

CHAPTER IV

CONCLUSION

Two trialkyltin monomers, tri-n-butyltin methacrylate (TBTM) and tri-n-butyltin acrylate (TBTA) were synthesized by esterification reaction. These monomers were obtained in high yield (90.0 and 95.0 % respectively). Each monomer was copolymerized with methyl methacrylate (MMA) or tertiary butylacrylate (t-Ba) in toluene solution using benzoyl peroxide (BPO) as initiator at $75 \pm 1^\circ \text{C}$. The homopolymerization of each monomer was also carried out in the same condition.

The polymerization condition was rigidly controlled to obtain a good molecular weight distribution and to keep all variable parameters constant. The yields of polymers were over 85% in all cases. Various mole ratio of monomer feeds were used for the preparation of copolymers, i.e., 0.08:0.02 , 0.06:0.04 , 0.05:0.05, 0.04:0.06 , 0.03:0.07 and 0.02:0.08 (mole/mole) of organotin monomer to (meth)acrylate comonomer.

The structures of all monomers and polymers were characterized by various spectroscopic technics, IR , ^1H NMR, ^{13}C NMR and $^{119\text{m}}\text{Sn}$ moessbauer. The formation of all copolymers and homocopolymers were confirmed by comparison of their IR and NMR spectra with those of the corresponding monomers.

IR spectra showed that all copolymers were quite similar and were characterized by two strong bands at 1645 and 1740 cm^{-1} due to (C = O) stretching of $\text{COOSn}(\text{C}_4\text{H}_9)_3$ and (C = O) stretching of $-\text{COOR}$ (where R = methyl or tertiary butyl group). Consequently, the intensity of the band at 1645 cm^{-1} (which is the characteristic peak of $-\text{COOSn}$ group) (15) increased when the mole fraction of tri-n-butyltin monomer increased.

^{13}C NMR spectra of copolymers showed two peaks of (C = O) at 180-183 ppm for the tin carboxylate group and at 175-178 ppm due to ester group of (meth)acrylate. In ^1H NMR spectra of the copolymers, a signal at 3.50-3.60 ppm was for methoxy protons ($-\text{OCH}_3$) of MMA and at 1.43 ppm due to methoxy protons ($(\text{CH}_3)_3\text{C}-\text{O}$) of the tertiary butyl group.

The $^{119\text{m}}\text{Sn}$ Moessbauer spectroscopy technic is very useful for investigating the stereochemistry and bonding of tin compounds in a solid state. Two important parameters, isomer shift (IS) and quadrupole splitting (Eq) were determined. The IS values of organotin monomers and their copolymers indicated that the alkyl groups, tri-n-butyl, were bonded to tin atom. Similary, Eq values of organotin monomers and their copolymers were in the same range which indicated a penta coordination or trigonal bipyramidal tin atom geometry with bridging carboxylate groups.

Each copolymer composition was determined by tin analysis using atomic absorption spectroscopy technic. The copolymerization

compositions curve of TBTM-MMA copolymer showed an azeotropic character at almost all compositions. The azeotropic compositions for TBTM-t-BA, TBTA-t-BA were in a wide range from 0.20-0.58 and from 0.20-0.36 of mole fraction of tri-n-butyltin monomer respectively. The results were not clearly understood as well as the TBTA-MMA copolymer system which gave no azeotropic compositions. The investigation should be carry on to make any conclusion.

The amounts of alkyl tin monomer in the polymer structure had great influence on some physical properties and films properties of the copolymers. It was observed that increasing proportion of organotin monomers in the copolymers resulted in decreasing of Tg. On the other hand, the drying time as well as the adhesion of polymer film increased. However, the disadvantage of long drying time can be overcome by the addition of dryers known in the art of paint formulations.

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