Synthesis of Organotin Polymers from Diallyl Terephthalate and Bu$_3$SnH

OSAMU MORIYA, *Department of Chemistry, The National Defense Academy, Hashirimizu, Yokosuka 239, Japan* and TAKESHI ENDO, *Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan*

Synopsis

Crosslinked polymers containing both ester and organotin moieties were obtained in high yields from diallyl terephthalate (DATP) and tri-n-butyltin hydride via radical processes. The tributyltin ester (**1**) and the hydrostannated derivatives of DATP (**2**) were prepared and employed for copolymerizations with DATP. The copolymerizations of **1** and **2** proceeded effectively to afford the corresponding organotin polymers, in which the tributyltin group was incorporated through O—Sn and C—Sn bonds, respectively.

INTRODUCTION

In recent years, various investigations on organotin polymers have been developed because of their unique physical, chemical, and biological properties.[1] Along with these developments, a number of methods for the synthesis of polymeric organotin compounds have been proposed.[2] Hydrostannation, which is a radical process, seems to be suitable for the preparation of organotin polymers having functional groups, since alkyltin hydrides are known to generate radical species readily under mild conditions and enable chemoselective reactions.[3,4] In fact, dialkyltin dihydrides have successfully been used with bifunctionally unsaturated compounds for the synthesis of organotin polymers.[5] On the other hand, the hydrostannation using trialkyltin hydrides has been noted as an effective process for the synthesis of organotin derivatives.[6] Such monohydrides may provide a facile technique for introduction of organotin moieties into polymers, since they are generally more stable and easily handled than the dihydrides.

During the course of our investigations on synthetic applications of organotin monohydrides, the polymerization of diallylcarbonate by the use of tri-n-butyltin hydride (Bu$_3$SnH) has been found to be possible and taken up as a convenient method for the preparation of crosslinked organotin polymers.[7] In this report, we present another application of the procedure for the synthesis of organotin polymers containing ester groups, in which diallyl terephthalate (DATP) is treated as the starting monomer.

EXPERIMENTAL

Benzene was refluxed on sodium metal and distilled before use. Other reagents were used as supplied from commercial sources. The density of crosslinked polymers was measured on a density gradient tube.

CCC 0021-8995/90/9-102095-07$04.00

Reaction of DATP with Bu₃SnH

Method A. To a solution of DATP (1.00 g, 4.06 mmol) and α,α'-azo-bis(isobutyronitrile) (AIBN) (0.007 g, 0.04 mmol) in benzene (5 mL) was added Bu₃SnH (1.18 g, 4.05 mmol). After stirring for 7 h at 80°C, the solution was concentrated on a rotary evaporator. The residual oil was distilled on a Kugelrohr apparatus to obtain tributylstannyl terephthalate (**1**) (66%) and allyl 3-(tributylstannyl)propyl terephthalate (**2**) (21%). **1:** bp 200°C/0.15 mm Hg (Kugelrohr); IR (neat) 2980, 2950, 1725, 1270, 1250, 1120, 1100, 730 cm⁻¹; ¹H-NMR δ 0.30–0.90 (m, 27H), 4.80 (d, 2H, J = 6.0 Hz), 5.20–5.48 (m, 2H), 5.80–6.20 (m, 1H), 8.05 (s, 4H).

    ANAL: Calcd for $C_{23}H_{36}O_4Sn$: C, 55.78; H, 7.32. Found: C, 56.03; H, 7.61%.

    2: bp 245°C/0.15 mm Hg (Kugelrohr); IR (neat) 2950, 2920, 1725, 1645, 1333, 1270, 1250, 1128, 1105, 735 cm⁻¹; ¹H-NMR δ 0.40–2.00 (m, 31H), 4.28 (t, 2H, J = 5.0 Hz), 4.83 (d, 2H, J = 6.0 Hz), 5.20–5.50 (m, 2H), 5.80–6.20 (m, 1H), 8.10 (s, 5H).

    ANAL: Calcd for $C_{26}H_{42}O_4Sn$: C, 58.12; H, 7.88%. Found: C, 58.31; H, 8.04%.

Method B. A solution of DATP (1.00 g, 4.06 mmol) and Bu₃SnH (1.18 g, 4.05 mmol) in benzene (5 mL) was degassed and irradiated (100 W high pressure mercury lamp) at room temperature for 7 h under argon. The resulting solution was treated in a similar manner as Method A to give **1** (57%).

Method C. A mixture of DATP (1.00 g, 4.06 mmol), Bu₃SnH (0.59 g, 2.03 mmol), and di-*tert*-butyl peroxide (DTBP) (0.01 g, 0.07 mmol) was heated at 120°C without a solvent for 5 h under argon. The mixture was then distilled under reduced pressure to give **1** (33%), **2** (12%), and a rubbery solid (0.30 g), as the residue.

Polymerization of DATP with Bu₃SnH

A mixture of DATP (0.45 g, 1.83 mmol), DTBP (0.003 g, 0.02 mmol), and Bu₃SnH (5.5, 6.8, 10.5, 22.0, 30.0, or 49.7 mol %) was degassed and heated at 140°C with no solvent in a sealed glass ampoule. After heating for 3 h, the resulting crosslinked polymer (**3**) was washed with acetone in a ultrasonic washing apparatus and dried in a vacuum oven at 50°C. The tin content of the polymers (**3**) was estimated on the value of ash (regarded as SnO_2) in elemental

TABLE I

Preparation of Crosslinked Polymer (3) from Diallyl Terephthalate (DATP) and Bu₃SnH

Init. content of Bu₃SnH/DATP (mol %)	Init. content of Sn (wt %)	Polymer (3)		
		Yield (%)	Content of Sn (wt %)	Density (g/cm³)
5.5	2.6	99	2.2	1.252
6.8	3.0	91	3.8	—
10.5	4.5	94	4.2	1.251
22.0	8.4	95	7.8	—
30.0	10.9	94	12.3	1.250
49.7	18.7	78	16.0	1.248

analysis (Table I). The IR data of **3** were as follows: IR (Nujol) 1725 (C=O), 1140 cm^{-1}.

Copolymerization of DATP with Allyl Tributylstannyl Terephthalate (1)

A mixture of DATP (0.60 g, 2.45 mmol), DTBP (0.01 g, 0.07 mmol), and **1** (4.9, 10.7, 23.0, or 47.0 mol %) was degassed and then heated at 140°C for 3 h in a sealed glass ampoule. Upon working up as in the homopolymerization, the crosslinked polymer (**4**) was obtained (Table II); IR (Nujor) 1725 (C=O) cm^{-1}.

Copolymerization of DATP with Allyl 3-(tributylstannyl) Terephthalate (2)

The copolymerization was carried out in a manner similar to that mentioned above using DATP (0.50 g, 2.03 mmol), DTBP (0.01 g, 0.07 mmol), and **2** (5.2, 11.3, 22.0, or 49.8 mol %) to give the crosslinked polymer (**5**) (Table II): IR (Nujor) 1725 (C=O) cm^{-1}.

Evaluation for Reactivities of the Organotin Monomers (1 and 2)

Copolymerizations of DATP were carried out to about 30 and 60% extent of reaction with an equimolar mixture of monomer (**1** or **2**) and DATP. The reaction mixture was poured into MeOH. The MeOH soluble part of the product was recovered by distillation under reduced pressure. The ratio of the residual monomers was estimated on the ^{1}H-NMR analysis of the distillates (Table III).

RESULTS AND DISCUSSION

As to the reduction of allyic esters by Bu$_3$SnH via a radical process, a few examples have been reported by Khoo.[8] Allyl benzoate is demonstrated to

TABLE II
Preparation of Crosslinked Polymers (**4, 5**) from Diallyl Terephthalate (DATP)
and Organotin Monomers (**1, 2**)

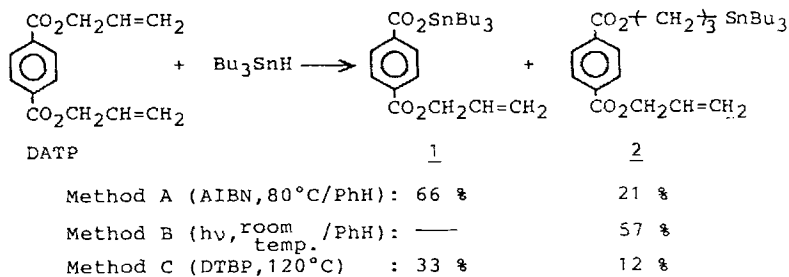| Monomer	Init. content of Monomer/DATP (mol %)	Init. content of Sn (wt %)	Polymers (**4, 5**)		
			Yield (%)	Content of Sn (wt %)	Density (g/cm^3)
1	4.9	2.1	98	2.5	1.252
	10.7	4.2	96	5.0	1.252
	23.0	7.5	98	7.9	1.251
	47.0	11.6	84	9.8	1.250
2	5.2	2.2	99	2.5	1.245
	11.3	4.3	96	5.2	1.245
	22.0	7.1	98	8.5	1.245
	˙ 49.8	11.4	88	9.8	1.244

TABLE III
Copolymerization of Diallyl Terephthalate (DATP) with an Equimolar Amount
of Organotin Monomers (1, 2)

Monomer	Reaction time (h)	MeOH insoluble substances (%)	Residual monomer ratio (1 or 2/DATP)
1	1.5	40	1.5
	2.5	60	2.1
2	2.5	33	1.7
	3.5	63	2.3

transform into tributyltin ester through the elimination of allyl group. This type of reaction was not observed in the previous cases using allylic carbonates with Bu_3SnH.[7] Accordingly, the crosslinked polymers obtained from these carbonates were simply assumed to contain tributyltin groups attached through C—Sn bond. The interesting difference of reaction patterns between allylic carbonates and esters led us to investigate the polymerizations of DATP by the use of Bu_3SnH, which seemed to afford the polymers having tributyltin ester groups.

On the basis of those considerations, the reaction of DATP, which was presumed to exhibit reactivity analogous to that of allylbenzoate, and Bu_3SnH was examined under three conditions (methods A, B, and C) to obtain some fundamental data for polymerizations using these compounds. By the reaction of DATP and Bu_3SnH carried out at 80°C in benzene with a catalytic amount of AIBN, the tributyltin ester derivative of DATP (1) was obtained as a main product in 66% yield (method A). This reaction seemed to proceed similarly to the reported one, in which the starting materials were irradiated with ultraviolet light at 80°C.[8] On the other hand, the hydrostannated derivative of DATP (2) was prepared in 57% yield by the reaction conducted at room temperature in benzene under the irradiation (method B). Next, the reaction was examined under more analogous conditions to those of the polymerizations, in which Bu_3SnH was treated with an excess amount of DATP at 120°C without solvent in the presence of DTBP as a catalyst (method C). In this case, tin ester 1 and hydrostannated derivative 2 were obtained in 33 and 12% yield, respectively. Thus, it was shown in those model reactions that the elimination of an allyl group from DATP to give the organotin ester (1) readily occurred at higher


```
    CO2CH2CH=CH2                CO2SnBu3            CO2(CH2)3SnBu3

        ⬡          +  Bu3SnH  ⟶      ⬡        +       ⬡

    CO2CH2CH=CH2                CO2CH2CH=CH2        CO2CH2CH=CH2

    DATP                            1                   2

        Method A (AIBN,80°C/PhH):  66 %             21 %
        Method B (hν,room temp. /PhH):  ——          57 %
        Method C (DTBP,120°C)    :  33 %            12 %
```

Scheme 1

reaction temperatures such as 80–120°C and the hydrostannation proceeded preferentially at lower temperatures such as 18–25°C.

The polymerizations of DATP with Bu_3SnH were carried out in bulk at 140°C in the presence of DTBP in degassed sealed ampoules. After heating for 3 h, the crosslinked polymers (3) containing both ester and organotin moieties were obtained in high yields (Table I):
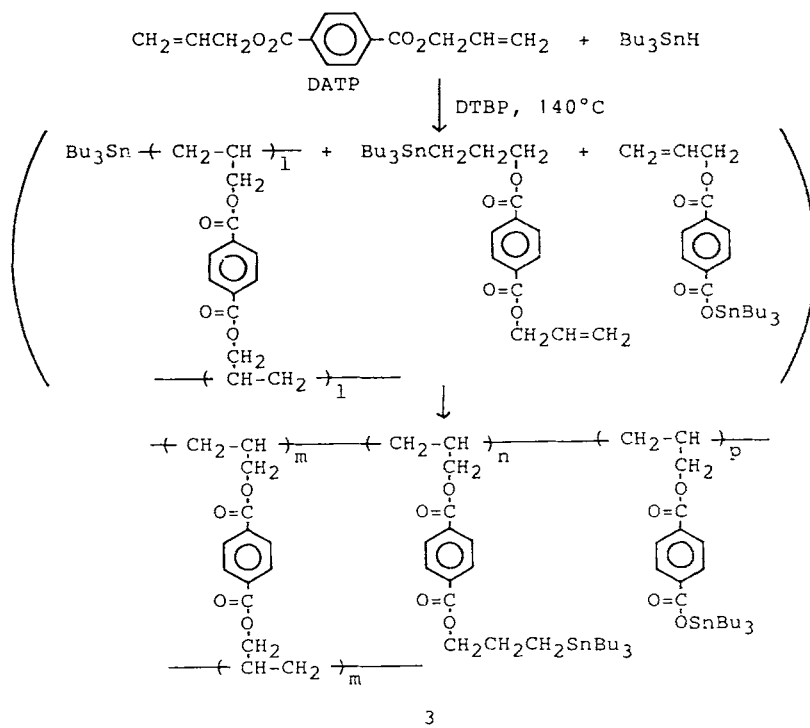
Scheme 2

The contents of Sn in the resulting polymers (3) were coincided closely with those in the monomer feed. The existence of ester groups and the transformation of the allylic double bond of DATP to a saturated bond were shown by the IR spectra of the polymer (3), in which a signal for $C=O$ was observed at 1725 cm^{-1} and a signal for $C=C$ at 1640 cm^{-1} became negligibly small. When a concentration of Bu_3SnH was less than 30 mol % against DATP, the organotin polymers (3) were formed almost quantitatively. A decrease of polymer yield was observed in the examples using 50 mol % of Bu_3SnH, in which the corresponding polymer was obtained in 78% yield. In polymer 3, the organotin moieties were presumed to consist principally of the tributyltin ester group on the basis of the results of the model reactions described above. The following results of copolymerizations of organotin derivatives 1 and 2 with DATP seem to support such a structure of the polymer 3.

The copolymerizations of DATP with 1 and 2, which were carried out under the conditions similar to those of the polymerizations using Bu_3SnH, afforded the corresponding organotin polymers 4 and 5 in high yields (Table II):
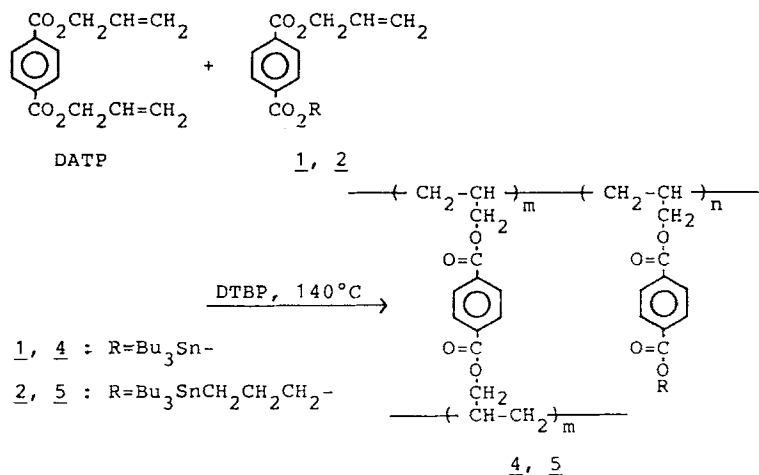
Scheme 3

Thus, two types of crosslinked polymers were obtained, one of which (4) contained tributyltin groups attached through an O$-$Sn bond and the other (5) through a C$-$Sn bond.

Comparison of the densities of polymers 3, 4, and 5 may provide information about the structures of organotin moiety contained in the crosslinked polymers. The densities of 3 and 4 changed in the region of 1.248 to 1.252. The density of the polymer 5 was invariably about 1.245. A marked change of densities with the tin contents was not observed. On the other hand, the density difference between 4 and 5 seems to reflect the different structures of the organotin moieties in the polymers; namely, the effects of introduction of the rather bulky tributyltin group, which is thought to bring about an increase of free volume in the polymer chain, may appear more clearly in polymer 5. Since the organotin moiety of 5, containing three methylene units between tin and oxygen atom, is bulkier than that of 4, in which tin is bonded directly to the ester oxygen. Another finding was that the densities of the polymer 3 and 4 lie close together in the vicinity of 1.250. Such results suggest a similarity of the structures of these polymers and support the presumption derived from the results of model reactions.

Next, the copolymerizations of DATP with an equimolar amount of 1 and 2 were conducted to evaluate the reactivities of these monoallylic organotin monomers. In these experiments, the ratio of the residual monomers was estimated by ^{1}H-NMR analysis (Table III). The residual monomer ratio of 1/DATP was 2.1 after 2.5 h in the copolymerization of DATP with the ester derivative 1; the ratio of 2/DATP was 2.3 after 3.1 h reaction. These results demonstrated that the organotin monomers were less reactive than DATP and needed a longer reaction time to accomplish the polymerizations. Therefore, these monomers, as well as the several organotin species reported before,[7,9] exert retarding effects on radical polymerizations.

References

1. C. J. Evans and S. Karpel, *Organotin Compounds in Modern Technology*, Elsevier, Oxford, 1985; T. Tahara, K. Seto, and S. Takahashi, *Polym. J.*, **19**, 301 (1987), and references are cited therein.

2. J. Kowalski, W. Stanczyk, and J. Chojnowski, *J. Rev. Silicon, Germanium Tin Lead Compd.,* **6,** 225 (1982).

3. P. J. Smith, *Organic Synthesis via Organotin Intermediates: Some Recent Developments,* Chem. & Ind., London, 1976; W. P. Neumann, *The Organic Chemistry of Tin,* Wiley, New York, 1970; R. C. Poller, *The Chemistry of Organotin Compounds,* Academic, New York, 1970.

4. H. G. Kuivila, *Synthesis,* 499 (1970); C. G. Gutierrez, R. A. Stringham, T. Nitasaka, and K. G. Glasscock, *J. Org. Chem.,* **45,** 3393 (1980).

5. G. J. M. van der Kerk, J. G. A. Luijten, and J. G. Noltes, *Angew. Chem.,* **70,** 298 (1958); J. G. Noltes and G. J. M. van der Kerk, *Rec. Trav. Chim.,* **80,** 623 (1961); W. P. Neumann and B. Schneider, *Ann. Chem.,* **707,** 20 (1967).

6. A. J. Leusink, H. A. Budding, and J. G. Noltes, *J. Organometal. Chem.,* **24,** 375 (1970); R. H. Fish, H. G. Kuivila, and I. J. Tyminski, *J. Am. Chem. Soc.,* **89,** 5861 (1967).

7. O. Moriya, S. Arai, and T. Endo, *J. Polym. Sci. Polym. Chem. Ed.,* **26,** 2573 (1987).

8. L. E. Khoo and H. H. Lee, *Tetrahedron Lett.,* 4351 (1968).

9. J. G. Noltes, H. A. Budding, and G. J. M. van der Kerk, *J. Organometal. Chem.,* **56, C11** (1973); J. W. Labadie, S. A. MacDonard, and C. G. Wilson, *Macromolecules,* **20,** 10 (1987).