

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

Part II *Poly(1,3-dioxolane-4-methyl methacrylate) and copolymers with methyl methacrylate*

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Photocross-linking of poly(1,3-dioxolane-4-methyl methacrylate) and copolymers with methyl methacrylate initiated by benzylsulphonium salt (BSS) has been explored. On photoirradiation, BSS directly produces benzyl cations which are capable of initiating cationic polymerization of side-chain cyclic ketals. The homopolymer and the copolymers were doped with BSS in the concentration range 0.05–5 mol % on the basis of the ketal units and the resulting films were irradiated at > 300 nm in air. The course of the photocross-linking of the sample films was followed spectroscopically by measuring the absorbance due to BSS (ultraviolet) and the absorbance due to dioxolane (infrared) as well as thermal analysis (differential scanning calorimetry) and chemical titration (ketal content). It was found that BSS is effective in inducing the cross-linking of the polymers, and the present system might be a promising candidate for a highly sensitive negative photoresist with an aqueous developing system.

1. Introduction

In a series of studies on photopolymers which exhibit changes in physical and/or chemical properties on photoirradiation, we explored in Part I the photocross-linking behaviour of poly(ethylene-co-glycidyl methacrylate) initiated by a photocationic initiator, benzylmethyl-4-hydroxybenzenesulphonium hexafluoroantimonate (BSS) [1]. Benzyl cations produced through photodecomposition of BSS attack the epoxy residues to initiate cationic polymerization, leading to interchain cross-linking of the copolymer. 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 [1]. Although the BSS/poly(ethylene-co-glycidyl methacrylate) system showed high sensitivity to incident light and excellent mechanical properties, poor solubility of the copolymer in conventional solvents owing to high contents of ethylene units (~ 96 mol %) will restrict the range of utility of this system to only a dry system where no developing process is required. Furthermore, the epoxy group used in this system as a functional group is subject to attack by both acidic and basic reagents; thus, for long-term stability of the copolymer, storage

in an acidic atmosphere or in a basic atmosphere must be excluded.

In the present paper, we report the photocross-linking behaviour of poly(1,3-dioxolane methacrylate) and copolymers with methyl methacrylate (MMA) initiated by BSS as a photocationic initiator. Choice of a cyclic ketal, 1,3-dioxolane, as a functional group is based on the fact that the cyclic ketal is very susceptible to attack by acids but is very stable in basic media. Furthermore, the solubility of the homopolymer and the copolymers with MMA in conventional solvents was high, and so sample films containing BSS could be prepared quite easily by a casting method. The copolymers were prepared in order to improve the mechanical strength of the sample films.

Another advantage of the present system may be possible development with acidic solution after exposure to light. Because the cyclic ketal is easily decomposed to ketone and diol in contact with aqueous acid, the homopolymer and the copolymers can be converted to water-soluble polymers by treatment with a dilute acid, unless they are cross-linked. Therefore, unexposed parts may be removed with a dilute acid, resulting in a cheap and nontoxic process in the development.

2. Experimental procedure

2.1. Materials

Benzylmethyl-4-hydroxybenzenesulphonium hexaflu-

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oroantimonate (BSS) was synthesised as reported previously [1].

2.1.1. Poly(2,2-dimethyl-1,3-dioxolane-4-methyl methacrylate) (I)

2,2-Dimethyl-1,3-dioxolane-4-methyl methacrylate (DDMMA) was synthesised by the method given by Roberts and Stille [2]. Polymerization was conducted in dimethylformamide (DMF) at 60 °C using azobisisobutyronitrile as an initiator. A polymerization tube was charged with 2.0 g monomer, 32 mg initiator and 10 ml DMF, and then degassed by several freeze-pump-thaw cycles under high vacuum, sealed off, and placed in a constant temperature bath at 60 °C. After 12 h, the polymerization tube was opened, and the reaction mixture was poured into an excess of methanol (100 ml). The precipitated polymer was filtered off, washed with methanol, and dried under vacuum. The polymer was purified by repeated precipitation from a methyl ethyl ketone (MEK) solution of the polymer into a large excess of methanol.

2.1.2. Poly(2,2-dimethyl-1,3-dioxolane-4-methyl methacrylate-co-methyl methacrylate) with various compositions (II-V)

Copolymers of DDMMA with MMA were prepared in a similar way to the homopolymer. Each polymerization tube was charged with the predetermined amount of DDMMA and MMA as listed in Table I, 2 mol % initiator (based on the total monomer concentration) and 10 ml DMF. Polymerization was carried out at 60 °C for 12 h. The copolymers were purified by repeated precipitation from the MEK

solution into methanol, followed by complete drying under vacuum.

2.2. Characterization of the polymers

The molecular weight of the polymers was determined by gel permeation chromatography (GPC; JASCO 880-PU; column, Shodex KF800P + KF802.5 + KF80M; eluent, chloroform) using a polystyrene standard. The values of the number-average molecular weight, M_n , of the homopolymer and the copolymers are listed in Table I.

Composition of the copolymers was evaluated by nuclear magnetic resonance (Jeol FX90Q) in dimethylsulphoxide- d_6 (DMSO- d_6) at 100 °C. Peaks due to α -methyl protons ($\delta = 1.1$ and 1.2 p.p.m.) and main-chain methylene protons ($\delta = 1.9$ p.p.m.) in DDMMA and MMA were all broad in the copolymers, while those of the methyl protons in the cyclic ketal ($\delta = 1.42$ and 1.48 p.p.m.) were sharp. These peaks were well separated, and so adequate for the determination of the composition. The composition of the copolymers thus determined, as well as the polymerization conditions and the abbreviations of the copolymers, are given in Table I.

2.3. Method

2.3.1. Preparation of samples

The sample films containing BSS were prepared by casting the polymer solution in MEK on to a Teflon sheet in a fixed frame made of Teflon, followed by evaporation of the solvent in air. The sample films were finally dried completely under vacuum and then stored in a desiccator.

TABLE I Preparation of I and poly(DDMMA-co-MMA) with various compositions^a

| Monomer feed (mol %) | | Conversion (%) | Polymer composition ^b (mol %) | | M_n ^c | Abbreviation | Structure |
|----------------------|-----|----------------|--|-----|--------------------|--------------|-----------|
| DDMMA | MMA | | DDMMA | MMA | | | |
| 100 | 0 | 68 | 100 | 0 | 28 000 | I | |
| 90 | 10 | 57 | 89 | 11 | 22 000 | II | |
| 70 | 30 | 60 | 70 | 30 | 24 000 | III | |
| 50 | 50 | 66 | 49 | 51 | 28 000 | IV | |
| 10 | 90 | 58 | 9 | 91 | 36 000 | V | |
| 0 | 100 | 84 | 0 | 100 | 16 000 | PMMA | |

^a Polymerization was conducted in DMF with AIBN as a radical initiator.

^b Composition of the polymers was determined by ¹H-NMR.

^c Number average molecular weight determined by GPC using polystyrene standards.

2.3.2. Photoirradiation

The sample films were irradiated in air by the use of a 300 W high-pressure mercury lamp through a Pyrex glass filter (> 300 nm) at room temperature.

2.3.3. 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 follow the photochemical reaction as reported previously [1]. The thermal properties of the sample films were evaluated by differential scanning calorimetry (DSC; Seiko I&E SSC-5000) at a heating rate of $10^{\circ}\text{C min}^{-1}$. At least four scans were performed for each sample to check reproducibility.

The change in ketal content in the polymers on photoirradiation was also followed by chemical titration using the procedure outlined in Part I [1]. The titration is simply based on the reaction of cyclic ketals with pyridinium chloride, followed by titration of the excess pyridinium chloride with a standard base.

2.3.4. Degree of swelling

The degree of swelling of the cross-linked films was determined in the following way. After photoirradiation, the sample film was placed in a vessel containing MEK and was left for stirring overnight in the dark. The cross-linked sample was recovered by filtration and washed thoroughly with MEK. The sample was then again placed in a vessel containing MEK and equilibrated by gentle stirring at room temperature over a period of 2 days in the dark. The equilibrated sample was removed from the vessel and the surface of the sample was wiped with filter paper to remove the solvent on the surface, and the weight of the swollen sample was measured, W_w . The sample was next dried completely under vacuum and the weight of the dried sample was measured, W_D . The degree of swelling was calculated from the ratio W_w/W_D .

3. Results and discussion

3.1. Photodecomposition of BSS

Fig. 1 shows the photodecomposition behaviour of BSS doped in the polymer films as a function of irradiation time, where the ratio of the absorbance at 255 nm before irradiation, $(A_{255})_0$, to that of t min irradiation, $(A_{255})_t$, is plotted for samples with various compositions. It may be realized that the rate of photodecomposition as evaluated by a parameter, $d[(A_{255})_t/(A_{255})_0]/dt$, and the degree of photoreaction estimated by the values in plateau in the curves, increased with the molar fraction of DDMMA.

Crivello and co-workers [3–5] have reported the photocationic polymerization of epoxides, cyclic acetals and vinyl ether initiated by sulphonium salts; dialkylphenacylsulphonium salts and dialkyl-4-hydroxyphenylsulphonium salts. Both sulphonium salts were found to generate Bønsted acid and the

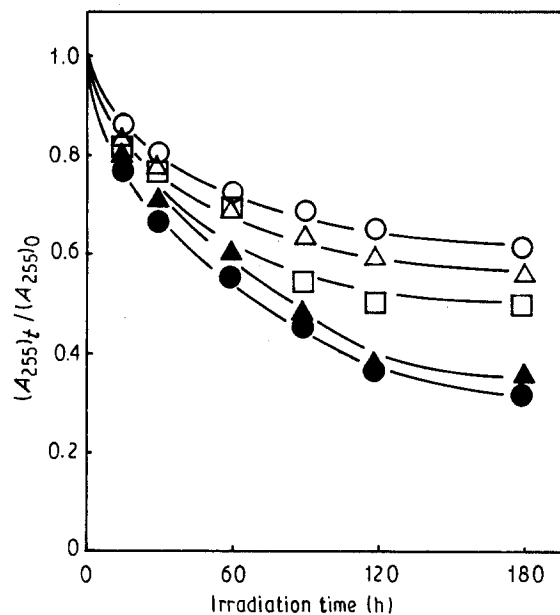


Figure 1 Photodecomposition behaviour of BSS doped in various polymer films as a function of irradiation time. (●) I, (▲) II, (□) III, (△) IV, (○) V. Initial concentration of BSS doped in the polymer films was 1 wt %. The ratio of absorbance at 255 nm after and before photoirradiation, $(A_{255})_t/(A_{255})_0$, is plotted as a function of time.

corresponding ylides on photoirradiation, but this process was proved to be reversible. Namely, the Bønsted acid and the ylide were combined to regenerate the sulphonium salts thermally. Although the detailed studies on the mechanism of photogeneration of the benzyl cation from BSS have not been yet performed, it seems likely that the photoproduction of benzyl cations is in equilibrium with a reverse process to restore BSS by analogy of the cases of dialkylphenacylsulphonium salts and dialkyl-4-hydroxyphenylsulphonium salts. In the present system, BSS is doped physically in polymer matrices, so that the mobility of BSS and its photoproducts (benzyl cation and 4-hydroxyphenylmethyl sulphide) is expected to be highly restricted and some cages may be present which prevent the diffusion of the photoproducts from the originally formed sites. This situation is explicitly favourable for the recombination of the photoproducts. If the matrix is inert to the photoproducts, the rate of photodecomposition of BSS should be the same. However, if the photoproduct reacts with the matrix, as is the present case, the rate should be dependent on the concentration of reactants. The observed trend that the rate of photodecomposition of BSS increased with the molar fraction of DDMMA is explicable in terms of equilibrium. In a polymer matrix where DDMMA is rich, the photogenerated benzyl cations are susceptible to react with 1,3-dioxolane and the cationic polymerization is initiated. Once benzyl cations react with the cyclic ketals, they are incorporated at the ends of the propagating chains and the reverse reaction to regenerate BSS is suppressed, leading to a higher rate of the photoreaction.

3.2. Photocross-linking behaviour

3.2.1. Solubility of irradiated samples

We examined the solubility of the irradiated samples

to confirm qualitatively the photocross-linking. All the samples with various compositions were irradiated in the absence of BSS for 3 h and their solubility in MEK was examined. The irradiated samples were all soluble in MEK at room temperature, indicating non-occurrence of the cross-linking. On the other hand, the samples irradiated in the presence of BSS became insoluble in MEK regardless of the ketal content in the copolymers, demonstrating that the photocross-linking took place. It is worth mentioning here that when the polymer samples doped with BSS were left in the dark they were all soluble in MEK at room temperature.

3.2.2. Change in infrared spectra

Fig. 2 shows the change in the infrared spectrum before and after photoirradiation. It is clearly seen that a peak due to cyclic ketal (1087 cm^{-1}) decreased after irradiation and a new peak appeared at 3450 cm^{-1} which can be assigned to an O-H stretching mode vibration. As in the case of photocross-linking of poly(ethylene-co-glycidyl methacrylate) with BSS, this result, as well as the results obtained from the ultraviolet absorption spectroscopy and the solubility test, indicate that photoirradiation of the sample films containing BSS in the present system resulted in decomposition of BSS, producing the initiation species which then reacted with the cyclic ketal in the polymers to bring about cross-linking, with simultaneous formation of products having an OH moiety. It is worth mentioning here that when BSS was doped in PMMA and irradiated under the same condition, no cross-linking took place and no peak appeared in the infrared spectrum in the wave number region where the OH stretching mode occurs, although the photodecomposition of BSS was confirmed by ultraviolet absorption spectroscopy. This control experiment suggests that the OH-containing product(s) result from the reaction between the photo-generated initiating species and the cyclic ketal.

Fig. 3 shows the change in peak intensity at 1087 cm^{-1} as a function of the irradiation time, where the intensity ratio after and before photoirradiation, $(I_{1087})_t/(I_{1087})_0$, is plotted for various polymers. Here, the concentration of BSS in the polymer films was kept constant (1 wt %) for all samples; thus, the con-

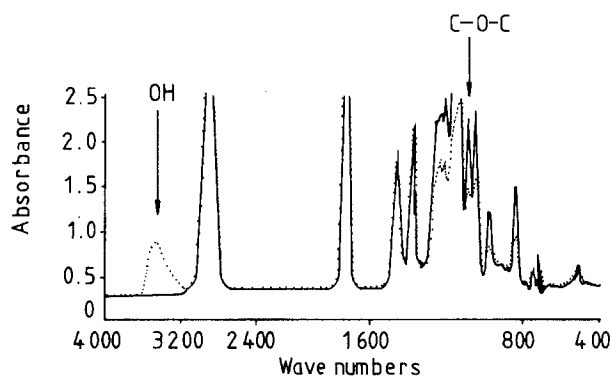


Figure 2 FT-IR spectra of polymer film II containing 1 wt % BSS (—) before and (· · ·) after 180 min photoirradiation.

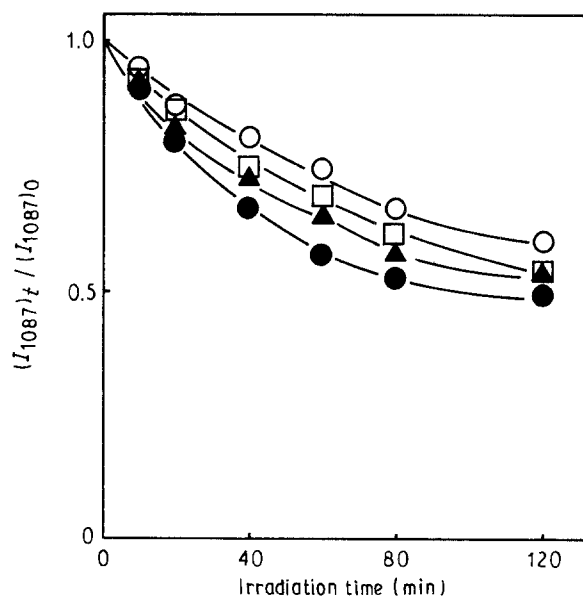


Figure 3 Change in the intensity at 1087 cm^{-1} in the infrared spectrum on photoirradiation. (●) I, (▲) II, (□) III, (○) V. Initial concentration of BSS doped in the polymer films was 1 wt %. The ratio of absorbance at 1087 cm^{-1} after and before photoirradiation, $(I_{1087})_t/(I_{1087})_0$, is plotted as a function of time.

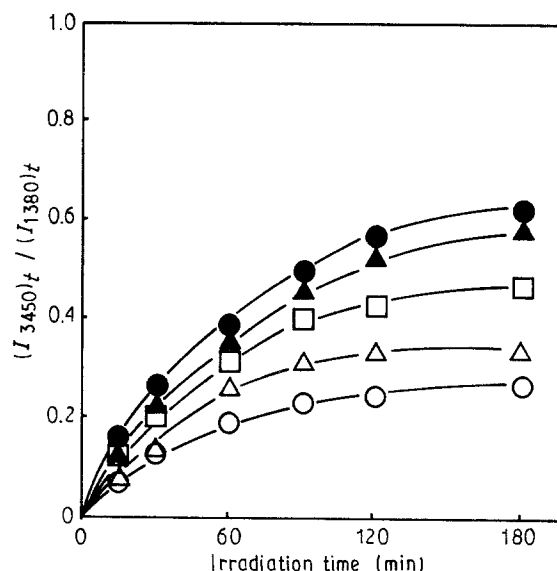


Figure 4 Change in the intensity at 3450 cm^{-1} in the infrared spectrum on photoirradiation. (●) I, (▲) II, (□) III, (△) IV, (○) V. Initial concentration of BSS doped in the polymer films was 1 wt %. The ratio of absorbance at 3450 cm^{-1} to that at 1380 cm^{-1} , $(I_{3450})_t/(I_{1380})_t$, is plotted as a function of time.

centration ratio of BSS to ketal, $[\text{BSS}]/[\text{DDMMA}]$, decreased with the molar fraction of the cyclic ketal. It can be seen that with photoirradiation the peak due to the cyclic ketal decreased in intensity and the rate of consumption of the cyclic ketal increased with the molar fraction of DDMMA. This result is in good agreement with the photodecomposition behaviour of BSS in various polymer matrices (Fig. 1). Namely, in a polymer matrix with higher compositional ratio of the cyclic ketal, the rate of photogeneration of benzyl cations is higher, leading to the higher rate of ring-opening reaction of the cyclic ketals.

Formation of the product(s) with the OH moiety is demonstrated in Fig. 4 as a function of the irradiation

time. Again, the concentration of BSS was 1 wt % for all samples. It is clear that the intensity at 3450 cm^{-1} increased with irradiation time, indicating that the amount of the product(s) with the OH moiety increased on photoirradiation. In Fig. 4 the ordinate indicates the ratio in the peak intensity at 3450 cm^{-1} to that of 1380 cm^{-1} , I_{3450}/I_{1380} , at various irradiation times. Choice of the internal standard, I_{1380} , is based on the fact that the peak at 1380 cm^{-1} , which can be assigned to rocking vibrational mode of the methyl group, scarcely changed on photoirradiation irrespective of the composition of the polymers. The formation of the product(s) with the OH moiety correlates well with the consumption of the cyclic ketals in the polymers.

The effect of the concentration of BSS in the polymer on the photocross-linking was explored for a copolymer with $[\text{MMA}]/[\text{DDMMA}] = 11/89$ (II). The concentration was varied from 0.12 wt % (0.05 mol % based on the ketal units) to 12 wt % (5.0 mol %) and the results are shown in Figs 5 and 6. The rate of the consumption of the cyclic ketals as well as the conversion increased with the concentration of BSS as shown in Fig. 5, and simultaneously the amount of the product(s) with the OH moiety increased monotonically with the concentration of the dopant.

3.2.3. Change in ketal content by titration

The ketal content in the irradiated samples was measured by the chemical titration method and the results are shown in Fig. 7 where the relative ketal content before and after photoirradiation estimated by titration is indicated, as well as that evaluated by Fourier transform-infrared spectroscopy (FT-IR). As in the case of poly(ethylene-co-glycidyl methacrylate) [1], the relative ketal content evaluated by the different

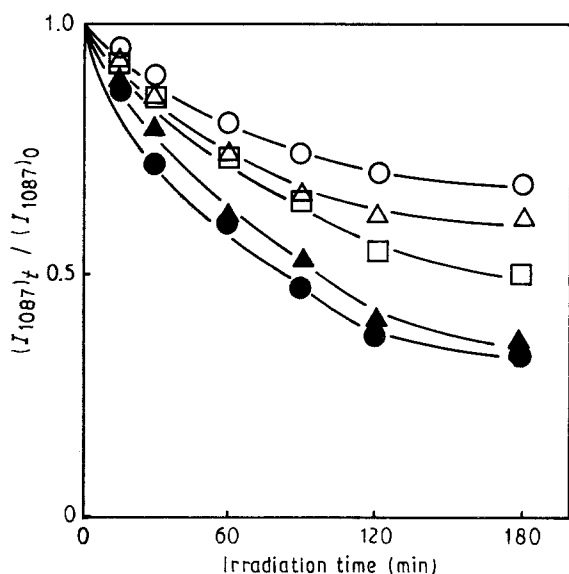


Figure 5 Change in the intensity at 1087 cm^{-1} in infrared spectrum on photoirradiation of II in the presence of various concentrations of BSS. (●) 5 mol %, (▲) 1 mol %, (□) 0.5 mol %, (△) 0.1 mol %, (○) 0.05 mol %. The ratio of absorbance at 1087 cm^{-1} after and before photoirradiation, $(I_{1087})_t/(I_{1087})_0$, is plotted as a function of time.

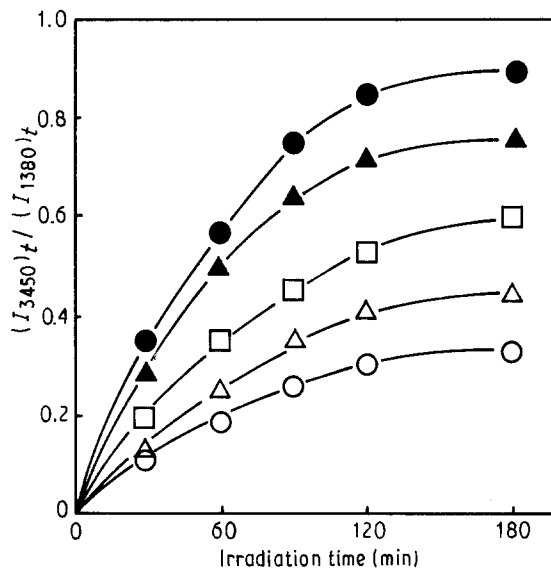


Figure 6 Change in the intensity at 3450 cm^{-1} in the infrared spectrum on photoirradiation of II in the presence of various concentrations of BSS. (●) 5 mol %, (▲) 1 mol %, (□) 0.5 mol %, (△) 0.1 mol %, (○) 0.05 mol %. The ratio of absorbance at 3450 cm^{-1} to that at 1380 cm^{-1} , $(I_{3450})_t/(I_{1380})_t$, is plotted as a function of time.

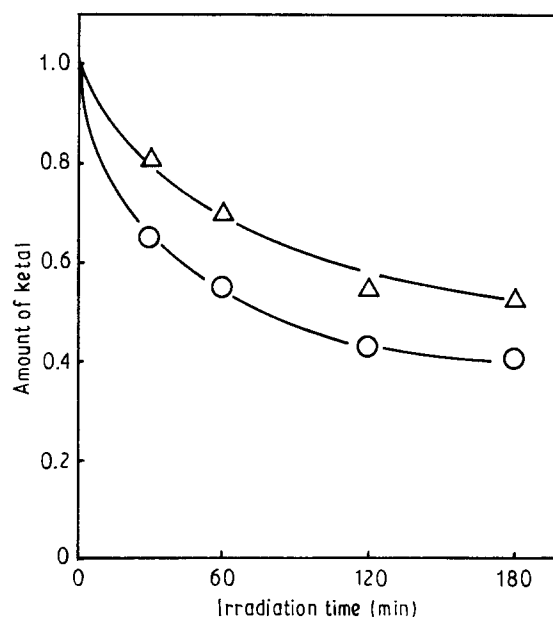


Figure 7 Change in ketal content in II films containing 1 wt % BSS on photoirradiation. (△) evaluated by FT-IR, (○) evaluated by titration.

methods did not agree each other completely, but it is at least certain that the ketal contents evaluated by FT-IR using the peak intensity at 1087 cm^{-1} reflect satisfactorily the ketal content in the polymer samples.

3.2.4. Thermal properties

In order to explore the change in glass transition temperature, T_g , of the polymers on photoirradiation, which was expected to reflect the cross-linking behaviour in a semiquantitative manner, DSC of the irradiated samples was measured. Unfortunately, however, no endothermic nor exothermic peaks were observed

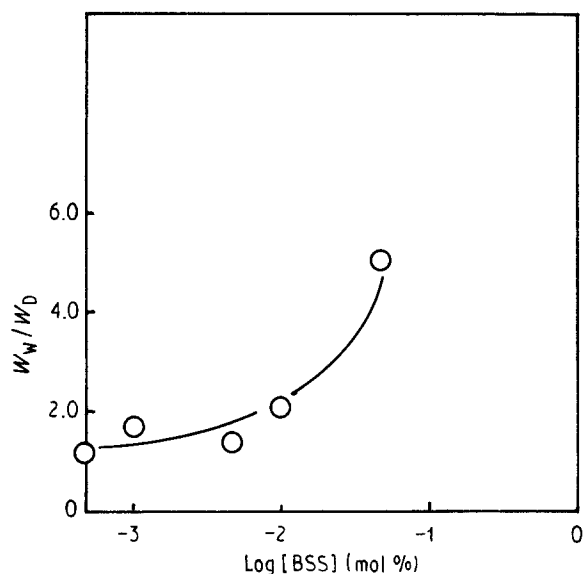


Figure 8 Degree of swelling of irradiated films of II containing various concentrations of BSS. The films were irradiated for 60 min.

of any samples (except PMMA) irrespective of photo-irradiation between 0 and 200 °C on heating.

3.2.5. Swelling behaviour of the irradiated samples

Fig. 8 shows the degree of swelling of the samples (II) irradiated for 1 h in the presence of various concentrations of BSS. These swelling profiles provide an interesting feature of the cross-linking behaviour of the present system. Fig. 8 indicates that the degree of swelling at the lower concentrations of BSS (up to 1 mol %) remains nearly constant and the value is very close to unity. This means that at the lower concentrations of BSS the swelling of the photocross-linked polymer films scarcely takes place. Usually, the degree of swelling of polymer gels increases with

decreasing cross-linking density and this density profile is interpreted in terms of equilibrium between osmotic pressure and mechanical strength of the gels [6]. In the present system, however, the concentration dependence of BSS on the swelling behaviour exhibits unusual profiles if we assume that the cross-linking density is linearly dependent on the concentration of BSS. This unusual swelling profile may be closely related to the formation of microgels with nonideal topological arrangements of the cross-linking points [7]. If the formation of such microgels predominates, the resulting gels are considered to be unfavourable in terms of swelling. Further increase in the heterogeneous cross-linking points will lead to the formation of macrogels with localized cross-linking points. Irrespective of the local structure, the formation of the macrogels is explicitly favourable for swelling. The concentration profile of Fig. 8, therefore, can be interpreted in terms of the formation of macrogels at the high concentration of BSS (5 mol %).

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