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## Long-range order in organotin monomers and polymers

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### ABSTRACT

Using gravitational mass spectroscopy (GMS) the long-range order (LRO) in organotin monomers and polymers (OTP) in the solid (film) and solved (highly dissolved in *p*-xylene) state was investigated. The GMS spectra of OTP, maleic anhydride (MA) – styrene (St) copolymer, etherified with bis(tri-*n*-butyltin)oxide, in solution (with subtracting the solvent signals) and in film were given further, those of the copolymers St-bis(tri-*n*-butyltin)maleinate and St-bis(tri-*n*-butyltin)fumarate and of the monomers bis(tri-*n*-butyltin)maleinate and bis(tri-*n*-butyltin)fumarate. The cluster of (<sup>+</sup>SnBu<sub>3</sub>)<sub>6</sub> and its associates was modeled. OTP were concluded to be thermodynamically unstable solid nanoemulsions of the first order of (<sup>+</sup>SnBu<sub>3</sub>)<sub>6</sub> clusters in the polymer matrix. The mechanism of the hydrolytic cleavage of OTP was discussed. It was analyzed how temperature influences LRO in the phenol formaldehyde OTP and how the thermal cross linking proceeds. © 2013 Trade Science Inc. - INDIA

### KEYWORDS

Organotin monomers;  
Polymers;  
Clusters;  
Structure;  
Properties;  
Long-range order.

### INTRODUCTION

Organotin polymers are used as protective antifouling<sup>[1]</sup>. However, the structure of solid OTP films at the level of LRO is not clear. It is believed that the solid OTP films for example, based on the maleic anhydride (MA) copolymer/terpolymers is a homogeneous system<sup>[1,2]</sup>. But this is questioned by a number of experiments<sup>[3]</sup>, first of all it is a permanent coating smell preventing the use of polymers with a high tin content in closed spaces. Further, high internal stresses form porous structures decreasing rapidly the antifouling effect. Studying with electron microscopy structural elements of heterogeneity resulting in phase separation and formation of porous materials, are reliably identified<sup>[4]</sup>.

2007 is even published an article on the use of organosilicon polymers based on St-MA to obtain a highly porous material<sup>[5]</sup>.

On the other side, the high difference in the melting temperatures of the low-molecular isomeric bis(tri-*n*-butyltin) maleate and bis(tri-*n*-butyltin) fumarate ( $\Delta 80$  K) is not explained yet. Since OTP, containing -SnBu<sub>3</sub> group, is the most frequently used polymer, these “strange” properties arising at polymer film formation could be caused by a strong cohesive- cooperative interaction of these groups with each other, leading to heterogeneities in solid polymers. A simple calculation shows that the cohesive energy for only one SnBu<sub>3</sub> group is more than 47 kJ/mol<sup>[6]</sup> (one-CH<sub>2</sub>-group = 2.8 kJ/mol, one CH<sub>3</sub> group = 7.1 kJ/mol) then the total cohe-

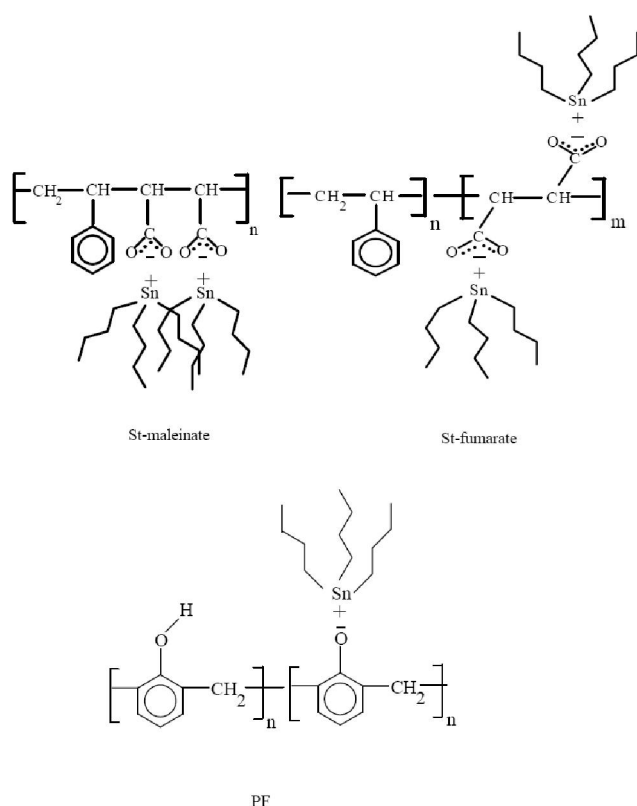
sive energy will exceed even that of a peptide group (37 kJ/mol). Therefore, with high probability heterogeneities in OTP and even splitting into two phases can be expected; understanding the reasons of these effects would be an upgrading of OTP.

It is interesting to get an idea on the energy of low-frequency movements in OTP macromolecules isolated from solvent influence. This could be realized using GMS, for example, by subtracting the solvent signals from those of the highly diluted polymer solution.

The aim of the present study is to investigate the cluster formation in organotin polymers by gravitational mass spectroscopy.

## MATERIAL AND METHODS

OTP and monomers (Figure 1) are synthesized according to the methods described in<sup>[7-9]</sup>, where *p*-xylene ( $n_D^{20} = 1.4959$ ) serves as solvent. The procedure for measuring the gravitational noises in films and solutions is given in the works<sup>[10,11]</sup>.

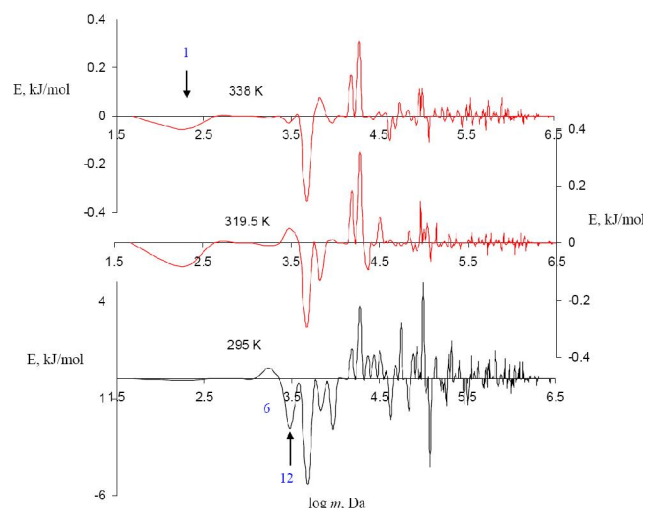


**Figure 1: Structural formulas of the investigated polymers. PF –phenol formaldehyde polymer (resole) etherified with bis (tri-n-butyl) tinoxide**

## RESULTS AND DISCUSSION

Figure 1 shows the structures of OTP analyzed in the present work they are basically different. It is reasonable to believe that the process of LRO formation in solid OTP for example, in films is strongly influenced by the configuration of organotin groups (OG) in OTP chains as well as their interaction with the surroundings. Continuously in the solid polymer run processes to minimize the potential energy of chains. This leads to thermodynamically favorable conformations of coils and to a stable coil interaction with the surroundings. The reconstruction processes are primary caused by the cohesive-adhesive interaction of chain fragments and functional groups in OTP. According to the old rule in chemistry - similar to similar- OG should approach each other and agglomerate to clusters however, the clustering can be forcibly accelerated both slowed under white gravitational noise<sup>[9]</sup>.

Figure 2 shows the energy GMS spectra of an alternating St-maleinate copolymer in diluted solution without solvent signals.



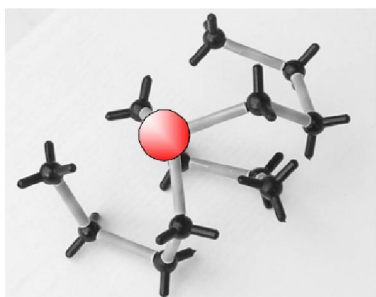
**Figure 2 : Subtraction GMS spectra of clusters in St-maleinate copolymer in diluted solution without solvent signals at different temperatures. Strong shock wave,  $p > 1N/m^2$  [9]**

The spectra are obtained by subtracting the signals of the solvent clusters (*p*-xylene) from those of the clusters in polymer solution ( $1.48 \cdot 10^{-3}$  mol/l, relative to tin). The solution is prepared applying one and the same solvent charge, before measuring both solvent and solution are kept at 295 K for 12 h, at the other temperatures - for 1 h. The wall effect<sup>[12]</sup> as a systematic error

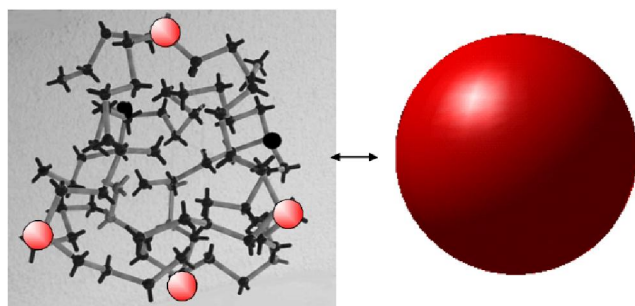
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is ignored. The cluster formation energies are very small indicating a strong cluster interaction with their neighbors and hence reduced clusters. Nevertheless, at the lower temperature of 295 K, the energy increases by an order of magnitude.

The weak signal of the small cluster referred in the Figure 2 with number 12 and being also present in the solid sample (Figure 4) shall be discussed in detail, its mass satisfactory agrees with that one of the hypothetical cluster consisting of 12 OG or 6 maleinate units. The signal of the cluster with number 1 is assigned to the hypothetical  $(^+\text{SnBu}_3)_1$  cluster (Figure 3).



A. Rod model of  $(\text{SnBu}_3)_2$ , 2.2 kHz



B. Rod model of  $(\text{SnBu}_3)_6$ , 7.4 kHz and its oscillator model (ball)

**Figure 3 : Rod cluster models. A –  $(\text{SnBu}_3)_2$ , B -  $(\text{SnBu}_3)_6$ . Small red balls – front tin cations. Calculated diameter of  $(\text{SnBu}_3)_6$  cluster is around  $1.1 \pm 0.1 \text{ nm}$**

The rod model of the organotin cluster is based on the cohesive-cooperative interaction of the butyl radicals in the heterogeneous coil polymer structure. Since the a polar styrene units and polar maleic acid anions are very different in nature the cohesive interaction between them should be strongly weakened. The total cohesion energy for  $(\text{SnBu}_3)_6$  is around 282 kJ/mol comparable to the energy required to break covalent bonds hence the thermodynamic stability of the cluster is real.

As seen in Figure 4, there are two types of oscillating clusters (expanded and collapsed) absorbing en-

ergy and releasing it at interaction with the shock wave spectrometer. The most intensive signals in these spectra are marked with the number 6 they belong to the cluster, which is modeled in Figure 3. This expanded cluster is more pronounced in the solid St-maleinate than in the diluted copolymer solution explained with its larger concentration as well as its higher individuality (weakened forces with surroundings<sup>[13]</sup>) in the polymer. When the polymer melt is cooled the signal disappears, and there appears a new weak one for the collapsed cluster. This reflects a shift of the balance between the expanded and collapsed cluster forms to the collapsed one. It is most likely to believe that this is one and the same cluster, but in different forms and with different neighbors. In solution, the cluster is partially destroyed by the solvent however, in the solid polymer, it is developing and individualizing because of cohesive forces of the alkyl groups and their cooperative interaction. Further, at cooling this cluster becomes denser. Similar processes take place with the participation of other clusters (12, 18 and 26) although in which expanded structures dominate, probably some larger clusters disintegrate into cluster-6.

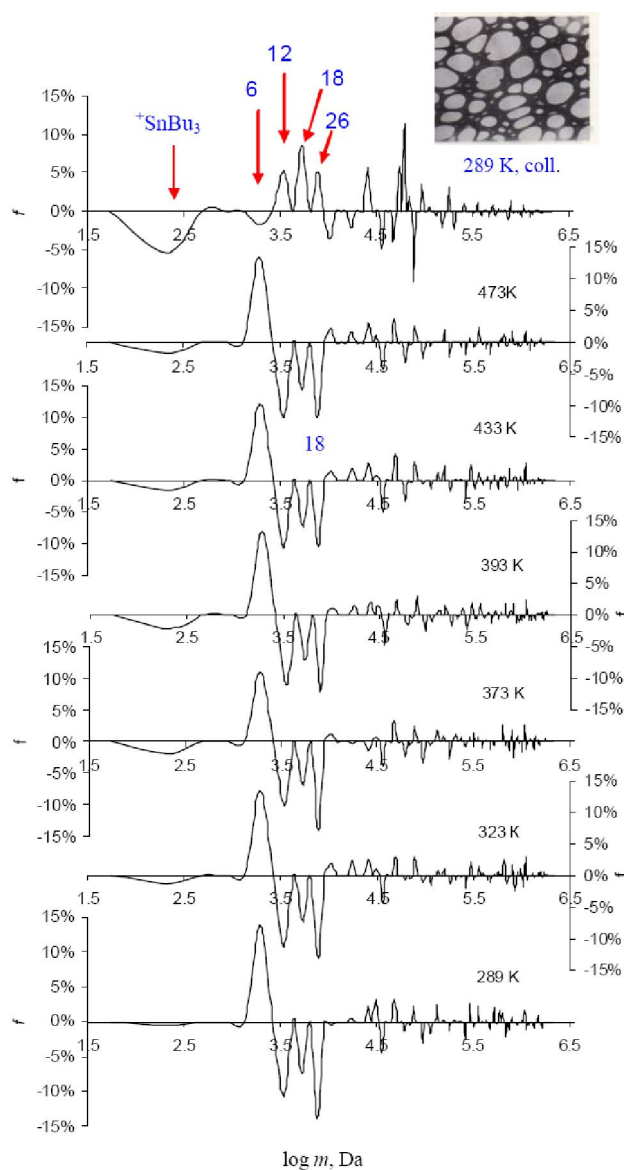
All these processes cause strong internal stresses in the polymer film with the formation of a foam like porous structure. The oscillating signals of  $^+\text{SnBu}_3$  clusters appear at  $\log m = 2.46$ .

When however, the melt of the bis (tri-*n*-butyltin)maleate monomer is cooled then the  $(^+\text{SnBu}_3)_6$  cluster will appear in the fumarate structure. Thus, the maleinate monomer is isomerized and in the small cluster range its GMS-spectrum agrees with that one of bis (tri-*n*-butyltin)fumarate (Figures 5 and 6). The strong signal of  $(\text{SnBu}_3)_6$  and the practical disappearance of  $\text{SnBu}_3$  at  $\log m = 2.46$  also points to a cluster agglomeration in the solid nanoemulsion at cooling (Figure 5).

Abnormally high internal stresses in OTP films were earlier observed for maleic anhydride co- and terpolymer being more than twice as high as in OTP without MA units<sup>[2]</sup>.

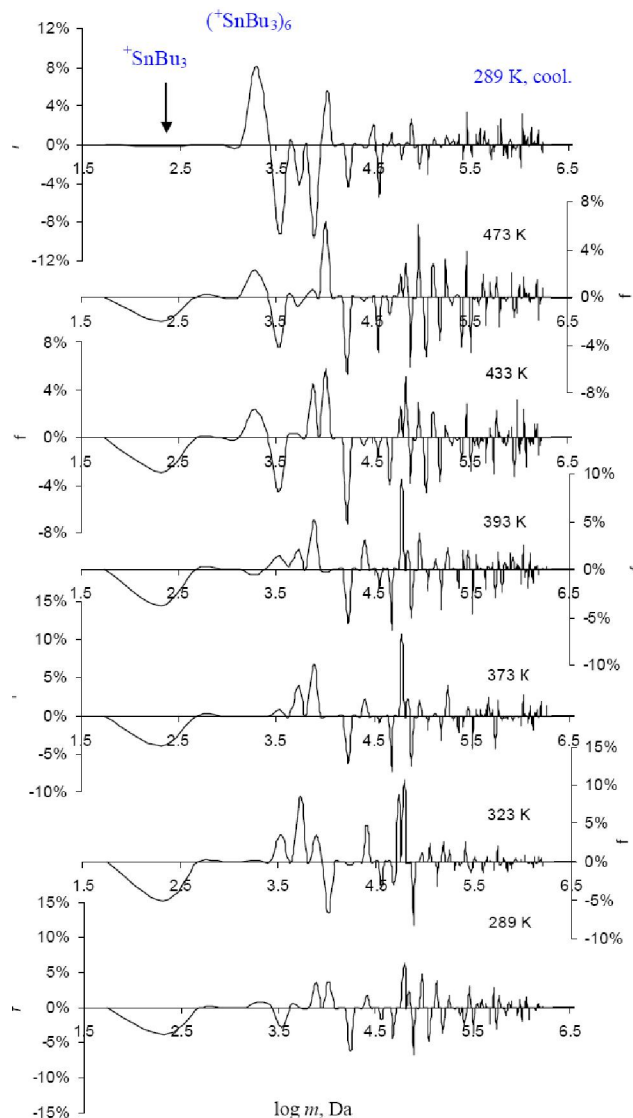
At heating OTP on MA base, in the IR spectra the carbonyl vibration band in the  $\text{COO}^-$  anion at  $1550 \text{ cm}^{-1}$  disappears instead of a new band appears at  $1640 \text{ cm}^{-1}$  (carbonyl group in the ester  $-\text{COOSnBu}_3$ ) [2, p. 211]. After cooling the film the IR spectrum agrees with that before the polymer was heated. These facts di-

rectly evidence the structural heterogeneities in OTP films on the base of MA co- and terpolymers. Modeling the heterogeneity in such polymers reveals two phases: the polymer matrix in form of a polyanion and the  $(^+SnBu_3)_n$  clusters (Figure 7). The dissociation constants for the first and second carboxyl groups in maleic acid are  $2.2 \cdot 10^{-3}$  and  $2.3 \cdot 10^{-4}$ , accordingly [2, p. 331]). As shown in Figure 7 the polyanions surround the cluster polycations. The formation process of a solid nanoemulsion (1)<sup>[14]</sup> and its partial destruction at heating (2) is given in this model (for 6 polymer units). The



**Figure 4 :** GMS spectra of solid St-maleate (289 K, soft pressing). Melt at 473 K and after natural cooling to 289 K. The numbers above the signals amounts to  $n$  in the cluster  $(SnBu_3)_n$ . Strong shock waves ( $p > 1N/m^2$ )

existence of a two-phase equilibrium was confirmed by Yin<sup>[15]</sup> using X-ray, further, he discovered two types of tin. Thus, part of OG is concentrated in clusters with  $n \geq 6$ , the remaining part is linked to the polymer chain by an ester bond ( $n = 1$ ).

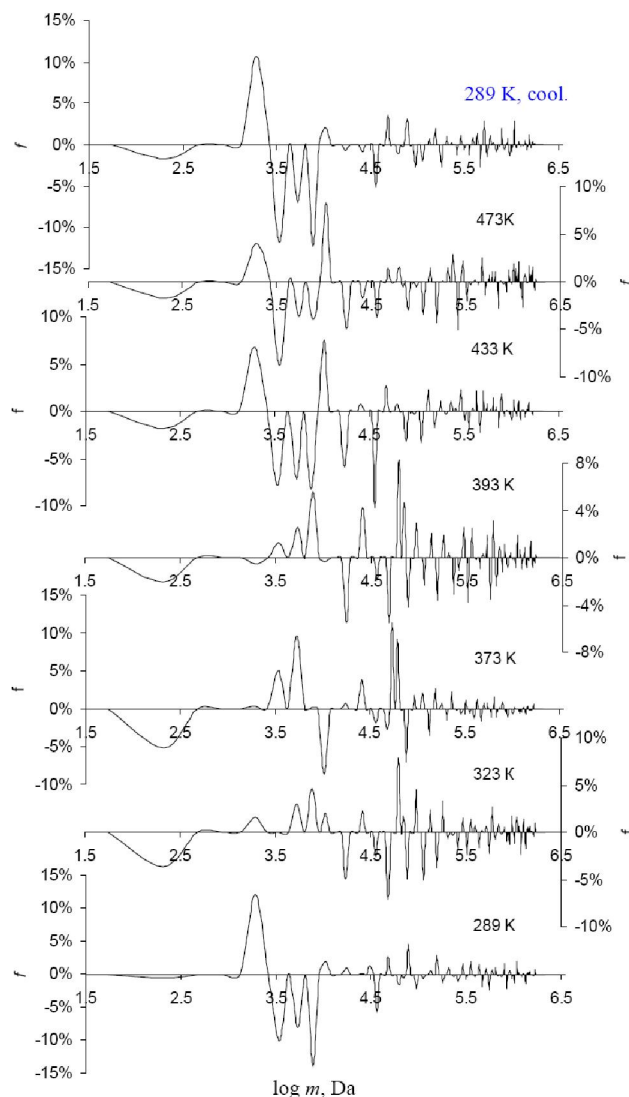


**Figure 5 :** GMS spectra of bis(tri-*n*-butyltin)maleate. The initial softly pressed sample (289 K) is melted at 473 K and then naturally cooled up to 289 K. Strong shock waves,  $p > 1N/m^2$

OTP films are known to exhibit piezoelectric properties<sup>[16]</sup> indicating that the polymers are characterized by a well organized nanostructure that under mechanical deformations generates electrical signals. Although, with rising temperature these properties weaken. A hypothetical deformation of the structure 1 (Figures 7, 15 and 16) should shift charges and induce an electrical

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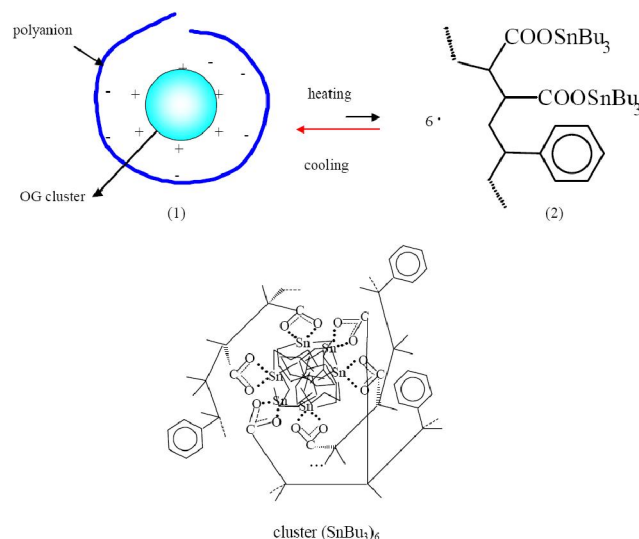
flow i.e. piezoelectricity. Thus, the piezoelectric properties of the OTP satisfactorily confirm the scheme in Figure 7 and the model for OG in Figures 15 and 16.



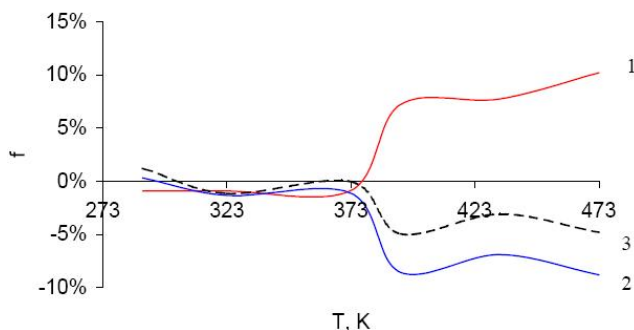
**Figure 6 :** GMS spectra of bis(tri-*n*-butyltin)fumarate. The initial softly pressed sample (289 K) at heating and after naturally cooling up to 289 K. Strong shock waves,  $p > 1\text{N/m}^2$

Strong tensions arise especially in thin OTP films based on St-MA copolymers, it leads to holes in the polymer resembling a “swiss cheese” (photo in Figure 4). These holes are typically, when strong internal tensions emerge in a two-phase, poorly miscible and unstable system. The separation of molecule groups in OTP according to the cohesive principles of preferential interaction should increase the internal tension in the film. This conclusion is evidenced by EM pictures of St-maleinate [2 p. 234] further, it proofs that the solid OTP acts as a nanoemulsion of OG clusters in the polymer matrix (Fig-

ures 3, 14 and 15). The GMS spectra (Figures 2 and 4) indicate on  $(^+\text{SnBu}_3)_n$  clusters in OTP, where  $n$  amounts to 6, 12, 18 and 26. A permanent smell of organotin compounds over all OTP films and coatings however, confirms that low-molecular tin substances are released. Hence the fast “wear and tear” of OTP antifouling coatings on the base of MA is not explained by the release of the  $(^+\text{SnBu}_3)$  cation [2, p. 327], but rather by  $(^+\text{SnBu}_3)_n$  clusters. It is hard to believe that this polycation is destroyed to monomer cations by water owing to strong cohesive interactions inside of the organotin clusters. Consequently, OTP offer large capacities to improve sustainable their protection properties. On the other hand, all attempts to detect these clusters in water with help of GMS are still unsuccessful, apparently because of the very low concentration  $(5...7) \cdot 10^{-7}$  mol/l, [2, p. 367]) and insufficient device sensitivity.

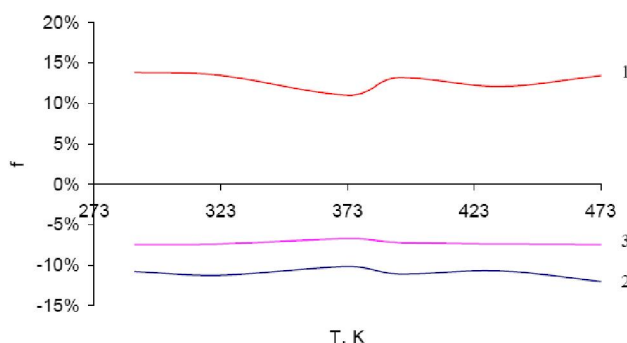


**Figure 7 :** Scheme of a solid nanoemulsion in MA based OTP (1) and its transformation to an one-phase state (2) at heating. The  $(\text{SnBu}_3)_6$  cluster formation is modeled below

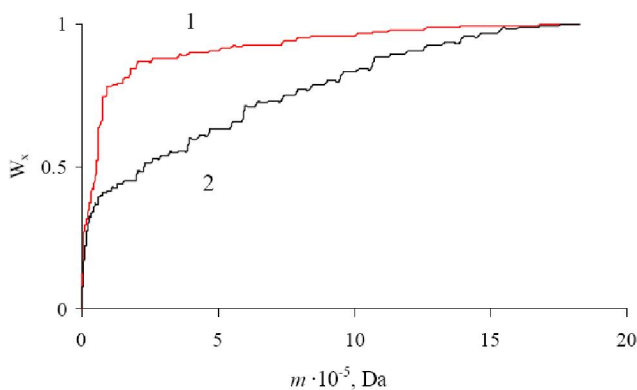


**Figure 8 :** Relative intensities of cluster signals in St-bis(tri-*n*-butyltin)fumarate versus heating temperature (see Figure 11). 1 - cluster  $(\text{SnBu}_3)_6$ , 2 - cluster  $(\text{SnBu}_3)_{12}$ , 3 - cluster  $(\text{SnBu}_3)_{18}$ . Slightly pressured (5 mg)

As shown in Figure 8 the copolymer St-bis(tri-*n*-butyltin)fumarate behaves like a block copolymer. The two blocks of the polystyrene and poly(bis (tri-*n*-butyltin)fumarate) chains differ significantly in their structure. Above 393 K the super structure of the polyfumarate block is destroyed, and the cluster oscillation becomes freer ( $|f| > 0$ ). Strong differences in the copolymerization constants of the monomers are a further evidence for the formation of a block copolymer. In contrary to St-fumarate the alternating St-maleinate copolymer does not show these regularities (Figure 9); the oscillation signals of clusters with the same mass (Figure 8) are constant over the whole temperature range (Figure 9).



**Figure 9 : Relative intensities of cluster signals in St-bis(tri-*n*-butyltin)maleinate versus heating temperature. 1 - cluster ( $\text{SnBu}_3$ )<sub>6</sub>, 2 - cluster ( $\text{SnBu}_3$ )<sub>12</sub>, 3 - cluster ( $\text{SnBu}_3$ )<sub>18</sub>. Slightly pressured (4 mg)**



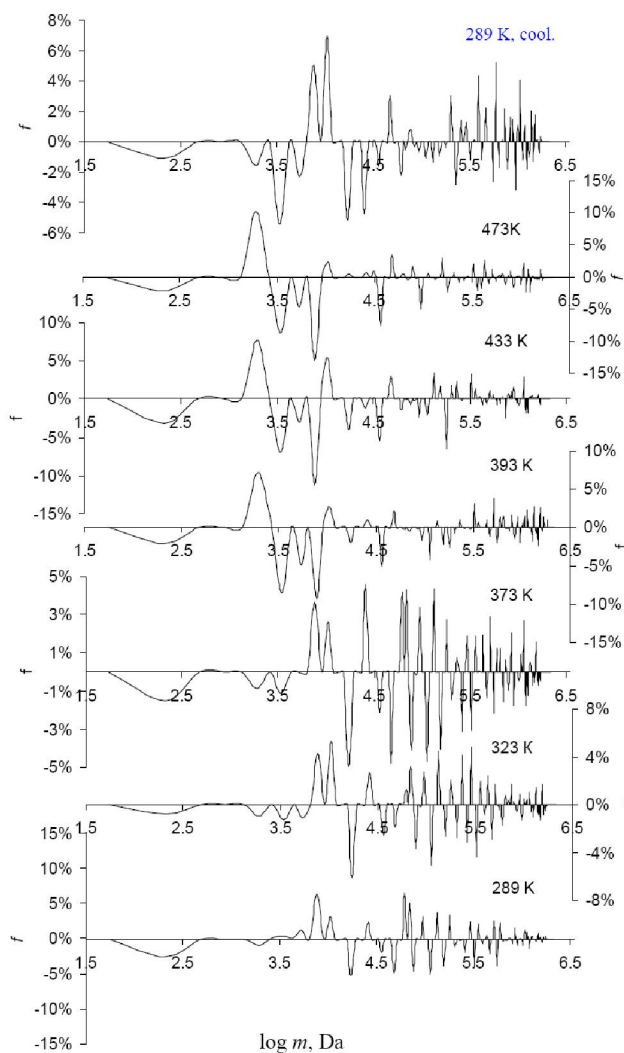
**Figure 10 : Integral distribution of cluster mass fractions in copolymers after cooling from 473 K to 289 K. 1 - St- bis (tri-*n*-butyltin) maleinate, 2 - St- bis(tri-*n*-butyltin)fumarate**

As visible from Figure 10, after cooling, the polymers are characterized by a different distribution of cluster mass fractions, especially in the middle range of molecular masses.

Comparison of skeletal clusters (signal reproducibility more than 95 %) regards a diametrically oppo-

site character in the cluster stability of polymers. For example, in St-maleinate copolymer, at heating strong changes take place in LRO the part of skeletal clusters is only 27 %, while that one for the copolymer St-fumarate amounts to 74 %. In St-maleinate, the content of collapsed clusters ( $\Sigma|f|/\Sigma|f|$ ) is found to be lower than in St-fumarate by 7 %. The number of cluster kinds remains about the same in both copolymers, in St-maleinate, it is 48-49 and in St-fumarate, it varies between 48 and 52. The proximity of both polymer GMS spectra at 473 K is remarkably, it however, regards to the cluster formation in the copolymers in the molten state, only.

OTP of the phenol formaldehyde type (PF) differ from the above discussed in the nature of the polymer chains and in the linking between tin and polymer matrix;



**Figure 11 : GMS spectra of solid St-fumarate at different temperatures,  $p > 1\text{N/m}^2$**

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the oscillation of OG clusters is especially pronounced (Figure 12). Heating the polymer to 473 K leads to cross-linking and after cooling its GMS spectrum changed little, only. Further, the part of collapsed clusters in PP is characterized by a distinctive minimum at 393 K, the average mass of clusters ( $M_{\text{GMS}} = \Sigma(f \cdot m)$ ) is strongly decreased at this temperature and at cooling from 473 K to 289 K the part of skeletal clusters becomes lower too (Figure 13). The formation of a spatial network prevents large clusters. The subsequent molecular mass rise of the clusters at  $T > 397$  K is due to LRO destruction, formation of a cross-linked structure and beginning depolymerization. The signal intensity of the  $\text{SnBu}_3$  clusters monotonically decreases at heating while that of  $(\text{SnBu}_3)_{12}$  clusters remain visible unchanged. The signal intensities of the  $(\text{SnBu}_3)_6$  clusters, however, first reduce strongly at heating to 323 K then remain almost unchanged up to 473 K. Thus, the formation of cross-linked structures in PF does not influence the cluster formation.

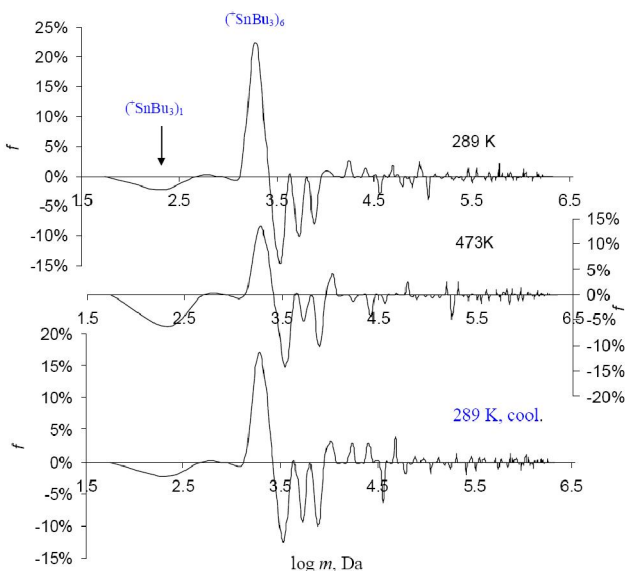


Figure 12 : GMS spectra of PF (viscous liquid, 5 mg) at different temperatures,  $p > 1\text{N/m}^2$

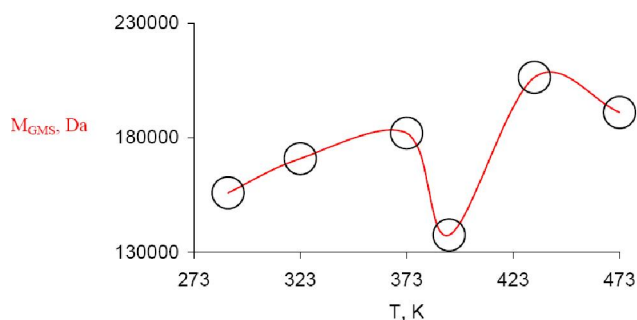


Figure 13 : Change of average cluster mass in PF at heating

TABLE 1 shows the mass of small clusters found in the monomers and the OTP.

TABLE 1 : Some cluster masses found with GMS in OTP and monomers, the masses are related to one  $(\text{SnBu}_3)_1$  group. \* Data for OTP are taken for a dilute *p*-xylene solution. ws - a weak signal. 289K

Substances	Organotin cluster, $(\text{SnBu}_3)_n$				
	n, (7.3 kHz)	n, (5.5 kHz)	n, (4.4 kHz)	n, (3.7 kHz)	n, (3.2 kHz)
Maleinate	6	12	ws	26	36
Fumarate	6	12	18	26	36
St-maleinate	6	12	18	26	ws
St-maleinate *	6	12	18	26	36
St-fumarate	6	12	18	26	36
PF	6	12	18	26	36

The TABLE 1 provides the data to get an idea on the cluster structure of the investigated substances additionally, to propose a model which is based on a cluster of one OG (Figures 14 and 15).

The structure of organotin clusters depends on temperature and can be represented in the collapsed and expanded form. The balance between collapsed and expanded structures is in both polymers and monomers characterized by something constancy with the participation of the collapsed  $(\text{SnBu}_3)_1$ ,  $(\text{SnBu}_3)_{12}$ ,  $(\text{SnBu}_3)_{18}$ ,  $(\text{SnBu}_3)_{26}$ ,  $(\text{SnBu}_3)_{36}$  and  $(\text{SnBu}_3)_6$  in the expanded form. A changed density of clusters and the cluster signal intensity provide information on the nature of their surroundings as well as on their interaction with it. Especially for OTP, it enables to understand the internal film structure at the level of macromolecule arrangement (fringed-micelle or associative) and their conformations.

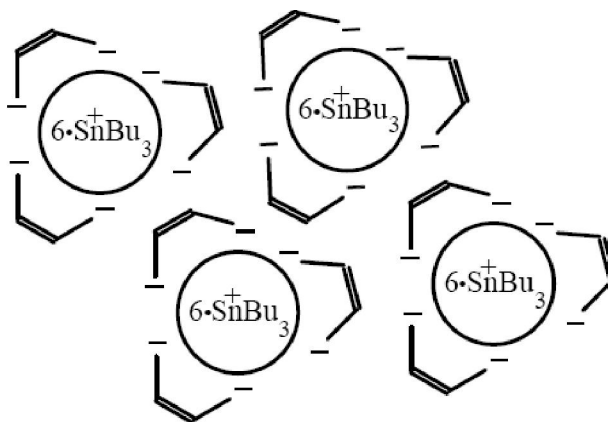
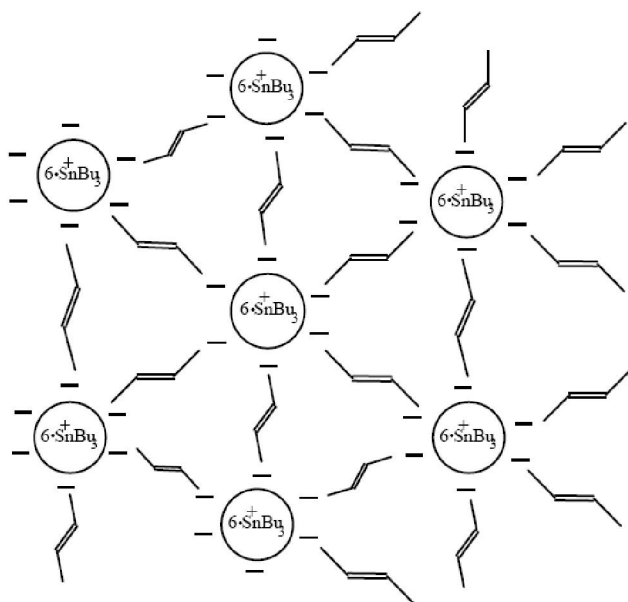


Figure 14 : Modeled cluster structure for a bis(tri-*n*-butyltin)maleinate fragment. Carboxyl groups ( $-\text{COO}-$ ) are not shown



**Figure 15 :** Modeled cluster structure for a bis(tri-*n*-butyltin)fumarate fragment. Carboxyl groups (-COO-) are not shown

The structures presented in Figures 14 and 15 differ externally, on the cluster level they are however the same and for both the OG clusters are the elements of the ensemble. Phase in which the clusters are depends on the cluster size and the experimental conditions (temperature, pressure). The larger the cluster and the higher the temperature the more it resembles the liquid and in contrary, the smaller the cluster and the lower the temperature the closer it is to the solid phase. The structures also satisfactorily explain the difference in the melting temperatures of fumarate and maleate. XRD<sup>[15]</sup> for organotin substances based on succinic acid ( $a = 2.0$  nm,  $b = 1.7$  nm and  $c = 2.1$  nm) gives also a good agreement with the periodic structures of the averaged models in Figures 14 and 15.

Molecule clusters are known to be formed in stationary shock waves (energy cluster, EC) in physical vacuum<sup>[10]</sup>. EC supply the molecule clusters with energy and “permit” for their existence. For organotin monomers and polymers, this process is enhanced by cohesive interaction of alkyl radicals. EC and various molecule clusters use extraterrestrial intelligence in the universe to communicate in real time with each other<sup>[17,18]</sup> OTP clusters are an interesting perspective, probably.

## CONCLUSIONS

The long-range order in OTP based on tri-*n*-butyltin

derivatives is represented as a thermodynamically unstable solid nanoemulsion, which is a direct emulsion of organotin clusters in the solid polymer matrix.

Clusters influence structure and properties of OTP.

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