JOURNAL OF MATERIALS SCIENCE 29 (1994) 2784–2788

# Electrical properties of tri-*n*-butyl tin acrylate–methylmethacrylate copolymers

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The copolymerization of tri-*n*-butyl tin acrylate (TBTA) with methylmethacrylate (MMA) has been investigated in dioxane. The composition of these copolymers was determined quantitatively by $^1$H nuclear magnetic resonance (NMR) spectroscopy. The tin contents were estimated by gravimetric as well as thermogravimetric techniques (TGA). The reactivity ratio of such copolymers was estimated by application of the Kelen–Tudos method. The dielectric properties of the copolymers have been studied over a frequency range of 100–50 kHz at different temperatures from 20 to 70 °C. The electrical conductivity for such copolymers was also measured. The results are interpreted in terms of the tin content of the copolymers.

## 1. Introduction

Organo-tin polymers find widespread applications as fungicides [1], pesticides [2], wood preservatives [3], antifouling coatings [4], more recently as mosquito larvicides [5] and finally as u.v. stabilizers [6, 7]. The copolymerization of tributyl tin acrylate and methacrylate monomers with a number of vinyl monomers containing functional groups was studied, and the reactivity ratios were determined. These values were expected to be very useful in selecting a suitable copolymer for obtaining cross-linking antifouling with optimum mechanical and physical properties [8]. It is evident that, the physical properties of organo-tin polymers and copolymers is greatly affected by organo-tin moiety in the copolymer chain.

In spite of the great practical interest in organo-tin polymers, not much work has been done concerning its dielectric properties.

In the present study, a series of high conversion TBTA–MMA copolymers were prepared and characterized by different methods (spectral, thermal, conductive and dielectric) in order to show the effect of TBTA moiety on the properties of such copolymers.

## 2. Experimental procedure

### 2.1. Materials

Methylmethacrylate (MMA) was first washed with 10% aqueous sodium hydroxide to remove the inhibitor, then distilled under nitrogen.

Tributyl tin oxide (TBTO), was provided by M&T Chemical Inc., Rahway, New Jersey.

Azobisisobutyronitrile (AIBN) was recrystallized from ethanol, m.p. 103 °C.

### 2.2. Preparation of tri-*n*-butyl tin acrylate (TBTA) monomer

TBTA prepared according to the method of Cummins and Dunn [9] based on the estrification of acrylic acid with tri-*n*-butyl tin oxide. Acrylic acid (24.16 g, 0.335 mol) was added dropwise to a cold 100 g, (0.167 mol) solution of tri-*n*-butyl tin oxide in light petrolium ether (300 ml), over a period of 2 h at room temperature. The reaction mixture was dried over anhydrous sodium sulphate, and was filtered. The resulting solution was left overnight in a refrigerator, and the precipitated monomer was collected by filtration and purified by recrystallization from petroleum ether as colourless needles; m.p. 75 °C, yield 93%.

### 2.3. Copolymerization

Copolymers were obtained by the solution polymerization method in the presence of 1 mol % AIBN, the free radical initiator. Predetermined amounts of comonomers were placed in glass tubes, and diluted with dioxane. The total monomer composition was about 2 mol l$^{-1}$. The tubes were flushed with oxygen free nitrogen for 10 min, capped and thermostatted at 65 °C for 2 h; conversions were limited within 10%. The copolymers were obtained by precipitation from methanol, and purified by washing several times with methanol, dried and weighed.

### 2.4. Determination of tin content

The tin content of the prepared (P) PTBTA, as well as TBTA–MMA copolymers, were determined gravimetrically through oxidation of the sample to tin oxide, according to the method of Gilman and Rosenberg [10]. Approximately 0.2 g of organo-tin copolymer was weighed in a 30 ml crucible. To this was added 20 drops (10 ml) of concentrated sulphuric acid, and five drops of concentrated nitric acid. The crucible was heated slowly over a flame until the sample turned

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black, and then continuous heating was maintained until the excess acid was removed. Subsequently, carbonaceous material formed by the action of acid was completely ignited (3 h) over high heat (700 °C), leaving tin oxide as a pale yellow solid residue. From the weight of this residue, the tin content of the sample was calculated as follows:

$$\text{Tin}\,\% = \frac{\text{weight of tin oxide} \times 119 \times 100}{\text{weight of sample} \times 151}$$

Since the atomic weight of tin equals 119, the molecular weight of tin oxide is 151.

## 2.5. Preparation of the copolymer films

Copolymers of TBTA–MMA (7 g) were separately dissolved in 100 ml distilled chloroform solution. A dry film of these copolymers was obtained by casting the chloroform solution onto a Petri dish, then drying in a vacuum oven at room temperature for about 7 days (film thickness $\simeq$ 2 mm).

## 2.6. Spectral measurements

$^1H$ NMR spectra, using $CDCl_3$ as a solvent and tetra methyl silane (TMS) as an internal reference, were obtained with a Varian EM-390 spectrometer operating at 90 MHz.

## 2.7. Thermogravimetric analysis (TGA)

Thermogravimetric analyses were measured in $N_2$ at a heating rate of 15 °C $min^{-1}$ using a DT-30B thermal analyser.

## 2.8. Dielectric measurements

Permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) were measured using an NF Schering bridge type decameter in the frequency range between 100 Hz to 50 kHz. A Guard ring capacitor, type NFM/5T, was used. The accuracy of the $\varepsilon'$ measurements was $\pm$ 1%, while for $\varepsilon''$ it was $\pm$ 3%. A description of the instrument and methods used are given in the instruction sheet by Wiss Tech. Werkstten Weilheim, OB, Germany (WTW) [11]. Measurements were carried out at temperatures between 20 and 70 °C, using an ultra-thermostat.

## 2.9. Electrical conductivity measurements

To measure electrical conductivity $\sigma$, for the copolymers investigated, a power supply unit, OM 45161/01, was used giving a stable d.c. voltage between 0 and 250 V, with a maximum permissible loading current of 1 mA. The potential difference ($v$) between the plates holding the sample was measured by a multimeter type URI BN 1050; while the current ($I$) flowing through it was measured using Picometer type 4/OA, Keithley, with an accuracy $\pm$ 2%. The cell used for electrical conductivity measurements is that used for dielectric measurements.

TABLE I Chemical shift of TBTA–MMA copolymers

| Resonance signal (ppm) | Proton | Assignment | Remarks |
|---|---|---|---|
| 3.8–3.0 | 3 | $-O-CH_3$ | 3 MMA |
| | | $x-CH_2-\overset{CH_3}{\overset{\vert}{C}}$ | 5 MMA |
| 2.2–0.4 | 35 | $y-CH_2-CH$ | 3 TBTA |
| | | $y-(C_4H_9)_3$ | 27 TBTA |

## 3. Results and discussion

Copolymers having different concentrations of TBTA moiety were prepared in dioxane at 65 °C in the presence of AIBN as a free radical initiator. The total monomer concentration was 2 mol $l^{-1}$. The two monomers are incorporated into the copolymers depending on their relative concentrations and reactivities. The composition of the copolymers was determined quantitatively by $^1H$ NMR spectroscopy. The tin content of the copolymers was determined using both gravimetric as well as thermogravimetric techniques, in order to compare the results of these two techniques with that of $^1H$ NMR spectroscopy. Table I shows the chemical shift of TBTA–MMA copolymers measured in deuterated chloroform. Analytical data for the different copolymer samples are depicted in Table II. The reactivity ratios for the comonomers were calculated using the Kelen–Tudos equations [12]. Fig. 1 shows a plot for this system; the intercept of the line at $\xi = 1$ is equal to $r_1$ (TBTA), and that of $\eta = 0$ is equal to $r_2/\alpha$ [13], where $\alpha$ is an arbitrary parameter. The monomer reactivity ratios for such copolymerization were found to be $r_1$ (TBTA) = 1.12 and $r_2$ (MMA) = 1.85, respectively.

Messiha *et al.* [14] have obtained different values for the same system: $r_1$ (TBTA) = 0.395, and $r_2$ (MMA) = 2.18. The difference between the present $r_1$ and $r_2$ values, and those reported by Messiha *et al.*, is a result of the difference in the technique for determination of $r_1$ and $r_2$; Messiha *et al.* used the percentage tin gravimetric method for determination of monomer reactivity ratios.

The obtained copolymer samples were white rubbery materials, soluble in most organic solvents. Table III represents the theoretical and determined percent-

TABLE II Analytical data for the copolymerization of TBTA with MMA. Solvent, dioxane; initiator, AIBN 1 mol %; temperature, 65 °C

| | Integral peak area | | $\alpha = 0.3076$ |
|---|---|---|---|
| $a$[a] | $CH_2-C-CH_3$, $CH_2-CH$, $(C_4H_9)_3$ (35 H) | $O-CH_3$ (3 H) | $b$[a] |
| 0.0526 | 71 | 36 | 0.0305 |
| 0.1111 | 122 | 53 | 0.0635 |
| 0.1764 | 138 | 51 | 0.1035 |
| 0.2500 | 187 | 60 | 0.1450 |
| 0.3333 | 114 | 31 | 0.2012 |
| 0.6667 | 159 | 22 | 0.5552 |

[a] $a$ and $b$ are the molar ratios $M_1/M_2$ of the monomer feed and copolymer, respectively.

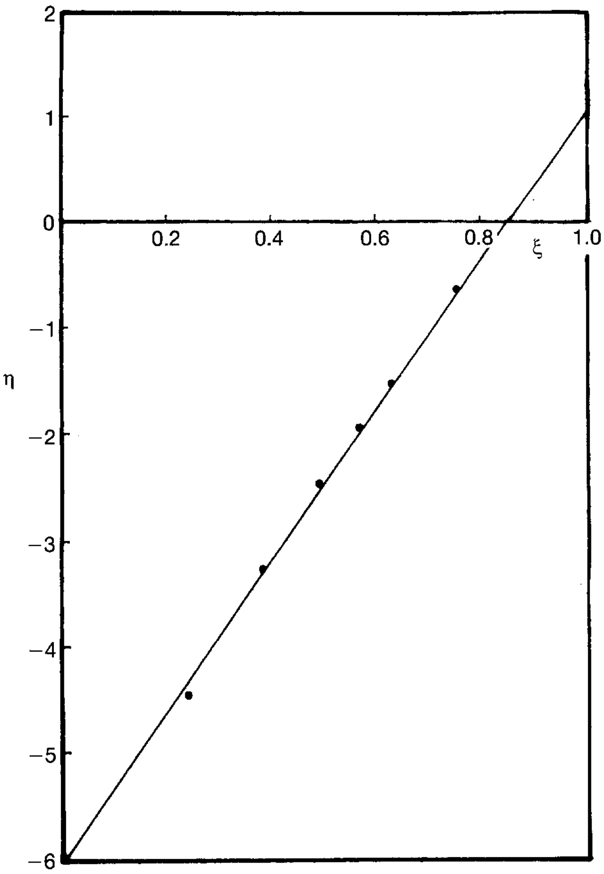

*Figure 1* Kelen–Tudos plots for the determination of copolymerization parameters. $\xi = a^2/\alpha b + a^2$ and $\eta = a(b-1)/\alpha b + a^2$, where $a$ and $b$ are the molar ratios ($M_1/M_2$) of the comonomer in the feed and copolymer, respectively, and $\alpha = a_{\min} \times a_{\max}/(b_{\min} \times b_{\max})^{1/2}$.

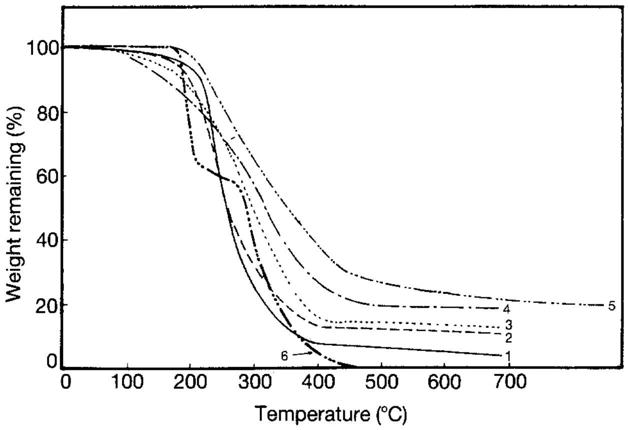

*Figure 2* Thermogravimetric curves for PTBTA, PMMA and their corresponding copolymers, heating was conducted in $N_2$; and the ratio of TBTA:MMA in the copolymer was (1) 2.7:97.3, (2) 5.96:94.04, (3) 13.1:86.9, (4) 31.94:68.06, (5) PTBTA, and (6) PMMA.

age tin in the copolymer compositions, estimated using $^1$H NMR, gravimetric and thermogravimetric techniques. The three estimated methods gave approximately similar results, within experimental error, when compared to each other.

Fig. 2 shows the TGA of PTBTA, PMMA and their corresponding copolymers having different percentage tin contents. From this figure it could be concluded that the weight remaining increased with increasing tin percentage in the copolymers.

The frequency dependence of permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) for TBTA–MMA copolymers having different tin contents at different temperatures are illustrated graphically in Fig. 3. $\varepsilon'$ is found to decrease with increasing frequency ($f$), and shows anomalous dispersion. The absorption curve relating $\varepsilon''$ and $\log f$ shows some sort of merging between the Maxwell–Wagner effect [15] and other processes which are more detectable at higher temperatures. These processes could be attributed largely to the α mechanism, but with β-relaxation superimposed at high frequencies. α-relaxation is associated with orientation of the copolymer main chain, while β-relaxation is generally associated with the rotation of the side chain. The presence of the Maxwell–Wagner effect in such relaxations could be attributed to an a.c. current, which is in phase with the applied potential. The current results from the difference in the conductivities and permittivities of the constituents of the copolymer; which introduces a time factor in the changing of the boundary surface. From Fig. 3, it is also noticed that $\varepsilon'$ and $\varepsilon''$ show an increase with increasing tin content. An abrupt increase is noticed at a concentration 14% tin, estimated by $^1$H NMR; while at a tin concentration of 20.73%, the values of $\varepsilon'$ and $\varepsilon''$ are so high that they could not be measured.

Due to the presence of tin in these copolymers, it is worth measuring the d.c. conductivity (σ). Ohm's law was applied to direct currents ($I$) flowing through the samples at different voltages (V) between 0 and 150 V. As an example, Fig. 4 shows the variation of $I$ with V for TBTA–MMA copolymers having a 14% tin content, estimated by $^1$H NMR. According to the

TABLE III Theoretical and estimated percentage tin in TBTA–MMA copolymers

| No. | Monomer feed (mol %) | | Copolymer composition | | Theoretical tin (%) | Estimated tin (%) | | |
|---|---|---|---|---|---|---|---|---|
| | $M_1$ TBTA | $M_2$ MMA | $m_1$ TBTA | $m_2$ MMA | | $^1$H NMR | Gravimetric | TGA |
| 1 | 5 | 95 | 2.70 | 97.30 | 5.26 | 3.00 | 2.95 | 3.15 |
| 2 | 10 | 90 | 5.96 | 94.04 | 9.44 | 6.14 | 5.68 | 6.34 |
| 3 | 15 | 85 | 9.41 | 90.59 | 12.83 | 8.99 | 8.06 | – |
| 4 | 20 | 80 | 13.10 | 86.90 | 15.59 | 11.62 | 10.73 | 10.63 |
| 5 | 25 | 75 | 16.96 | 83.04 | 18.00 | 14.00 | 12.22 | – |
| 6 | 40 | 60 | 31.94 | 68.06 | 23.29 | 20.73 | 19.39 | 19.70 |

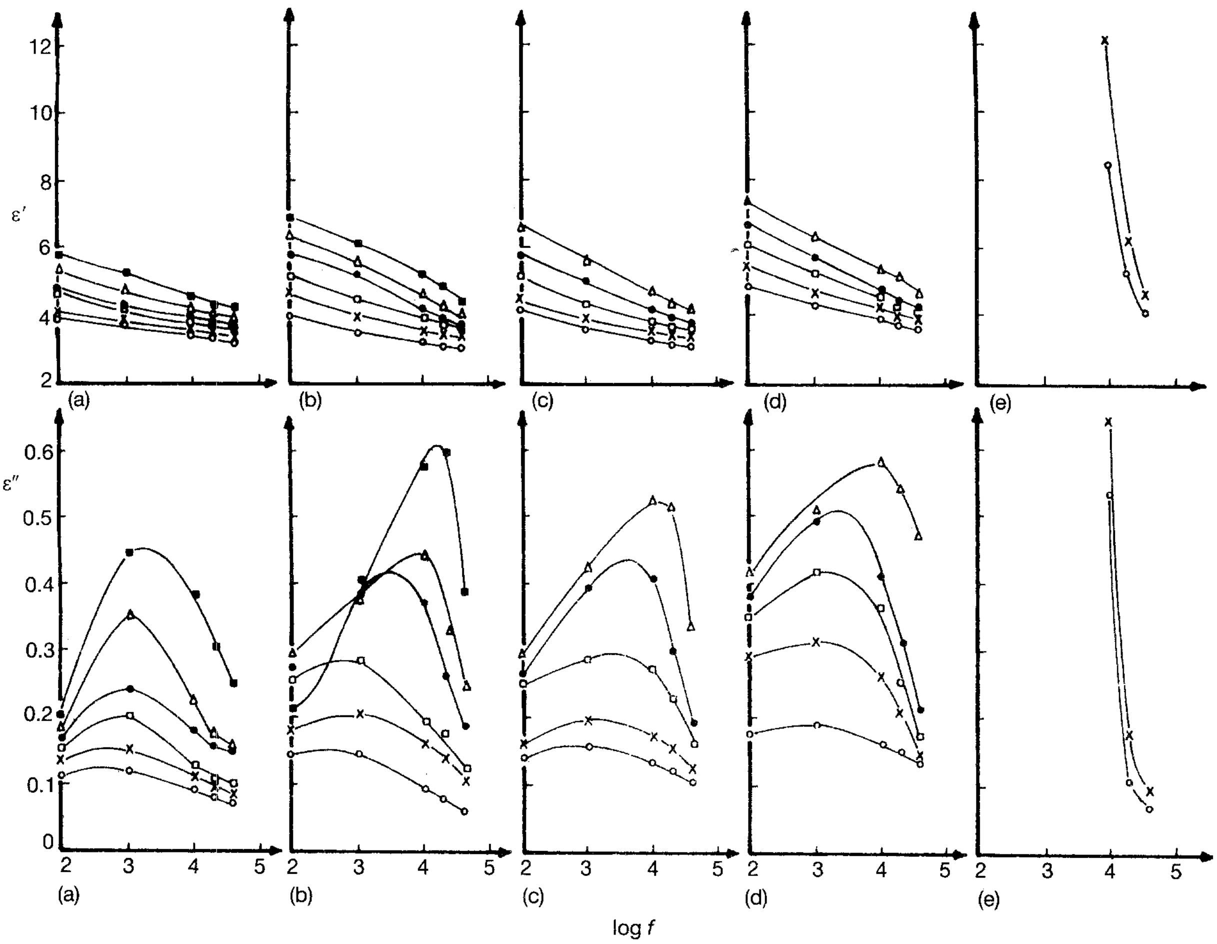

*Figure 3* Variation of permittivity (ε′) and dielectric loss (ε″) with frequency ($f$) at (○) 20 °C, (×) 30 °C, (□) 40 °C, (●) 50 °C, (△) 60 °C and (■) 70 °C. (a) PMMA, (b) TBTA–MMA copolymer 2.7:97.3, (c) TBTA–MMA copolymer 9.41:90.59, (d) TBTA–MMA copolymer 13.1:86.9, and (e) TBTA–MMA copolymer 16.96:83.04.

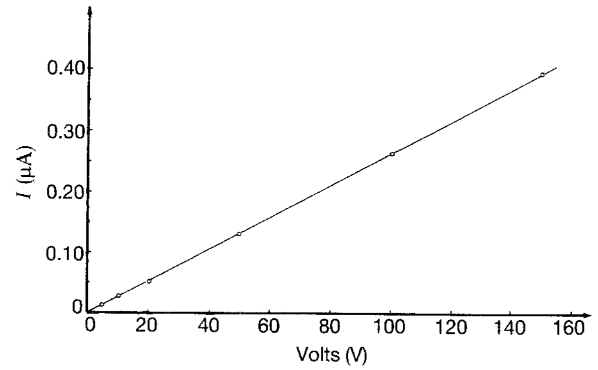

*Figure 4* Variation of $I$ (μA) versus V (volts) for TBTA–MMA copolymers having a 14% tin content, estimated by $^1$H NMR.

equation:

$$\sigma = \frac{d}{V} \times \frac{I}{A}\,\Omega^{-1}\,\mathrm{cm}^{-1}$$

where $d$ is the thickness of the sample in cm, and $A$ its surface area in cm$^2$. Conductivity (σ) was calculated and illustrated graphically versus the tin content in Fig. 5. From this figure it is seen that at low concentrations of tin, up to 11.62% estimated by $^1$H NMR, a very small increase in σ is noticed. This increase becomes extremely high at a certain concentration of tin, which could be attributed to interfacial polarization between the different constituents of the copolymer. This result is supported by the dielectric data given in the text. Similar behaviour was found previously in case of neoprene and butyl rubber carbon black mixtures [16, 17].

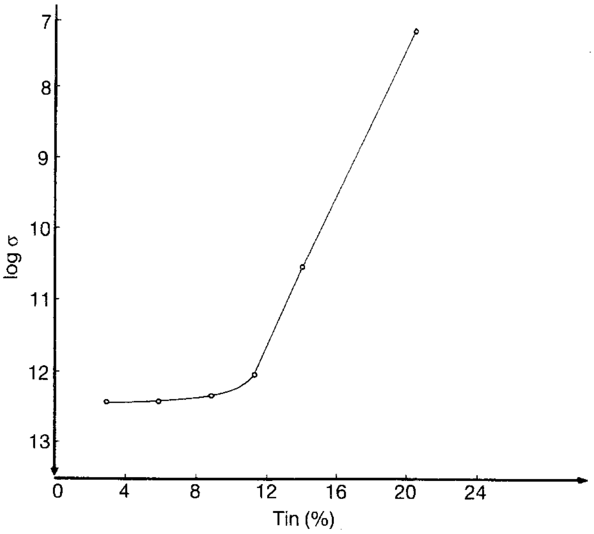

*Figure 5* Dependence of conductivity (σ) on tin content (%) estimated by $^1$H NMR in TBTA–MMA copolymers.

To be sure that losses (ε″), up to a concentration of 11.62%, are not due to d.c. conductivity, losses at various frequencies (ω) were calculated using the relation [18]:

$$\varepsilon''_{\mathrm{d.c.}} = \frac{9 \times 10^{11} \times 4\pi \times \sigma}{\omega}$$

These values are found to be very small and could be neglected when compared with experimental values of ε″.

From these results it could be concluded that the TBTA–MMA copolymer may lose its insulation properties at tin concentrations $\leqslant$ 11.62%. This is an interesting result, because this copolymer is largely used in marine biocidal paints.

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*Received 4 September 1992*
*Revised 27 September 1993*