

# Postcrosslinking of Linear Polyesters. II. UV-Induced Crosslinking Agents Having Carboxyl Reactive Group

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## Synopsis

A previous article reported that polyallyl compounds such as triallyl cyanurate could be applied as an effective melt-blend-type ultraviolet (UV)-induced crosslinking agent for linear polyesters to improve their thermal resistances without sacrificing their melt processabilities. The present article reports the results from further investigation to seek more effective crosslinking agents for the polyesters. Compounds having both allyl and carboxyl reactive groups, such as diallyl glycidyl isocyanurate and 2- $\beta$ -(3,5-diallylisocyanuro)ethyl]carbamoyl-2-oxazoline have been proved to be more effective UV-induced crosslinking agents than the simple polyallyl compounds reported previously. The former compounds were coupled with carboxyl terminal groups of the polyesters by reaction in the melt and act as an effective UV-induced crosslinking agent, which was proved by the observation that the polyester having more carboxyl terminals resulted in higher UV crosslinkabilities. Addition of such compounds to the polyester did not seriously affect the melt stability of the mixtures.

## INTRODUCTION

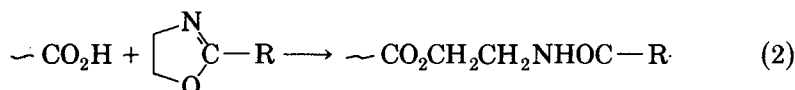
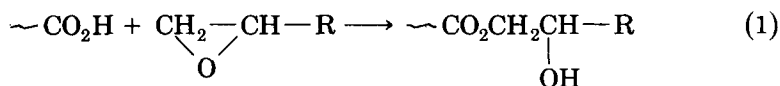
Poly(ethylene terephthalate) (PET) is well known to be one of the most commercially important polymers, used as synthetic fibers, biaxially oriented films, blow-molded bottles, and plastics. In applications where high thermal and chemical resistances of the fabricated products were very important, a technology to crosslink such linear polyesters without sacrificing their melt processabilities has been desired.

We have been making efforts to develop practically applicable crosslinking agents which can be incorporated into polyesters by melt blending to act as effective ultraviolet (UV)-induced crosslinking agents after shaping.

In the previous article,<sup>1</sup> we reported that such polyallyl compounds as triallyl isocyanurate and triallyl cyanurate had proved to be such effective melt-blend-type UV-induced crosslinking agents. The crosslinking mechanism of the polyester by these polyallyl compounds includes both the polymerization of the allyl compound to form semi-interpenetrating polymer networks and the reaction of the polyester backbone and the allyl moiety of the polyester. As is easily understood, the latter reaction should be preferable to the former reaction for effective crosslinking, but in the above case the former proved to predominate. Therefore, we can expect more effective crosslinking if we can introduce allylic groups to the polyester chain.

We report our attempts to find UV-induced crosslinking agents which react with polyester chain terminals in the melt, resulting in the polyester having

UV-sensitive terminal groups. We have selected epoxy and oxazoline groups as a group to react with carboxyl terminals of the polyester, as shown below.



As the UV-induced crosslinking group, we have chosen allyl group which was proved to be effective in the previous report.

## EXPERIMENTAL

### Materials

Diallyl glycidyl isocyanurate (DAGI) was prepared as follows. A mixture of 115 g of diallyl isocyanurate,<sup>2</sup> 23 g of sodium hydroxide, 25 g of water, and 690 g of epichlorohydrin were heated at 100°C for 4 h. After cooling, water and excess epichlorohydrin were distilled off under vacuum. The resultant mixture was extracted with methylene chloride and the extract was washed with water and distilled to yield 102 g of DAGI having boiling point of 145–148°C (0.4 mmHg).

ANAL. Calcd. for  $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_4$ : C, 54.3%; H, 5.7%. Found: C, 54.2%; H, 5.7%.

2- $[\beta$ -3,5-diallylisocyanuro]ethyl]carbamoyl-2-oxazoline (DAIO) was prepared as follows. A solution of 41 g of sodium diallyl isocyanurate in 450 mL of *N,N* dimethylformamide was added dropwise to a solution of 70 g of *N,N'*-bis( $\beta$ -chloroethyl) oxamide<sup>3</sup> in 9000 mL of *N,N*-dimethylformamide at 80°C. The mixture was kept at 80°C for 4 h more, and after cooling *N,N*-dimethylformamide was removed by distillation under vacuum. The residual mixture was extracted with methylene chloride and methylene chloride evaporated to result in 52 g of *N*- $[\beta$ -(3,5-diallylisocyanuro)ethyl]-*N'*-( $\beta$ -chloroethyl)oxamide having mp 135–138°C. This oxamide (27 g) was added to a solution of 4.0 g of potassium hydroxide in 200 mL of ethanol and heated under reflux for 1 h. The reaction mixture was filtered and the filtrate was concentrated and recrystallized from ethanol to yield 15.3 g of DAIO having mp 121–123°C.

ANAL. Calcd. for  $\text{C}_{15}\text{H}_{19}\text{N}_5\text{O}_5$ : C, 51.6%; H, 5.5%. Found: C, 51.5%; H, 5.3%.

Triallyl isocyanurate (TAIC) and benzil dimethyl ketal (BDMK) were obtained from Tokyo Kasei Kogyo Co., Ltd. and triglycidyl isocyanurate (TGIC) was obtained from Nissan Chemical Ind. Co., Ltd.

PET having various intrinsic viscosity ( $[\eta]$ ) and carboxyl content (CV) were prepared by changing reaction conditions such as temperature, pressure, or time from dimethyl terephthalate and ethylene glycol by the ordinary polycondensation method using  $\text{Sb}_2\text{O}_3$  (0.03 mol%) and  $\text{Mn}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$  as catalyst and  $(\text{CH}_3\text{O})_3\text{P}=\text{O}$  (0.05 mol%) as a stabilizer.

### **Incorporation of the UV-Induced Crosslinking Agent to PET by Melt Treating**

To a 100 mL three-necked, round-bottom flask, equipped with a mechanical stirrer, nitrogen inlet and outlet tubes, 30 g of the polymer chips were added and the system was evacuated and purged with nitrogen. Then the system was evacuated again and the flask was placed in a salt bath heated at 280°C. When all the polymer chips melted, 0.6 g of the UV-induced crosslinking agent and 0.3 g of BDMK as a photoinitiator were added under stirring. After 5 min mixing under a nitrogen flow, the resulting composition was pulverized to about 10–20 mesh and provided for UV irradiation test or analysis.

### **UV Irradiation Method**

One layer pulverized particles obtained above was placed on a hot plate heated at 150°C in air and exposed to UV light for predetermined period of times. The lamp used was an Ushio Electric high-pressure mercury lamp (Type UM-103B). The light from the lamp was focused into a parallel beam by a reflector and the distance between the lamp and the sample was set to 10 cm. Light intensities incident on the samples were measured with an ORC UV intensity meter (Model UV-MO1:sensor UV35) and found to be 17 mW/cm<sup>2</sup>.

### **Analytical Procedure**

$[\eta]$  was measured in *o*-chlorophenol at 35°C. CV (eq/10<sup>6</sup> g polymer) was measured by Conix method.<sup>4</sup> Degree of crosslinking (GV) was determined as follows.

The sample (100 mg) was dissolved in 10 mL of *o*-chlorophenol at 140°C for 1 h. After removal of the soluble portion by filtration, the insoluble gel was washed well with acetone, dried, and weighed. Percentage by weight of the insoluble gel was defined as GV.

## **RESULTS AND DISCUSSION**

The results from the evaluation of the carboxyl reactive allyl compounds as the UV-induced crosslinking agent for PET are summarized in Table I and Figure 1. Results using the polyallyl compound having no melt reactive group (TAIC) and polyepoxy compound having no allyl group (TGIC) are also shown as controls. As shown in Table I, in all cases except TAIC, CV of PET was lowered by the melt treating. This indicates that those compounds reacted with carboxyl end groups of the polyesters. The results from GV measurements show that all of the allyl compounds used here are effective as a UV-induced crosslinking agent. In case of TGIC, gelation was not observed before irradiation, although a slight branching might occur. Therefore, the GV result suggests that epoxy groups themselves may be involved in the UV-induced crosslinking reaction under the tested conditions. The compound having both allyl and carboxyl-reactive groups has been proved to be more effective than those having only either allyl or carboxyl-reactive group such as TAIC and TGIC. Further, in cases of the former compounds, PET having higher initial CV results in higher GV. To evaluate the above observation

TABLE I  
 Melt Reactivities and UV Crosslinkabilities of UV-Induced Crosslinking Agents

UV-induced crosslinking agent	Change in $[\eta]$ /CV of PET by melt treating		GV after 15 min UV irradiation
	Before treatment	After treatment	
$\begin{array}{c} \text{CH}_2=\text{CHCH}_2 \diagdown \text{N}-\text{C}=\text{O} \\ \text{O}=\text{C} \diagup \text{N}-\text{C}=\text{O} \\ \text{CH}_2=\text{CHCH}_2 \diagdown \text{N}-\text{C}=\text{O} \end{array} \text{N}-\text{CH}_2\text{CH}(\text{O})-\text{CH}_2$	0.59/54	0.57/12	63
(DAGI)	0.65/35 0.62/11	0.61/10 0.58/4	58 50
$\begin{array}{c} \text{CH}_2=\text{CHCH}_2 \diagdown \text{N}-\text{C}=\text{O} \\ \text{O}=\text{C} \diagup \text{N}-\text{C}=\text{O} \\ \text{CH}_2=\text{CHCH}_2 \diagdown \text{N}-\text{C}=\text{O} \end{array} \text{NCH}_2\text{CH}_2\text{NHOC}-\text{C} \begin{array}{l} \diagup \text{N}-\text{CH}_2 \\ \diagdown \text{O}-\text{CH}_2 \end{array}$	0.59/47	0.57/3	65
(DAIO)	0.63/33 0.61/8	0.61/2 0.59/2	60 46
$\begin{array}{c} \text{CH}_2-\text{CHCH}_2 \diagdown \text{N}-\text{C}=\text{O} \\ \text{O}=\text{C} \diagup \text{N}-\text{C}=\text{O} \\ \text{CH}_2-\text{CHCH}_2 \diagdown \text{N}-\text{C}=\text{O} \end{array} \text{N}-\text{CH}_2\text{CH}(\text{O})-\text{CH}_2$	0.65/33	0.62/7	22
(TGIC)	0.60/8	0.57/3	13
$\begin{array}{c} \text{CH}_2=\text{CHCH}_2 \diagdown \text{N}-\text{C}=\text{O} \\ \text{O}=\text{C} \diagup \text{N}-\text{C}=\text{O} \\ \text{CH}_2=\text{CHCH}_2 \diagdown \text{N}-\text{C}=\text{O} \end{array} \text{N}-\text{CH}_2\text{CH}=\text{CH}_2$	0.64/33	0.60/37	25
(TAIC)			

more precisely, in Figure 2 are plotted GV versus  $\Delta\text{CV}$  which is calculated as follows;

$$\Delta\text{CV} = \text{CV}_0 - \text{CV}_1 \quad (3)$$

where  $\text{CV}_0$  and  $\text{CV}_1$  mean the CV of the initial PET and the treated PET, respectively.  $\Delta\text{CV}$  means the number of the carboxyl groups coupled with these agents. Figure 2 shows that GV increases as  $\Delta\text{CV}$  increases. This result indicates that the UV-reactive groups coupled with the polyester act more effectively to the UV-crosslinking of the polyester than the uncoupled ones. Figure 2 also shows the UV crosslinkability of epoxy groups is inferior to that of allyl groups under the tested condition.

To evaluate the stabilities of the UV-reactive groups in the polyester melt, changes in  $[\eta]$  were measured when PET was treated with the UV-induced crosslinking agent and BDMK at 280°C under a stirring with a nitrogen flow (Fig. 3). In case of the epoxy compounds,  $[\eta]$  increased, after a slight decrease, especially in case of TGIC finally gelation occurred. As for DAIO, only a slight decrease in  $[\eta]$  was observed and any unfavorable reaction such as gelation did not occur.

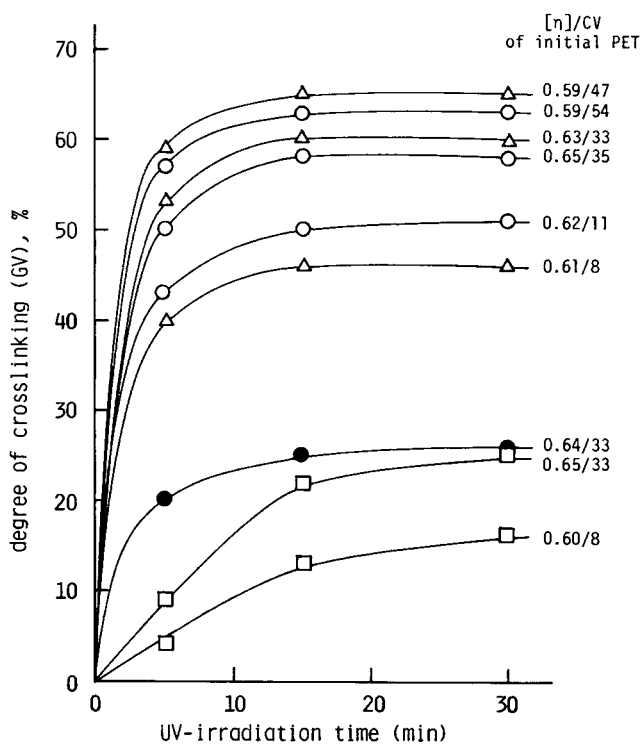


Fig. 1. UV-induced crosslinking of PET using DAGI (○), DAIO (Δ), TGIC (□) and TAIC (●). Changes in GV with UV-irradiation time.

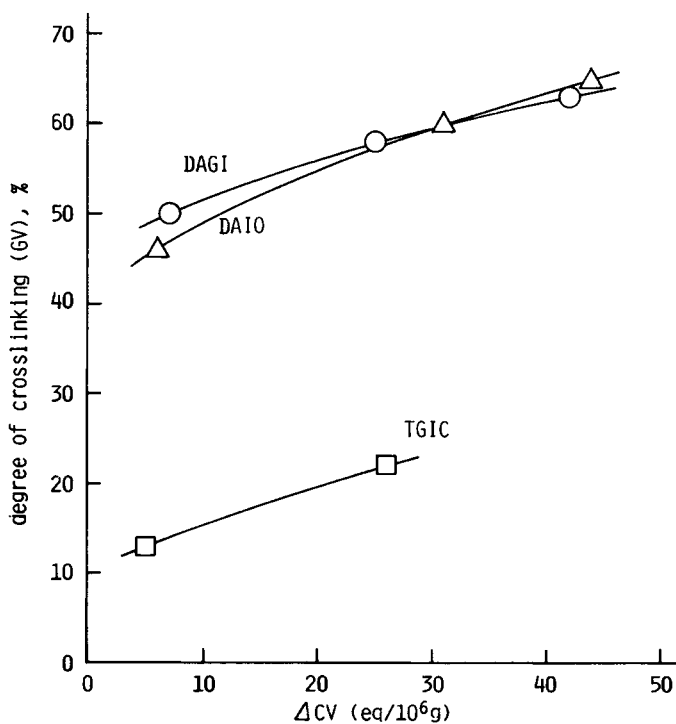


Fig. 2. UV-induced crosslinking of PET using DAGI (○), DAIO (Δ) and TGIC (□). Effect of  $\Delta CV$  on GV after 15 min UV irradiation.

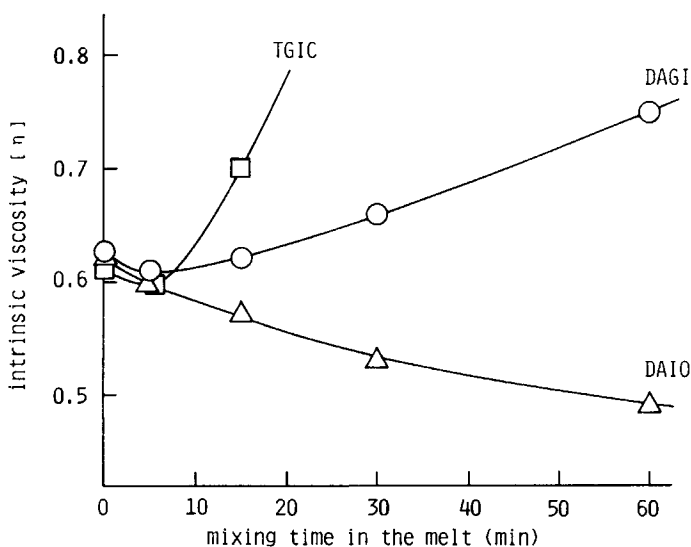


Fig. 3. Melt stabilities of UV-induced crosslinking agents. Changes in  $[\eta]$  of PET by melt treating with 2 wt% of the UV-induced crosslinking agent and 1 wt% of BDMK at 280°C under a nitrogen flow.

### CONCLUSION

The compounds having both allyl and carboxyl-reactive groups, such as diallyl glycidyl isocyanurate and 2- $[\beta$ -(3,5-diallylisocyanuro)ethyl]carbamoyl-2-oxazoline, were found to be more effective melt-blend-type UV-induced crosslinking agents than simple polyallyl compounds having no carboxyl-reactive groups. UV crosslinkability increased with an increase of the number of the agents coupled with the carboxyl terminals of the polyesters. This result indicates that the UV-induced crosslinking agent coupled with the polyesters leads to the more effective crosslinking than the semi-interpenetrating polymer networks made by the polymerization of the simple polyallyl compounds in the polyester matrix.

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