

Postcrosslinking of Linear Polyesters. I

Melt-Blend-Type UV-Induced Crosslinking Agents

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Synopsis

Postcrosslinking of such linear polyesters as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are known to be attractive means to improve their thermal resistances without sacrificing their melt processibilities. Effective melt-blend-type ultraviolet-induced crosslinking agents were investigated among allyl compounds. Such polyallyl compounds as triallyl cyanurate and triallyl isocyanurate were found to be practically promising agents from the viewpoints of crosslinkability and stability in the polyester melt. The crosslinkability of the allyl compounds increased with increasing the number of the allyl groups in the molecule and electron-withdrawing property of the neighboring group to which the allyl group was attached. The crosslinking mechanism likely includes both the polymerization of the allyl compound to form semi-interpenetrating polymer networks in the polyester matrix and the reaction between the polyester and the allyl compound moiety. The crosslinked PET and PBT showed good mechanical properties even above the melting points of the ordinary PET and PBT.

INTRODUCTION

Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are well known as commercially important polymeric materials. Many studies have been carried out to improve their performances. Among these studies, a technology to improve mechanical properties at high temperature without sacrificing their melt processibilities has been regarded as a very important target development. In particular, polyester sheets and films which can be used at high temperature have been desired for electrical applications.

Postcrosslinking of the polyesters after melt processing seems an attractive method. But is very difficult to apply conventional thermally induced crosslinking for that purpose, since a temperature to generate the crosslinking should be lower than that for melt processing. Applications of radiation-induced crosslinking are expected to be suitable means to overcome the difficulties. It was reported that PET itself can be crosslinked by ultraviolet (UV) irradiation.¹ But such self-crosslinking is of no practical value, since it takes many hours to achieve the crosslinking and simultaneous UV-induced degradation is an unavoidable accompaniment.

Many studies on the applications of UV-induced crosslinking agents to postcrosslinking of linear polyesters have been carried out. Crosslinking agents used for that purpose can be classified as follows.

(i) Copolymerization-type agent. (a) Having a photoreactive unsaturated group, and (b) having a photosensitive group to couple each other or with another group.

(ii) **Blend-type agent.** Stilbene dicarboxylic acid² and 5-maleimidylisophthalic acid³ are known as the type i-a comonomers. Such difunctional benzophenone derivatives as benzophenonedicarboxylic acid⁴ and *N,N'*-bis(β -hydroxyethyl)benzophenone-3,3',4',4'-tetracarboximide⁵ have been reported to be effective type i-b crosslinking agents. The unsaturated groups contained in the type i-a crosslinking agents are relatively active at a high temperature, and tend to cause gelation during usual melt polycondensation procedures. In contrast, the type i-b crosslinking agents are generally more thermally stable and more easily copolymerizable without trouble.

Blend-type agents (type ii) have several advantages over the copolymerization-type agents. For example, the former can be applied directly to commercially available polyesters such as PET and PBT. In other words, a copolymerization procedure as is essential to the copolymerization-type agents is unnecessary for the blend-type agents. In addition, more thermally sensitive materials can be used, since the blending procedure, even the melt blending, needs lower heating temperature and time than the copolymerization procedure.

For several years, we have been attempting to find more effective postcrosslinking agents for linear polyesters, especially the blend-type UV-induced crosslinking agents. In the present article, we would like to report the results from our investigation on the melt-blend-type crosslinking agents having allyl groups as a photoreactive group. The allyl groups are, as a radically polymerizable unsaturated group, characterized by short propagation chain length and high chain-transfer efficiencies. From the practical viewpoint, they have advantages of storage stability without inhibitors and no polymerization inhibition by air. Moreover, under certain conditions they can act as a stabilizer against oxidative degradation.⁶ These characteristics were expected to be suitable for the postcrosslinking agents.

EXPERIMENTAL

Materials

All allyl compounds evaluated here as crosslinking agents are summarized in Table I along with their melting or boiling points.

Triallyl cyanurate (Ia) and triallyl isocyanurate (IVb) were obtained from Tokyo Kasei Kogyo Co., Ltd. Triallyl trimesate (Ib) was obtained from Nakarai Chemicals Co., Ltd. and diallyl isophthalate (Ic) was obtained from Wako Pure Chemical Ind. Ltd. These allyl compounds were used after distillation *in vacuo*.

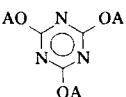
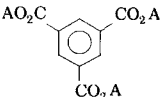

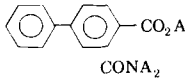
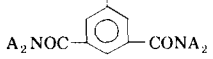

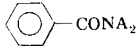
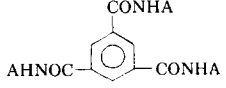
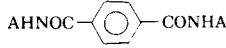
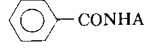
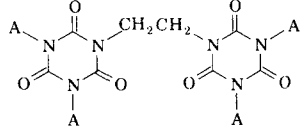
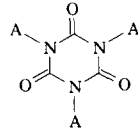
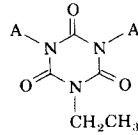
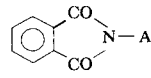
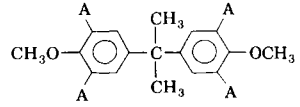
Benzil dimethyl ketal (BDMK) was obtained from Tokyo Kasei Kogyo Co., Ltd. and used without further purification.

Allyl biphenyl-4-carboxylate (Id) was prepared as follows. Biphenyl-4-carbonyl chloride (10.1 g) allyl alcohol (50 mL) and pyridine (5 mL) were heated at 90°C for 3 h. The reaction mixture was extracted with chloroform and distilled *in vacuo* to yield 8.5 g of Id.

ANAL. Calcd for $C_{16}H_{14}O_2$: C, 80.6%; H, 5.9%. Found: C, 80.2%; H, 6.1%.

N,N-diallyl- or *N*-allylcarboxamide compounds (IIa ~ c, IIIa ~ c) were prepared from the corresponding carboxylic acid chlorides and diallyl- or allyl amines according to the literature.⁷⁻⁹

TABLE I
 Allyl Compounds Evaluated as Crosslinking Agent

Compound (A-; CH ₂ =CHCH ₂ -)	Characterization
	(I-a) bp. 160–161°C (3.5 mmHg)
	(I-b) bp. 204–205°C (0.9 mmHg)
	(I-c) bp. 179–181°C (4 mmHg)
	(I-d) bp. 167–169°C (1.0 mmHg)
	(II-a) mp. 51–52°C (hexane-toluene)
	(II-b) mp. 106–108°C (ethanol)
	(II-c) bp. 95–98°C (0.3 mmHg)
	(III-a) mp. 226–228°C (ethanol)
	(III-b) mp. 210–213°C (chloroform-ether)
	(III-c) bp. 140–141°C (1.0 mmHg)
	(IV-a) mp. 60–62°C (ethanol-water)
	(IV-b) bp. 110–115°C (0.5 mmHg)
	(IV-c) bp. 120–121°C (0.8 mmHg)
	(IV-d) mp. 68–70°C (ethanol)
	(V) bp. 206–207°C (0.5 mmHg)

α,β -Bis[5-(1,3-diallylisocyanuro)]ethane (IVa) and diallyl ethyl isocyanurate (IVc) were prepared from the reaction of ethylene bromide and ethyl bromide, respectively, with sodium salt of diallyl isocyanurate as described in the previous reports.^{10,11}

N-allylphthalimide (IVd) was prepared from phthalic anhydride and allylamine.¹²

2,2-Bis(3,5-diallyl-4-methoxyphenyl)propane (V) was prepared as follows. To the mixture of 19.4 g of 2,2-bis(3,5-diallyl-4-hydroxyphenyl)propane, which had been prepared according to the method proposed by G. E. Green,¹³ and 4 g of sodium hydroxide in 150 mL of 90/10 (v/v) water-acetone, 12.6 g of dimethyl sulfate was added dropwise under ice cooling. After 2 h the reaction mixture was concentrated and distilled *in vacuo* to yield 12.9 g of V.

ANAL. Calcd for $C_{29}H_{36}O_2$: C, 83.6%; H, 8.7%. Found: C, 83.4%; H, 8.4%.

PET was prepared from dimethyl terephthalate and ethylene glycol by the ordinary melt polycondensation using Sb_2O_3 (0.03 mol%) and $Mn(OCOCH_3)_2 \cdot 4H_2O$ (0.04 mol%) as catalysts and $(CH_3O)_3P=O$ (0.05 mol%) as a stabilizer. The molten polymer obtained was cooled and pulverized, which has (η) of 0.68.

PET was prepared from dimethylterephthalate and 1,4-butanediol by the ordinary melt polycondensation using $Ti(O-nC_4H_9)_4$ (0.02 mol%) as a catalyst. The resultant PBT had [η] of 0.97.

Blending Method

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 in case of PET and at 250°C in case of PBT. When all the polymer chips melted, a prescribed amount of the UV crosslinking agent and 0.3 g of BDMK as a photoinitiator were added under stirring. After 5 minutes of mixing, resulting composition was pulverized to about 10–20 mesh and provided for UV irradiation test or analysis.

UV Irradiation Method

The sample was placed on a hot plate heated at 150°C in air and exposed to UV light for a predetermined period of time. 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 (Mode UV-M01: sensor UV35) and found to be 17 mW/cm².

Preparation of Crosslinked Polyester Films

A prescribed amount of the UV crosslinking agent and 10 g of BDMK were mixed thoroughly with 1 kg of polyester chips and then melt-extruded by a 30 mm ϕ extruder equipped with a T-die at about 280°C in case of PET and about 250°C in case of PBT. The melt extrudate was quenched on a cool drum

TABLE II
UV-Induced Crosslinking with Allyl Compounds

Allyl compound	$[\eta]$ of PET after blending of crosslinking agents	GV(%) or $[\eta]^a$ when GV = 0 after 15 min of UV irradiation
Ia	0.62	42
Ib	0.61	40
Ic	0.62	25
Id	0.63	0.60 ^a
IIa	0.60	28
IIb	0.61	21
IIc	0.61	3
IIIa	0.63	9
IIIb	0.62	3
IIIc	0.62	0.59 ^a
IVa	0.61	36
IVb	0.63	33
IVc	0.60	18
IVd	0.60	0.61 ^a
V	0.62	0.72 ^a
not added	(0.68)	0.65 ^a

^aAmount of allyl compound is 3 wt%/PET

to obtain a transparent film of a thickness of about 100 μm . Then the film was UV irradiated for 15 minutes as described above.

Analytical Procedure

$[\eta]$ was measured in *o*-chlorophenol at 35°C.

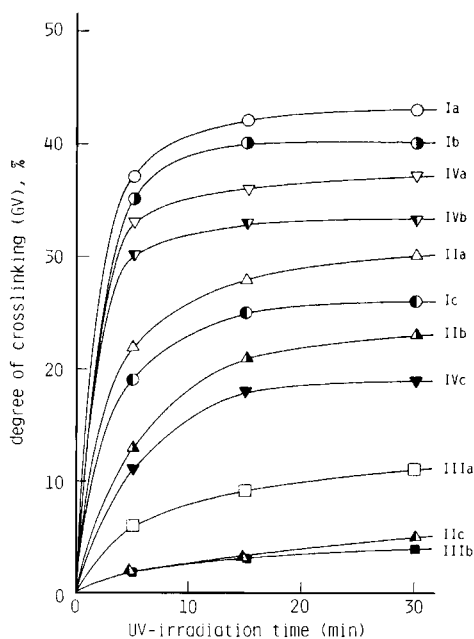
Degree of crosslinking (GV) was determined as follows. The sample (100 mg) was dissolved in 10 mL of *o*-chlorophenol at 140°C for 1 h. After removal of the soluble portion by filtration, the insoluble gel was washed well with acetone, dried, and weighed. Percentage by weight of the insoluble gel was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

Young's modulus of the film was measured at a pulling speed of 100% per minute using an Instron Engineering Company Model TM-M tensile tester.

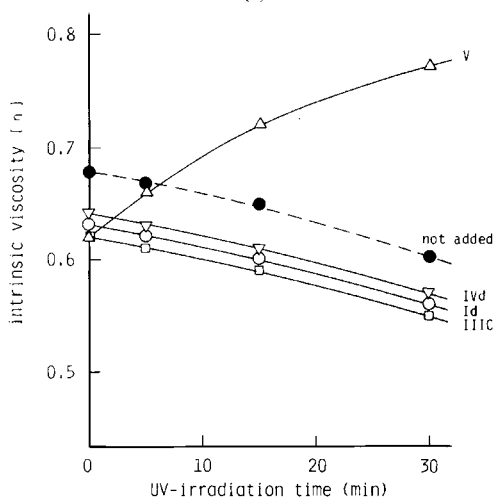
RESULTS AND DISCUSSION

UV-Induced Crosslinkability and Melt Stability of the Allyl Compounds

The results from the evaluation of the allyl compounds shown in Table I as the UV-induced crosslinking agent for PET are summarized in Table II and Figure 1. In all cases, added amounts of the allyl compound were 3 wt%/polymer. The crosslinkability was criticized by GV or $[\eta]$ after the irradiation. The results indicate that polyallyl compounds having more than one allyl group in each molecule are effective as the crosslinking agent, whereas monoallyl compounds show no effect. To compare the crosslinkability of each allyl group more precisely, GV versus the number of allyl groups in the molecule are plotted as shown in Figure 2. The reactivity of the crosslinking agent



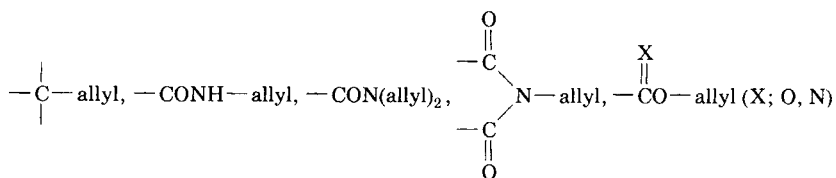
(a)



(b)

Fig. 1. UV-induced crosslinking of PET using allyl compounds. Change in GV(a) and $[\eta]$ (b) (when GV = 0) with UV irradiation time. Added amount of allyl compound: 3 wt%/PET.

varies with the neighboring group of the allyl group and increases in the following order;



This indicates that electron-withdrawing property of the neighboring group

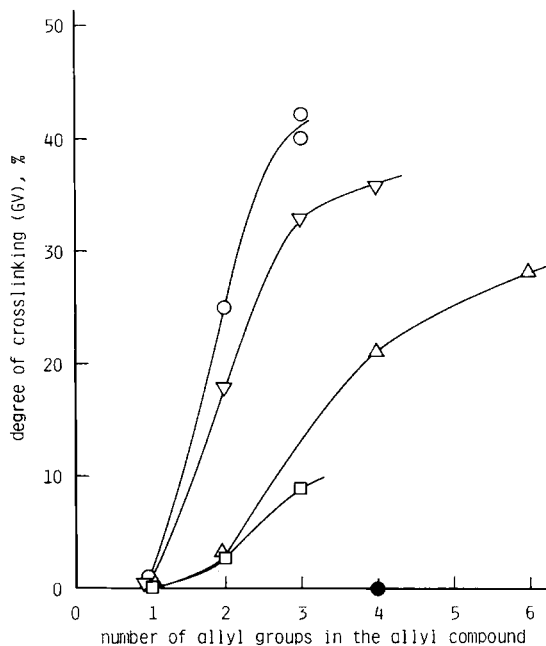


Fig. 2. UV-induced crosslinking of PET using allyl compounds. Effect of the number of allyl

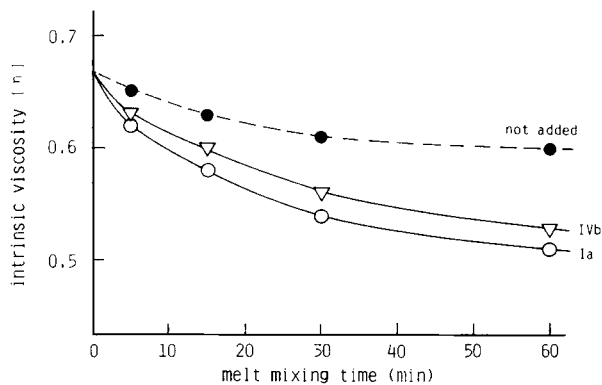
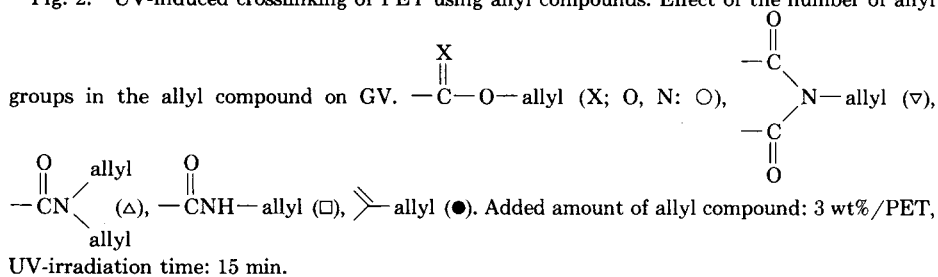


Fig. 3. Melt stability of allyl compounds. Change in $[\eta]$ of PET in the presence of 3 wt% of allyl compound and 1 wt% of BDMK at 280°C under a nitrogen flow.

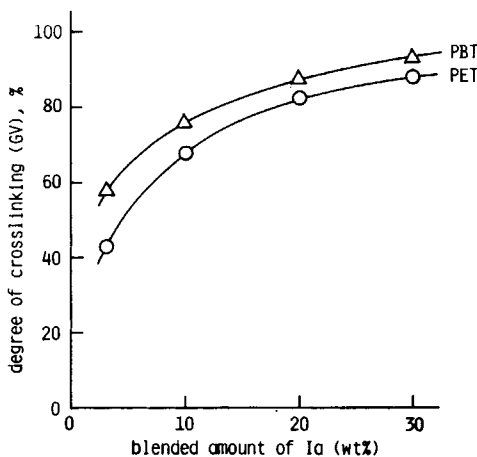


Fig. 4. UV-induced crosslinking of PET and PBT. Effect of the blended amount of Ia on GV. UV-irradiation time: 15 min.

promotes the reactivity of the allyl group. It is also shown that the crosslinkability increases with increasing the number of the allyl groups in the molecule.

As for the stability of the allyl compounds in the polyester melt, $[\eta]$ of PET after melt blending, shown in Table II, indicates that all the compounds tested here are stable under the blending conditions. To evaluate such a stability under more severe conditions, changes in $[\eta]$ were measured when PET composition containing 3 wt% of the allyl compound and 1 wt% of BDMK was kept in the melt at 280°C for 1 h under a stirring and a nitrogen flow (Fig. 3). A slight decrease in $[\eta]$ was observed, but any unfavorable reaction such as gelation did not occur.

Crosslinking Mechanism

Two types of the crosslinking mechanism can be proposed for the UV-induced crosslinking of polyesters by the polyallyl compounds. One is the formation of semi-interpenetrating polymer networks by the UV-induced homopolymerization of the polyallyl compound in the polyester matrix, the other is the formation of the linkage between the polyester and the polyallyl compound moiety.

It is well known that, in case of radical polymerization of monomers in a polymer matrix, the matrix polymer should be involved in the polymerization reaction to form graft polymers or the like unless the chain transfer constant of the matrix polymer is very small. The results from the UV-induced crosslinking of PET and PBT using Ia as the crosslinking agent are shown in Figure 4. UV crosslinkability increases as the added amount of Ia increases, as is to be expected. Another feature of the results shown in Figure 4 is that GV is always higher in case of PBT than in case of PET at the same added amount of the crosslinking agent. It can be understood that the chain transfer constant of PBT is larger than that of PET since tetramethylene glycol moiety seems more susceptible to a radical attack than ethylene glycol moiety.

As shown in Figure 5, the effect of initial $[\eta]$ of PET on the resultant GV has been investigated. GV is strongly dependent on the initial $[\eta]$, that is, higher initial $[\eta]$ results in the higher GV.

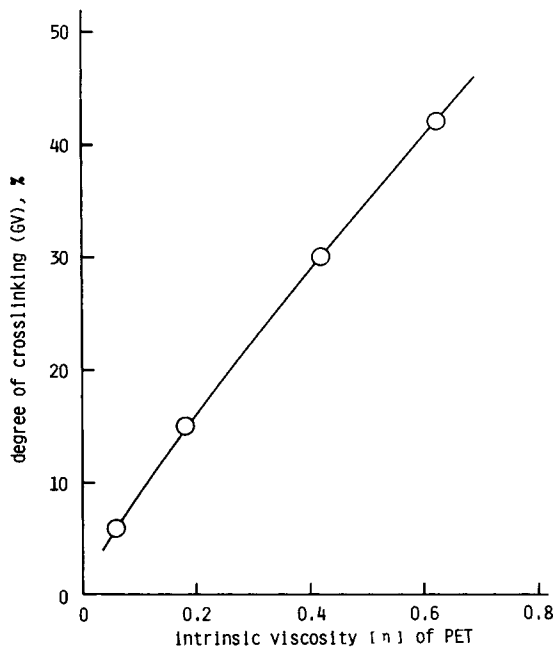


Fig. 5. UV-induced crosslinking of PET. Effect of initial $[\eta]$ of PET on GV. Added amount of Ia: 3 wt%/PET, UV-irradiation time: 15 min.

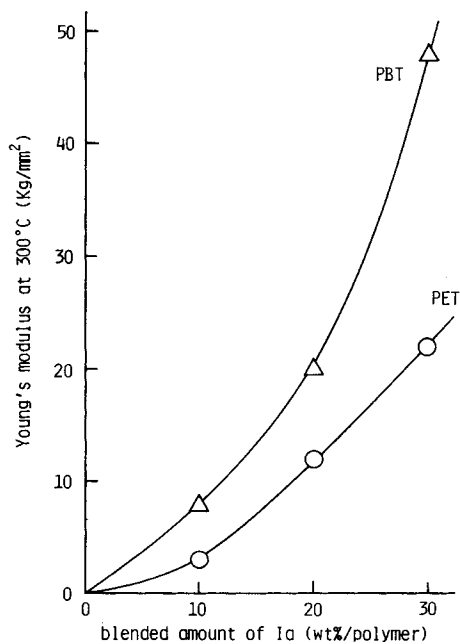


Fig. 6. Heat resistance of the UV-crosslinked polyester films.

All the results above reasonably suggest that both the polymerization of the allyl compound and the reaction between the polyester matrix and the allyl compound moiety occur during the UV-induced crosslinking.

Thermal Properties of the Crosslinked Polyesters

Young's modulus of the crosslinked PET and PBT films using various amounts of the polyallyl compound (Ia) was measured at 300°C (Figure 6). The crosslinked films showed a good heat resistance even at above the melting points of the ordinary PET and PBT. As is expected from the results in Figure 4, PBT has higher Young's modulus than PET at the same amount of Ia.

CONCLUSION

Some polyallyl compounds have proved to be very effective as melt blend-type UV-induced postcrosslinking agents for linear polyesters such as PET and PBT. The crosslinkability of the polyallyl compounds increased with increasing the number of the allyl groups in the molecule and electron-withdrawing property of the neighboring group to which the allyl group was attached.

The crosslinking mechanism of the polyester by the allyl compounds includes both the polymerization of the allyl compounds to form semi-interpenetrating polymer networks and the reaction between the polyester matrix and the allyl compound moiety. The crosslinked PET and PBT films using such effective allyl compounds as triallyl cyanurate (Ia) or triallyl isocyanurate (IVb) showed considerable mechanical properties even above the melting points of the ordinary PET and PBT.

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