

Thermal Behavior of *p*-Acryloyloxy-tri-*n*-butyltin Benzoate–Acrylonitrile Copolymers

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SYNOPSIS

The copolymerization of *p*-acryloyloxy-tri-*n*-butyltin benzoate (ABTB) with acrylonitrile (AN) has been investigated in dimethylformamide (DMF), using azobisisobutyronitrile (AIBN) as an initiator. The prepared homopolymer of (ABTB), as well as the copolymers, were characterized by a variety of analytical, spectral, and thermal methods. Thermogravimetry (TG) and differential thermal analysis (DTA) data showed a little improvement in the thermal behavior of the investigated copolymer. A mechanism for the initiation of ABTB units in the nitrile oligomerization in the copolymer was also proposed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Organotin polymers find widespread applications as fungicides,¹ pesticides,² wood preservatives,³ and antifouling coatings,⁴ and more recently as mosquito larvicides⁵ and, finally, as UV stabilizers.^{6,7} The copolymerization of different organotin monomers with acrylonitrile (AN) was studied and the reactivity ratios were determined.⁸ It is evident that the physical properties of the organotin polymer and copolymers are greatly affected by the organotin moiety in the copolymer chain. In spite of great practical interest in organotin polymers, not much work has been done concerning their thermal properties.

The technological importance of polyacrylonitrile (PAN) is known to suffer from several disadvantages: weak moldability, color instability, and weak dyeability. Beside other efforts to abolish these difficulties, several monomers have been used as comonomers for the production of AN copolymers^{9,10} with improved the thermal stability.

In the present work, a series of azobisisobutyronitrile (ABTB)–AN copolymers were prepared and characterized by a variety of analytical, spectral, and thermal methods to determine the effect of ABTB on thermal behavior.

EXPERIMENTAL

Materials

Acrylonitrile (AN) (BDH) was purified by distillation before polymerization. Tri-*n*-butyltin oxide (TBTO) was provided by M&T Chemical Inc., Rahway, NJ. Acrylic acid, supplied by Aldrich, was distilled twice under reduced pressure. *p*-Hydroxybenzoic acid was from BDH, *N,N*-Dicyclohexylcarbodiimide (DCCI), and azobisisobutyronitrile (AIBN) were from Merck.

Synthesis of *p*-Hydroxy-tri-*n*-butyltin Benzoate (HBTB) and *p*-Acryloyloxy-tri-*n*-butyltin Benzoate (ABTB)

p-Hydroxy-tri-*n*-butyltin benzoate (HBTB) was prepared through the esterification of *p*-hydroxybenzoic acid with tri-*n*-butyltin oxide, whereas *p*-acryloyloxy-tri-*n*-butyltin benzoate (ABTB) was prepared by the reaction of acrylic acid with HBTB in the presence of DCCI as a dehydrating agent according to our previous work.¹¹

Polymerization

Polymerization ampules of Pyrex glass were charged with the monomers (1.5M), dimethylformamide (DMF) and AIBN (1 mol % based on the total

monomer concentration). The ampules were covered with serum caps, cooled, and purged with a slow stream of purified N_2 . The polymerization was carried out in a thermostated water bath at $75^\circ C$. The reaction was terminated by opening the ampules and pouring the contents into a large amount of methanol. The precipitated homopolymer and copolymers were collected and washed repeatedly with methanol. The polymers were dried to constant weight at $50^\circ C$. The polymer compositions were calculated on the basis of their tin content by the method of Gilman and Rosenberg.¹²

Spectral Measurement

IR spectra were measured as thin films on NaCl plates, using $CHCl_3$ as solvent, and as KBr discs using a Perkin-Elmer 598 ($4000\text{--}200\text{ cm}^{-1}$) spectrophotometer.

Thermal Analysis

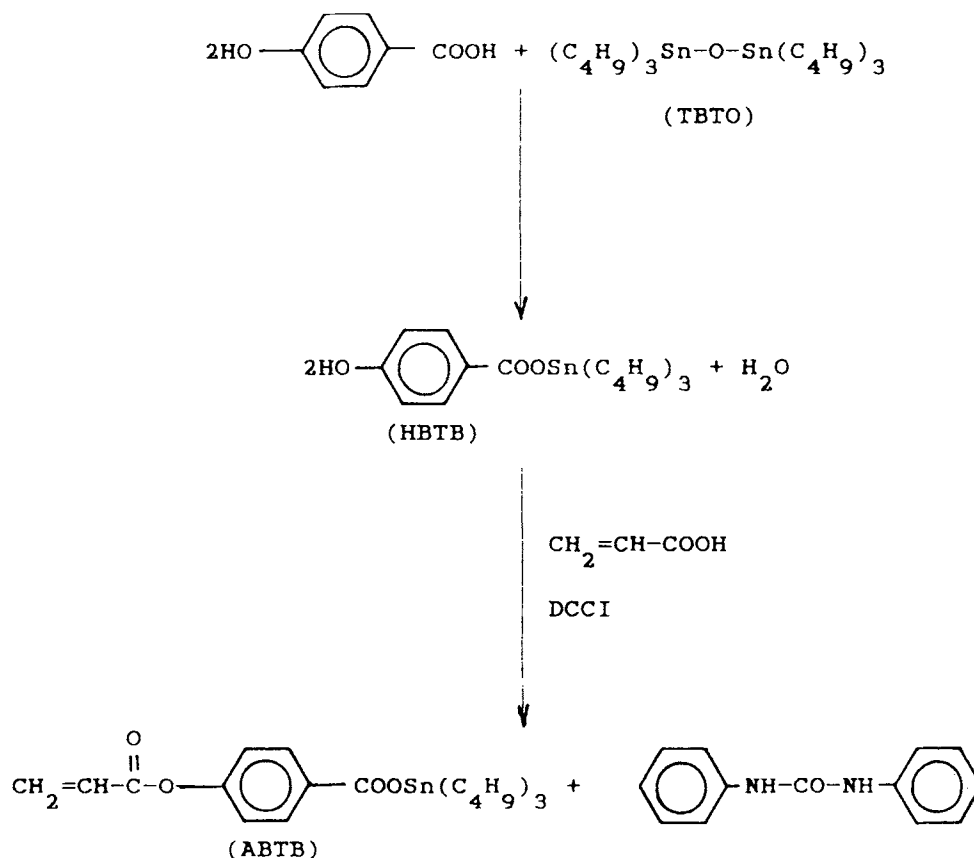
Differential thermal analysis (DTA) was performed in air at a heating rate of $15^\circ C\text{ min}^{-1}$ using a Shimadzu XD-30 thermal analyzer. Thermogravimetry

(TG) thermograms were obtained in air at a heating rate of $15^\circ C\text{ min}^{-1}$ using a DTA 30-B thermal analyzer (Shimadzu, Kyoto, Japan).

RESULTS AND DISCUSSION

The organotin monomer ABTB was prepared by the reaction of *p*-hydroxybenzoic acid with bis-tri-*n*-butyl tin oxide. The obtained *p*-hydroxy-tri-*n*-butyltin benzoate was reacted with acrylic acid in the presence of DCCI according to Scheme 1.

The spectral analysis of HBTB, ABTB monomer, *p*-ABTB homopolymer, and *p*-ABTB-AN copolymers have been discussed previously.¹¹ The prepared organotin monomer ABTB was found to polymerize and copolymerize with AN in the presence of AIBN as a free-radical initiator. The reactivity ratios for the copolymerization of ABTB with AN were calculated using the Kelen-Tüdös equation.¹³ The calculated values of r_1 (ABTB) = 0.007 and r_2 = 2.853 indicated that the growing radical ending with ABTB unit prefers the M_2 monomer over the M_1 monomer in the propagation stage. The monomer



Scheme 1

Table I IR Spectral Data for HATB, ABTB, PABTB, and P(ABTB-co-AN)

Compound	$\nu_{\text{C=O}}$ (cm^{-1})		$\nu_{\text{C=C}}$ (cm^{-1})	$\nu_{\text{C}\equiv\text{N}}$ (cm^{-1})
	$\begin{array}{c} \text{---C---O---} \\ \\ \text{O} \end{array}$	$\begin{array}{c} \text{---C---Sn} \\ \\ \text{O} \end{array}$		
HBTB	—	1620	1600	—
ABTB	1730	1640	1600	—
PABTB	1740	1640	—	—
P(ABTB-co-AN)	1740	1640	—	2240

reactivity ratios ($r_1 \cdot r_2$) of such copolymers are greater than unity, which shows that the monomer sequence consists of large blocks of the comonomer units interrupted by single molecules of ABTB.

The prepared p-ABTB was a rubbery, colorless material and the yield was 88%, whereas the copolymers were colorless, were soluble in most organic solvents, and had film-forming properties. The

structure of prepared ABTB monomer, PABTB, as well as copolymers with AN, were investigated by IR spectroscopy, and the results are represented in Table I and Figures 1 and 2.

The tin content in the copolymers was determined gravimetrically and calculated using the method of Gilmann and Rosenberg and the results are represented in Table II.

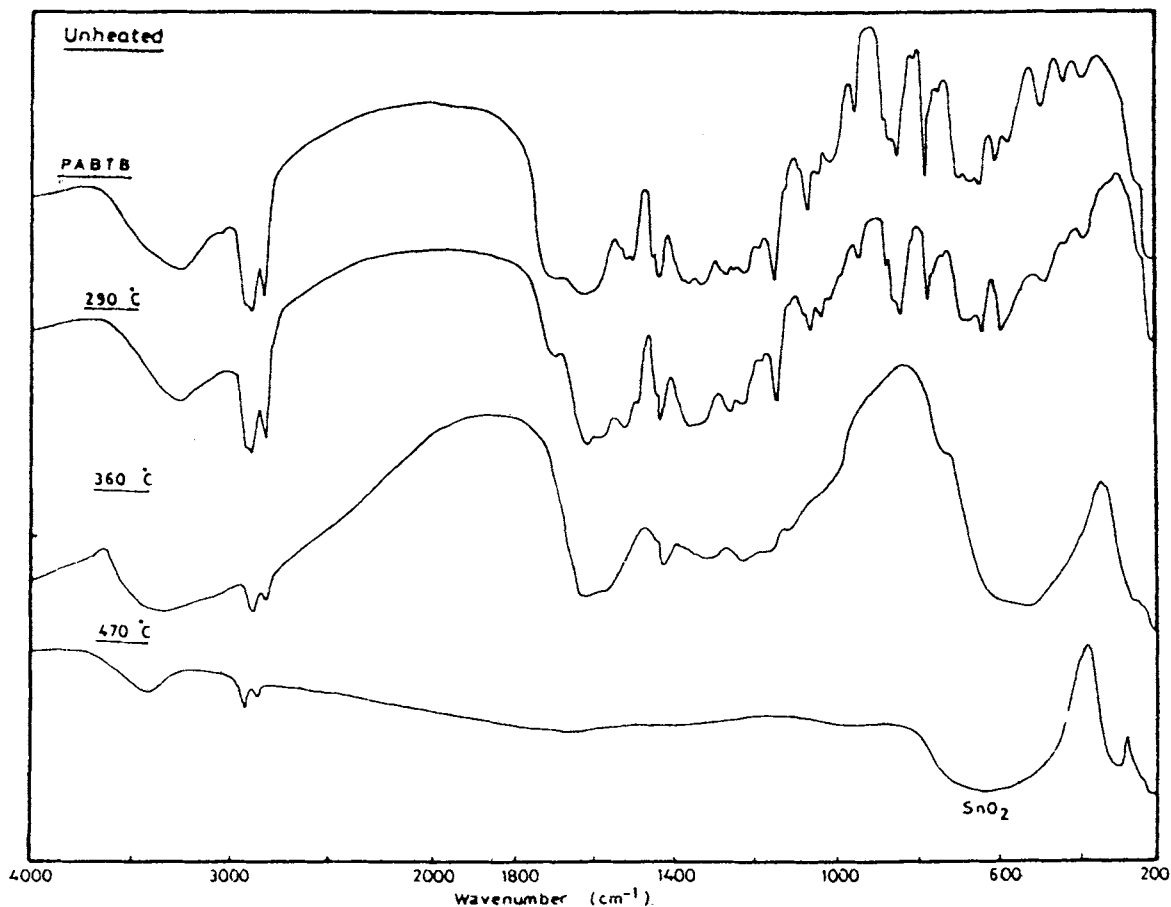


Figure 1 IR spectra of unheated and heated homopolymer PABTB at different temperatures.

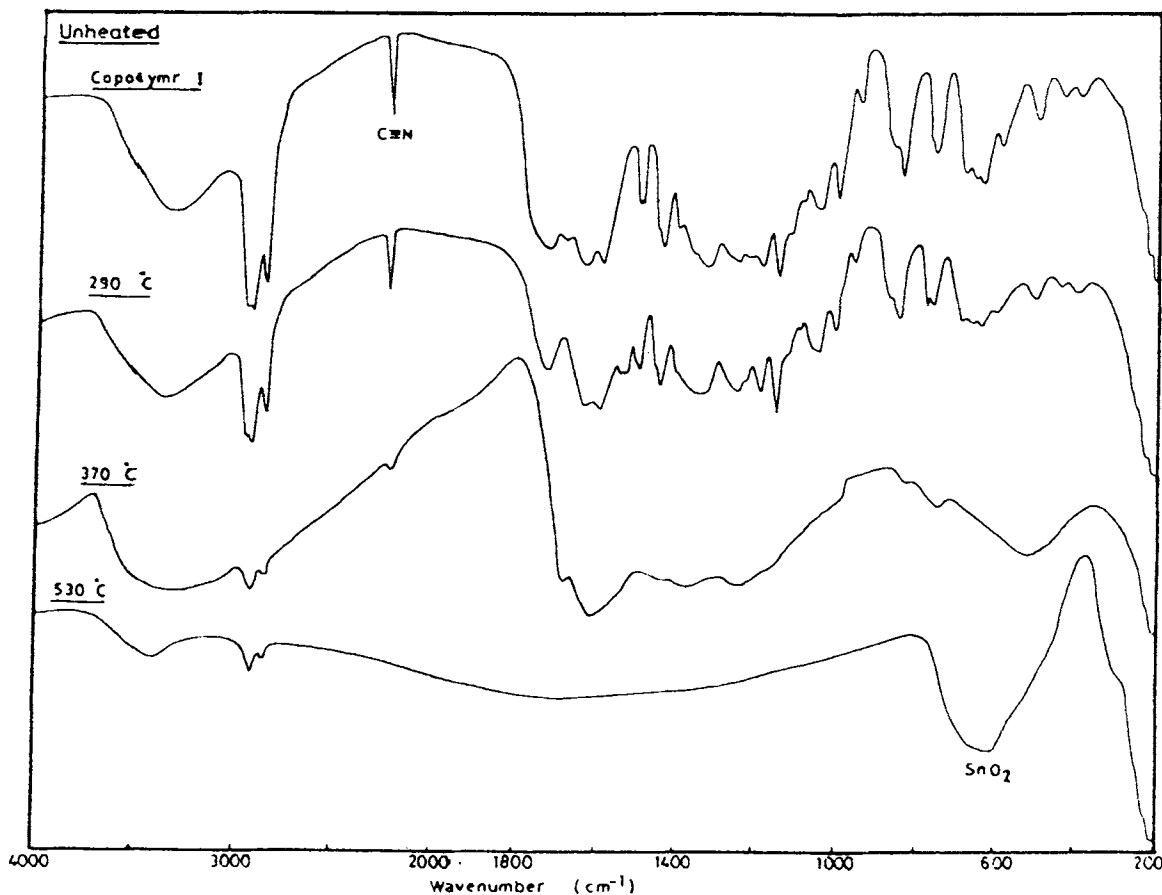


Figure 2 IR spectra of unheated and heated copolymer I (ABTB-AN) at different temperatures.

Thermal Behavior

The thermal degradation of PAN and its copolymers in air as well as under nitrogen was investigated by Coleman et al.¹⁴⁻¹⁶ Intramolecular, cyclization, intermolecular cross-linking, and water elimination were proposed. Grassie and McGuchan^{17,18} investigated the effect of copolymerization on the oligomerization of the nitrile groups of PAN on heating. It has been argued that, since the comonomer is an integral part of the polymer chain, it may influence

the cyclization reaction of the nitrile group by initiation, participation, or inhibition. Acrylic acid and acrylamide act as initiators for the cyclization reaction. A free-radical mechanism followed by homolytic scission of the amide C—N bond has been proposed. Methyl and benzyl acrylates and methyl methacrylates participate in the cyclization process and cause a decrease in the intensity of exotherm without a strong intensity effect. Styrene and α -methyl styrene and vinyl acetate, on the other hand, act as blocking agents for the nitrile oligomerization.

Table II Copolymerization Data for the ABTB (M_1)-AN (M_2) System in DMF at 65°C

Copolymers	Monomer Feed (wt %)		Tin Content (%)		Conversion (%)
	M_1	M_2	Theoretical	Experiment	
I	10	90	2.45	0.92	7.48
II	20	80	4.91	1.12	9.24
III	30	70	7.37	1.32	6.88

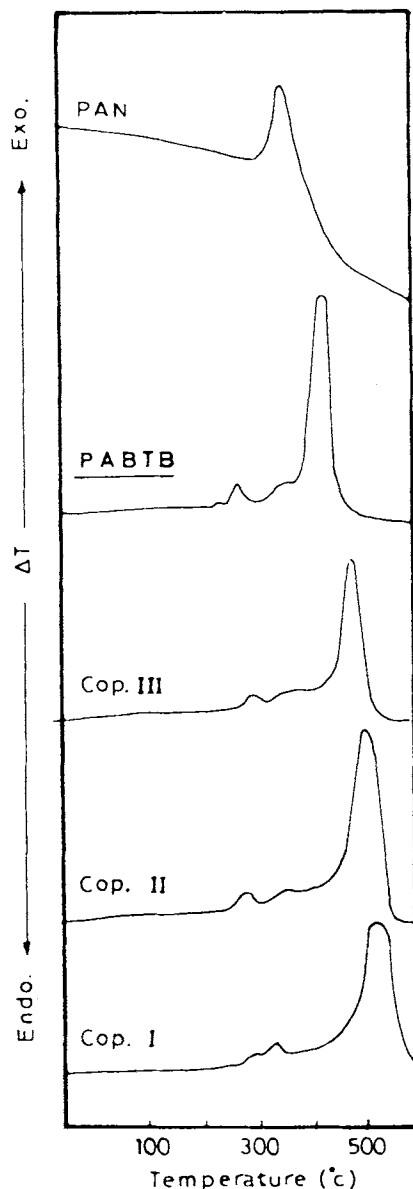
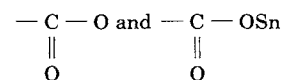


Figure 3 DTA curves for PAN, PABTB, and copolymer (ABTB-AN) in air.

El-Sabee et al.¹⁹ also reported that glycidyl methacrylate belongs to the first category of the Grassie classification.¹⁸

The thermal behavior of PAN was studied in detail by Grassie.²⁰ In the present investigation, the thermal analysis of PAN is given as a reference, i.e., the comparison between the DTA and TG data of PAN and those of the copolymers will illustrate the effect of ABTB comonomer on the thermal behavior of the products. The DTA curves of PAN and PABTB and those of the copolymers are shown in Figure 3. The thermal analysis of PAN in air shows

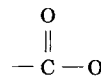
the usual thermogram with an initial decomposition at 310°C and an exotherm with a maximum at 340°C, which results from the oligomerization of the nitrile groups and formation of some aromatic structures.²⁰ On the other hand, the DTA curve of PABTB shows exotherms with maxima at 290, 350, and 470°C. The IR spectra of unheated PABTB and PABTA samples at different temperatures are shown in Figure 1. The spectra show no change in most of the functional groups present upon heating to 290°C. Above this temperature, the characteristic bonds attributed to



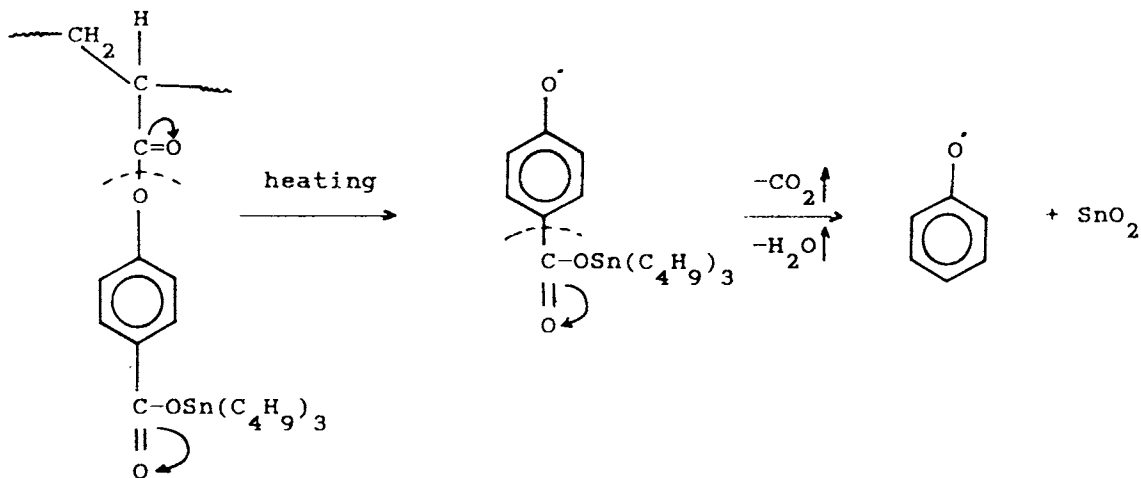
at ν 1730 and ν 1640 cm^{-1} start to disappear and, finally, a new broad band at ν 600 cm^{-1} , assigned to SnO_2 , appears after the complete homolytic scission at \sim 470°C. This indicates that a homolytic scission takes place as shown in Scheme 2.

The exothermic band at 470°C is attributed to a complete depolymerization and decomposition of the polymer. The DTA curves of the ABTB-AN copolymers in air (Fig. 2) show exotherms at 290 and 350°C, reflecting many processes probably including scission, cyclization, cross-linking, and decomposition at the higher temperature exotherm. The first stage of degradation is a scission of the C—O bond, in a manner similar to that occurring with PABTB, followed by cyclization. The DTA peaks of the copolymers were shifted to lower temperature relative to that of PAN, indicating an initiating effect of the ABTB comonomer by the cyclization process.

The IR spectra of the ABTB-AN copolymer (I) before and after heating at 290, 370, and 530°C are given in Figure 2. The spectra show an appreciable broadening and decreasing in the intensities of the nitrile band at ν 2240 cm^{-1} . The carbonyl at ν 1740 cm^{-1} merges into a band at ν 1690 cm^{-1} . The bands at ν 1620 and ν 1690 cm^{-1} , characteristic for ethylene and imino groups, are enlarged and broadened.¹⁸ These spectral changes reveal a radical change in the copolymer structure and must also be due to a direct interaction between the nitrile group and the



functional group of the comonomer. The new broad band at ν 600 cm^{-1} , which appears after a complete homolytic scission at 530°C, indicates the presence of SnO_2 , similar to that obtained for the homolytic scission of PABTB.



Scheme 2

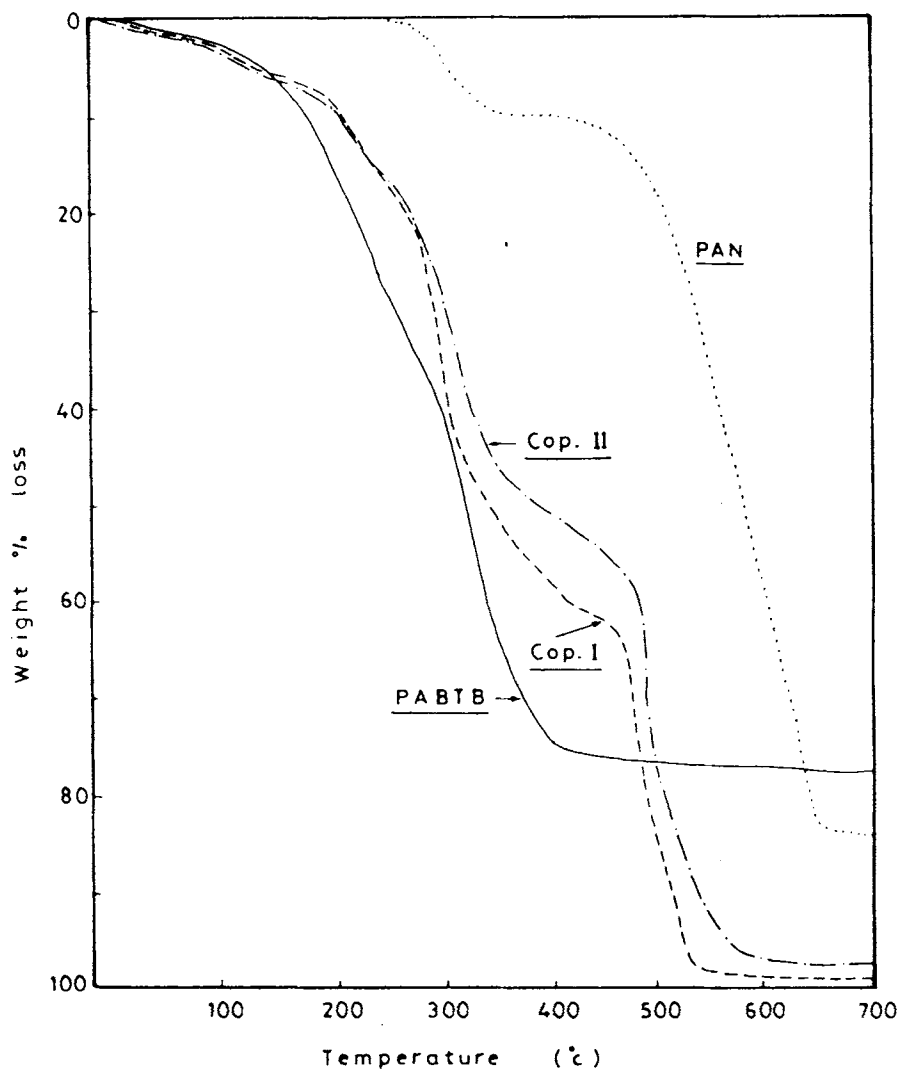
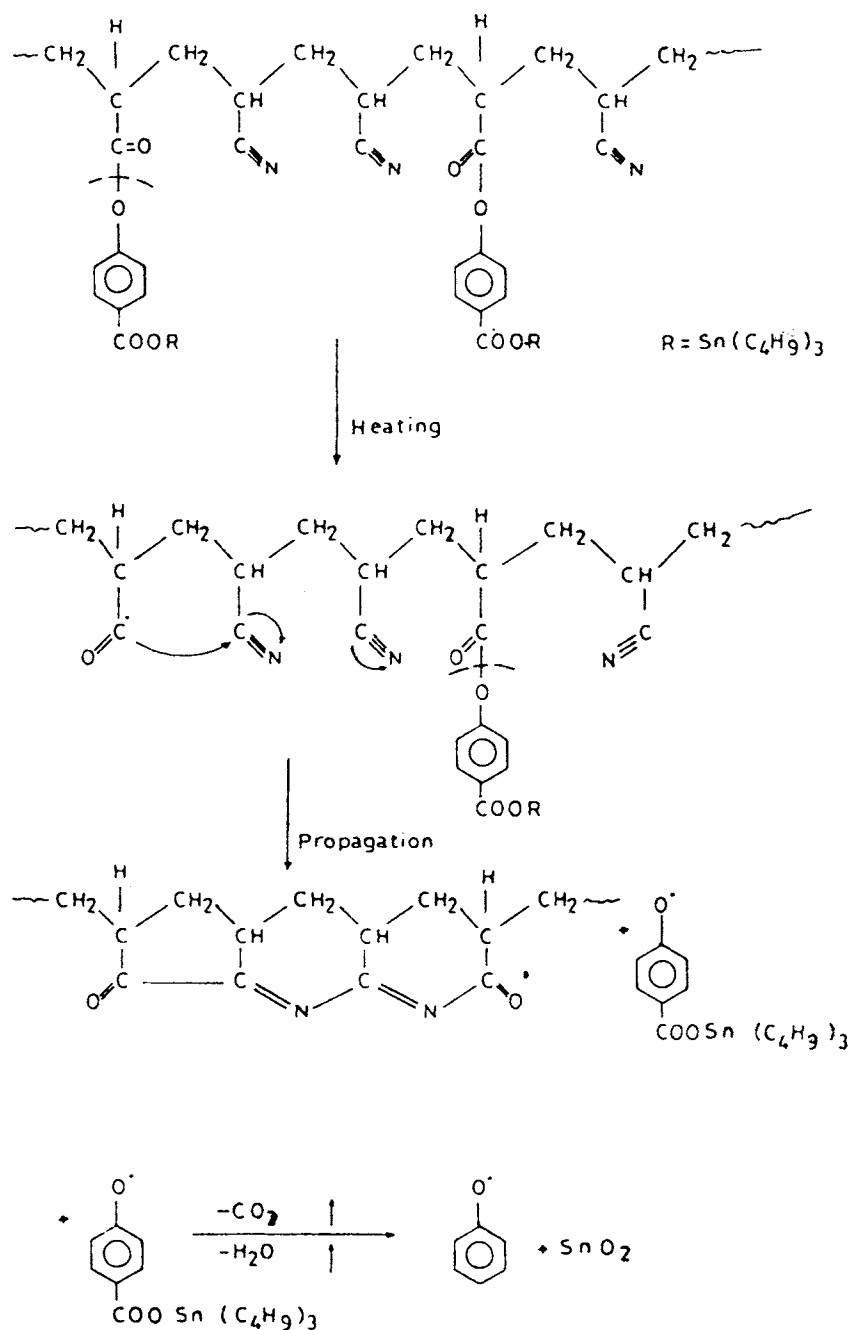


Figure 4 TG curves for PAN and copolymers I and II. (ABTB-AN).



Scheme 3

The TG thermogram in air for PAN, PABTB, and two concentrations of copolymers (10-90) and (20-80) are given in Figure 4. The analysis shows the existence of two transitions, probably reflecting more than one process during the thermal degradation reaction. Also, the TG curve shows an increase in the weight loss of the copolymer relative to that of PAN. This could be confirmed when the ABTB-AN copolymer was heated for about 5 min

at 370°C; a black insoluble mass was left, indicating an appreciable cross-linking reaction due to the cyclization process. Also, the constant weight percentage remaining, which appeared from 530 to 700°C, is attributed to the presence of a yellow tin oxide residue left in the final degradation process.

Based on the above-mentioned thermal and spectral data, the mechanism shown in Scheme 3 is suggested for the thermal degradation of copolymers.

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