

## **THERMAL DEGRADATION BEHAVIOR OF BLENDS OF PHENYL METHACRYLATE-STYRENE COPOLYMERS WITH ALUMINUM ISOPROPOXIDE**

*S. Zulfiqar\**, *K. Masud* and *Q. Ameer*

Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

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### **Abstract**

Thermal degradation studies were carried out of copolymer phenyl methacrylate-styrene in the presence of aluminum isopropoxide to assess the stability and alteration of degradation mechanism using thermogravimetry-differential thermogravimetry (TG-DTG) in inert atmosphere and under vacuum using thermal volatilization analysis (TVA). After collecting the condensable volatile degradation products from TVA experiments and separating them by sub-ambient TVA, investigation and identification were effected out by IR spectroscopy and gas chromatography-mass spectrometry (GC-MS) techniques. The degradation products from the blends consisted of some additional products, i.e., isopropanol, phenol, methacrylic acid, ethyl benzene, benzene and a cyclic compound apart from similar products obtained from the degradation of pure copolymers. The mechanism of newly formed degradation products has been discussed in detail.

**Keywords:** degradation, isopropoxide, phenyl methacrylate-styrene

### **Introduction**

In our previous communications [1, 9], the results of thermal degradation of phenyl methacrylate-styrene (PMA-ST) have been reported. In the present work, the behavior of blends of PMA-ST copolymers was studied with an additive  $\text{Al}(\text{}^{i\text{so}}\text{OC}_3\text{H}_7)_3$  with the help of same techniques.

Flammability is a well-known parameter which inhibits the full scale replacement of conventional stuff, i.e., wood by polymeric materials. Research studies are being pursued to modify this risk from fire by using the additives with polymers.

Antimony oxide and halogenated compounds have shown promise as fire retardants in some cases. However, researchers have started finding non-halogenated additives [2] due to the toxicity and corrosive effects of halogen containing fire retardants. The use of inorganic fillers as fire retardants have been found effective by many workers [3–5]. The present work has been carried out to establish the possible

\* Author for correspondence: E-mail: Shagufta\_z@hotmail.com

chemical interactions between PMA-ST copolymers and an additive  $\text{Al}(\text{isoOC}_3\text{H}_7)_3$ . For better understanding of the mechanism of decomposition of the polymeric blends, the degradation was followed under vacuum and all the volatile products were collected and characterized.

## Experimental

### *Preparation and composition of blends*

The blends of PMA-ST copolymers with aluminum isopropoxide were prepared by mixing the two components thoroughly in agate mortar for 5 min (film preparation was not possible due to the absence of common solvent) [6]. Melt compounding did not produce desired results as the components began to decompose before melting in inert atmosphere. The composition by mass of the blends are given in Table 1.

**Table 1** Sample codes and composition of blends of PMA-ST copolymers with  $\text{Al}(\text{isoOC}_3\text{H}_7)_3$

Blend Code	PMA in copolymer/mol%	Additive
PS1I	90	25% $\text{Al}(\text{isoOC}_3\text{H}_7)_3$
PS2I	75	25% $\text{Al}(\text{isoOC}_3\text{H}_7)_3$
PS3I	50	25% $\text{Al}(\text{isoOC}_3\text{H}_7)_3$
PS4I	25	25% $\text{Al}(\text{isoOC}_3\text{H}_7)_3$
PS5I	10	25% $\text{Al}(\text{isoOC}_3\text{H}_7)_3$

Aluminum isopropoxide was synthesized by mixing aluminum powder (Aldrich) with absolute isopropanol (Fluka) in the presence of mercuric chloride and few crystals of iodine as reported [7]. The product melted at 118°C and kept in a desiccator for future use.

### *Thermal degradation*

The thermal degradation of the blends were carried out using thermogravimetry-derivative thermogravimetry (TG-DTG) and thermal volatilization analysis (TVA) under vacuum. Programmed heating rate at 10°C min<sup>-1</sup> was employed in each case. In TVA experiments, the main product fractions consisting of non-condensable gases, condensable gases and volatile liquids, cold ring fraction (CRF) and residue were all available for subsequent analysis. The condensable gases and volatile liquids were separated first by sub-ambient TVA (SATVA) and then investigated by IR spectroscopy and gas chromatography-mass spectrometry (GC-MS) techniques, as appropriate, for the identification of the degradation products. The experimental procedures adopted have already been reported previously [1].

TG-DTG curves were recorded using a Netzsch simultaneous thermal analyser STA-409 under dynamic nitrogen with a flow rate of 50 mL min<sup>-1</sup> (30 mg sample heated from ambient temperature to 500°C).

The TVA experiments were performed on a line with the TVA system at a programmed heating rate of 10°C min<sup>-1</sup> to 500°C under vacuum (10<sup>-3</sup> mm Hg).

## Results

### Thermogravimetry

The TG-DTG curves were recorded for the blends are given in Fig. 1 and the relevant data in terms of  $T_{\text{threshold}}$  (temperature at which degradation starts) and  $T_{\text{max}}$  (temperature corresponding to maximum mass loss) are summarized in Table 2. The predicted behavior of each blend, assuming no interaction between the components, was calculated from the TG curves of the components and their relative amounts.

**Table 2** TG in nitrogen at 10°C min<sup>-1</sup>\*

Sample code	$T_{\text{thresh}}/^{\circ}\text{C}$	$T_{50}/^{\circ}\text{C}$	$T_{\text{max}}/^{\circ}\text{C}$ from DTG	Residue at 600°C/%
PS1I	21, 360 (21, 340)	380 (359)	312.5, 392.5 (100, 375)	12 (14)
PS2I	23, 365 (23, 335)	385 (365)	394 (120, 387.5)	15 (13)
PS3I	20, 385 (20, 370)	367.5 (465)	395 (125, 400)	12.5 (14.5)
PS4I	24.5, 390 (24.5, 375)	396 (395)	420 (150, 412.5)	17 (15)
PS5I	26, 375 (26, 350)	397 (395)	425 (150, 418)	18 (15.5)

Figures in parentheses are calculated values assuming no interaction between the components;

$T_{\text{thresh}}$  is the temperature at which mass loss is first detected;

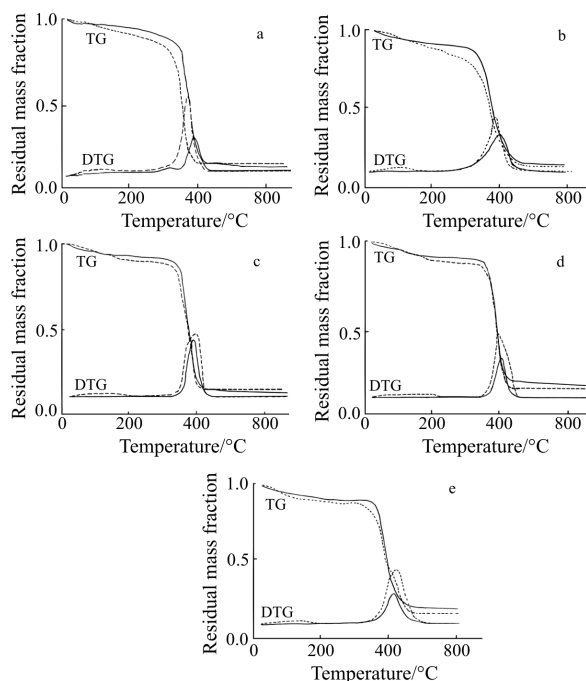
$T_{50}$  is the temperature for 50% mass loss;

$T_{\text{max}}$  is the temperature at which rate of mass loss reaches a maximum (from DTG curve).

The TG curves for pure PMA-ST1-5 copolymers exhibited mass loss between 284–381°C and occurred in single step [1]. The pure additive (TG not illustrated) began to lose mass at about 124°C.

The first stage of degradation of blend PS1I [PMA-ST1, 25% Al(<sup>iso</sup>OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub>] which was attributed to the decomposition of Al(<sup>iso</sup>OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub> to Al<sub>2</sub>O<sub>3</sub>, C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>7</sub>OH (isopropanol), commenced at 21°C and finished around 360°C (Fig. 1a) with  $T_{\text{max}1}$  at 312.5°C. The second stage began immediately and showed  $T_{\text{max}2}$  at 392.5°C. The amount of residue at the completion of degradation (600°C) was 12%, 2% less than the expected value. There was initial destabilization up to a mass loss of 4.5%, however, after this stabilization up to 40°C was observed almost till the end.

The blend PS2I [PMA-ST2, 25% Al(<sup>iso</sup>OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub>] showed a single stage degradation (Fig. 1b). It started around 23°C due to the decomposition of additive and reached  $T_{\text{max}}$  at 394°C. The residue at 600°C was 15%, 2% more than the calculated value. After initial destabilization up to mass loss of 4%, stabilization was noticed which reached from 10 to 50°C.



**Fig. 1** TG and DTG curves for a – PS1I, b – PS2I, c – PS3I, d – PS4I and e – PS5I; (— experimental; - - - calculated)

The mass loss initiated at 20°C for the blend PS3I [PMA-ST3,  $\text{Al}(\text{isoOC}_3\text{H}_7)_3$ ] and reached its  $T_{\text{max}}$  at 395°C (Fig. 1c). The residue was 12.5% at 600°C, 2% less than the expected value. Despite initial destabilization up to mass loss of 7%, stabilization of up to 40°C was evident in different temperature zones.

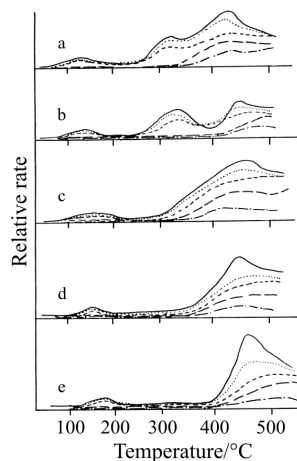
Blend PS4I [PMA-ST4, 25%  $\text{Al}(\text{isoOC}_3\text{H}_7)_3$ ] began to lose mass around 24.5°C and showed  $T_{\text{max}}$  at 420°C (Fig. 1d). The residue at 600°C was found to be 17%, 2% more than the calculated value. Destabilization was noticed up to mass loss of 9% and then stabilization went up to 45°C at different points during degradation.

The mass loss for blend PS5I [PMA-ST5, 25%  $\text{Al}(\text{isoOC}_3\text{H}_7)_3$ ] commenced around 26°C and reached  $T_{\text{max}}$  at 425°C. The amount of residue at the completion of degradation was 18%, 2.5% more than the expected value. This blend also showed initial destabilization up to a mass loss of 2% and then stabilization ranging from 15 to 50°C was noticeable in different temperature zones.

#### *Thermal volatilization analysis (TVA) and SATVA*

##### Separation of condensable degradation products

The TVA experiments were performed on a line with the TVA system at a programmed heating rate of  $10^\circ\text{C min}^{-1}$  to 500°C under vacuum ( $10^{-3}$  mm Hg). The TVA curves for the current blends are reproduced in Fig. 2a–e.



**Fig. 2** TVA curves (vacuum  $10^{\circ}\text{C min}^{-1}$ ) for a – PSII, b – PS2I, c – PS3I, d – PS4I and e – PS5I; — 0;  $\cdots$  – 45; - - - 75; - · - · - 100 and - - - - 196°C

The first two blends, i.e., PSII and PS2I exhibited three-step whereas the remaining three showed two-stage degradation (pure copolymers either degraded in two stages, i.e., PMA-ST1 and PMA-ST2 or in a single step, i.e., PMA-ST3-5) [1]. Products of various volatilities were found at the last stage including non-condensables.

The pure copolymers began to volatilize in the range of 265 to  $367^{\circ}\text{C}$  [1] whereas the volatilization of blends commenced between 69 and  $131^{\circ}\text{C}$ .  $T_{\text{max}}$  for the last stage in the case of pure copolymers was found 382 to  $410^{\circ}\text{C}$  and from 410 to  $430^{\circ}\text{C}$  for the blends.

#### Characterization of degradation products

Non-condensable gaseous products were separated, detected and identified by on-line GC-MS; Varian-3700 with a quartz capillary column and Leda-Mass Multi quad quadrupole mass spectrometer (Varian MAT-44) soon after their formation. Methane (major) and carbon monoxide were identified in appreciable amounts whereas traces of hydrogen were also found.

#### Condensable volatile products

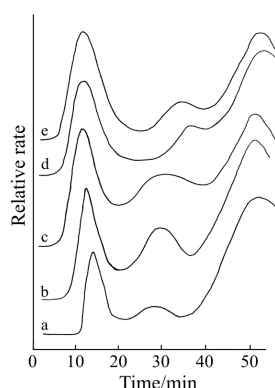
The condensable gases and liquid products collected from each TVA experiment were further separated by SATVA. The gaseous products at each SATVA peak were collected in gas cells and analyzed by MS and FTIR spectroscopy while the liquid was characterized mainly by GC-MS and IR. SATVA traces for the blends are presented in Fig. 3a-e and analytical data is given in Table 3.

**Table 3** Analytical data for degradation products of blends PS1I-PS5I

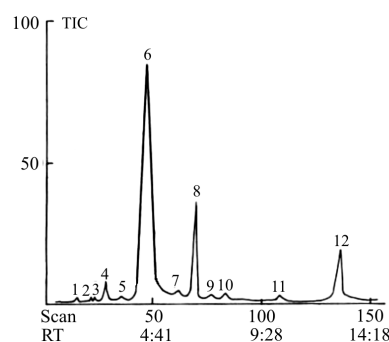
IR/cm <sup>-1</sup>	MS ( <i>m/e</i> )	Degradation products
	16, 15, 14	Methane (non-condensable)
	28, 16, 12	Carbon monoxide (non-condensable)
3702, 2360, 688	44, 28, 16	Carbon dioxide
3130, 2940, 1820, 1670 1450, 990, 910	41, 39, 42	Propene
2180, 2141		Dimethyl ketene
3350, 2980, 1410, 1130	45, 43, 29, 27	Isopropanol
	91, 92, 39, 65	Toluene
	117, 118, 115, 91, 103, 77	$\alpha$ -Methyl styrene
	91, 106, 92, 77, 51	Ethyl benzene
	91, 132, 39, 65	4-Phenyl-1-butene
	91, 146, 39, 65	4-Phenyl-2-methyl-1-butene
	78, 52, 51, 50, 39, 77	Benzene
3335, 3048, 1589, 1495 1468, 1217	94, 66, 65, 39, 40	Phenol
3090, 3058, 2950, 1602, 741, 699	104, 103, 78, 51, 77	Styrene
	41, 86, 39, 40, 28, 45	Methacrylic acid
	39, 41, 69, 94, 162	Phenyl methacrylate
	121, 93, 125, 42, 56, 97, 141 77, 218	Phenyl ester of cycloheptanoic acid (cyclic compound)

All the blends showed three peaks. The gaseous products identified were: CO<sub>2</sub>, propene and dimethyl ketene. The amount of propene showed an increase when compared with the amount of degradation products of pure copolymers of same sample size, the additional quantity was attributed to the decomposition of additive.

Vaporization along with depolymerization during degradation is characteristic for polymers like PMMA [10] and polystyrene. The major components of the liquid fractions for blends studies were monomers, i.e., PMA and ST. The other products identified in the liquid fraction were: isopropanol, toluene,  $\alpha$ -methyl styrene, ethyl benzene, 4-phenyl-1-butene, 4-phenyl-2-methyl-1-butene, benzene, phenol, methacrylic acid and a cyclic compound (phenyl ester of cycloheptanoic acid). Isopropanol, ethyl benzene, benzene, phenol, methacrylic acid and the cyclic compound were not present in the degradation products of the pure copolymers. The liquid fraction was further separated and characterized by GC-MS and a typical chromatogram is shown in Fig. 4. The amounts of phenyl methacrylate and styrene showed a slight decrease as revealed by the area under GC peaks when compared with equal sample size of pure copolymers. The amount of propene has shown an increase as is clear from SATVA (peak 2).



**Fig. 3** Subambient TVA curve for warm up from  $-196$  to  $0^{\circ}\text{C}$  of condensable volatile degradation products from degradation of 1 – PS1I, 2 – PS2I, 3 – PS3I, 4 – PS4I and 5 – PS5I copolymer blends to  $500^{\circ}\text{C}$  at  $10^{\circ}\text{C min}^{-1}$  under TVA conditions



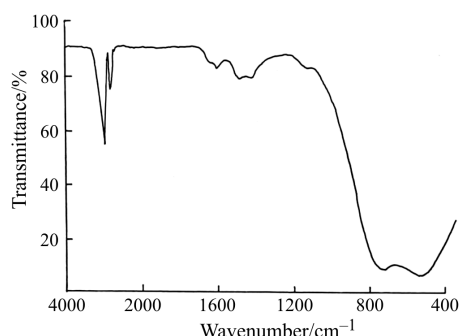
**Fig. 4** GC-MS chromatogram of liquid fraction from degradation of PS3I blend to  $500^{\circ}\text{C}$  under TVA conditions; 1 – isopropanol, 2 – methacrylic acid, 3 – phenol, 4 – toluene, 5 – benzene, 6 – styrene, 7 – cyclic compound (phenyl ester of heptanoic acid), 8 –  $\alpha$ -methyl styrene, 9 – ethyl benzene, 10 – 4-phenyl-1-butene, 11 – 4-phenyl-2-methyl-1-butene, 12 – phenyl methacrylate

#### Cold ring fraction

The CRFs collected from the blends were colorless in appearance. The FTIR spectra (Nicolet Magna-550) of CRFs of the blends were similar, in most respects, to those of pure copolymers [1], indicating that CRFs consisted essentially of copolymer chain units. A strong absorption at  $1638\text{ cm}^{-1}$  was ascribed to unsaturation. Moreover, some new bands at  $3335$ ,  $3048$ ,  $1580$ ,  $1495$ ,  $1468$ ,  $1217$  along with  $750$  and  $680\text{ cm}^{-1}$  suggested the presence of phenol. It was, therefore, concluded that the CRFs comprised of short chain fragments containing both type of monomer units and some unsaturation.

#### Residue

The residues from the blends were brown powders in appearance. The typical FTIR spectrum (Fig. 5) besides C–H absorptions, was similar to that of  $\text{Al}_2\text{O}_3$ . However,

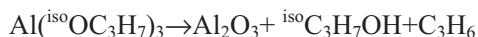


**Fig. 5** IR spectrum of the residual fraction from the degradation of PS3I blend to 500°C under TVA conditions

few peaks in the region of 1642–1537 and 1493–1450  $\text{cm}^{-1}$  were observed which are known to be exhibited by acid salts.

## Discussion

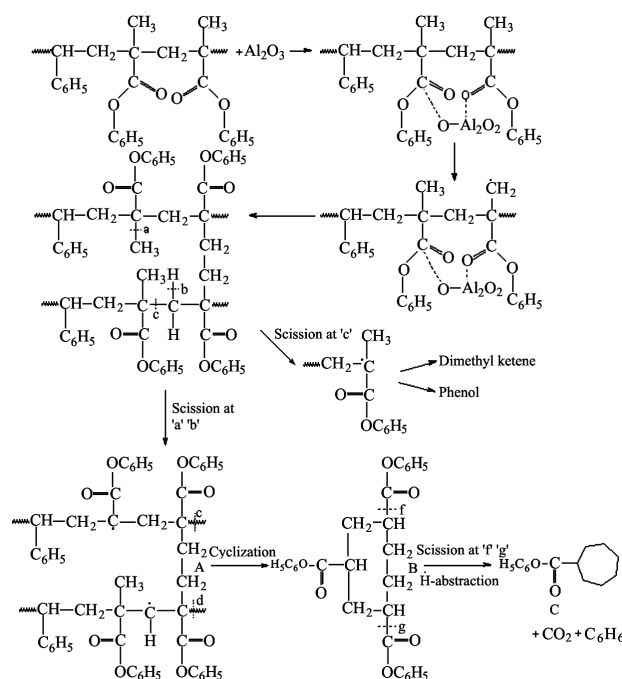
The degradation studies of copolymers of PMA-ST have already been reported earlier [1]. The blends (PS1I-PS5I) give appreciable amounts of gaseous products similar to those given by the pure copolymers, i.e.,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ , dimethyl ketene and propene. The amount of propene showed an increase which was attributed to the decomposition of additive. These minor products became more significant at higher PMA content (going from PS5I to PS1I). The slight increase in the amounts of other gaseous products suggest the involvement of additive. The additive  $[\text{Al}(\text{isoOC}_3\text{H}_7)_3]$  in the blends decomposes on heating and forms alumina, isopropanol and propene [8].



The results obtained reveal that the copolymers have shown early destabilization in the presence of additive apparently due to the low temperature decomposition of the additive ( $T_i=124^\circ\text{C}$ ). The  $\text{Al}_2\text{O}_3$  so produced can also react with the acid group forming corresponding ionic salts which are more stable than the acid groups in the copolymer chain. The subsequent stabilization, in the presence of stable residue from the decomposition of additive which may also act as filler at later part of degradation, is thought to occur due to reduction in flexibility of copolymer pendent groups which allow it to twist and change shape. The following factors lead to the restriction of mobility of the copolymer chains in the presence of additive: (i) the bonds due to copolymer-additive adsorption (the additive does not decompose completely because of adsorption factor) and (ii) steric hindrance due to the presence of solid particles of the additive and their aggregates.

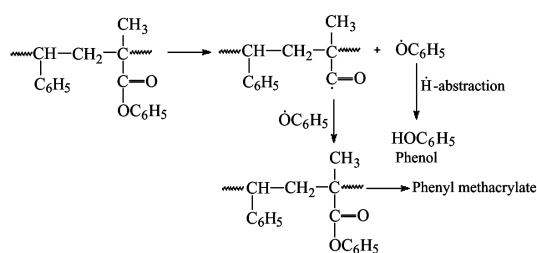
It is also noteworthy that the production of methane and carbon dioxide, in the presence of additive, has increased as compared to copolymers when degraded alone. The following mechanism has been proposed for the development of the interactions between  $\text{Al}_2\text{O}_3$  and the pendent groups of copolymers (Scheme 1).





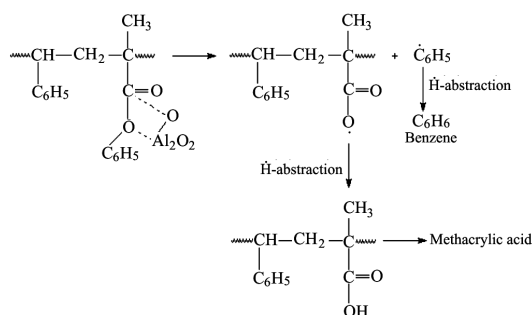
Scheme 1

The two radicals combine and the formation of a cyclic compound (C), phenyl ester of cycloheptanoic acid, may be facilitated by the pyrolysis of (B) which may act as an intermediate. The presence of phenol in CRF along with unsaturation indicates interaction between stable residue from the degradation of additive and copolymer (Scheme 2). The stable residue binds PMA units in such a way that it promotes cyclization on one hand and the production of phenol, on the other. It is interesting to note that only 25% mass/mass ratio of additive is very effective for the observed stabilization.



Scheme 2

Benzene and ethyl benzene are the degradation products of styrene units, however, these were absent when copolymers were degraded alone [1]. Some interaction between copolymer and additive takes place which is not clearly understood at present. The pres-



Scheme 3

ence of methacrylic acid (it was absent in copolymers' degradation products) suggest interaction between PMA units of copolymers and additive (Scheme 3).

## Conclusions

Decomposition of additive furnishes free radicals which may initiate early degradation of copolymers.

Despite early destabilization, it appears that additive has stabilized the copolymer at higher temperatures. The interaction is not only physical but also chemical.

The amounts of methane and carbon dioxide have shown an increase because of the binding effect of additive (stable residue from additive decomposition, i.e.,  $\text{Al}_2\text{O}_3$ ).

Some portion of additive also sublimates, thus, providing a barrier between heat source and degrading copolymer. This process withdraws heat from the surroundings and raises the temperature of copolymer degradation.

The stable residue from the additive plays important role in the production of new compounds at later stage of degradation.

Additive also facilitates cyclization (phenyl ester of cycloheptanoic acid is produced in this way) which is one of the causes of stability of the system.

## References

- 1 S. Zulfiqar, K. Masud, B. Siddique and A. Piracha, *Polym. Degrad. Stab.*, 52 (1996) 293.
- 2 G. F. Beekman, S. Petrie and L. Keating, In: *Proc 44<sup>th</sup> Ann. Tech. Conf.*, Boston 1986, p. 1167.
- 3 I. C. McNeill and M. H. Muhammad, *Polym. Degrad. Stab.*, 48 (1995) 189.
- 4 L. Delfosse, C. Baillet, A. Brault and D. Brault, *Polym. Degrad. Stab.*, 23 (1989) 337.
- 5 J. Rychly and L. Rychla, *J. Thermal Anal.*, 35 (1989) 77.
- 6 A. Jamieson and I. C. McNeill, *J. Polym. Sci. Polym. Chem.*, 16 (1978) 2255.
- 7 G. Brauer ed., *Handbook of preparative inorganic chemistry*, Vol. 1., New York, Academic Press 1963.
- 8 G. P. Shulman, M. Trusty and J. H. Vickers, *J. Org. Chem.*, 28 (1963) 907.
- 9 S. Zulfiqar, K. Masud and Q. Ameer, *Polym. Degrad. Stab.*, 77 (2002) 457.
- 10 E. Inoue, M. Tsuchiya, K. Ishimaru and T. Kojima, *J. Therm. Anal. Cal.*, 70 (2002) 747.