Functionalized Allyl Resins. I. Photosensitivity of Partially Cinnamoylated Allyl Resins

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Synopsis

The preparation of photosensitive allyl resins is described. The introduction of cinnamoyl groups into allyl resins is attempted for imparting successfully photosensitive functionality. Thus, the photosensitivity of cinnamoylated poly(allyl benzoate) was first examined in detail as a model photoreaction of cinnamoylated allyl resins. Cinnamoylated poly(diallyl phthalate) was then UV-irradiated to yield crosslinked resin, and its photosensitivity was compared with that of other allyl resins. The highest photosensitivity was observed for cinnamoylated poly(diallyl phthalate), although the mobility of the main polymer chain was considered to be lowest; this may be ascribed to the function of phthaloyl groups as photosensitizers.

INTRODUCTION

The commercial interest in allyl resins can be attributed to their excellent electrical properties and ability to maintain these under conditions of high temperature and humidity, their excellent dimensional stability, and their chemical resistance. Diallyl phthalate (DAP) and diallyl isophthalate (DAI) resins are in widest use, being supplied as monomers and B-staged prepolymers for conversion to thermosetting molding compounds, preimpregnated glass cloth and paper, sealants, coating, etc. The DAP and DAI prepolymers are dry, free-flowing white powders that are stable on storage and, even when compounded by using catalysts decomposing at high temperatures, do not polymerize at room temperature. Under heat and pressure as in molding and laminating, they soften, flow, and crosslink to yield three-dimensional insoluble thermosets, being used in critical electrical/electronic applications requiring high reliability such as electronic connectors in communications, computer, and aerospace system.[1,2]

In spite of these excellent properties, application of these allyl resins is rather limited since useful three-dimensional insoluble thermosets are prepared only under severe conditions using heat and pressure because of low polymerizability of allyl groups responsible for crosslinking. In this sense, functionalization of allyl resins would be required for versatile applications.

Thus, this article describes the preparation of photosensitive allyl resins that are photocrosslinkable even without heat. The introduction of cinnamoyl groups into allyl resins is attempted for endowing them with photosensitive functionality because cinnamoylated polymers, represented by poly(vinyl cinnamate),[3,4] are well known as photosensitive polymers, the photocrosslinking mechanism of

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which is quite established.[5,6] Moreover, the excellent properties of allyl resins mentioned above are expected to be maintained or strengthened by cinnamoylation.   In addition, cinnamoylated derivatives are included in the most important class of photocrosslinking systems from the economical viewpoint.[7]

EXPERIMENTAL

Allyl Monomers

DAP, DAI, and allyl acetate (AAc) were commercially available reagents.   Allyl benzoate (ABz) was prepared as described previously.[8]   Allyl glycolate (AG) was synthesized by esterification of glycolic acid (1 mol) with allyl alcohol (1.5 mol) under reflux in benzene (300 mL) using p-toluenesulfonic acid as a catalyst. These monomers were purified by vacuum distillation under nitrogen.

Preparation of Partially Cinnamoylated Allyl Resins

DAP, DAI, ABz, or AAc was copolymerized with AG in bulk at 80°C using 0.06 mol/L benzoyl peroxide as an initiator; the polymerization procedure was similar to that in the literature.[8]   After a definite reaction time, the polymer produced was precipitated by pouring the reaction mixture into a large amount of ethyl ether–petroleum ether mixture as precipitant, the ethyl ether volume fraction of which was high in the copolymerization system, with a large molar fraction of AG in feed.   It was then washed several times with a small amount of precipitant and dried *in vacuo*; conversion was kept less than 10%.

The polymers thus obtained, having hydroxyl groups as AG units, were subjected to cinnamoylation.   Thus, a 1.5 mol equivalent excess of cinnamoyl chloride in pyridine as a HCl acceptor was added to a benzene solution (3 g/100 mL) of the polymer having hydroxyl groups, although a benzene–pyridine mixture was used as a solvent for the highly hydroxylated polymer which is poorly soluble in benzene, and the solution was stirred at 60°C for 4 h.   After filtration of the pyridinium salt, the filtrate was condensed and then poured into chilled methanol (−78°C) to precipitate cinnamoylated allyl resins.

UV Irradiation

Cinnamoylated allyl resin was cast on a UV cell or on a glass plate from the dioxane solution, followed by evaporating the solvent under vacuum to obtain a film.   The film was then irradiated with UV light from a high-pressure mercury lamp made by Ushio Denki Co. (100 W) at a distance of 10 cm from the lamp at room temperature.   The film was transparent and its thickness was around 2 μm.   The photodimerization rate of the cinnamoyl group was estimated from the change of absorbance at 300 nm in its UV spectrum (Fig. 2).   After irradiation on a glass plate, the film was immersed in tetrahydrofuran (THF) for 2 min, and then the insoluble part was successively reimmersed in fresh THF for 30 s, dried *in vacuo*, and weighed.

Analyses

UV spectra of the polymers were recorded in dioxane solutions with a Shimazu UV-210 UV spectrophotometer. The measurement of IR spectra was registrated on a KBr disk with a JASCO A-202 IR spectrophotometer. The molecular weight and/or polydispersity coefficient ($\overline{M}_w/\overline{M}_n$) of the polymer was determined by vapor pressure osmometry (VPO) or gel permeation chromatography (GPC). VPO measurements were done by using a Hewlett–Packard 302 vapor pressure osmometer in benzene at 37°C.

GPC measurements were carried out with a Waters Associates model ALC/ GPC 501 apparatus at room temperature under the following conditions: solvent, tetrahydrofuran; polystyrene gel column combination, 10^3, 10^4, and 10^5 Å (Waters designation); polymer concentration, 0.5% (w/v); and flow rate, 1 mL/min. GPC curves were analyzed by using the calibration curve obtained with standard samples of monodisperse polystyrene to estimate the number-average and weight-average molecular weights ($\overline{M}_n$, $\overline{M}_w$).
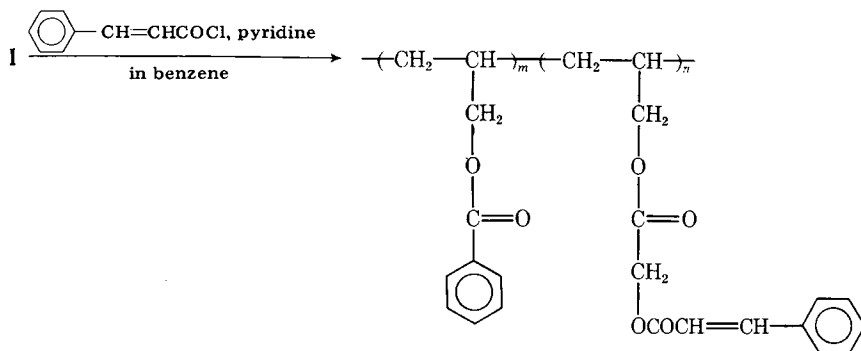
RESULTS AND DISCUSSION

Preparation and Characterization of Partially Cinnamoylated Allyl Resins

Allyl resins having cinnamoyl groups were prepared via the following reaction paths as exemplified for cinnamoylated poly-ABz:
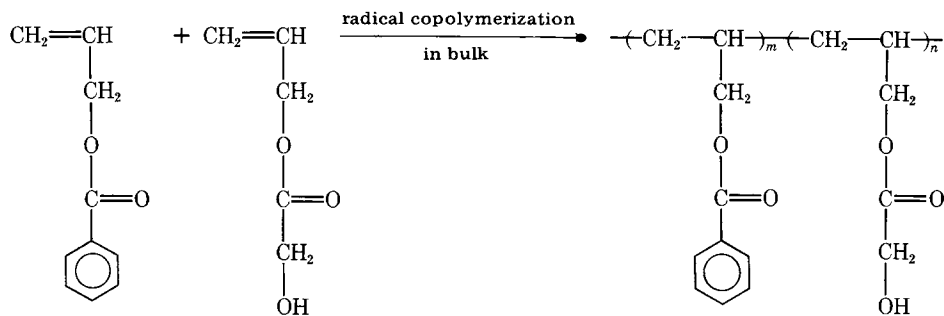
This synthetic method was carefully checked for the preparation of cinnamoylated poly-ABz, and other cinnamoylated allyl resins were prepared similarly. Thus, ABz was radically copolymerized in bulk with AG under different feed monomer composition, and the composition of the copolymers obtained at less than 10% conversion was determined by elemental analysis and/or UV spectroscopy using the absorption band at 275.5 nm; Figure 1 shows the copolymer composition curve.

The monomer reactivity ratios were estimated to be $r_{ABz} = 0.88$ and $r_{AG} = 1.39$ from the Fineman–Ross plot[9] based on the data of Figure 1. These copolymers of known composition were then subjected to the reaction with cinnamoyl chloride to give cinnamoylated poly-ABz. The complete reaction of AG units in the copolymer with cinnamoyl chloride was tentatively checked by the absence of absorption due to hydroxyl groups in its IR spectrum. Furthermore, the content of cinnamoyl groups in the cinnamoylated poly-ABz was determined as corresponding to that of AG units in the poly(ABz-co-AG) from its UV spectrum in dioxane solution using the absorption band at 300 nm. The structure of the polymers thus obtained was further confirmed by NMR spectroscopy. In the case of other cinnamoylated allyl resins, the content of cinnamoylated groups in the polymer was determined only by UV spectroscopy. The cinnamoylated allyl resins had number-average molecular weights in the range 2000–3500, and their polydispersity coefficients were less than 2, i.e., they were rather homogeneous.

Photosensitivity of Cinnamoylated Poly-ABz

First, cinnamoylated poly-ABz was tentatively irradiated by UV light to investigate a model photocrosslinking reaction of cinnamoylated allyl resins, be-
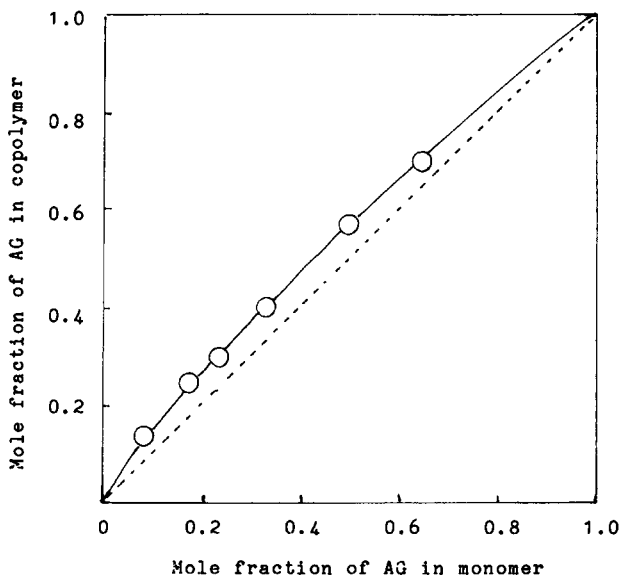

Fig. 1. Copolymer composition curve for the bulk copolymerization of AG with ABz.

cause ABz-homopolymer shows no photosensitivity and has a polymer skeleton analogous to DAP-homopolymer as a typical allyl resin.

Figure 2 shows the time dependence of UV spectra of poly-ABz having 30 mol % cinnamoyl groups under UV irradiation; the absorption due to cinnamoyl groups ($\lambda_{max} \simeq 282$ nm) decreased rapidly at an early stage of the irradiation. Figure 3 also shows the change in IR spectra of the above cinnamoylated poly-ABz by UV irradiation; a remarkable reduction of the absorption due to car-bon–carbon double bonds of cinnamoyl groups was observed at 1630 cm^{-1} for the gelled polymer obtained by UV irradiation for 60 min. Furthermore, the variation of GPC curves of the cinnamoylated poly-ABz under the solid photo-crosslinking reaction is shown against UV irradiation time in Figure 4 until the gel formation starts. Evidently, the crosslinking leading to three-dimensional network formation occurred effectively. These results for the poly-ABz having 30 mol % cinnamoyl groups clearly demonstrate the possibility of the successful functionalization of poly-ABz as a model polymer of allyl resins by cinnamoy-lation.

Figure 5 shows the dependence of photosensitivity of cinnamoylated poly-ABz on the content of cinnamoyl groups; the percentage conversion reached up to about 80% after 30 min, although the photosensitivity seemed to be enhanced slightly with an increase in the cinnamoyl group content. The expanded diagram of Figure 5 is illustrated in Figure 6 to disclose in detail the early stage of pho-
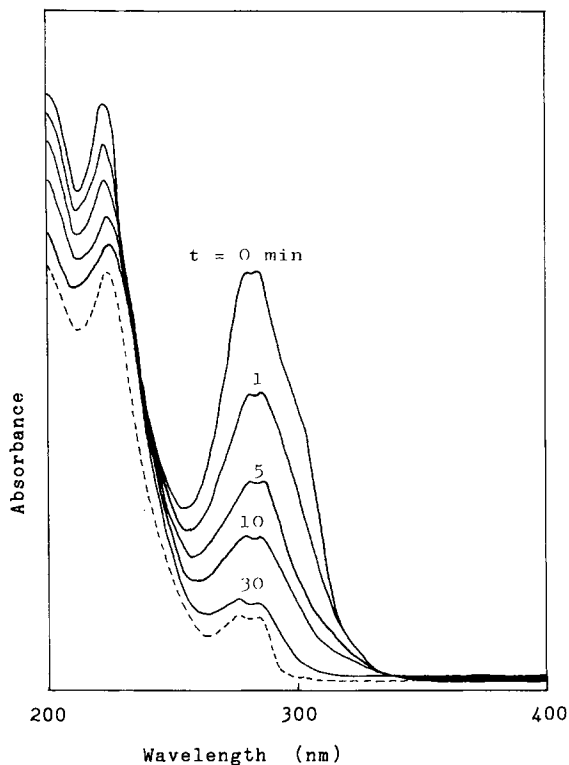

Fig. 2. Change in UV spectra of cinnamoylated poly-ABz by irradiation at 10 cm from the mercury lamp: (——) cinnamoylated poly-ABz; (- - -) poly(ABz-co-AG).
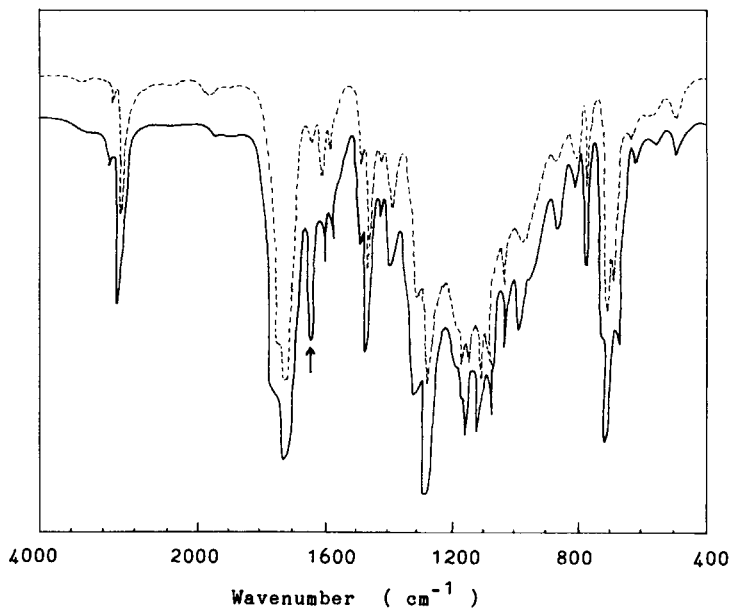
Fig. 3. Change in IR spectra of cinnamoylated poly-ABz by irradiation at 10 cm from the mercury lamp: (——) nonirradiated polymer; (- - -) gelled polymer.

todimerization. Interestingly, the photosensitivity at the early stage was slightly reduced with an increase in the content of cinnamoyl groups, contrary to the later stage, being probably attributed to the increased glass transition temperature (T_g) with increasing amount of cinnamoyl groups, as is the case in the cinnamoylated polydienes.[10] However, exact determination of T_g by DSC was unsuccessful.
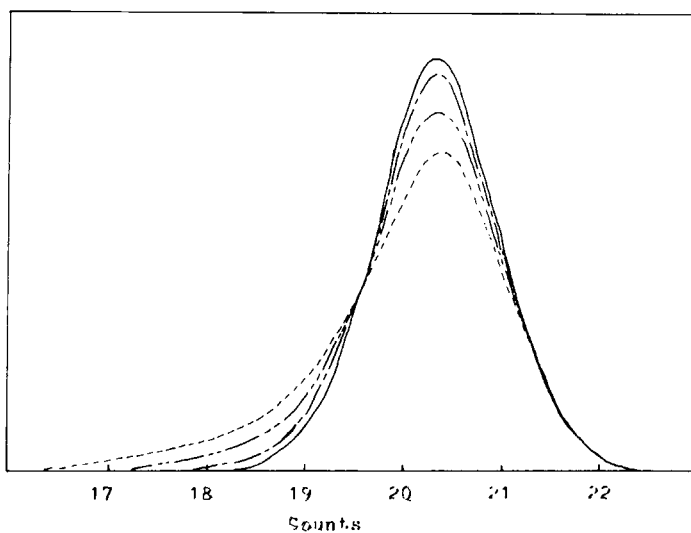
Fig. 4. Variation of GPC curves of cinnamoylated poly-ABz with irradiation time: (——) 0 min; (— - —) 0.5 min; (— ·· —) 2 min; (- - -) 4 min.
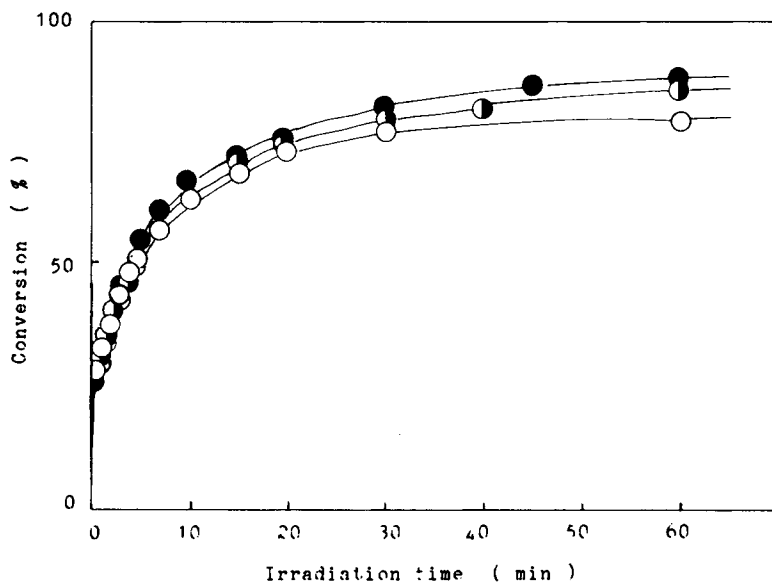
Fig. 5. Time–conversion curves for photopolymerization of poly-ABz having (O) 6.4, (◐) 29.6, and (●) 45.3 mol % cinnamoyl groups.
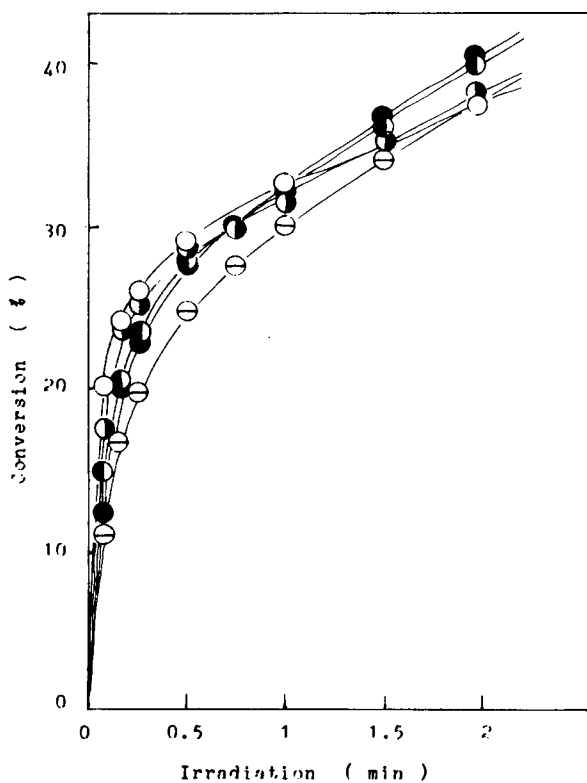

Fig. 6. Time–conversion curves for photopolymerization of poly-ABz having (O) 6.4, (◐) 29.6, (◑) 45.3, (●) 64.3, and (⊖) 90.3 mol % cinnamoyl groups.
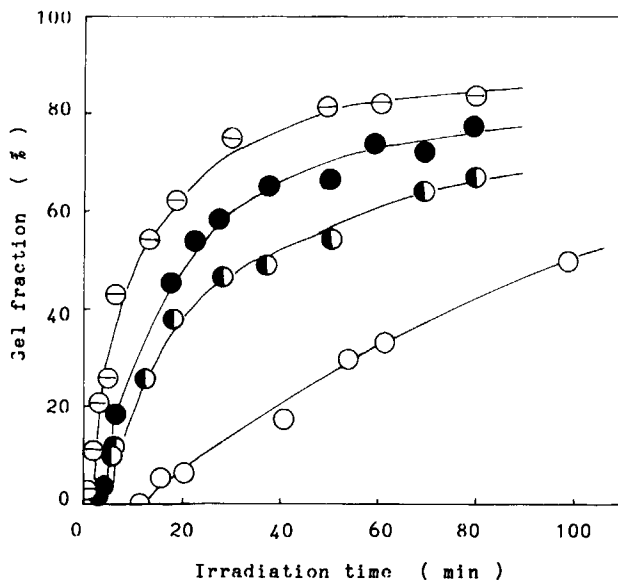
Fig. 7. Gel formation in the photopolymerization of poly-ABz having (○) 6.4, (◐) 45.3, (●) 64.3, and (⊖) 90.3 mol % cinnamoyl groups.

Figure 7 demonstrates the photocrosslinking results.   Gel formation was clearly enhanced with increased cinnamoylation, as expected.

Photosensitivity of Cinnamoylated Poly-DAP

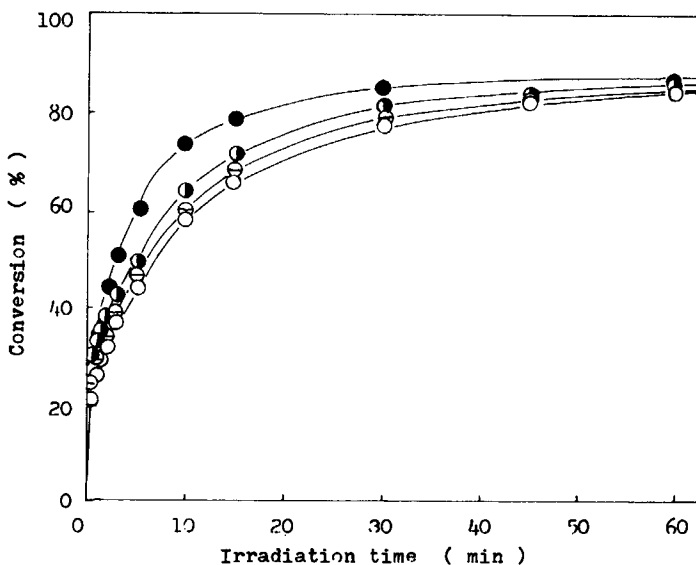Figure 8 shows the time–conversion curves of cinnamoyl groups in the cin-

Fig. 8. Time–conversion curves for photopolymerization of poly-DAP having (●) 7.2, (◑) 33.6, (⊖) 67.5, and (○) 81.7 mol % cinnamoyl groups.

namoylated poly-DAP under UV irradiation. The photosensitivity was quite high and, interestingly, increased with a decrease in the content of cinnamoyl groups in the photopolymer. The photocrosslinking reaction of cinnamoylated poly-DAP was then examined in terms of gel formation as shown in Figure 9. The gel fraction reached around 80% after 40 min although the gel formation was favored for the polymers of higher molecular weight.

Here, it should also be noted that the photosensitivity of cinnamoylated poly-DAP having a low content of cinnamoyl groups was higher than that of cinnamoylated poly-ABz, as is evident from a comparison of results shown in Figures 5 and 8. In general, the photosensitivity of the polymer in a solid state is related to the mobility of the main polymer chain; the more mobile, the higher it is.[11]

In contradiction to this point, the mobility of the main polymer chain in cinnamoylated poly-DAP of high photosensitivity is considered to be lower than that in cinnamoylated poly-ABz. This was further examined by comparison with the photosensitivity of cinnamoylated poly-AAc, the polymer chain of which is quite flexible, as shown in Figure 10. Again, the photosensitivity of flexible allyl resin was low. In this connection, the photosensitivity of cinnamoylated poly-DAP was quite enhanced by a decrease in the content of cinnamoyl groups or by an increase in the content of DAP units. These results may suggest an unusual behavior for photodimerization of cinnamoylated poly-DAP, some reasons for which were tentatively searched from the following standpoint.

First, the effect of unreacted pendent allyl groups, the content of which can be calculated to be about 56% of DAP units in the cinnamoylated poly-DAP in terms of cyclopolymerization mechanism,[8] was carefully checked because the polymers having allyl groups or allyl resins are known to show some degree of photosensitivity by themselves.[12] That is, when the photosensitivity due to
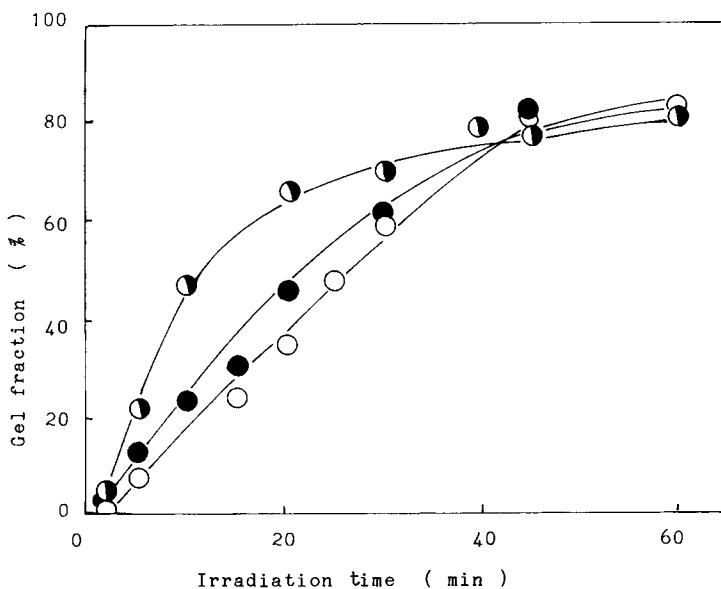

Fig. 9. Gel formation in photopolymerization of poly-DAP having (O) 33.6, (●) 51.2, and (◐) 81.7 mol % cinnamoyl groups.
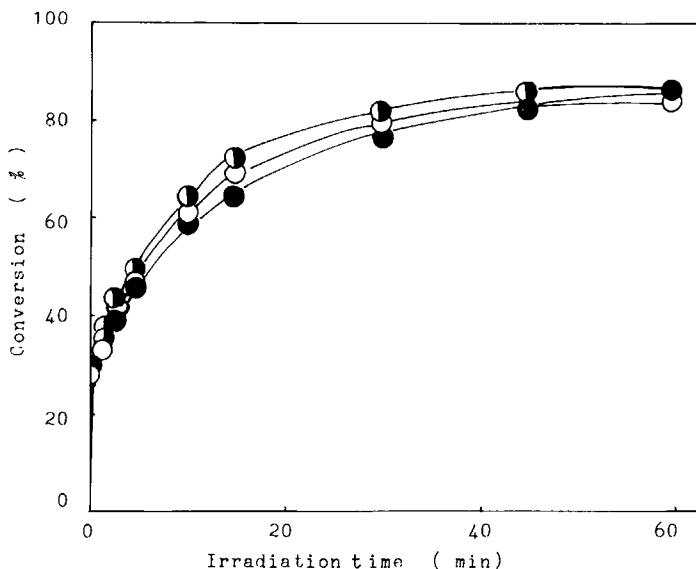
Fig. 10. Effect of chain flexibility on photopolymerization of various allyl resins having about 30 mol % cinnamoyl groups: (●) poly-AAc; (○) poly-ABz; (◐) poly-DAP.

unreacted allyl groups is superimposed on that due to cinnamoyl groups, the photosensitivity of cinnamoylated poly-DAI should be greater than that of cinnamoylated poly-DAP because cinnamoylated poly-DAI contains a larger amount of unreacted pendent allyl groups[13] and, moreover, its chain is more flexible.   However, a low photosensitivity was observed for cinnamoylated poly-DAI (Fig. 11) in comparison with cinnamoylated poly-DAP, suggesting the
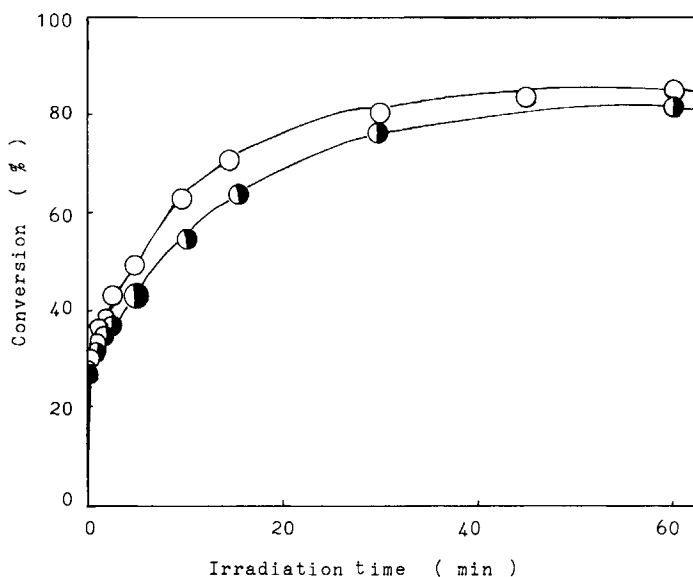
Fig. 11. Comparison of photosensitivity of (○) poly-DAP and (◑) poly-DAI having about 30 mol % cinnamoyl groups.

ineffectiveness of unreacted pendent allyl groups for the explanation of enhanced photosensitivity of cinnamoylated poly-DAP.

Second, it may be considered that the phthaloyl groups of DAP units, especially 44% of cyclic units, in cinnamoylated poly-DAP act as photosensitizers for photodimerization of cinnamoyl groups because irradiation occurred with unfiltered UV light. Thus, high-energy light of less than 300 nm might excite the phthaloyl groups, the excitation energy being transferred to cinnamoyl groups through a long-range singlet–singlet energy transfer and/or a short-range triplet–triplet energy transfer mechanism. Moreover, the rigidity of the main polymer chain of cinnamoylated poly-DAP, especially that due to cyclic structures, may delay the nonradiative energy dissipation of the excited phthaloyl groups to the ground state leading to a long life at the excited state as a result of reduced segmental motion. The possibility of the energy transfer to cinnamoyl groups would be increased. Thus, the photosensitivity of cinnamoylated poly-DAP and poly-AAc were compared for the irradiation of UV light of more than 300 nm, although the high-energy light of less than 300 nm was cut by using a Toshiba UV filter No-29; the photosensitivity of both samples was reduced and no difference was found, as expected. Elucidation of the details of the function of phthaloyl groups as photosensitizer is now in progress.

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