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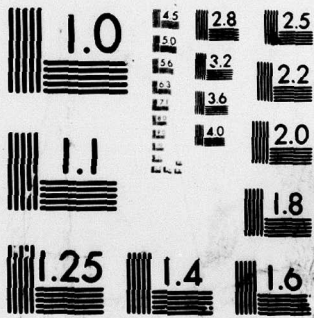
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Variable Temperature  $^{119}\text{mSn}$  Mössbauer Study of Organotin -  
Substituted Styrene Monomers and Polymers.

by

K. C. Molloy and J. J. Zuckerman  
H. Schumann and G. Rodewald

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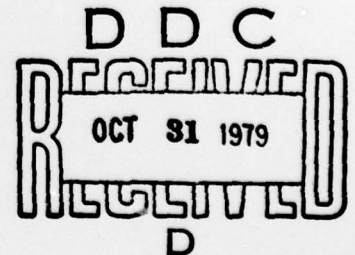
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Variable Temperature  $^{119}\text{mSn}$  Mössbauer Study of Organotin -  
Substituted Styrene Monomers and Polymers.

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SUMMARY

Variable temperature  $^{119}\text{mSn}$  Mössbauer spectroscopy can detect the enhanced binding of the tin atom in organotin(IV)-substituted styrenes on polymerization.

Tin-containing organometallic polymers (OMPs) are being actively investigated as potential marine antifouling materials. The OMPs are unique in containing the organotin pesticide chemically bound to a polymer backbone, resulting in controlled release into the marine environment.<sup>1</sup> The binding at the tin site is crucial to the rate at which the release will take place. We report here the first application of a method based upon Mössbauer spectroscopy for distinguishing the state of binding of the tin atoms in organotin-substituted monomers and polymers.

Di-para-tolyldi-para-styryltin(IV) (I) (mp 83-84°C) and tetra-para-styryltin(IV) (II) (mp 134.5-135.5°C) are solids formed by treatment of the corresponding tin chloride with the para-styryl Grignard reagent. The monomers are polymerized to (Ia) and (IIa) by gentle heating to infusible solids.<sup>2</sup> The tin-119m Mössbauer Isomer Shift (IS) and Quadruple Splitting (QS) values for the monomers (I: IS=1.23±0.02; QS=0mm/s and II: IS=1.17±0.02; QS=0mm/s) do not change outside of experimental error on polymerization (Ia: IS=1.21±0.02; QS=0mm/s and IIa: IS=1.20±0.02; QS=0mm/s).<sup>3</sup> These values are typical of simple tetraorganotin compounds,<sup>4</sup> and the failure to detect any change in their magnitudes on polymerization has been noted before for trimethyl-<sup>5</sup> and triphenyl-para-styryltin(IV).<sup>6</sup>

It has been recently found that logarithmic plots of the Mössbauer resonance areas vs. temperature are linear over an accessible temperature range as expected according to the Debye model of solids in the high temperature limit. For a thin absorber the recoil-free fraction,  $f(T)$ , is directly related to this area,  $A(T)$ , and may be used to investigate the lattice dynamics at the tin site. It is found that the more tightly bound the tin atoms, the slower will be the decrease in  $f$ , and hence  $A(T)$ , as the temperature is raised. Compounds of known structure, consisting of non-interacting monomeric molecules exhibit slopes  $[a = \frac{d \ln (A_T/A_{77})}{dT}]$  of ca.  $-1.8 \times 10^{-2} K^{-1}$ . Solids in which one-, two- or three- dimensional association is present exhibit slopes of ca.  $-0.9 \times 10^{-2} K^{-1}$  or less.<sup>7</sup>

Figure 1 displays the logarithmic plot of the area under the Mössbauer resonances, normalized to 77K for ease of comparison of data, vs. temperature

in the range 77 to 140K for monomers I and II and their polymers Ia and IIa. The spectral intensities in the case of the monomers decays rapidly [I:  $a = -2.13 \times 10^{-2} \text{K}^{-1}$  (regression analysis,  $r = -0.990$ , intercept 1.64, 4 points); II:  $a = -2.08 \times 10^{-2} \text{K}^{-1}$  ( $r = -0.998$ , 1.60, 3)], and it becomes impossible, even over extremely long counting times, to obtain usable data above ca. 100K. By contrast the spectral intensities for the materials after polymerization show slower decays [Ia:  $a = -1.79 \times 10^{-2} \text{K}^{-1}$  ( $r = -0.993$ , 1.36, 8); IIa:  $a = -1.95 \times 10^{-2} \text{K}^{-1}$  ( $r = -0.999$ , 1.51, 6)], and spectra can be obtained up to ca. 140K.

The effect of polymerization in locking the tin atom in its position must necessarily be very small, yet the effect is detectable by Mössbauer techniques in two ways. Firstly, the temperature dependences of the recoil-free fractions are discernably greater for the monomers than for their polymers. Secondly, the Debye model by which the slopes in Figure 1 are linear, itself begins to break down, and for the monomers the resonance areas above ca. 100K are very much smaller than expected by extrapolation of the linear plots in the range 77 to 100K.

While the tin atoms are clearly more free to move in the monomers, the added constraint on polymerization is not as marked as when tin atoms are bound rigidly by bridging, directly-attached electronegative substituents.<sup>7</sup> In the case of the tetraorganotins studied here, the tin atoms continue to be held by bonds to four carbons and, moreover, the polymerized lattice itself may itself be quite porous owing to the steric bulk of the atoms attached to tin.

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Figure Caption

Figure 1. Logarithmic plot of the area under the Mössbauer resonances [A(T)] normalized to 77K vs. temperaturer in the range 77 to 140K for Di-para-tolyl-di-para-styryltin(IV) and tetra-para-styryltin(IV) and their polymers.

$\text{Log}_e[A(T)/A(77)]$

