

NOTES

Copolymerization of Dibutyltin Maleate with Styrene and Methyl Methacrylate

INTRODUCTION

In recent years considerable progress has been made in the synthesis of new organotin polymers and in their application in various branches of technology.¹ Although there has been much interest and research because of the application of organotin polymers as biocides, stabilizers, antifouling, and antimicrobial coatings, etc., little is reported about synthesis and application of di-alkyl-(aryl)tin polymers with pendent organotin groups. Yamada et al.² studied polymerization of dimethyltin dimethacrylate. Kauto et al.³ reported synthesis of copolymers of di-alkyltin dimethacrylate with vinyl monomers. Copolymers of dibutyltin maleate with vinyl monomers could be used as coatings which had good stability, leveling property, and yellowing resistance in patent literature.^{4,5} In the present investigation we report the preparation and characterization of copolymers of dibutyltin maleate with styrene and methyl methacrylate.

EXPERIMENTAL

Materials and Preparation of Comonomer

Benzene was distilled before use. Styrene (St) and methyl methacrylate (MMA) were distilled under reduced pressure prior to use. Benzoyl peroxide (BPO) was twice recrystallized from methanol and then dried under vacuum at room temperature.

Dibutyltin maleate (DBTM) was synthesized from dibutyltin oxide and maleate anhydride in benzene in 95% yield. The crude DBTM was recrystallized from benzene (mp 101–102°C).

ANAL: Calcd for $C_{12}H_{20}O_4Sn$: C, 41.83; H, 5.81; Sn, 34.29. Found: C, 41.50; H, 5.84; Sn, 34.28. Infrared (IR) (KBr): 2960, 2920 and 2860 cm^{-1} ($n-C_4H_9$); 1710 cm^{-1} (C=C); 1610–1550 cm^{-1} (COO-); 576–561 cm^{-1} (O–Sn–O). ¹H-NMR (in $CDCl_3$): 6.29 ppm (–CH=CH–, 2H); 1.75–1.79 ppm (–CH–Sn–CH–, 4H); 1.34–1.43 ppm (–CH₂CH₂–, 4H); 0.91–0.99 ppm (–CH₃, 6H).

Copolymerization

Predetermined amounts of DBTM, St or MMA, BPO and benzene were charged into a polymerization tube, followed by degassing. The tubes were sealed, and the polymerizations were conducted at 75°C. After the desired reaction intervals, the resulting polymer solutions were precipitated into a large excess of methanol. The polymers were further purified by repeated dissolution and reprecipitation. Then copolymers were dried in a vacuum oven at 50°C. Overall conversion was calculated from the weight of polymer obtained from a known amount of reaction mixture. The tin content of the copolymers was determined by the method of Gilman and Rosenberg.⁶

Infrared Spectra

IR spectra were obtained on a Perkin–Elmer 577 spectrometer. The absorption mode was used on finely powdered samples prepared as KBr discs.

Proton NMR Spectra

Proton NMR spectra of DBTM and polymers in $CDCl_3$ were obtained on a Varian FT-80A spectrometer operating at 80 MHz at ambient temperature. Tetramethylsilane (TMS) was used as an internal standard, and all chemical shifts were reported downfield from TMS.

TABLE I
Copolymerization of Styrene (M_1) with Dibutyltin Maleate (M_2)^a

Copolymer code	Mole fraction of M_2 in feed	Yield (%)	Percentage of tin in copolymer	Mole fraction of M_2 in copolymer
PSDM ₁	0.10	8.3	4.96	0.048
PSDM ₂	0.20	6.4	9.23	0.10
PSDM ₄	0.40	4.0	16.75	0.22
PSDM ₅	0.50	6.9	20.79	0.32
PSDM ₆	0.60	7.8	22.88	0.38
PSDM ₇	0.70	10.9	24.74	0.44
PSDM ₈	0.80	6.8	26.32	0.497

^a Polymerization conditions: solvent, benzene; (M) = 2 mol/L; initiator, (BPO) = 1.0×10 mol/L; $75 \pm 0.2^\circ\text{C}$; precipitant, methanol.

Thermal Analysis

Thermogravimetric analyses (TGA) were performed on a 4.1 module different thermobalance in static air. The heating rate was $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

The experimental data of copolymerization of DBTM with St and MMA are summarized in Tables I and II, respectively. The Kelen-Tüdös method⁷ was employed to determine the monomer reactivity ratios. The r_1 , r_2 , Q_2 , and e_2 values obtained are summarized in Table III.

Table I shows that St-DBTM copolymers contain a greater proportion of St than the feed. This phenomenon is more pronounced for the MMA-DBTM copolymers (Table II). The DBTM mole fractions in St-DBTM copolymers and MMA-DBTM copolymers were less than 0.5, because DBTM didn't homopolymerize under our experimental condition.⁹ It's expected to synthesize St-DBTM alternating copolymer when the ratio of DBTM to St in the comonomer is enough large under our experimental condition. However, it's difficult to synthesize MMA-DBTM copolymer with high DBTM content, because the polymerization ability of DBTM is great different from that of MMA.

St-DBTM and MMA-DBTM copolymers are white, fine powders. St-DBTM copolymer (DBTM content: 13.1 mol %, (η) = 0.14 dL/g in CHCl_3 at 30°C) and MMA-DBTM copolymer (DBTM content: 10.9 mol %, (η) = 0.17 dL/g in CHCl_3 at 30°C) were found soluble in benzene, toluene, chloroform, and dioctyl phthalate, partly soluble in THF and insoluble in alcohol, acetone, petroleum ether, ethyl acetate, dioxane, DMF, and DMSO.

TABLE II
Copolymerization of Methyl Methacrylate (M_1) with Dibutyltin Maleate (M_2)^a

Copolymer code	Mole fraction of M_2 in feed	Yield (%)	Percentage of tin in copolymer	Mole fraction of M_2 in copolymer
PMMDM ₂	0.20	10.7	0.42	0.0035
PMMDM ₃	0.30	9.0	0.63	0.0054
PMMDM ₄	0.40	9.2	1.04	0.0089
PMMDM ₅	0.50	8.5	1.37	0.012
PMMDM ₆	0.60	3.5	2.13	0.019
PMMDM ₇	0.70	5.8	3.46	0.031

^a Polymerization conditions: solvent, benzene; (M) = 2 mol/L; initiator, (BPO) = 1.0×10 mol/L; $75 \pm 0.2^\circ\text{C}$; precipitant, methanol.

TABLE III
Radical Copolymerization Parameters for St(M_1) or MMA(M_1) and DBTM(M_2) Systems^a

Polymer	r_1	r_2	$r_1 r_2$	Q_2^*	e_2^*
St-DBTM	2.08	0.22	0.46	0.24	0.08
MMA-DBTM	73.9	0	0		

^a Q_2 and e_2 values were calculated by Alfrey-Price eq.,⁸ thus $Q_1 = 1$, $e_1 = 0.8$ for Styrene.^a

Infrared Spectra

The IR absorption spectra¹⁰⁻¹⁴ of Polystyrene (PS) and St-DBTM copolymers with various DBTM content are shown in Figure 1. The spectra of St-DBTM copolymers indicated a band at 1730 cm^{-1} due to the C=O stretching vibration and a characteristic band in the region $1610\text{--}1550\text{ cm}^{-1}$ due to the COO— asymmetric stretching vibration. From Figure 1, it could be seen that the intensity of the bands due to the C—H out-of-plane bending vibration in monosubstituted benzene at 770 cm^{-1} and 700 cm^{-1} , and the intensity of the overtone and combination bands due to the C—H out-of-plane deformation vibration at 1942 cm^{-1} , 1869 cm^{-1} , 1801 cm^{-1} , and 1750 cm^{-1} decreased with the increasing of the DBTM content in St-DBTM copolymers. The overtone and combination bands disappeared in the IR spectrum of St-DBTM alternating copolymer (Spectrum E). The intensity of the band in the region $1610\text{--}1550\text{ cm}^{-1}$ due to the COO— asymmetric stretching vibration increased with the increasing of the DBTM content in St-DBTM copolymers.

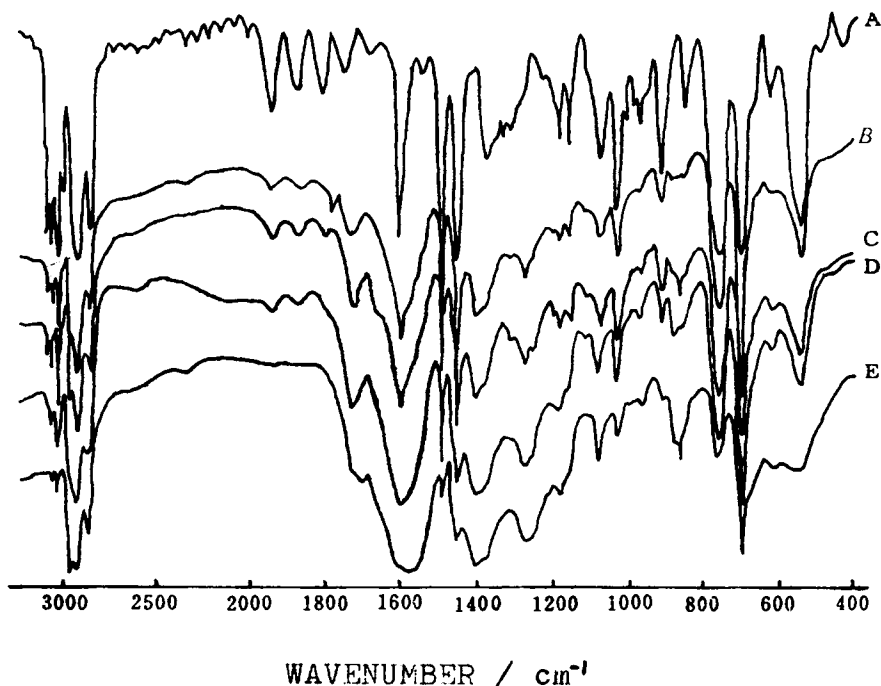


Fig. 1. IR spectra of PS and St-DBTM copolymers with various DBTM content; (A) Polystyrene (PS), (B) St-DBTM copolymer (4.8 mol % DBTM content), (C) St-DBTM copolymer (13.1 mol % DBTM content), (D) St-DBTM copolymer (22.2 mol % DBTM content), (E) St-DBTM copolymer (49.7 mol % DBTM content).

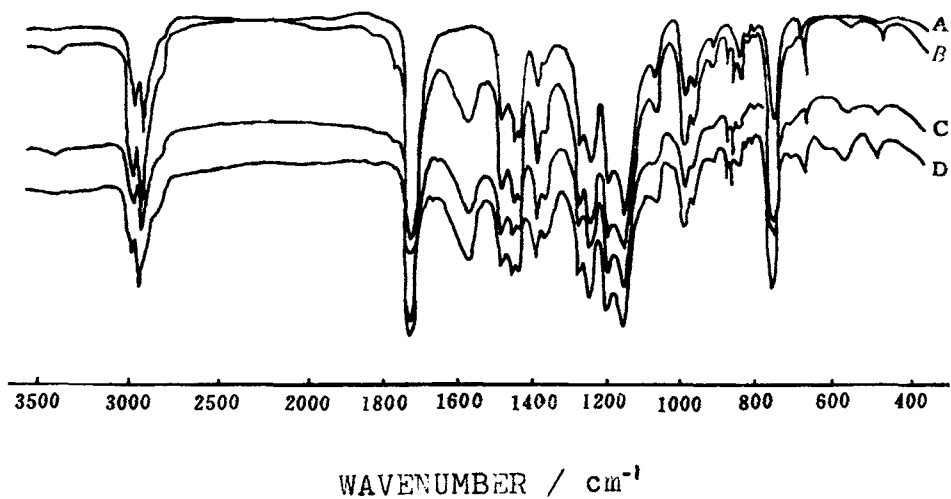


Fig. 2. IR spectra of PMMA and MMA-DBTM copolymers with various DBTM content; (A) Polymethyl methacrylate (PMMA), (B) MMA-DBTM copolymer (3.5 mol % DBTM content), (C) MMA-DBTM copolymer (7.3 mol % DBTM content), (D) MMA-DBTM copolymer (10.9 mol % DBTM content).

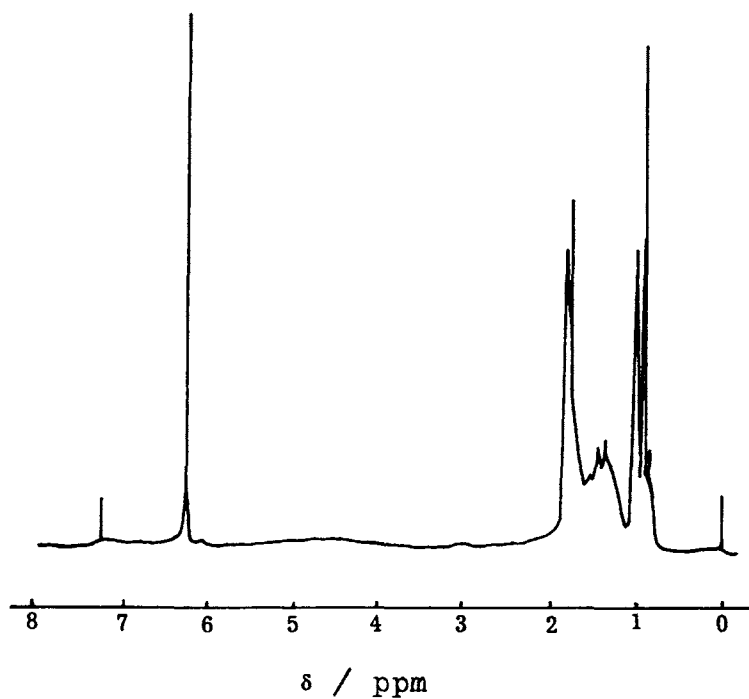


Fig. 3. ¹H-NMR spectrum of DBTM in CDCl₃.

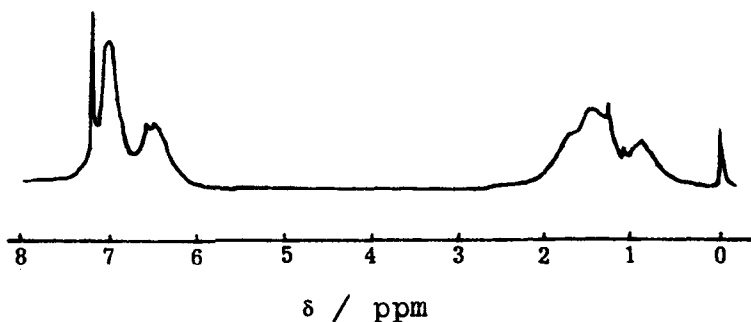


Fig. 4. $^1\text{H-NMR}$ spectrum of St-DBTM copolymer with 13.1 mol % DBTM content in CDCl_3 .

The IR absorption spectra of Polymethyl methacrylate (PMMA) and MMA-DBTM copolymers with various DBTM content are shown in Figure 2. The spectra of MMA-DBTM copolymers indicated a characteristic band in the region $1610\text{--}1550\text{ cm}^{-1}$ due to the CCO — asymmetric stretching vibration and a band in the region $576\text{--}561\text{ cm}^{-1}$ due to the O-Sn-O symmetric stretching vibration. The absorption peaks above increased with the increasing of the DBTM content in MMA-DBTM copolymers.

Proton NMR Spectra

The $^1\text{H-NMR}$ spectra of DBTM, St-DBTM copolymer (13.1 mol % DBTM content) and MMA-DBTM copolymer (10.9 mol % DBTM content) are shown in Figure 3, 4, and 5, respectively.^{13,14} Figure 3 shows a signal of vinyl protons ($-\text{CH}=\text{CH}-$) in DBTM at 6.29 ppm, which disappears

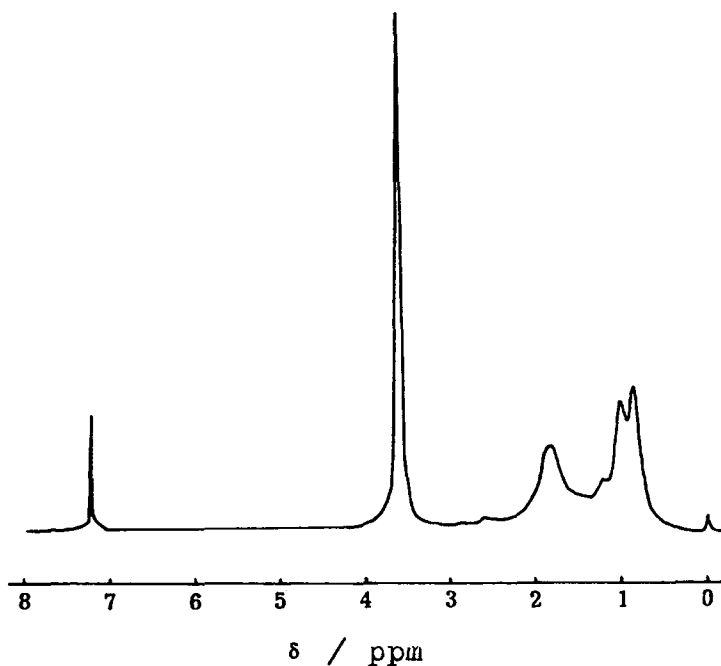


Fig. 5. $^1\text{H-NMR}$ spectrum of MMA-DBTM copolymer with 10.9 mol % DBTM content in CDCl_3 .

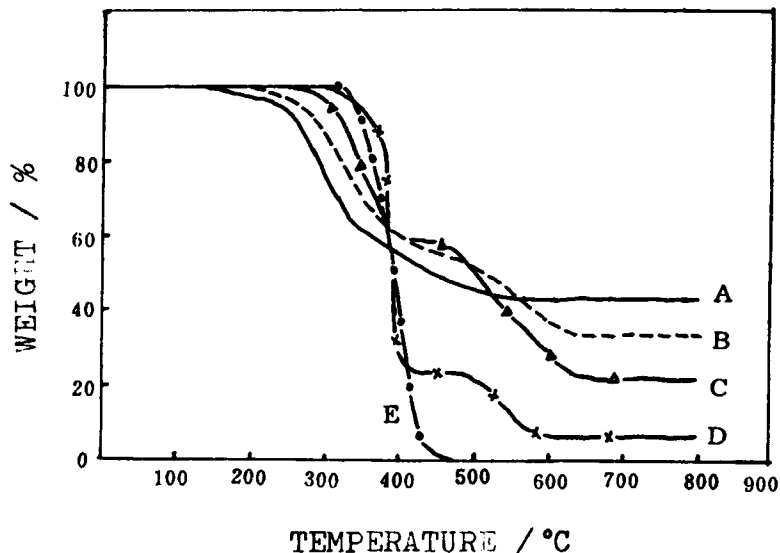


Fig. 6. TGA curves of DBTM, PS and St-DBTM copolymers with various DBTM content in air; (A) DBTM, (B) St-DBTM copolymer (49.7 mol % DBTM content), (C) St-DBTM copolymer (22.2 mol % DBTM content), (D) St-DBTM copolymer (4.8 mol % DBTM content), (E) Polystyrene (PS).

in Figure 4 and 5. The spectrum of St-DBTM copolymer shows a broad signal of aromatic protons at 7.05–6.55 ppm which results from overlapping multiplets of the five spin system. The spectrum of MMA-DBTM copolymer shows a signal of methoxyl protons ($-\text{OCH}_3$) at 3.60 ppm.

Thermal Behavior

The thermal properties of St-DBTM copolymers, MMA-DBTM copolymers, DBTM, PS, and PMMA were studied by TGA method. Figure 6 and Table IV show the thermal behavior of St-

TABLE IV
Thermogravimetric Analyses of St-DBTM Copolymers, MMA-DBTM Copolymers, DBTM, PS and PMMA

Sample	DBTM content (mol %)	Initial decomposition temperature IDT (°C)	Decomposition temperature at various weight loss DT (°C)		
			10%	30%	70%
DBTM	100	151	261	315	— ^a
St-co-DBTM	49.7	203	265	346	— ^a
St-co-DBTM	22.2	239	315	360	595
St-co-DBTM	4.8	272	336	367	405
PS	0	276	340	378	407
PMMA	0	192	255	288	346
MMA-co-DBTM	3.5	202	263	294	352
MMA-co-DBTM	7.3	215	270	298	365
MMA-co-DBTM	10.9	231	280	312	376

^a Weight loss was less than 70%.

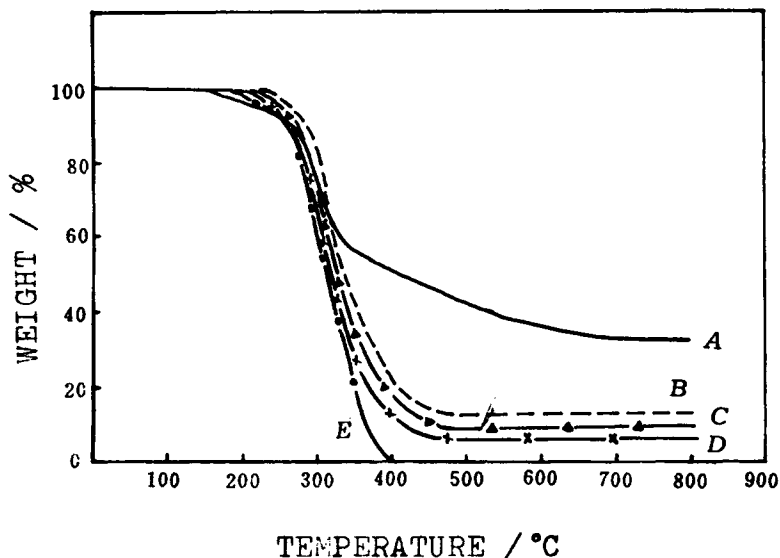


Fig. 7. TGA curves of DBTM, PMMA and MMA-DBTM copolymers with various DBTM content in air; (A) DBTM, (B) MMA-DBTM copolymer (10.9 mol % DBTM content), (C) MMA-DBTM copolymer (7.3 mol % DBTM content), (D) MMA-DBTM copolymer (3.5 mol % DBTM content), (E) Polymethyl methacrylate (PMMA).

DBTM copolymers with various DBTM content exceeds that of DBTM, but inferior to that of PS. And the initial decomposition temperature (IDT) and the decomposition temperature (DT) at various weight losses of St-DBTM copolymers decreased with the increasing of DBTM content in these copolymers due to introducing of butyl group ($n\text{-C}_4\text{H}_9\text{-}$) with poor thermal property. Figure 7 and Table IV show the thermal behavior of MMA-DBTM copolymers with various DBTM content exceeds that of DBTM and PMMA. The IDT and DT at various weight losses of MMA-DBTM copolymers increased with the increasing of DBTM content in these copolymers, since the thermal depolymerization speed of MMA block unit decreased because of existing of DBTM unit on MMA-DBTM copolymer backbones.¹⁵

The St-DBTM and MMA-DBTM copolymer may be used as polyfunctional PVC stabilizers. The effect of them on PVC stability will be reported in our following article.

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