Studies on Tributyl Tin Methacrylate (TBTM). VI. Thermal and Tensile Behavior of Copolymer of Tri-n-Butyl Tin Methacrylate and Methyl Methacrylate

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SYNOPSIS

The thermal and tensile properties of polytributyl tin methacrylate (PTBTM) and n-tributyl tin methacrylate–methyl methacrylate (TBTM–MMA) copolymers have been studied. Thermogravimetric study showed that with increasing the TBTM content in the copolymer the thermal stability decreases. The glass transition temperature (T_g) decreases continuously as the TBTM content increases. All the polymers showed multistep decomposition. MS study showed that in addition to monomer formation several other side reactions also take place during degradation, leading to formation of other products. Studies on tensile properties show that the tensile strength decreases with increasing TBTM content, whereas elongation at break increases. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Copolymers of tri-n-butyl tin methacrylate TM) and methyl methacrylate (MMA) have evoked considerable interest in recent years due to their controlled release of tributyl tin oxide/hydroxide, leading to long-life antifouling action.[1-6] Recently, a number of studies have been reported on homopolymerization and copolymerization of TBTM with different monomers and on properties of homopolymers and copolymers.[7-12] The properties of copolymers are dependent on TBTM content. In a study of solution property, the characteristic ratio ($\bar{r}^2/\bar{r}_0^2$) of polytributyl tin methacrylate (PTBTM) was found to be slightly higher than that for PMMA.[13] But this does not provide much information on the physicomechanical properties of the material.

The major application of these types of copolymers in the paint industry is their use as antifouling coating material on underwater structures. In a coating formulation, polymer being the most important component, knowledge of its properties such as glass transition temperature, mechanical properties, and stability is essential, because the performance of the coating greatly depends on these properties.

The present study involves the measurement of thermal characteristics and tensile properties of PMMA, PTBTM, and TBTM–MMA copolymer having different compositions.

EXPERIMENTAL

Materials

The homopolymer (PTBTM) and copolymers (TBTM–MMA), used for the present study, were synthesized by a bulk polymerization technique, the details of which were reported earlier.[7,12]

Characterization Techniques

The thermogravimetric analyses (TGA) of PMMA, PTBTM, and TBTM–MMA copolymer were carried out using a DuPont thermal analyzer, 951 TGA model, under N_2 atmosphere. The samples were heated from ambient temperature to 800°C at a heating rate of 10°C/min.

Differential scanning calorimetry (DSC) experiments were performed using a DuPont 910 system

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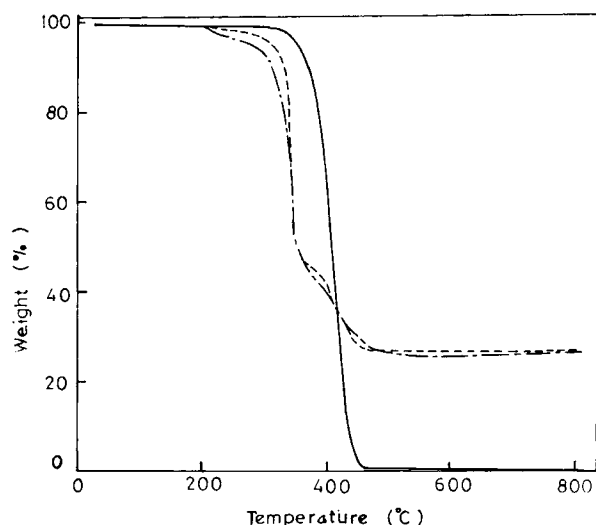
Figure 1 TGA thermograms of (———) PMMA,
(— · —) PTBTM, and (— — —) TBTM–MMA (80 : 20)
copolymer.

under a N_2 system. A heating rate of 10°C/min was
maintained for all the samples.

Thermomechanical analyses (TMA) were carried
out by employing a DuPont thermomechanical an-
alyzer (943 TMA). The measurements were done
by using a dilatometric probe in the temperature
range of −90 to 120°C, under a constant load of 20
g. Liquid air was used for the low-temperature mea-
surement. For all the analyses, a heating rate of 3°C/
min was maintained. The IR spectra of the polymers
in the form of a KBr pellet were recorded using a
5DX Nicolet FTIR spectrophotometer.

A Jeol JMS-DX300 mass spectrophotometer
having a TMS-200 data processing system was used
for recording mass spectra. The polymer samples
were pyrolysed on the injection probe at 350°C and

the pyrolysed products were then fed to the ionizing
chamber. The temperature of the ionizing chamber
was maintained at 250°C. For the tensile study, the
samples were prepared from thin film (0.2–0.3 mm
thick) obtained by casting from a 20% solution of
the polymer in toluene on a glass plate. The films
were dried to constant weight at 40°C for 7 days
under vacuum. The dried films were cut into strips
for the tensile measurement according to ASTM D-
88-83. The tensile behavior of the samples were de-
termined by a tensile tester (Instron 1123) using a
gauge length of 10 cm, crosshead speed of 20 mm/
min, and full-scale load of 10 kg.

RESULTS AND DISCUSSION

On copolymerization of MMA and TBTM, the na-
ture of the material changes from a brittle (for
PMMA) to an elastomeric material (for PTBTM).
All the copolymers and homopolymer (PTBTM) are
thermally stable under ambient conditions. How-
ever, they are susceptible to slow hydrolysis when
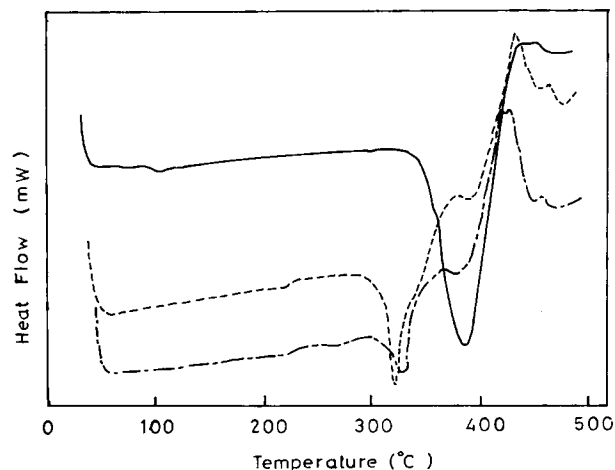kept in air for a prolonged period.

Thermal Stability

The thermal stability of PMMA, PTBTM, and
TBTM–MMA copolymers was investigated by TGA.
From the thermograms (a few representative ther-
mograms are presented in Fig. 1), various param-
eters such as initial decomposition temperature
(IDT) and integral procedural decomposition tem-
perature (IPDT) were calculated and are presented
in Table I. From the results it can be seen that the
IDT value of PMMA is 360°C, whereas for PTBTM,
it is 321°C. In the case of the copolymer, on increas-

**Table I   Results of Thermogravimetric Analysis of PMMA, PTBTM,
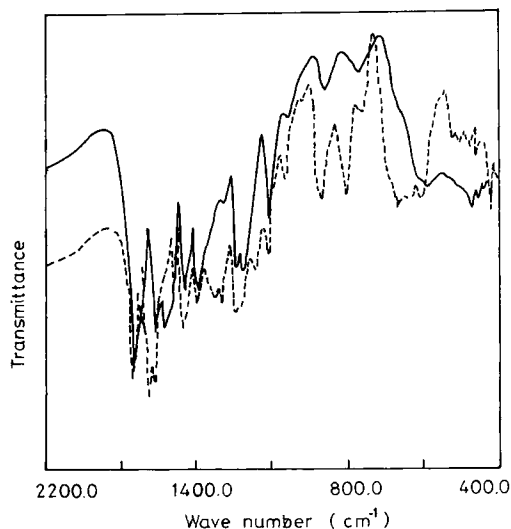and TBTM–MMA Copolymer under N_2 Atmosphere**

Samples	Temperature at Various Wt % Losses (°C)				IDT (°C)	IPDT (°C)
	10	20	30	70		
PMMA	350.0	380.0	400.0	415.0	360.0	447.7
TBTM : MMA						
12 : 88	300.0	345.0	365.0	423.0	317.0	492.0
32 : 68	332.5	337.5	340.0	432.5	327.5	497.5
50 : 50	332.5	340.0	342.5	440.0	331.7	493.3
80 : 20	320.0	335.0	342.5	442.5	330.0	482.3
91 : 09	330.0	332.5	340.5	442.5	331.8	450.1
PTBTM	342.5	345.0	352.5	480.0	321.5	451.1

ing the TBTM content, the value decreases. This indicates that PTBTM has lower thermal stability compared to PMMA because of the presence of the tributyl tin ester group. IPDT, which governs the overall thermal stability, shows a different trend. Thus, the IPDT value of PMMA and PTBTM are almost the same. But the copolymers have higher IPDT compared to homopolymers. This is probably because of the difference in the nature of degradation of PMMA, PTBTM, and TBTM–MMA copolymers. Comparison of the thermograms of PMMA, PTBTM, and their copolymers shows that PMMA follows a single-stage decomposition, whereas PTBTM and copolymers follow a two-stage decomposition. DSC results (Fig. 2) also show a similar trend. Thus, PMMA shows a single endothermic peak at 380°C, whereas both PTBTM and copolymer show two peaks: one endothermic peak at 325°C and one exothermic peak at 425°C.

Several workers have studied the degradation mechanism of PMMA and reported that PMMA degradation proceeds through unzipping into the monomer.[14-16] Thus, the peak at 380°C in the DSC thermogram is due to monomer formation. Hosaka et al.[17] in a study of poly-n-alkyl methacrylate (homologs of methyl methacrylate) observed that the decomposition products were alkenes along with their respective monomers. They also observed that secondary and tertiary alkyl methacrylate polymers, after ester group decomposition, give a more stable product, such as polymethacrylic anhydride. In a pyrolysis study of poly(*tert*-butyl methacrylate), it was observed that the polymer follows two-stage decomposition and the nature of decomposition is temperature-dependent.[18] The monomer formation

Figure 3   IR spectra of heat-treated (——) PTBTM and (-----) TBTM–MMA (25 : 75) copolymer.

was taking place from 140 to 320°C, whereas from 320 to 500°C, it was the formation of isobutylene. In the present case, it seems that for both PTBTM and copolymer the first peak is due to unzipping and the second peak is due to ester decomposition. The ester decomposition was ascertained by IR spectroscopy. PTBTM and TBTM–MMA (25 : 75) copolymer were heated in the thermobalance up to 350°C for 30 min. IR spectra of the heat-treated samples were recorded and are presented in Figure 3. Both PTBTM and TBTM–MMA copolymers have been analyzed by an IR spectrophotometer and the results have been reported earlier.[12] From the spectra it has been found that in case of PTBTM the peak due to the carbonyl group appears at 1642 cm^{-1}, whereas in the case of copolymer, two peaks have been observed: one for the MMA unit at 1737 cm^{-1} and one for TBTM unit at 1640 cm^{-1}. In the present case for PTBTM, the carbonyl peak appeared at 1720 cm^{-1}, essentially from the carboxyl group. In addition, a new peak at 1008 cm^{-1}, characteristic of the anhydride ($C-O-C$) group, is observed. Similarly, in case of copolymer, the carbonyl peak appeared at 1766 cm^{-1}, whereas the anhydride peak appeared at 1016 cm^{-1}. These observations indicate that, first, the ester group decomposed to carboxyl and carbonyl groups (later on confirmed by MS study) and then the anhydride structure is formed by cyclization of adjacent carboxyl and carbonyl groups.

To identify the possible products of decomposition, PTBTM was subjected to pyrolysis in the injection probe of a mass spectrometer and the de-
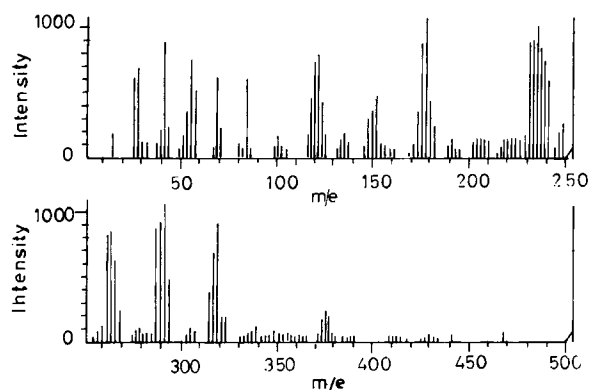

Figure 2   DSC thermograms of (——) PMMA, (----) PTBTM, and (— · —) TBTM–MMA (25 : 75) copolymer.

Figure 4 Mass spectrum of PTBTM.

composed gaseous products have been analyzed. The mass spectrum showed a large number of peaks (Fig. 4) and the prominent ones have been identified (Table II). In the mass spectrum, a small molecular ion peak at 375 (m/e) responsible for TBTM was

observed. Peaks due to dibutyl hydrogen tin methacrylate (319 m/e) and monobutyl dihydrogen tin methacrylate (263 m/e) are also present. There was no peak of higher fragmentation (> M^+), which indicates that there was no oligomer present during degradation. Verma et al.[19] studied the mass spectra of higher acrylates and proposed a mechanism for degradation. In the present case, a similar type of mechanism appears to be operative. From the spectrum it is evident that although TBTM unzips there are other reactions that occur through ester decomposition. Thus, peaks due to tributyl tin hydride (291 m/e), dibutyl tin dihydride (235 m/e), and monobutyl tin trihydride (179 m/e) have appeared. In case of copolymer, similar types of peaks appeared. An additional peak due to MMA at 100 (m/e) has also been found. It seems that the degradation mechanism of copolymer is similar to that of PTBTM. From IR as well as from mass studies, a probable mechanism for degradation of PTBTM has been presented in Scheme 1:
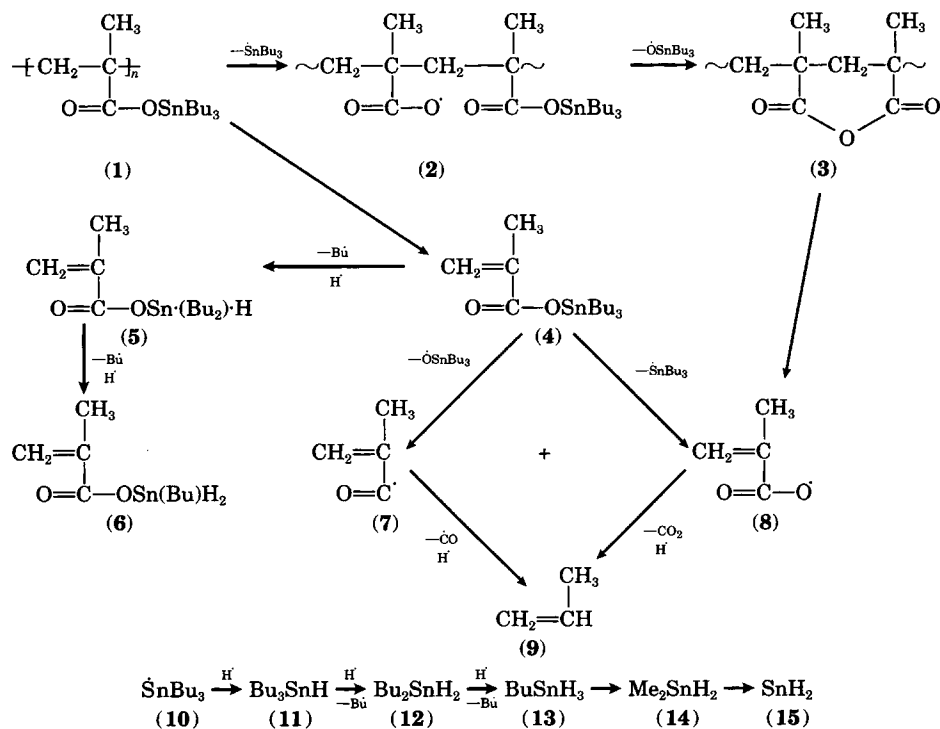
Scheme 1

Glass Transition Temperature

Glass transition temperature (T_g) of TBTM–MMA copolymers with varying TBTM content was measured using a thermomechanical analyzer. The results signifying the variation of T_g with TBTM con-

tent of the polymers has been presented in Figure 5. The results show that with a small introduction of TBTM (around 12 mol %) along the PMMA chain the high T_g of PMMA, i.e., 100°C, decreases to 38°C. On further introduction of TBTM, the T_g
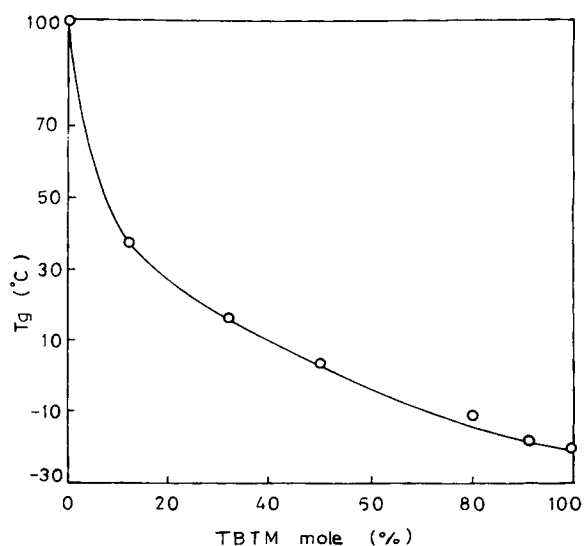
Table II   Compounds Identified in the Mass Spectrum of PTBTM

Compounds/Groups	m/e
Carbon monoxide	28
Ethyl	29
Propenyl	41
Carbon dioxide	44
Butene	56
2-Methyl vinyl carbonyl	69
2-Methyl vinyl carboxyl	85
Tin dihydride	121
Dimethyl tin dihydride	151
Monobutyl tin trihydride	179
Dibutyl tin dihydride	235
Monobutyl dihydrogen tin methacrylate	263
Tributyl tin hydride	291
Dibutyl hydrogen tin methacrylate	319
Tributyl tin methacrylate	375

Table III   Tensile Properties of PMMA, PTBTM, and TBTM–MMA Copolymers

Sample	Tensile Strength (kg/mm^2)	% Elongation at Break
PMMA	3.13	2.5
TBTM : MMA		
12 : 88	3.49	6.6
32 : 68	1.61	74.0
50 : 50	0.83	242.0
PTBTM	0.19	435.0

decreases continuously and reaches a value of $-20°C$ for PTBTM.

PMMA is a brittle polymer under ambient condition having a T_g of $100°C$. On copolymerization of MMA with TBTM, the stiffness of the chain decreases due to the presence of bulky tributyl tin containing ester pendant groups along the polymer chain, which prevents closer packing of the macromolecular chain, resulting in an increase of free volume and a decrease of T_g.

The decrease in T_g with an increase in TBTM content is not linear but exponential. This type of

decreasing trend has been reported by others[20] and is typical for the random copolymer.

Tensile Properties

The tensile characteristics of PMMA, PTBTM, and TBTM–MMA copolymers have been presented in Table III. It can be seen from the results that with the increase in TBTM content in the copolymer the tensile strength decreases, whereas elongation at break increases. PMMA has a tensile strength of 3.13 kg/mm^2, whereas the elongation at break is only 2%. On incorporation of the bulky TBTM moiety onto the PMMA chain, T_g decreases, indicating the decrease in compactness of the chain. The increase in elongation at break is due to the plasticizing effect of TBTM. Marize et al.[21] reported in their study of grafting of propylene oxide onto PMMA that on increasing the graft branches the tensile strength decreased while elongation increased. They have explained the phenomenon on the basis of the flexible nature of grafted branches. In the present case, segments containing TBTM offer softness to the overall copolymer, resulting in higher elongation.

Figure 5   Variation of T_g with respect to TBTM content in the polymer.

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