

Synthesis of New Di(tri-n-butyltin) Citraconate and Its Copolymer

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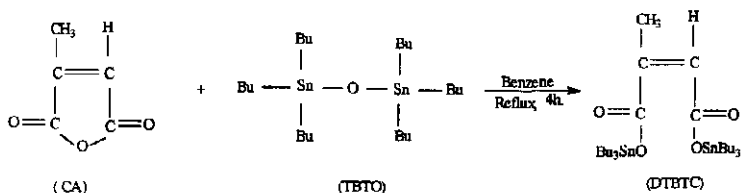
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Abstract. A new monomer of Di(tri-n-butyltin) citraconate has been synthesized by the reaction of citraconic anhydride and bis(tri-n-butyltin) oxide. This monomer was copolymerized with styrene using 2,2-azobisisobutyronitrile (AIBN) as a free radical initiator. The monomer and copolymer were identified by elemental analysis, IR and NMR spectroscopy.

Introduction

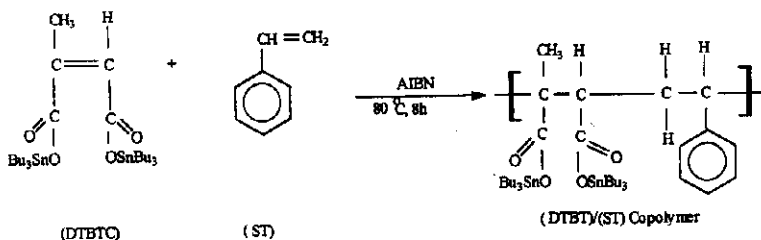
It has been shown previously that organotin polymers are efficient marine antifouling substances and wood preservatives [1-7]. As part of our extended studies, recently we have synthesized a new organotin monomer Di(tri-n-butyltin) citraconate (DTBTC) by reacting citraconic anhydride (CA) and tri-butyltin oxide (TBTO). This monomer was then copolymerized with styrene (ST) to obtain a polymer derivative, which may have strong efficacy against marine fouling. As demonstrated previously, the tin atoms in the organotin monomer and its copolymer are attached to the backbone of the polymer through O-Sn bond [2].

First the two active tin alkyl groups were attached to citraconic anhydride as shown in scheme I below:



(Scheme I)

The organotin monomer was then reacted with styrene to obtain a stable solid product as demonstrated in scheme II below:



(Scheme II)

Experimental Design

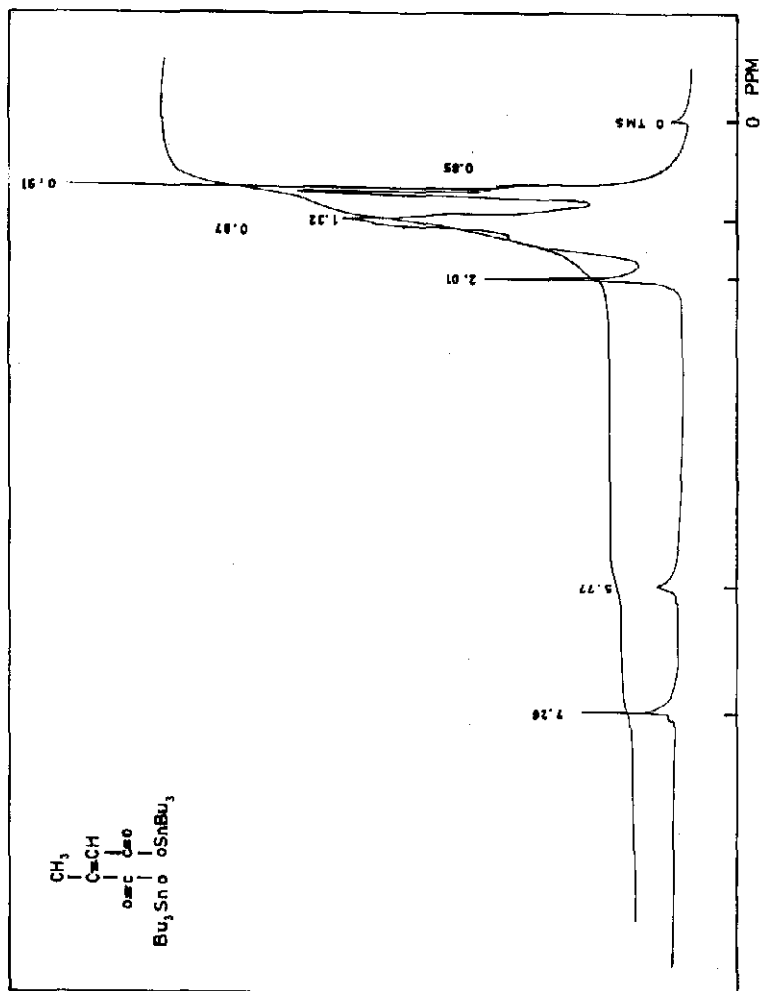
The new Di(tri-n-butyltin) citraconate monomer was synthesized by reacting tri-n-butyltin oxide (TBTO) with the citraconic anhydride (CA) in the presence of benzene and refluxed for 4hr. The liquid monomer was purified by distillation under reduced pressure. Copolymerization was carried out at 80°C in a sealed tube under nitrogen atmosphere and in the presence of catalyst 2,2'-azobisisobutyronitrile (AIBN; 1 mol %). After 8hrs, the reaction was stopped, product was dissolved in benzene and poured into excess petroleum ether. The copolymer was filtered, washed and dried vacuum at 50°C for 24hr until the weight was constant.

Results and Discussion

The presence of active SnBu₃ group was characterized by ¹³C-NMR spectrum, which exhibited four peaks between 13.68 and 27.84δ which was due to the proton moieties. There was a broad peak at 0.85 - 2.01 δ in ¹H-NMR spectrum due to organotin moiety and -CH₃ group of the monomer (Fig. 1).

The analysis of the presence of tin atoms in the monomer and copolymer has been performed by the method of Gillman and Rosenberg [8]. The most striking signal, for the copolymer was detected in the I.R. spectrum (KBr disc): which gave an absorption band at 1645 Cm⁻¹ due to the carbonyl group. The ¹H-NMR spectrum of the copolymer (CDCl₃) also showed a broad peak between 0.8 to 1.8 δ due to organotin moiety. The characteristic peak was due to the aromatic protons of styrene between 6.4 to 7.28 δ. (Fig. 1, 2).

There were no peaks noticeable for the vinyl groups of the monomers indicating that a copolymer has been formed. The monomer and copolymer will be tested for possible biological activity and will be the subject of a future publication.

Fig. 1. $^1\text{H-NMR}$ spectra of (DTBTC) monomer.

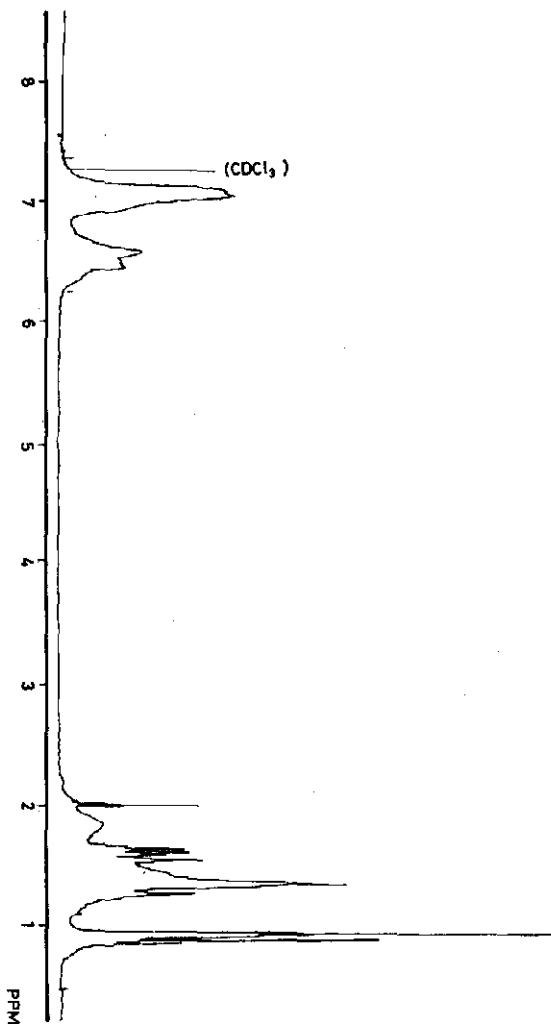


Fig. 2. $^1\text{H-NMR}$ spectra of (DTBTC)/(ST) copolymer.

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References

- [1] Al-Diab, S.S. "Synthesis of Novel Organotin Copolymer." *J. Chem. Res.*, (1986), 306-307.
- [2] Mufti, A.S. and Poller, R.C. "Stabilization of Polyvinyl Chloride by Organotin Malcate." *Chem. Abst.*, 13889 (1968), 68.
- [3] Gary, B.K., Corredor, J. and Subramanian, R. V. "Copolymerization of Tri-n-butyltin Acrylate and Tri-n-butyltin Methacrylate Monomers with Vinyl Monomers Containing Functional Group." *J. Macromol. Sci. Chem.*, All. No. 9 (1977), 1567-1601.
- [4] Al-Diab, S.S., Barcelon, M.A., Mark, J.E. and Zimmer, H. "Synthesis and Polymerization of Styrene-type Monomers Containing Phenyl-tin Alkyl Group." Presented at: *the 183rd Am. Chem. Soc. Meeting*, March, 1982.
- [5] Al-Diab, S.S., Baldwin, L. and Barcelon, J.E. and Zimmer, H. "Synthesis and Some Properties of Certain Functionally Substituted Organotin-and Silicon Compounds." Presented at the *185th Am. Chem. Soc. Meeting*, March, 1983.
- [6] Hof, T. "Review of Literature Concerning the Evaluation of Organotin Compound for the Preservative of Wood." 4, No. 23 (1969), 19-26.
- [7] Josli, R.R. and Gupta, S.K. "Synthesis, Characterization Biototoxicity and Antifouling Study of a New Organotin Monomer and Polymer." *Eur. Polym. J.*, 32, No. 5 (1996), 613-616.
- [8] Gilman, H. and Rosenberg, S.D. "Method of the Quantitative Analysis for Tin in Organotin Compounds." *J. Am. Chem. Soc.*, 75 (1953), 3592.

تحضير الأحادي الجديد ثنائي (ثلاثي - ن - بيوتيل قصدير) ستراكونيت والبلمرة المشتركة له

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ملخص البحث . تم تحضير الأحادي الجديد ثنائي (ثلاثي - ن - بيوتيل القصدير) ستراكونيت من تفاعل حامض الستراكونيك اللامائي مع مركب بس (ثلاثي - ن - بيوتيل أكسيد القصدير) والبلمرة المشتركة له مع الستايرين . وتمت دراسة الأحادي والبوليمر المشترك الجديدين بواسطة طيف الأشعة تحت الحمراء وطيف الرنين النووي المغناطيسي .