Study on Triazine Thiols. II. Curing Reaction of Unsaturated Polyesters by 6-Dibutylamino-1,3,5-triazine-2,4-dithiol

INTRODUCTION

It is well known that unsaturated polyesters are cured by monomers such as styrene, vinyltoluene, acrylonitrile, methyl methacrylate, diallyl phthalate, and unsaturated fatty acid oils, in the presence of peroxides.[1] No attention, however, is paid to the curing reaction of unsaturated polyester with dithiols.[2] In this note, the curing reaction of unsaturated polyesters with 6-dibutylamino-1,3,5-triazine-2,4-dithiol (DB) was investigated for curing temperature, curing time, DB content, and the degree of unsaturation of unsaturated polyester. The investigation will serve to develop new applications for unsaturated polyesters and triazine thiols.[3-6]

EXPERIMENTAL

Preparation of Unsaturated Polyesters

A 500-ml, four-necked flask was equipped with a stirrer, siphon, nitrogen inlet, and thermometer, all reaching below the surface of the solution and a side arm with condenser set for distillation. In the flask were placed diols (1.1 mol), which were heated to 80°C. Then, maleic anhydride (1.0 mol) was added. The temperature was raised to 150°C over 1 h, then to 190°C over 2 h, and was maintained at 190°C; a vacuum of 100–200 mm Hg was applied. When the acid number of unsaturated polyesters approached a desired value, the temperature was lowered to room temperature.

The obtained sample was analyzed for hydroxyl and carboxyl end groups in Ogg's manner.[7] The sum of the hydroxyl and carboxyl numbers permits calculation of the number-average molecular weight; the total hydroxyl and carboxyl ends equals twice the number of polymer. The results are summarized in Table I.

Curing Reaction

Unsaturated polyesters and DB (Sankyo Kasei Co., Osaka, Japan) obtained commercially were placed on a Petri dish and thoroughly mixed. The mixture was cured by heating at 60–170°C for 0.5–5 h in a gear oven.

The cured sample (0.2 g) was added to a conical flask containing 20 ml tetrahydrofuran (THF) and allowed to stand for 24 h at 30°C. The insoluble parts in THF were taken out of the flask and weighed after drying for 24 h at 100°C. The insoluble fraction (G, %) of the cured mixture in THF is

$$G = \frac{\text{THF} - \text{insoluble parts}}{\text{cured sample (0.2 g)}} \times 100$$

The G values show the curing degree in the curing reaction of unsaturated polyester with DB.

Reaction of Dimethyl Maleate with DB

A 200-ml, three-necked flask was equipped with a stirrer, nitrogen inlet, and thermometer. In the flask were placed dimethyl maleate (0.02 mol) and DB (0.01 mol). After stirring at 100°C for 24 h, the mixture was extracted with ether. A part of the ether extract was column-chromatographed to give 2,4-bis(1,2-dimethylcarboxyl)ethylthio-6-dibutylamino-1,3,5-triazine (BDT) in a 96% yield: ANAL. Found: C 49.0%, H 6.6%, N 10.1%, S 11.4%. Calcd for $C_{23}H_{36}N_4O_8S_2$: C 49.26%, H 6.47%, N 9.99%, S 11.44%. IR (KBr): C=O, 1750 cm^{-1}, —N=C— (triazine ring): 860, 790 cm^{-1}.

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TABLE I
Unsaturated Polyesters

No.	Acid	Diol	Molar ratio	Polyester	Nu[a]	Molecular weight
I	$(CHCO)_2O$	$HOC_2H_4OC_2H_4OH$	1/1	$HO(COCH{=}COOC_2H_4OC_2H_4O)nH$	4.1	762
II	$(CHCO)_2O$ $C_6H_4(COOH)_2$	$HOCH_2CHOH$ $\vert$ CH_3	0.6/0.4/1	—	3.8	1465
III	$C_6H_4(COOH)_2$	$HOCH_2CHOH$ $\vert$ CH_3	0.6/0.4/1	—	8.1	3551
IV	$(CHCO)_2O$	HOC_4H_8OH	1/1	$HO(COCH{=}CHCOOC_4H_8O)nH$	2.7	455
V	$(CHCO)_2O$	HOC_4H_8OH	1/1	$HO(COCH{=}CHCOOC_4H_8O)nH$	2.3	400
VI	$(CHCO)_2O$	HOC_4H_8OH	1/1	$HO(COCH{=}CHCOOC_4H_8O)nH$	3.2	544
VII	$(CHCO)_2O$	HOC_4H_8OH	1/1	$HO(COCH{=}CHCOOC_4H_8O)nH$	3.8	644
VIII	$(CHCO)_2O$	HOC_4H_8OH	1/1	$HO(COCH{=}CHCOOC_4H_8O)nH$	5.5	941
IX	$(CHCO)_2O$	$HOC_{10}H_{20}OH$	1/1	$HO(COCH{=}CHCOOC_{10}H_{20}O)nH$	9.9	2697

[a] Number of unsaturation in polyester molecule.

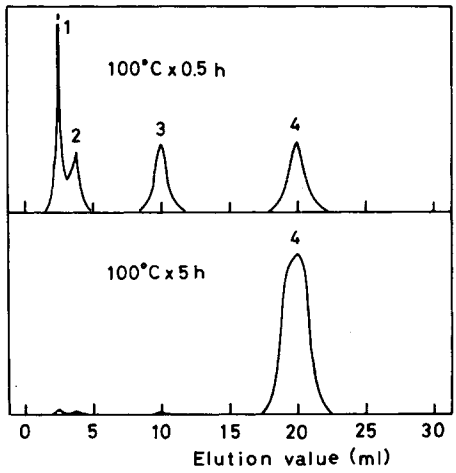
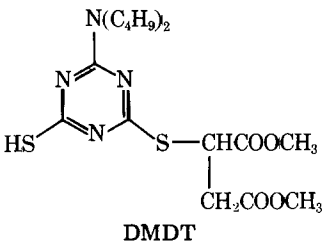
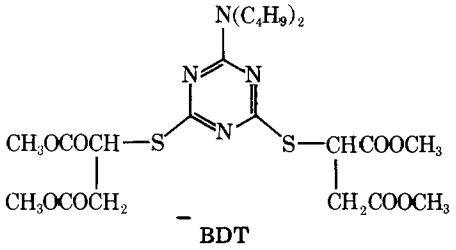


Fig. 1. Liquid chromatographs of the reaction mixture of DB (0.01 mol) with dimethyl maleate (0.02 mol) at 100°C. (1) DB; (2) dimethyl maleate; (3)



DMDT



BDT

RESULTS AND DISCUSSION

Curing Reaction

It is well known that the addition reaction of mercaptans with unsaturated compounds having electron-attractive groups in the α position of double bonds proceeds easily in the presence of alkali catalyzers.[8,9] No attention, however, has been paid to the addition of unsaturated polyesters to DB, which is a tautomer of the thiol-thione type. Figure 1 shows the liquid chromatographs of the reaction mixture of DB (0.01 mol) with dimethyl maleate (0.02 mol), which was used as a model

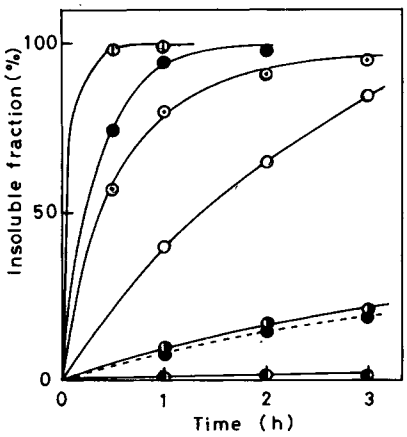


Fig. 2. Effect of curing time on the curing reaction of unsaturated polyester (I) by DB: (——) I 100 parts, DB 35.7 phr, [I]/[DB] = 1; (- - -) I 100 parts; (◐) 60°C; (◑) 80°C; (○) 100°C; (◎) 130°C; (●) 150°C; (◍) 170°C.

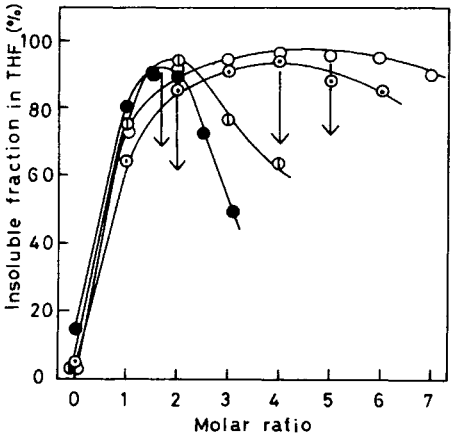
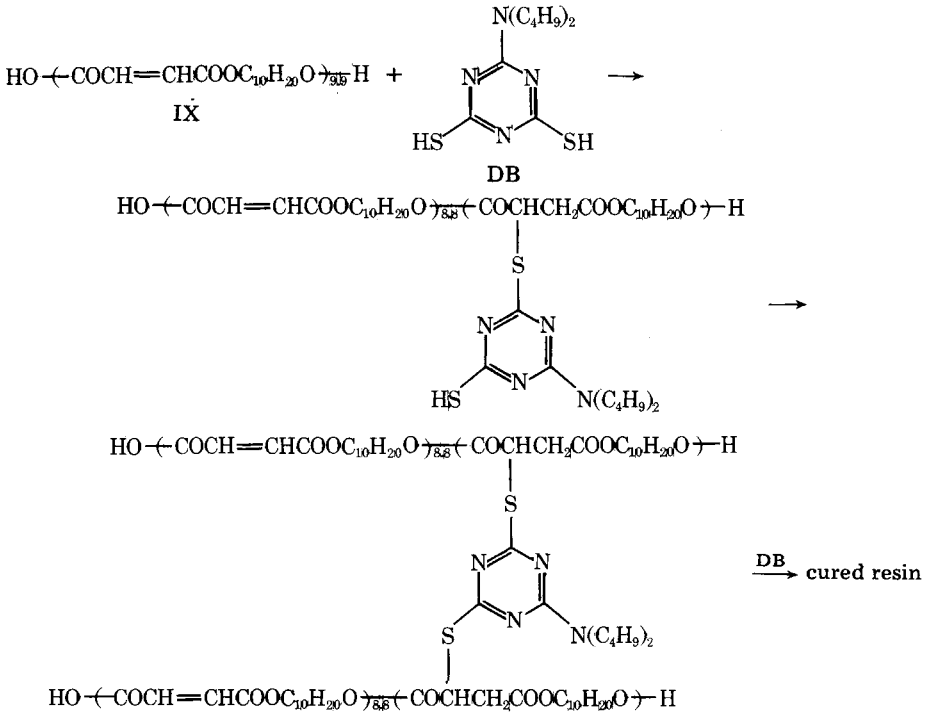


Fig. 3. Effect of moler ratio of DB to unsaturated polyesters on the curing reaction at 130°C for 3 h: (Φ) I, *Nu* = 4.1; (●) II, *Nu* = 3.8, (⊙) III, *Nu* = 8.1; (○) IV, *Nu* = 9.9.

compound of unsaturated polyesters. The chromatographs of the reaction mixture after heating for 0.5 h at 100°C showed four peaks, which are based on DB, dimethyl maleate, 2-(1,2-dimethylcarboxyl)ethylthio-4-mercapto-6-dibutylamino-1,3,5-triazine (DMDT), and BDT in the order of elute, respectively. Further, on heating for 5 h at 100°C, the preceding three peaks nearly disappeared, and only the intensity of the peak for BDT increased. The results suggest that the curing reaction of unsaturated polyesters (IX) with DB proceeds easily and irreversibly at 100°C as shown in following scheme:



On heating a mixture of unsaturated polyester (IX, 10 g) and DB (2 g) at 100°C for 5 h, the cured polyester insoluble in THF was obtained in 98% yield (found: N 4.0%, S 4.9%. Calcd: N 4.12%,

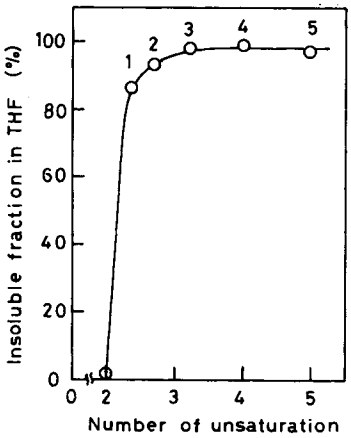


Fig. 4. Effect of number of unsaturation (Nu) per polyester molecule (IV–VIII) on the curing reaction by DB at 130° for 3 h. [DB]/[polyesters] = 1: (1) IV, molecular weight (M_w) = 400, Nu = 2.3; (2) V, M_w = 455, Nu = 2.7; (3) VI, M_w = 544, Nu = 3.2; (4) VII, M_w = 644, Nu = 4.0; (5) VIII, M_w = 941, Nu = 5.5.

S 4.72%); IR (KBr): C=O (ester), 1750 cm,$^{-1}$ —N=C— (triazine ring), 790, 850 cm.$^{-1}$ The results confirm that the above addition scheme. The addition proceeds, very easily and irreversibly, even in the absence of alkali catalyzers.

The presence of imidazole as an alkali catalyzer gave a large insoluble fraction, even at a low temperature (85% at 80°C for 3 h); but at a high temperature the insoluble fraction decreased because alkali catalyzers give rise to the reversible reaction.[10]

Effect of Curing Temperature

Figure 2 shows the effect of curing temperature on the curing reaction of unsaturated polyesters with DB in the absence of alkali catalyzer. The reaction did not take place at all at 80°C for 3 ; insoluble parts hardly resulted in the mixture. Unsaturated polyesters by DB were found to show an appreciable curing degree at temperatures above 100°C. A curing temperature of 130 or 150°C may be most desirable since a high degree of curing is obtained at a short time and the cured resin does not discolor. At a temperature above 170°C, the resin discolored.

The gellation of unsaturated polyesters in the absence of DB proceeded slightly, even at 150°C. Therefore, in the presence of DB, the self-gellation seems to be negligible.

Effect of Amount of DB

The curing degree of unsaturated polyesters is closely related to the amount of DB. The effect of the molar ratio of DB to unsaturated polyester is summarized in Figure 3. The curing degree increased first with increase in the molar ratio, reached a maximum value, and then decreased. This tendency was noted for all unsaturated polyesters used in the present experiments. The highest curing degree was obtained when half a mole DB is used with the mole number of unsaturation in the polyester polymer. In unsaturated polyesters containing a low number of unsaturation, the tendency is remarkable.

Effect of Amount of Unsaturation

The effect of the number of unsaturation in the polyester molecule on the curing degree is shown in Figure 4. The number of unsaturation over two units per polymer molecule is, on calculation, required to form the cured polyester. The curing degree increased with an increase in the number of unsaturation over two units and reached a constant value over about three units. The results suggest that no high molecular weight was necessary to obtain a sufficient curing degree.

The low number of unsaturation may give excellent resistance against heat and sunlight. The low molecular weight may lead to excellent processing.

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