexation. The next step is evidently the hydrogen exchange within the exciplex leading to photoreduction of benzophenone groups by aromatic tertiary amines.

Preliminary experiments on 4-methylbenzophenone and p-dimethylaminotoluene have shown that the quantum yield of photoreduction of the phenone in benzene solution at room temperature is equal to 0.35 ± 0.04, and is independent of the phenone and tertiary amine concentrations. On the other hand, data's of Davidson(10) on the photoreduction of benzophenone with dimethylaniline indicate that 60 % of the phenone is transformed into benzpinacol and only 12 % in aminoalcohol, the cross-combination product, which can further dehydrate into enamine.
Similar radical processes will be admitted for our copolymers and will be responsible for intra- and intermolecular cross-linking reactions in the solid films.

It is however not possible to detect by infrared or NMR spectrometry structural differences between soluble and insoluble parts of the copolymers during and after irradiation. Nevertheless molecular weight changes are easily followed by GPC and must result necessarily from structural modifications of the copolymers.

The photolysis of a co(VB 53-DAS 47)polymer is represented in Fig. 11 in which the normalized GPC-curves show the changes of molecular weight and their distribution after 2 and 5 hrs. The increase of molecular weight results from chain branching by combination of radicals; further irradiation produces a large increase of gel formation while the soluble part shows some degradation. In these systems intermolecular cross-linking is largely predominant if compared to macrocyclization and/or chain scission.
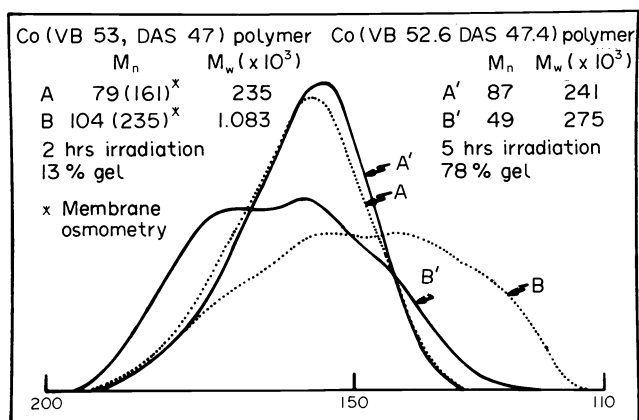

Fig. 11. Normalized GPC-curves of Co(vinylbenzophenone-dimethylaminostyrene) polymers before (A) and after (B) irradiation in benzene solution (2 wt.%). Influence of time of irradiation.

Changes of molecular weight before insolubilization have been followed in function of the time of irradiation (λ_{irr} 350 nm) for copolymers with different compositions in benzene solution, the concentration of VB-units at time zero (3.5×10^{-3} molar) being kept constant. The results are represented in Fig. 12 and can be summarized as follows :
i) at high phenone content M_w decreases in the begin of irradiation; the copolymers behave similarly to PVB, chain scission being predominant. Afterwards M_w increases by progressive branching.
ii) at high DAS-amine content M_w increases during the whole course of irradiation; branching reactions are prevalent.
iii) although Fig. 12 refers to copolymers of different initial molecular weights, a similar trend has been observed for three different copolymers of similar molecular weights of which the molar DAS-contents were 22, 47 and 74 %. In these cases the reciprocals of the incipient
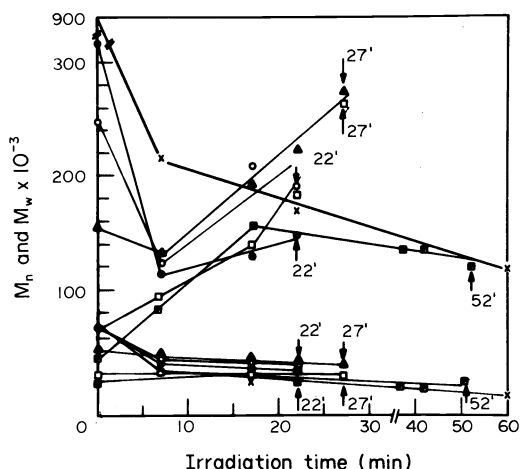
Fig. 12. Changes of molecular weight of polyvinylbenzophenone and
co(vinylbenzophenone-dimethylaminostyrene)polymers during irradiation
in function of time.
Molar percent VB : x-x-x 100; •-•-• 88.9; o-o-o 79.5; ▲-▲-▲ 52.6;
□-□-□ 25; ■-■-■ 16.5
Arrows indicate incipient gelation times.

gelation time were approximately proportional to the VB molar content of the copolymers.

From chemical point of view it is assumed that the excited triplet state of the carbonyl
group abstracts a hydrogen atom from the backbone of the polymer chain, when insufficient
H-donors or electron donor groups are present. It results in Norrisch II-chain scission,
even in a 4 weight % solution.

At high electron donor content, chain branching followed by gel formation prevails. It should
be noticed that these GPC-data, especially those related with chain degradation, have been
confirmed by intrinsic viscosity measurements. In the case of a PVB sample M_n, measured by
membrane osmometry, decreases on irradiation from 248.000 to 55.000 after 7 min. irradiation
time. Such results disagree with the interpretation of David and al. (12) concerning the
degradation of polyvinylbenzophenone, and should be compared with the data of Sanchez (13).

d. Photolysis of vinylbenzophenone-dimethylaminostyrene-Bu. acrylate terpolymers in solid
    state.
Copolymers (VB/DAS) present a high glass transition temperature and high absorption extinction
coefficient. Both properties make it difficult to prepare self-supporting films with an
adequate optical density. Therefore photolytic experiments were carried out on VB/DAS/butyl-
acrylate terpolymers. Cross-linking was followed gravimetrically i.e. by measuring the in-
creasing weight fraction of insoluble products. Worthwhile to mention is the small difference,
if any, between experiments carried out in air and under nitrogen atmosphere for the (BA 56-
VB 22-DAS 22) terpolymer. Oxygen exerces thus a small or negligible effect on the cross-
linking reactions on account of the competition between exciplex formation and oxygen quenching
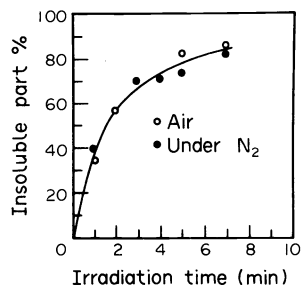(Fig. 13).

Fig. 13. Insolubilization with time of irradiation of co(BA 56-VB 22-DAS 22)
terpolymers.
λ_{irr} : 367 nm I_o : 4.7 x 10^{-3} wcm^{-2} o : air •:under N_2-atmosphere

The influence of the chemical composition of the terpolymers was examined in air conditions (18°C) with three polymers with about 50 mole percent butyl acrylate but varying ratios benzo-phenone/tertiary amine groups. Again the influence is rather weak; a high phenone content is apparently favorable but high degrees of insolubilization are reached in all cases (Fig. 14).
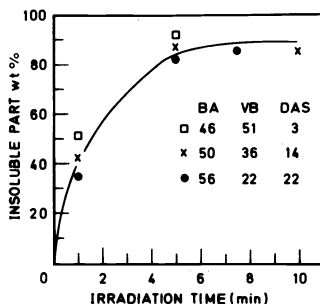

Fig. 14. Insolubilization with time of irradiation. Dependence on terpolymer composition.
λ_{irr} : 367 nm I_o = 3.5 x 10^{-3} wcm^{-2}

On the basis of Shultz equation (14,15) a quantum yield of cross-linking of terpolymer is estimated to 0.06.

CONCLUSION

Between the two free radical photocross-linking reactions which have been studied in solid state, the reaction based on the formation of photoexcited EDA complexes is practically unsen-sitive to air inhibition and to copolymer composition. On the contrary the reaction based on the photoinitiated polymerization of unsaturated side group shows a strong dependence of the content of unsaturated groups and is, as expected, air sensitive.

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