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Photocross-Linkable Polymers

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Several processes of photocross-linking of polymers are based on the photodimerization of unsaturated groups and on the photodissociation of light labile groups, such as azides. In the present paper we will consider three different methods of cross-linking:

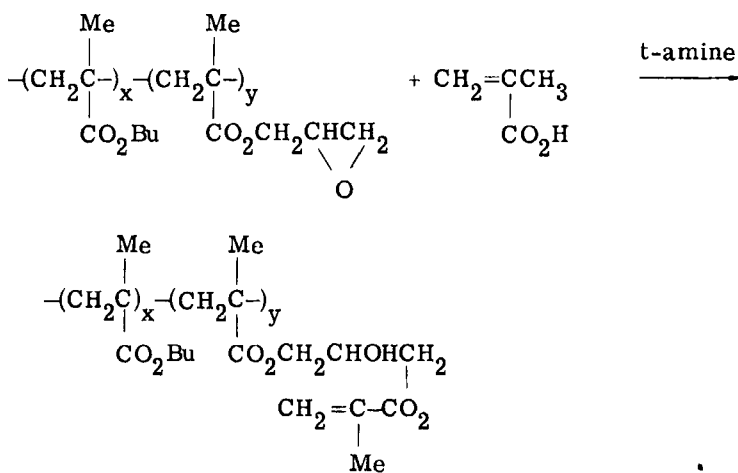
1. Photoinitiation of free radical polymerization of unsaturated side groups attached to a polymer molecule in the presence of a suitable photoinitiator, such as benzoin alkyl ether.
2. Photoinitiation of cationic polymerization of oxirane side groups in the presence of photolabile amine salts, such as diazonium salts, giving rise to the formation of Lewis acid.
3. Electron donor/acceptor complexation of side groups which on photoexcitation exchange an hydrogen atom; this results in cross-linking by free radical combination.

While the two first methods are based on the photochemical initiation of free radical/ionic polymerization processes, the third one involves an interaction of two donor and acceptor groups without any amplification phenomena.

These three different methods will be considered on the basis of recent experimental data which were obtained on solid polymer films. Finally some new perspectives will be commented on briefly.

PHOTOCROSS-LINKING BY FREE RADICAL
CHAIN POLYMERIZATION [1]

Unsaturated polymethacrylic esters were synthesized by reaction of methacrylic acid with copolymers of *n*-butyl methacrylate and glycidyl methacrylate. Their photoinitiation was obtained by photodissociation of benzoin isopropyl ether (350 nm) and the reaction followed by differential scanning calorimetry, infrared spectrometry, and gravimetry.



The DSC technique is based on the heat evolution rate resulting from the onset of polymerization. It was previously shown that a linear relationship exists between the unsaturated groups content and the initial rate by which the exotherm peak is reached. From the experimental point of view the irradiation is carried out directly under nitrogen atmosphere inside the sample holder; the method is very simple and facile and allows measurements of relative rates of cross-linking of small samples, eventually in the presence of polyfunctional unsaturated triacrylate. It is illustrated in Fig. 1 where the DSC exotherms of a copolymer containing 40 mol% unsaturation are represented in the presence of increasing pentaerythritol triacrylate concentration (Fig. 1). On the other hand, by working at different temperatures, an activation energy of 15 ± 0.5 kcal can be evaluated, independently of the degree of unsaturation of the copolymers.

The infrared spectrometry was used for obtaining more quantitative data. It is based on the decrease with time of the optical density of the C=C stretching band at 1640-^{-1} . The films were casted ($10 \mu\text{m}$) directly onto the sodium chloride windows. Surprisingly, the reaction follows second-order reaction kinetics, as can be seen from Fig. 2

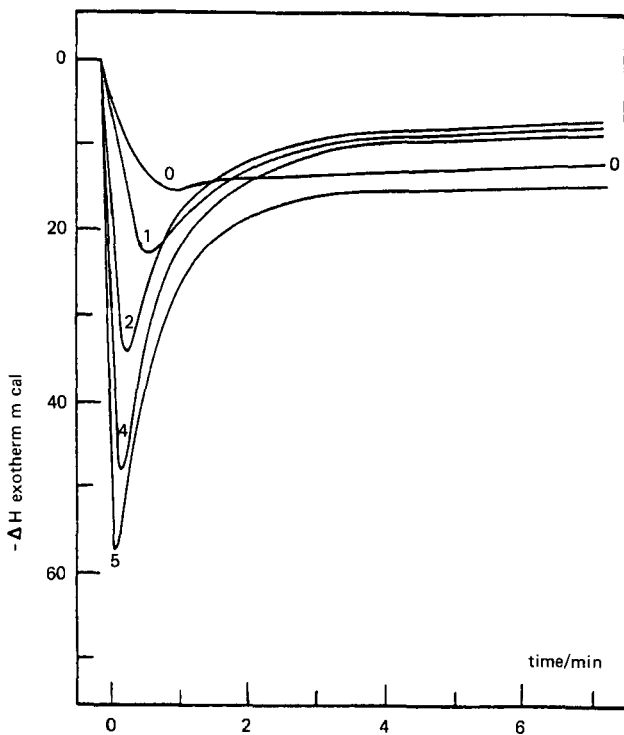


FIG. 1. Differential scanning calorimetry exotherms of copolymer-40% unsaturated, containing increasing concentrations of pentaerythritol triacrylate (0, 1, 2, 4, and 5 wt%): 60°C.

where the reciprocal of unsaturation content is plotted against time. The rate constants vary slightly with the degree of unsaturation; apparently they increase with decreasing unsaturation. Here again, an overall activation energy of 13.7-14 kcal is obtained for reactions under an inert atmosphere.

For comparison, cross-linking was also followed by the gravimetric method, i.e., by determination of the increasing insoluble fraction of copolymer with the time of irradiation. As could be expected, the rates of insolubilization exceed considerably (by a factor of 10-15) those determined by infrared.

Insolubility indeed occurs when cross-links are formed independently of the presence of pendent unreacted groups. Again, second-order kinetics are found and the rate constants apparently decrease with increasing unsaturation of the copolymer.

The second type of photoinitiated polymerization is represented by the cationic systems where polyglycidyl methacrylate and glycidyl

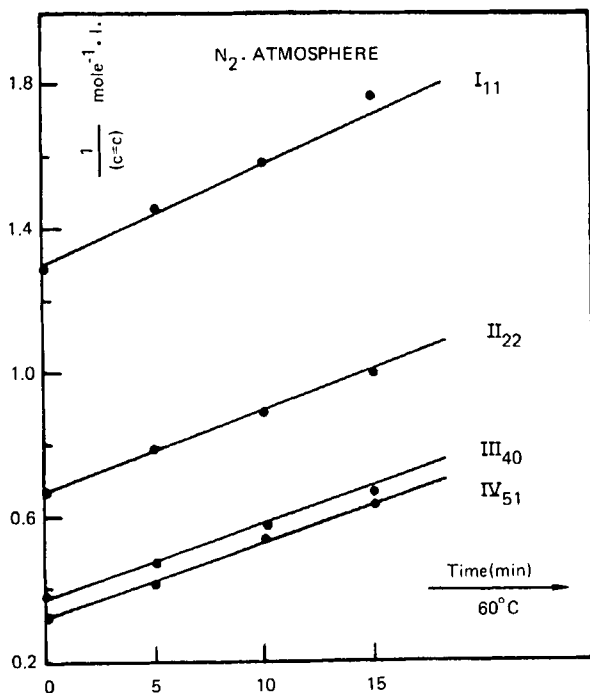
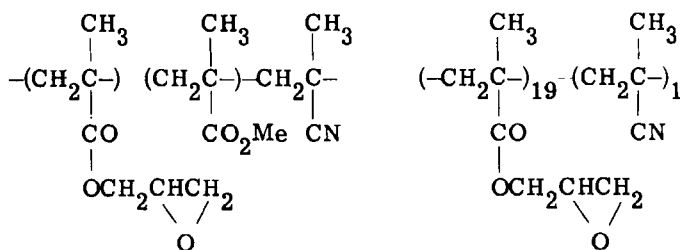
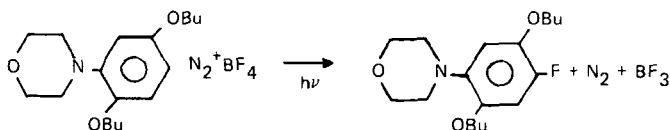


FIG. 2. Second-order diagram of the decrease of unsaturation (infrared) against the time for copolymers with 11, 22, 40, and 51 mol% side methacrylic groups.

methacrylate-methyl methacrylate copolymers are cross-linked in the presence of morpholinodibutyl-aryldiazonium tetrafluoroborate (MDBDZ) as light sensitive onium salts [2]. The polymers and copolymers always contained 5 mol% methacrylonitrile in order to improve the solubility of the diazonium salt in the film.



On irradiation with $\lambda_{\text{irr}} 404 \text{ nm}$, MDBDZ photolyses and yields a Lewis acid (BF_3) which is responsible for the cationic ring-opening polymerization of the oxirane groups and the resulting cross-linking.



The quantum yield of the decomposition of the diazo salt amounts to 0.5. This can be amplified considerably by a free radical chain mechanism if the reaction is carried out under an inert atmosphere. The cross-linking reaction necessitates after irradiation a thermal development at 70°C , i.e., above the glass transition temperature, in order to improve the diffusion of the boron trifluoride and the chain segment mobility. Figure 3 shows the progress of insolubilization with

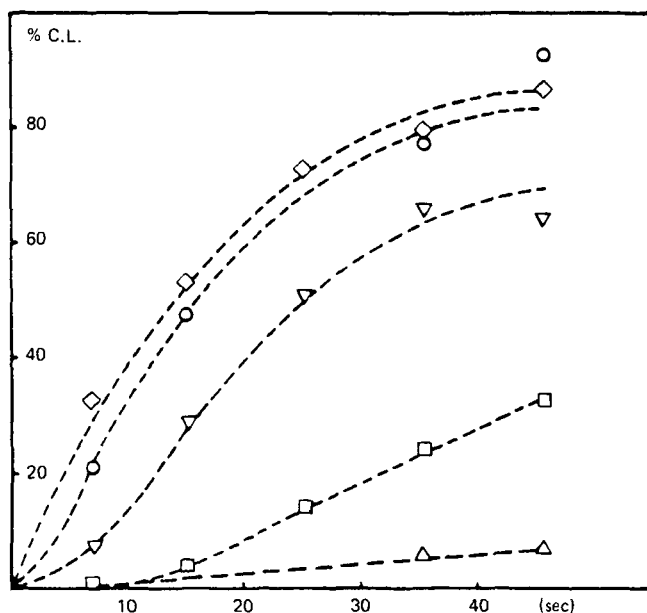
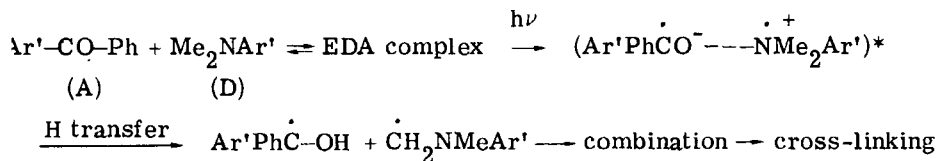


FIG. 3. Cross-linking of glycidyl/methyl methacrylate copolymers as a function of time of irradiation ($\lambda_{\text{irr}} 404 \text{ nm}$). Influence of the copolymer composition (% glycidyl side groups): (◇) 95, (○) 70, (▽) 50, (□) 20, and (△) 10%. Photoinitiator: MDBDZ-tetrafluoroborate.

the time of irradiation for five copolymers of different composition. It can be seen that copolymer 70 cross-links as efficiently as copolymer 95; copolymer 50 is, however, noticeably slower. A relatively high epoxide content is thus required for efficient cross-linking. The rate of cross-linking evidently depends on the nature of the diazonium cation and also on its complex anion.

Noteworthy indeed is that the ring-opening polymerization, i.e., the cross-linking efficiency, is higher with the tetrafluoroborate than the hexafluoroantimonate of the same diazonium cation. The reason for this effect again resides in the importance of the diffusion phenomena in solid films; the molecular volume of SbF_5 is evidently much larger than that of BF_3 and is more hindered in its diffusion into the epoxide. In solution experiments the reverse order is observed as indicated by Crivello and Lamm [3].

A third cross-linking process to be considered is based on the interaction between electron donor and electron acceptor groups attached as side groups along a polymeric chain [4]. In the present study copolymers of vinyl benzophenone (A) and p-dimethylaminostyrene (D) as well as their terpolymers with butylacrylate are considered and compared with the behavior of their model compounds, 4-methylbenzophenone (A) and p-dimethylaminotoluene (D). The basic principle of the cross-linking reaction is an hydrogen atom exchange within the photoexcited EDA complex with the production of two radicals; the combination of these radicals results in cross-linking. The reaction can be represented as follows for the model compounds:



where $\text{Ar}' = \text{p-CH}_3\text{-C}_6\text{H}_4$

EDA complex formation can easily be observed for vinylbenzophenone dimethylaminostyrene copolymers; a new absorption band is formed around 340 nm even in dilute solutions (vinylbenzophenone 10^{-4} mol/L). This absorption cannot be observed for mixtures of the two corresponding homopolymers or with dilute solution of the two model compounds. Only at high amine concentration (1.5 M) can broadening of the absorption be found. The formation of the intramolecular EDA complex in the ground state must therefore be admitted; it is evidently enhanced by the high crossed diad concentration. The complexation equilibrium constant was evaluated at 29-30 mol/L with the molar extinction coefficient around 175.

Incorporation of both donor and acceptor groups in the same macromolecule is therefore also favorable for the formation of intramolecu-

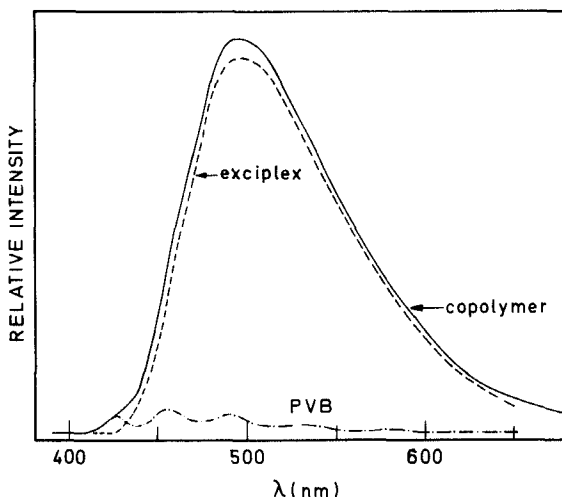


FIG. 4. EDA-complex emission spectrum of co(vinylbenzophenone-79-dimethylaminostyrene 21) polymer at 77 K in MeTHF. $[VB] = 4.4 \times 10^{-3}$, $[DAS] = 1.2 \times 10^{-3}$.

lar excited EDA complexes whose emission spectrum can be observed at low temperature.

Figure 4 shows the exciplex emission spectrum of co(vinyl benzophenone 79-dimethylaminostyrene-21)polymer in methyltetrahydrofuran at 77 K. The emission spectrum of homopolyvinylbenzophenone (at the same concentration of VB) is also shown; the contribution of locally excited benzophenone is almost negligible. The emission spectrum of the copolymer therefore corresponds to the excited EDA complexes.

In the case of terpolymers with methyl methacrylate in which vinylbenzophenone and dimethylaminostyrene are more or less separated from each other by dilution in the same macromolecule, intermediate cases are observed. Noteworthy is that even in the case of a terpolymer VB8/DAS 5/MA87 for which crossed EDA-diad probability is practically negligible, exciplex emission is nevertheless observed. Remote group participation in the excited state complex formation must therefore be admitted.

Exciplex formation is only the first step in the photochemical cross-linking process. It must be followed by hydrogen exchange in which the phenone is reduced by the tertiary amine. Measurements on the model compounds indicated a quantum yield of reduction of methylbenzophenone equal to 0.35. With the copolymers it is, however, not possible to detect by infrared or NMR spectrometry structural modifications caused by irradiation. Only modifications of molecular weight and

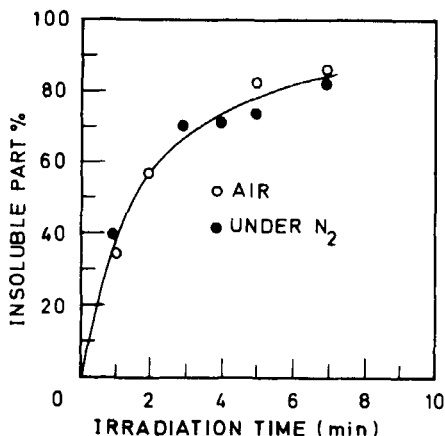


FIG. 5. Insolubilization of co(Bu acrylate 56-VB 22-DAS 22) polymers with time of irradiation (λ_{irr} 367 nm).

molecular weight distribution before insolubilization can be followed with gel permeation chromatography as a function of the time of irradiation. It was found that for copolymers with a high percentage of benzophenone units, the molecular weights first decrease by Norrish II chain scission. This decrease of molecular weight was confirmed by intrinsic viscosity measurements. Afterwards the molecular weight increases by progressive branching. On the contrary, at high dimethylaminostyrene units content the molecular weight steadily increases.

It is concluded that ultraviolet absorption and emission spectra as well as GPC measurements confirm the reaction scheme as written above, at least for solution experiments.

In the solid state, photolytic experiments were also carried out on vinylbenzophenone-dimethylaminostyrene-butylacrylate terpolymers. The presence of butylacrylate is required to obtain self-supporting films with an appropriate optical density. The cross-linking was followed by measuring the increasing weight fraction of insoluble material. It is remarkable that these solid-state reactions are practically insensitive to air inhibition as can be seen from Fig. 5 in the case of a co(Bu acrylate 56-VB 22-DAS 22) polymer. Radical combination probably follows H-exchange within the cage, and is therefore apparently not influenced by oxygen.

CONCLUSION

The present data obtained on solid polymer films clearly stress the influence of the reaction medium on the chemical cross-linking reac-

tions. While the diffusion of a Lewis acid onto the oxirane rings (the second method) necessitates thermal development for achieving rapid cross-linking, in the EDA complexation method the combination of radicals in the reaction cage increases considerably the cross-linking efficiency and makes it insensitive to the presence of air oxygen.

The same consideration applies to the photochemical degradation/depropagation of photolabile polymers even above their ceiling temperature. It can easily be shown experimentally that the quantum yield of chain scission is much lower or even insignificant in solid films while relatively high (0.5-0.8) in solution [5], and these discrepancies are again due to diffusion problems.

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