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Photocross-linking of polymers initiated by benzylsulphonium salts as cationic initiators

Part I *Poly(ethylene-co-glycidyl methacrylate)*

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Photocross-linking behaviour of poly(ethylene-co-glycidyl methacrylate) (EGMA) initiated by benzylsulphonium slats (BSS) has been investigated in relation to negative photoresist. Unlike triarylsulphonium slats which produce Brønsted acids, following the reaction with solvents or monomers, BSS directly produces benzyl cation on photoirradiation at > 300 nm and the resulting benzyl cation attacks the epoxy residues in EGMA to initiate cationic polymerization, leading to interchain cross-linking of the polymer. In this photocross-linking reaction, the efficiency was found to be so high that only 0.15 mol% BSS (based on the epoxy content in the copolymer) was enough to produce an insoluble network of the copolymer. This fact strongly suggests the presence of domains where the epoxy moieties and BSS are concentrated, thereby once initiating species (benzyl cation) are formed photochemically, the cationic polymerization takes place effectively in these domains.

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1. Introduction

Many studies have been conducted on photopolymers which exhibit changes in physical and chemical properties when exposed to light. These changes in properties are closely related to a development process in microlithography and many photopolymers have been used as photoresists in microimage fabrications. In negative photoresists, photocross-linking has been a major reaction to produce insoluble parts along the exposed sites because the first practical example of poly(vinyl cinnamate) [1, 2], in which cinnamoyl moieties in the side chains of polymers undergo interchain photodimerization to form cyclobutane structure. Thereafter, many chromophores which are capable of photodimerization have been examined as photofunctional groups in photoresists, such as chalcones, coumarins and styrylpyridinium salts [3].

Highly sensitive photoresists have been successfully prepared with the aid of photopolymerization. Photoirradiation of mixtures of binder polymers, such as poly(vinyl alcohol), polyamides and polyesters, and multifunctional acrylates containing photoinitiator results in photopolymerization of the acrylate monomers with simultaneous formation of insoluble networks where the binder polymers are included. Because this process involves a chain reaction (polymerization), a small amount of photoenergy is enough to produce a large change in the physical properties of the system. In this way, high sensitivity can be achieved [3].

Photocationic initiators possess an advantage over radical initiators in that curing can be performed in the presence of air. Since the first report on aryldiazonium salts by Schlesinger [4, 5], many photocationic initiators have been explored; diaryliodonium salts [4–8], triarylselenonium salts [9] and triarylsulphonium salts [10–12]. In diaryliodonium salts and triarylsulphonium salts, a C–I bond and a C–S bond are cleaved homolytically to produce Brønsted acids, following the reaction with solvents or monomers. The Brønsted acids thus formed can initiate cationic polymerization of various monomers such as epoxides, cyclic ethers, cyclic acetals and vinyl monomers. Furthermore, in the initiation process, it is reported that oxygen does not affect the quantum yield for the photodecomposition of the salts, and the effect of counter ions has also been investigated in full detail.

Recently, it has been reported that benzylsulphonium salts act as latent thermal cationic initiators, and they have been employed for curing of epoxides [13]. In addition to the thermal latency, their activities as photocationic initiators have been recognized and the cationic polymerization of epoxides with these salts has been conducted successfully under photoirradiation at > 300 nm [14]. The mechanistic studies of the photocationic polymerization of phenyl glycidyl ether with benzylsulphonium salts have revealed that the initiation species is benzyl cation produced by photodecomposition of the salts. This fact is in sharp contrast to the initiation mechanism of the diaryliodonium and triarylsulphonium salts which produce Brønsted acids as the initiation species.

In a series of studies on photocross-linking of polymers having polymerizable functional groups, we will

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explore the photocross-linking by means of benzylsulphonium salts as cationic initiators for various polymerizable groups. In the present paper, we report the photocross-linking behaviour of poly(ethylene-co-glycidyl methacrylate) in which the glycidyl moieties are expected to polymerize cationically to produce the cross-linking.

2. Experimental procedure

2.1. Materials

The benzylsulphonium salt used in this study, benzylmethyl-4-hydroxybenzenesulphonium hexafluoroantimonate (BSS; Fig. 9), was synthesized and purified as reported previously [13].

2.1.1. Poly(ethylene-co-glycidyl methacrylate) (PEGM)

The copolymer was prepared by radical polymerization. The molecular weight of the copolymer was determined by gel permeation chromatography (GPC) under the following conditions: solvent *o*-dichlorobenzene; temperature 135 °C; flow rate 1.0 ml min^{-1}; standard, linear polyethylene. The number-average molecular weight, M_n, and the polydispersity index thus obtained were 1.78×10^4 and 6.4, respectively. The composition of the copolymer was determined by ^{13}C NMR in *o*-dichlorobenzene at 80 °C and the content of the glycidyl methacrylate units in the copolymer was estimated as 3.4 mol % (15 wt %).

2.2. Method

2.2.1. Preparation of samples

Because the major component of the copolymer is poly(ethylene), the solubility of the copolymer in conventional solvents at room temperature was very poor. The copolymer was soluble in *o*-dichlorobenzene and toluene, but only at elevated temperatures. Cooling of the copolymer solution in hot *o*-dichlorobenzene or hot toluene to room temperature resulted in precipitation of the copolymer. At first, we attempted to prepare the copolymer films containing BSS by a casting method, but it was unsuccessful. Because of the thermal latency of the sulphonium salt, BSS decomposed in hot *o*-dichlorobenzene or in hot toluene. Then, we investigated an alternate way for the preparation of the sample films. BSS was soluble in dioxane, and chloroform showed high affinity toward the copolymer, leading to swelling of the copolymer surfaces to some extent; thus, we conducted incorporation of BSS into the copolymer by an immersion method. BSS was dissolved in dioxane/chloroform mixture and to this solution an appropriate amount of the copolymer film (100 μm thick) was immersed and left in the dark for 1 day at room temperature. The sample film was then taken from the immersion bottle and its surface was washed with dioxane to remove BSS from the sample surfaces. The sample films were finally dried under vacuum. The amount of BSS in the sample films was estimated by absorption spectroscopy on the basis of the molar extinction coefficient of the sulphonium salt separately determined in solution.

2.2.2. Photoirradiation

The sample films were irradiated in air using a 300 W high-pressure mercury lamp through a pyrex glass filter (> 300 nm) at room temperature.

2.2.3. Evaluation of photocross-linking

After photoirradiation, the sample films were subjected to spectroscopic measurements, infrared spectra (Jeol FT–IR 3505) and ultraviolet absorption spectra (Hitachi UV-320), in order to monitor the decrease in epoxy content (infrared) and BSS (ultraviolet), respectively. The thermal properties of the sample films were evaluated by differential scanning calorimetry (Seiko I&E SSC-5000) at a heating rate of 10 °C min^{-1}. At least four scans were performed for each sample to check reproducibility.

The change in epoxy content in PEGM on photoirradiation was also followed by chemical titration using the procedure outlined by Bell [15] with some modification. The titration procedure involved the reaction of epoxy group with pyridinium chloride, followed by titration of the excess pyridinium chloride with a standard base. The epoxy content of the sample was calculated from the difference between the titre and a control titre for the pyridinium chloride alone.

3. Results and discussion

3.1. Photodecomposition of BSS

Fig. 1 shows the change in absorption spectrum of BSS in ethanol (2.1×10^{-4} M) on photoirradiation. It is clearly observed that the absorbance at 255 nm (maximum) decreased on photoirradiation and an isosbestic point appeared at ~ 240 nm. A similar change in absorption spectrum was observed for BSS-doped in the PEGM films.

Fig. 2 shows the photodecomposition behaviour of BSS-doped PEGM films as a function of irradiation time, where the ratio of the absorbance at 255 nm of

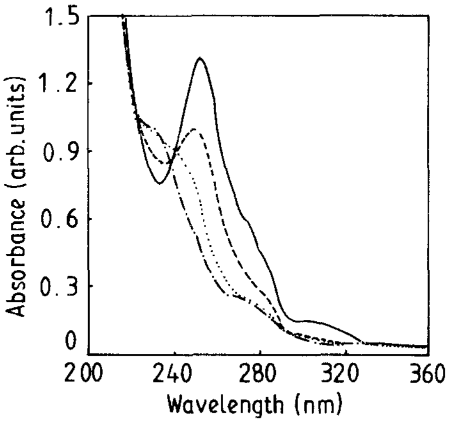

Figure 1 Change in absorption spectrum of BSS in ethanol on photoirradiation in air. Irradiation time: (——) 0; (– – – – –) 10; (·······) 30, (·—·—) 60 min. [BSS] = 2.1×10^{-4} M.

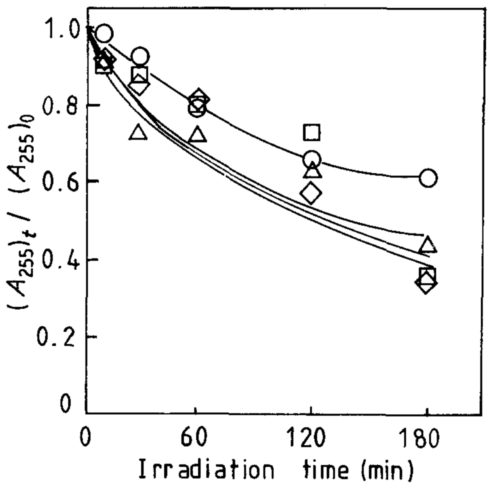

Figure 2 Photodecomposition behaviour of BSS-doped PEGM films as a function of irradiation time. Initial BSS concentration doped in PEGM: (○) 0.19 mol %; (△) 0.22 mol %; (□) 0.26 mol %; (◇) 0.29 mol %. The ratio of absorbance at 255 nm after and before photoirradiation, $(A_{255})_t/(A_{255})_0$, is plotted as a function of time.

t min irradiation, $(A_{255})_t$, to that before irradiation, $(A_{255})_0$, is plotted for samples with various initial BSS concentrations. These PEGM films with various BSS concentrations were prepared by immersing the PEGM film into BSS solution with various BSS concentrations while the immersion period was kept constant. The initial concentration of BSS was varied from 0.15–0.29 mol % on the basis of the glycidyl methacrylate units in PEGM. One may realize that the rate of photodecomposition as evaluated by the parameter $d[(A_{255})_t/(A_{255})_0]/dt$, is not affected significantly by the initial concentration at least in this concentration range, although a tendency is observed that the higher the initial concentration, the higher is the decomposition rate of BSS.

3.2. Photocross-linking behaviour

3.2.1. Solubility of irradiated samples

Although the solubility of PEGM film in conventional organic solvents was very poor at room temperature, PEGM became soluble in some solvents at elevated temperatures, as described before. In fact, PEGM was highly soluble in toluene at 80 °C. We examined the solubility of the PEGM film after photo-irradiation in order to confirm qualitatively the photocross-linking. In the absence of BSS, the PEGM film was soluble in toluene at 80 °C after photoirradiation for 3 h, indicating the non-occurrence of the cross-linking. On the other hand, in the presence of BSS, the film became insoluble and there was no soluble parts at all even after 10 min irradiation. It must be mentioned here, however, that in the presence of BSS the PEGM film became insoluble in toluene at 80 °C even when it had been left in the dark. This is simply because BSS acts as a latent thermal cationic initiator, so that curing of the epoxy rings can take place at 80 °C through thermally generated benzyl cations, leading to the cross-linking of PEGM.

3.2.2. Change in infrared spectra

Fig. 3 shows the change in infrared spectra before and after photoirradiation. It can clearly be observed that the peaks due to epoxy C–O stretching vibrations, 846, 912 (epoxy 11 μm band) and 763 cm^{-1}, decreased after irradiation and new peaks appeared at 3450 cm^{-1} (O–H stretching) and at 1050 cm^{-1} (C–OH stretching). Coupled with the results obtained from the ultraviolet absorption spectroscopy and the solubility test, this result indicates that photoirradiation of the PEGM film containing BSS resulted in decomposition of BSS, producing the initiation species which then reacted with epoxy groups in PEGM to bring about cross-linking with simultaneous formation of products having a COH moiety. Figs 4–6 show the intensity ratio of the peak at 912 cm^{-1} (epoxy 11 μm band), $(I_{912})_t/(I_{912})_0$, at 3450 cm^{-1}, $(I_{3450})_t/(I_{1380})_t$, and at 1050 cm^{-1} (C–OH), $(I_{1050})_t/(I_{1380})_t$, respectively, as a function of irradiation time. Choice of the peak at 1380 cm^{-1} as an internal standard for the determination of the concentration of the photoproduct(s) is based on the fact that it does not change on photoirradiation. Clear correlation can be recognized that the concentration

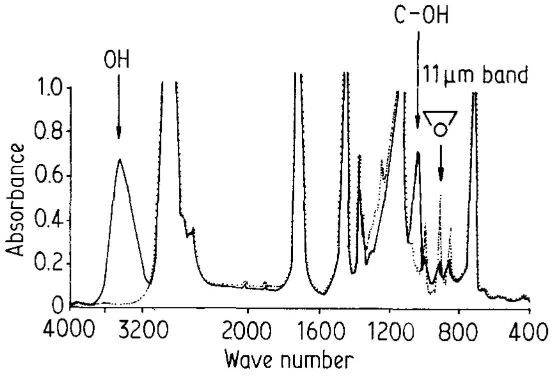

Figure 3 FT–IR spectra of PEGM films containing BSS (···) before and (——), after 60 min irradiation.

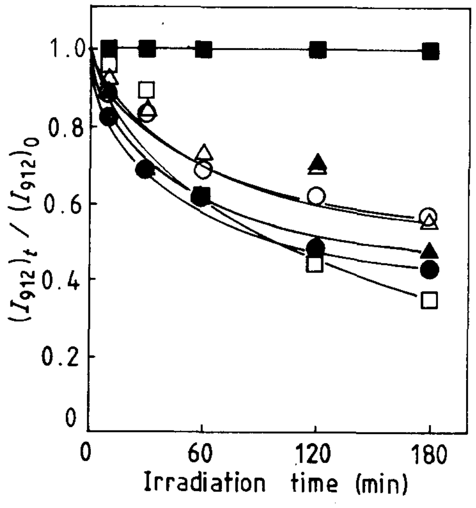

Figure 4 Change in the intensity of epoxy 11 μm band in the infrared spectrum on photoirradiation. Initial BSS concentration doped in PEGM: (■) without BSS; (○) 0.15 mol %; (△) 0.19 mol %; (□) 0.22 mol %; (▲) 0.26 mol %; (●) 0.29 mol %. The ratio of absorbance at 912 μm after and before photoirradiation, $(I_{912})_t/(I_{912})_0$, is plotted as a function of time.

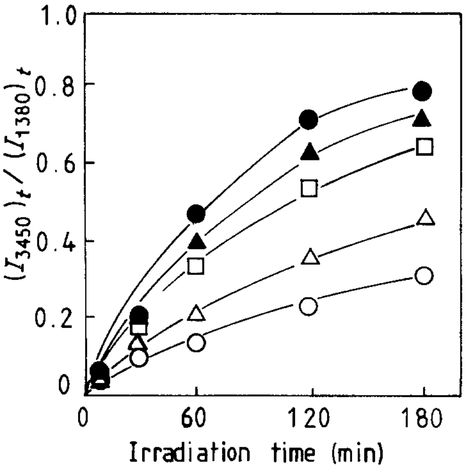

Figure 5 Change in the intensity at 3450 cm^{-1} in the infrared spectrum on photoirradiation. Initial BSS concentration doped in PEGM: (○) 0.15 mol %; (△) 0.19 mol %; (□) 0.22 mol %; (▲) 0.26 mol %; (●) 0.29 mol %. The ratio of absorbance at 3450 cm^{-1} to that at 1380 cm^{-1}, $(I_{3450})_t/(I_{1380})_t$, is plotted as a function of time.

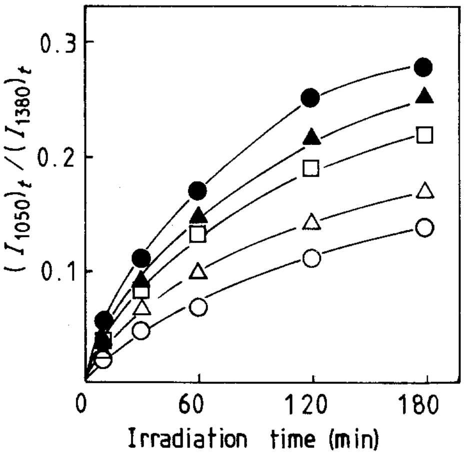

Figure 6 Change in the intensity at 1050 cm^{-1} in the infrared spectrum on photoirradiation. Initial BSS concentration doped in PEGM: (○) 0.15 mol %; (△) 0.19 mol %; (□) 0.22 mol %; (▲) 0.26 mol %; (●) 0.29 mol %. The ratio of absorbance at 1050 cm^{-1}, to that at 1380 cm^{-1}, $(I_{1050})_t/(I_{1380})_t$, is plotted as a function of time.

of the epoxy group decreases and that of product(s) with the COH structure increases on irradiation.

3.2.3. Change in epoxy content by titration

The epoxy content of the PEGM films containing BSS was measured at various irradiation times by the chemical titration method and the results are shown in Fig. 7, where the relative epoxy content estimated by the titration, as well as that by the infrared spectra, are indicated for comparison. These two values did not agree completely, probably because in the chemical titration method the formation of the network structure due to cross-linking affected the consumption of pyridinium chloride; thus, this method is accompanied by greater error than that of the infrared spectroscopy. However, it may be appreciated that the intensity ratio at the 11 μm band in the infrared spectra, $(I_{912})_t/(I_{912})_0$, reflects the epoxy content in the sample films rather satisfactorily.

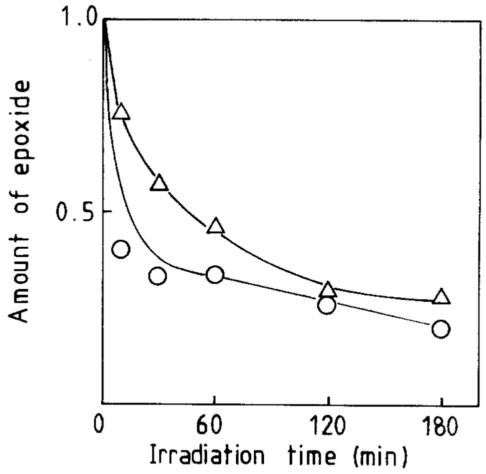

Figure 7 Change in epoxy content in PEGM films containing BSS on photoirradiation, (△) evaluated by FT–IR (○) evaluated by titration.

3.2.4. Thermal properties

Fig. 8 shows the DSC thermograms of PEGM films containing BSS at various irradiation times. Before irradiation, an endothermic peak was observed at 105 °C, which may correspond to the melting of the copolymer. After photoirradiation, the peak became broader while the peak maximum remained nearly at the same temperature. The broadening of the endothermic peak may be best interpreted in terms of network formation which produced a heterogeneous environment with respect to the mobility of the polymer chains and led to heterogeneous distribution of the endothermic event. The broadening of the endothermic peak after photoirradiation again supports the occurrence of cross-linking.

3.3. Mechanism of photocross-linking

Unlike the triarylsulphonium salts and the diaryliodonium salts which produce Brønsted acids, following

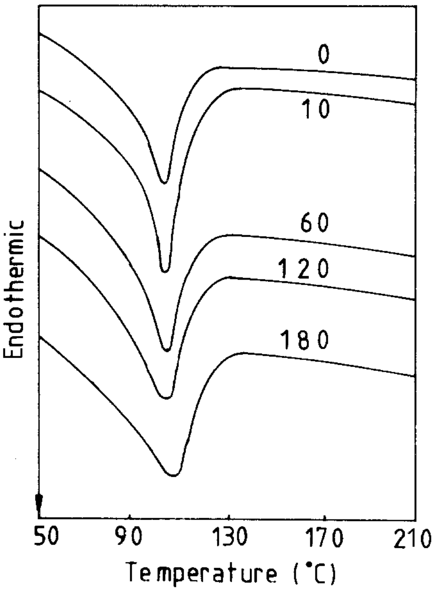

Figure 8 DSC thermograms of PEGM films containing BSS at various irradiation times. The numbers indicate the irradiation time (min).

the reaction with solvents or monomers, BSS produces benzyl cations directly from the photoexcited state. Although the photophysical properties of BSS have not been explored in detail at the present time in such aspects as what state is responsible for the generation of benzyl cations (single or triplet) and the quantum yield for the process, it is at least certain that the benzyl cation is formed by photoirradiation in air. The benzyl cation thus formed is expected to attack the epoxy rings to initiate the cationic polymerization. It is worth mentioning here that the efficiency of photocross-linking is quite high in the present system. The concentration of BSS is only 0.15 mol % based on the epoxy residue, of which the content in PEGM is 3.6 mol %, but cross-linking takes place effectively in the presence of air. It is true that only one covalent bonding between a pair of polymer chains is enough to form cross-linking of polymers; however, the efficiency of cross-linking in the present system is still regarded as quite high. Because of the nature of the two components in the copolymer, ethylene and glycidyl methacrylate, it may be expected that the glycidyl moieties tend to aggregate in the polymer solid. Furthermore, the photoinitiator, BSS, is an ionic species, thereby it is more stable thermodynamically in a polar environment. Therefore, if the glycidyl residues form a domain in which the fraction of the glycidyl moieties is high in the PEGM film, it is reasonably assumed that BSS is distributed in the polar domain and not in the ethylene-rich domain. Under such circumstances the photogenerated benzyl cations are expected to initiate the ring-opening reaction of epoxy rings quite effectively.

Another important point that must be discussed here is diffusion or mobility of the reactive species. In solution, reactants diffuse freely to collide with each other. However, in polymer solids, the diffusion of dopants is usually highly restricted, particularly below the glass transition temperature, T_g, of the polymers, so that bimolecular reactions are expected to occur very slowly [16]. Even unimolecular reactions are still depressed to some extent, depending on the activation volume (ΔV) of the reaction, although in the polymer matrix they are considered to take place at similar rates to those of solutions because they require no diffusion of the reactants [16]. It is well known that there are free volumes in the polymer solids. The size of the free volumes and their distribution depend on the nature of polymers, and these properties are closely related to the rate and the final degree of the unimolecular reactions in the polymer solids. In the present system, polymerization of epoxy groups is a bimolecular reaction, requiring the close proximity of a propagating species and an epoxy residue; thus, the high efficiency of photocross-linking observed for the present system strongly suggests the presence of domains where the photoinitiator and the epoxy residues are concentrated and the polymerization takes place without diffusion of the reactants.

The suspected mechanism of photocross-linking for the present system is illustrated schematically in Fig. 9. Although the degree of polymerization of epoxy groups is unknown, the propagating cation may be terminated with basic species, most probably water in air. This view is supported by the fact that on photoirradiation the amount of product having COH

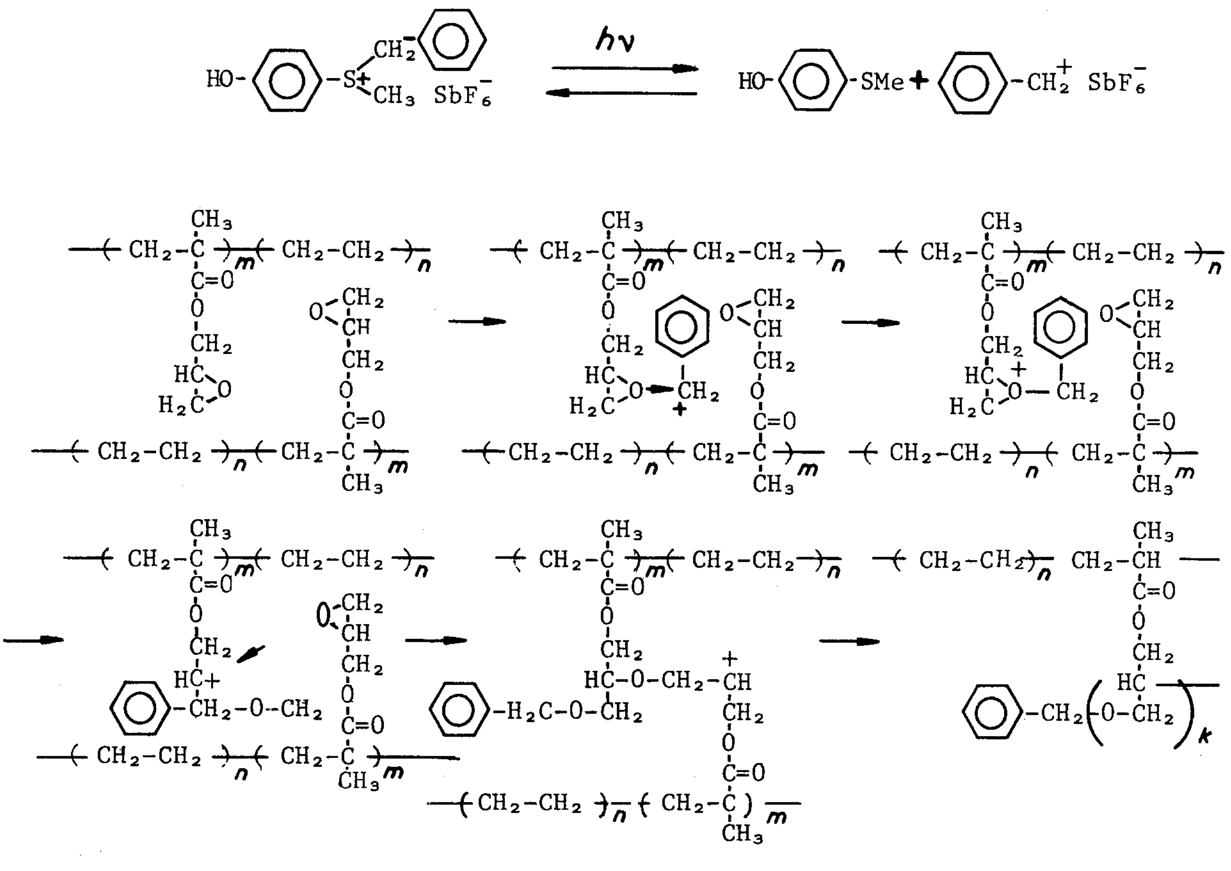

Figure 9 Schematic illustration of the photocross-linking mechanism.

moieties increases as evinced by FT–IR measurements (Figs 5 and 6).

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