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THERMOGRAVIMETRIC STUDY OF THE THERMAL STABILITY OF POLY(METHYL METHACRYLATE) CONTAINING STERICALLY HINDERED AMINE GROUPS

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ABSTRACT

Sterically hindered amine groups were incorporated into PMMA by copolymerizing methyl methacrylate and 2,2,6,6-tetramethylpiperidinyl methacrylate. In contrast to the two-stage degradation of PMMA, the copolymer showed a three-stage degradation. The activation energies for the various copolymers and PMMA were evaluated from TG curves.

INTRODUCTION

Sterically hindered amines (SHA) from the 2,2,6,6-tetramethylpiperidine series represent a relatively new class of polymer stabilizers [1–5]. A notable example of SHA stabilizers, also known as HALS (hindered amine light stabilizers), is bis-(2,2,6,6-tetramethyl-4-piperidinyl) sebacate. HALS are highly efficient as thermal and photo-stabilizers for polymers.

One problem commonly encountered in the stabilization of polymers using low molecular weight stabilizers is the loss of the stabilizers due to their volatility and extractability. The problem can be overcome by using high molecular weight stabilizers or incorporating stabilizing groups into the base polymers [6,7]. Polymers containing 2,2,6,6-tetramethylpiperidinyl groups have been used as stabilizers [8–14].

Although the thermal degradation of PMMA was the first polymer degradation to be studied in detail [15], it is still the subject of many recent investigations [16–19]. We have studied the miscibility of PMMA containing 2,2,6,6-tetramethylpiperidinyl groups with poly(styrene-co-acrylonitrile) and with poly(α-methyl styrene-co-acrylonitrile) [20]. The thermal stability of PMMA containing such SHA groups is reported in this communication. The SHA groups were incorporated into PMMA by copolymerizing methyl

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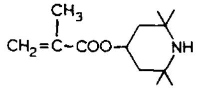
methacrylate (MMA) and 2,2,6,6-tetramethylpiperidinyl methacrylate (TPMA).



(TPMA)

EXPERIMENTAL

Materials

PMMA was obtained from DuPont (Elvacite 2010); its weight-average molecular weight was 120 000 as determined by intrinsic viscosity measurement. It was purified by precipitating the polymer from 2-butanone solution by methanol.

TPMA was prepared by ester exchange reaction between 2,2,6,6-tetramethyl-4-piperidinol and methyl methacrylate according to the method of Lu et al. [11]. The MMA–TPMA copolymers were prepared by copolymerizing MMA and TPMA in bulk at 333 K for 18 h using 0.3% by weight of azobisisobutyronitrile as initiator. The resulting copolymers were purified by precipitating the copolymers from 2-butanone solutions by *n*-hexane. Three MMA–TPMA copolymers were prepared. The TPMA contents as determined by elemental analysis, together with the glass transition temperatures (T_g) and the intrinsic viscosities ($[\eta]$) of the three copolymers are given in Table 1.

Equipment

The TG curves of PMMA and various MMA–TPMA copolymers in an atmosphere of nitrogen were obtained using a Perkin-Elmer TGA-7 thermogravimetric analyzer. The nitrogen flow rate was 20 ml min^{-1} and the

TABLE 1

Description of MMA–TPMA copolymers

Copolymer	Wt% of TPMA	T_g (K) [a]	$[\eta]$(dl g^{-1}) [b]
MMA–TPMA-1	1.5	382	0.44
MMA–TPMA-2	7.8	391	0.16
MMA–TPMA-3	14.5	395	0.41

[a] Determined by DSC.

[b] In 2-butanone at 303 K.

heating rate was 20 K min^{-1}. The sample size was 4–5 mg. The activation energy of degradation was calculated using the method of Coats and Redfern [21] assuming first-order kinetics.

RESULTS AND DISCUSSION

The thermal degradation of PMMA is well understood. It degrades in two stages. The first stage is due to depolymerization initiated at unsaturated chain ends and the second stage is initiated by random chain scission. The TG curve of PMMA is shown in Fig. 1. A two-stage degradation is apparent from the TG curve. The Coast–Redfern plot for PMMA, as shown in Fig. 2, also indicates a two-stage degradation. The first stage is up to 615 K (11% weight loss) with an activation energy of 77 kJ mol^{-1} and the second stage has an activation energy of 157 kJ mol^{-1}. Some of the reported activation energy values of degradation for PMMA are given in Table 2. In general, the activation energy of the first stage ranges between 30 and 110 kJ mol^{-1}, while the activation energy of the second stage is about 200 kJ mol^{-1}. The values obtained in this work are quite close to these values. Malhotra et al. [16] reported a rather low value of 42 kJ mol^{-1} for the main degradation stage. They reported that their experimental results fitted the Coats–Redfern equation better when zero-order kinetics were assumed. However, our data fit the Coats–Redfern equation well with first-order kinetics as shown in Fig. 2.

The TG curves of the three MMA–TPMA copolymers are shown in Fig. 1. These TG curves are distinctively different from that of PMMA. The

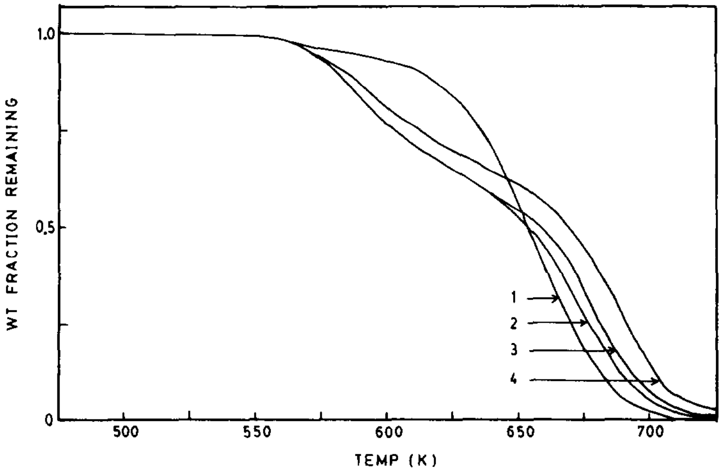


Fig. 1. TG curves of polymers: (1) PMMA; (2) MMA–TPMA-1; (3) MMA–TPMA-2; (4) MMA–TPMA-3.

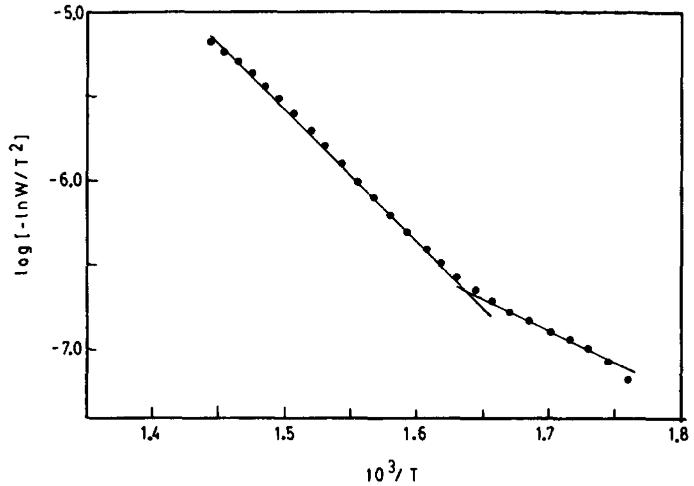


Fig. 2. Coats–Redfern plot for PMMA.

copolymers suffer greater weight loss than PMMA below 650 K but they appear to be more stable than PMMA at higher temperatures.

The Coats–Redfern plots of the copolymers are shown in Figs. 3–5. A three-stage degradation is indicated in these plots. The first stage occurs below 590 K (up to about 17% weight loss); the second stage occurs between 590 and 660 K (weight loss between 17 and 50%); and the third stage occurs above 660 K. The activation energies of the three stages for each copolymer are given in Table 3. The activation energies of the second and third stages are virtually the same for the three copolymers; but the activation energy of the first stage for MMA–TPMA-3 is lower than those for the other two copolymers.

TABLE 2

Activation energy of degradation for PMMA

Reference	Stage	E_a (kJ mol^{-1})	Remarks
18	1st	31 ($n = 1$)	From TG using Kissinger's method
	2nd	210 ($n = 1$)	From isothermal heating; both stages follow first-order kinetics
19	1st	33 ($n = 0.8$)	From TG using the Freeman–Carroll method
	2nd	197 ($n = 1.1$)	
16	2nd	42 ($n = 0$)	From TG using the Coats–Redfern method
22	1st	113	
	2nd	207	
23	1st	96	
	2nd	275	

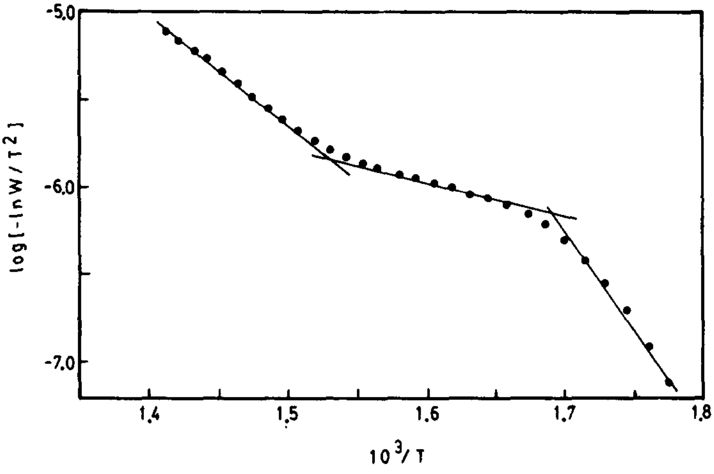


Fig. 3. Coats–Redfern plot for MMA–TPMA-1.

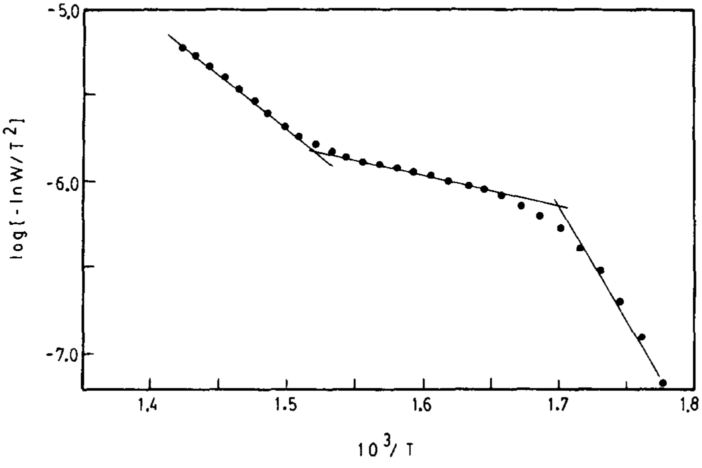


Fig. 4. Coats–Redfern plot for MMA–TPMA-2.

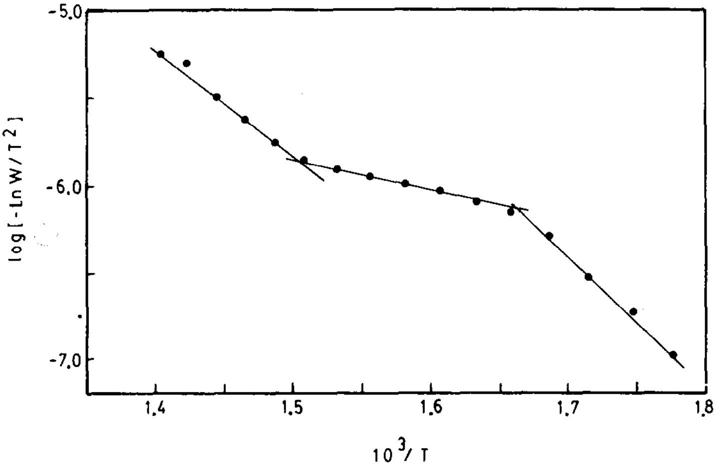


Fig. 5. Coats–Redfern plot for MMA–TPMA-3.

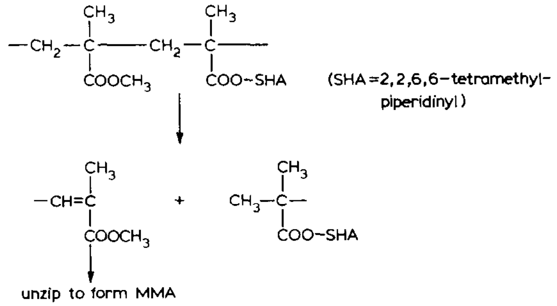
TABLE 3

Activation energies of degradation for MMA–TPMA copolymers

Stage	E_a (kJ mol^{-1})		
	MMA–TPMA-1	MMA–TPMA-2	MMA–TPMA-3
1st	210	241	158
2nd	41	33	36
3rd	115	121	117

The thermal stability of a number of copolymers of MMA have been studied in detail [24]. A small concentration of a second comonomer may, at one extreme, render the copolymer very unstable, while at the other extreme, an improvement in stability is observed. For example, the incorporation of maleic anhydride units into PMMA led to a very rapid decrease in molecular weight and autocatalytic production of monomer [24]. The observation was explained on the basis of chain scission by disproportionation producing terminal MMA units with unsaturated degradable chain ends.

It is conceivable that the incorporation of TPMA units into PMMA also leads to the initial chain scission between TPMA and MMA units by disproportionation as follows.



Such a mechanism would explain the greater weight loss of the copolymers in the early stage as compared with PMMA. It is not clear why the copolymers suffer smaller mass losses than PMMA in the latter stage. Nonetheless, the replacement of pendant methyl groups by 2,2,6,6-tetramethylpiperidinyl groups does produce a significant effect on the thermal stability of PMMA.

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