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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Synthesis and Study of Polymeric Ultraviolet Absorbers. I

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**To cite this Article** Patel, Mahendra , Parmar, J. S. , Patel, M. R. and Patel, M. M.(1986) 'Synthesis and Study of Polymeric Ultraviolet Absorbers. I', Journal of Macromolecular Science, Part A, 23: 11, 1363 – 1380

**To link to this Article:** DOI: 10.1080/00222338608081128

**URL:** <http://dx.doi.org/10.1080/00222338608081128>

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## Synthesis and Study of Polymeric Ultraviolet Absorbers. I

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### ABSTRACT

Polymeric ultraviolet absorbers have been synthesized by free-radical solution copolymerization in cyclohexanone at 70°C of methyl methacrylate and 2-hydroxy-4-acryloyloxybenzophenone at low (below 10%) conversion of monomers. The composition of the copolymers was determined by UV, IR, and NMR. The reactivity ratios were determined and the effect of copolymer composition on viscosity was studied. The copolymers were also studied by TGA and DSC. The latter showed the effect of copolymer composition on the glass-transition temperature.

### INTRODUCTION

Polymerizable functional groups have been attached primarily to the 4-hydroxy group of 2,4-dihydroxybenzophenone to prepare polymerizable UV absorbers. Tocker [1-4] synthesized 2-hydroxy-4-

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acryloyloxybenzophenone (2H-4-AB) by reacting acryloyl chloride with 2,4-dihydroxybenzophenone (2,4-(OH)<sub>2</sub>-BP). He obtained polymeric UV stabilizers by radical homopolymerization and copolymerization of these compounds with ethylene, vinylidene chloride, and acrylate esters. Copolymers of 2H-4-AB with acrylates and acrylonitrile have also been prepared [5]. Osawa [6, 7] polymerized 2H-4-AB and copolymerized it with styrene, while Tocker [8] prepared 2-hydroxy-2'-methacryloyloxybenzophenone and copolymerized it with ethylene. Oo and Tahan [9] polymerized 2H-4-AB and terpolymerized with styrene and acrylonitrile in the presence of polybutadiene latex to obtain a polymeric UV absorber.

The present communication deals with the synthesis of UV absorbers from 2H-4-AB and its copolymers with methyl methacrylate. These polymers are characterized by various methods.

## EXPERIMENTAL

### Materials

Monomer, 2H-4-AB, was prepared by reacting acryloyl chloride with 2,4-(OH)<sub>2</sub>-BP in the presence of hydroquinone and N,N-dimethylaniline. It was purified by column chromatography using active alumina and recrystallized in ethanol, mp 80-81°C [7].

The solvents were purified by appropriate chemical methods [10].

Methyl methacrylate (MMA) was freed from inhibitor (hydroquinone) by washing with 5% aqueous NaOH solution followed by several washings with distilled water, dried over anhydrous sodium sulfate, and distilled under vacuum. The initiator azobisisobutyronitrile (AIBN) was purified by recrystallizing twice from methanol.

### Polymerization

Free-radical solution polymerization was adopted for the preparation of copolymers of seven compositions (Table 1) with AIBN as the initiator and cyclohexanone as the solvent. In each case the contents were added to a round-bottom flask equipped with a condenser. Nitrogen gas was bubbled through the contents while they refluxed at 70°C for 1 h so that the conversion to polymer reached ~10%. The copolymers were precipitated by adding methanol. They were purified by the cyclohexanone/methanol system three times and dried under vacuum at 30°C.

TABLE 1. Preparation and Copolymer Composition of MMA-2H-4-AB Copolymers<sup>a</sup>

No.	Copolymer	Mole fraction in the feed		Conversion, %	Mole fraction of 2H-4-AB in the copolymer determined by		
		2H-4-AB	MMA		UV	IR	
						(1 620 cm <sup>-1</sup> )	(1 595 cm <sup>-1</sup> )
1	MMA-2H-4-AB-0 <sup>b</sup>	0.0	1.0	4.0	0.000	0.000	0.000
2	MMA-2H-4-AB-1	0.2	0.8	8.2	0.260	0.259	0.257
3	MMA-2H-4-AB-2	0.3	0.7	8.5	0.403	0.403	0.404
4	MMA-2H-4-AB-3	0.5	0.5	13.0	0.652	0.654	0.652
5	MMA-2H-4-AB-4	0.7	0.3	9.2	0.830	0.834	0.834
6	MMA-2H-4-AB-5	0.8	0.2	9.7	0.900	0.900	0.900
7	MMA-2H-4-AB-6 <sup>c</sup>	1.0	0.0	12.5	1.000	1.000	1.000

<sup>a</sup> Polymerization conditions: solvent, cyclohexanone (30 mL); initiator, AIBN (60.8 μmol); temperature, 70 ± 0.2°C; time, 1 h ± 5 min.

<sup>b</sup> Poly(MMA).

<sup>c</sup> Poly(2H-4-AB).

### Spectral Study

UV spectra of the polymers in solution in tetrahydrofuran were recorded on a Beckman-36 spectrophotometer in the range of 220-360 nm.

IR spectra of the polymers were recorded on a Carl Zeiss "UR-10" IR spectrophotometer equipped with a potassium bromide cell of path length 0.1 mm on 1.0% solutions of polymer in chloroform.

High-resolution  $^1\text{H}$  NMR spectra were obtained by using a 90-MHz Varian spectrometer, Model EM-390. Polymers were dissolved in  $\text{CDCl}_3$ , and tetramethylsilane was used as reference.

### Viscometric Study

Viscosity measurements were made in three different solvents at  $30^\circ\text{C}$  with an Ubbelohde suspended-level viscometer (Table 5).

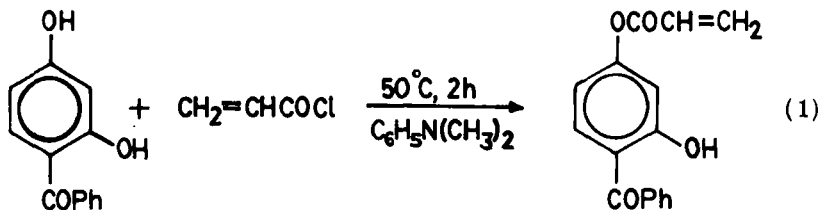
### Thermal Behavior

A Linseis thermal analyzer (West Germany) was used for thermogravimetric analysis (TGA) in air at a heating rate of  $8.5^\circ\text{C}/\text{min}$ . The order of reaction and energy of activation were evaluated.

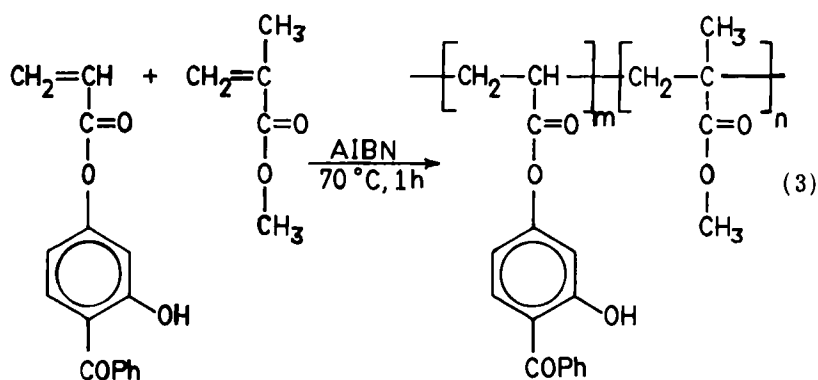
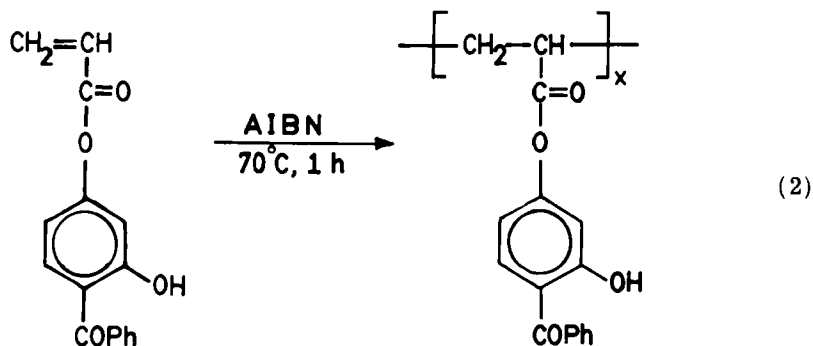
Differential scanning calorimetry (DSC) of the polymer sample was done with a Du Pont 900 Thermal Analyzer at a heating rate of  $10^\circ\text{C}/\text{min}$  in air.

## RESULTS AND DISCUSSION

2,4-Dihydroxybenzophenone was reacted with acryloyl chloride, to give 2H-4-AB. This product contains a polymerizable vinyl group as well as an ultraviolet-light-absorbing group, 2-hydroxybenzophenone:



This product, 2H-4-AB, undergoes homopolymerization to give poly(2H-4-AB) (Eq. 2) as well as copolymerization with MMA to give a copolymer MMA-2H-4-AB (Eq. 3):



### Copolymer Composition and Characterization

Table 1 shows the feed compositions and the composition of the resulting copolymers found by IR, UV, and NMR techniques. The UV optical density (o.d.) at 333 nm was used for calculating the content of 2H-4-AB in the copolymer since this peak is not observed in the spectra of poly(MMA).

The IR absorbance peak at  $1620\text{ cm}^{-1}$  is considered to be due to the benzophenone moiety [11, 12]. The values of  $P_0$  and  $P$  at this peak were found as shown in Fig. 1. From the values of  $\log P_0/P$  and a standard curve of  $\log P_0/P$  vs % 2H-4-AB, the mole fraction of 2H-4-AB in each copolymer was found.

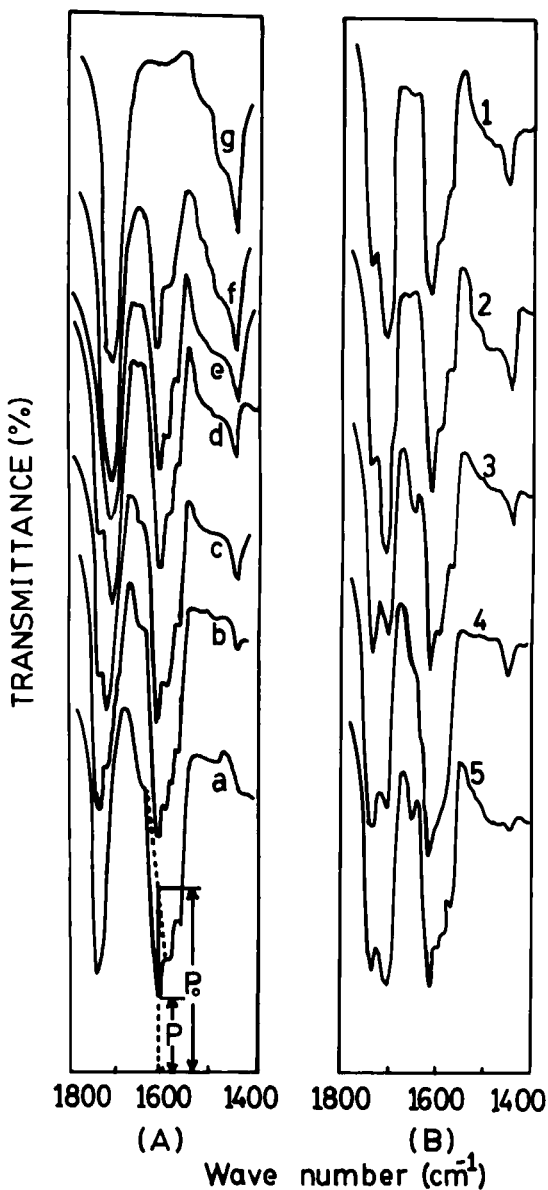


FIG. 1. (A) IR spectra in  $\text{CHCl}_3$  of mixtures of poly(2H-4-AB) (x) and poly(MMA) (y). a: 100% x; b: 80% x, 20% y; c: 60% x, 40% y; d: 50% x, 50% y; e: 40% x, 60% y; f: 20% x, 80% y; and g: 100% y. (B) IR spectra of copolymers in  $\text{CHCl}_3$ . 1: MMA/2H-4-AB-1; 2: MMA/2H-4-AB-2; 3: MMA/2H-4-AB-3; 4: MMA/2H-4-AB-4; and 5: MMA/2H-4-AB-5.

The NMR resonance peak at 3.5-3.6 ppm is due to the  $-\text{OCH}_3$  protons of MMA (M), and that at 7.4-7.6 ppm is due to the aromatic protons of the benzophenone (P). The average mole fraction of benzophenone (A) was determined by

$$A = \frac{3X}{5 + 3X} \quad (4)$$

where X is the ratio of the integrated heights P/M.

The UV spectrum of 2,4-(OH)<sub>2</sub>-BP (Fig. 2) shows one band at 333 nm due to the  $n-\pi^*$  transition, and two bands at 290 and 245 nm due to  $\pi-\pi^*$  transitions [13]. The UV spectra of 2H-4-AB show one band at 333 nm due to the  $n-\pi^*$  transition and a second band with a hypsochromic shift at 290 to 273 nm due to the  $n-\pi^*$  transition. The second  $\pi-\pi^*$  transition band at 245 nm in 2H-4-AB disappears, which indicates the formation of O-R bond in 2H-4-AB at the 4-position. Similar bands are observed for poly(2H-4-AB) and its copolymers [7] because there is no further change in the structure during polymerization.

The results of these three methods (Table 1) are in very good agreement. Further, the mole fraction of 2H-4-AB in each copolymer is found to be higher than in the monomer feed. This reflects the high reactivity of 2H-4-AB (discussed later) during copolymerization with MMA.

The IR spectrum of poly(2H-4-AB) shows a strong absorption peak at  $1\ 620\ \text{cm}^{-1}$  corresponding to the ketonic  $>\text{C}=\text{O}$  group, whereas the spectrum of poly(MMA) shows a strong band at  $1\ 730\ \text{cm}^{-1}$  due to the ester  $>\text{C}=\text{O}$  group. As expected, the copolymers of 2H-4-AB and MMA show both these peaks. The IR spectra of poly(2H-4-AB) and poly(MMA) also differ in other respects, e.g., the former shows a band due to the phenyl ring ( $1\ 595\ \text{cm}^{-1}$ ) which is not observed in PMMA. Both bands were used to determine the composition and gave good agreement (Table 1).

Table 2 shows other characteristic bands of poly(2H-4-AB), poly(MMA), and MMA-2H-4-AB copolymer. The bands in the region  $2\ 800-3\ 200\ \text{cm}^{-1}$  show the presence of intramolecularly hydrogen-bonded OH groups [11], and those at  $1\ 350-1\ 360\ \text{cm}^{-1}$  the presence of C-O stretching of phenolic OH groups [14].

The NMR study (Table 3) helps in the confirmation of the structure of copolymer. The signals in the 6.6-7.9 ppm range are due to aromatic protons [11, 15]. The 7.95 ppm multiplet corresponds to the proton of ArOH, the 7.5 ppm signal to protons of monosubstituted phenyl rings, and the doublet at 7.1 ppm is expected to be due to trisubstituted phenyl rings. The signals in the 1.0 to 2.9 ppm range are due to aliphatic protons: that at about 1.0 ppm probably due to  $\alpha\text{-CH}_3$  groups [16], that at about 3.5 ppm due to methoxy ( $-\text{OCH}_3$ ) protons.



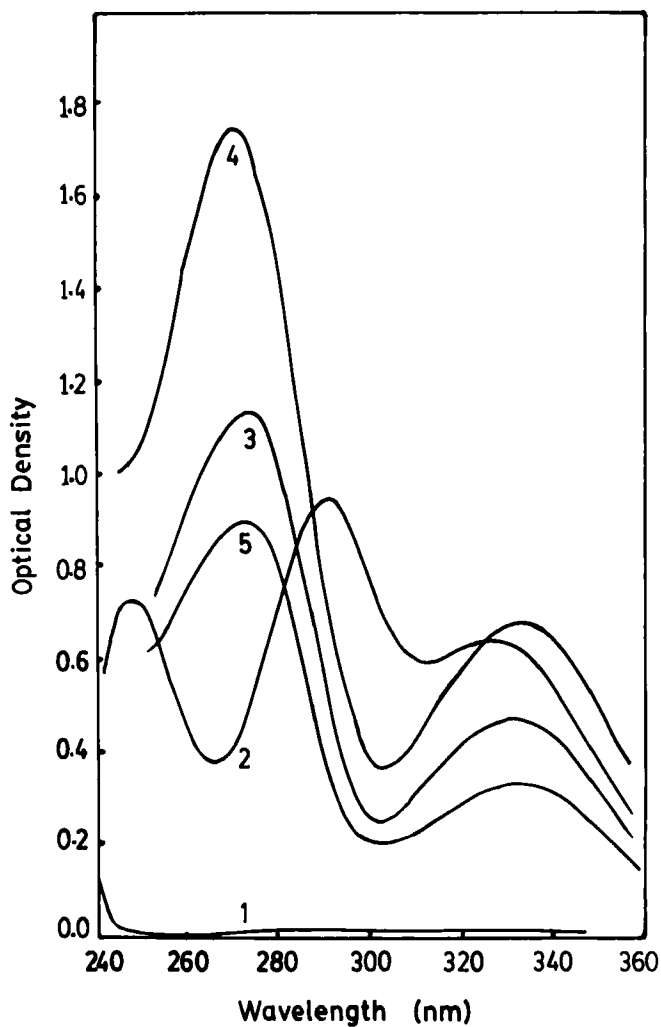


FIG. 2. UV spectra in THF. 1: Poly(MMA); 2: 2,4-dihydroxybenzophenone; 3: 2H-4-AB; 4: Poly(2H-4-AB); and 5: MMA/2H-4-AB-3.

TABLE 2. IR Spectral Data ( $\text{cm}^{-1}$ ) in Chloroform<sup>a</sup>

Compound	C=C stretching (aromatic)	C=O stretching (ketone)	C=O stretching (ester)	OH/OCH <sub>3</sub> stretching	-O- stretching (ester)	-OCH <sub>3</sub> bending	-CH <sub>3</sub> bending	$\nu$ -CH stretching	$\nu$ -CH <sub>2</sub> stretching
MMA-2H-4-AB-0	-	-	1730(vs)	2900(sb) (OCH <sub>3</sub> )	1150(s) 1285(m)	1445(s) 1470(w)	990(s)	-	1430(w)
MMA-2H-4-AB-3	1595(b)	1620(vs)	1710(vs) 1740(vs)	1350(s) 2800- 3200(b)	1110(s)	1470(w)	980(s)	730(w)	1430(w)
MMA-2H-4-AB-6	1595(b)	1620(vs)	1740(vs)	1350(s) 2800- 3200(b)	1110(s)	-	-	730(w)	1430(w)

<sup>a</sup>vs = very strong, s = strong, w = weak, m = medium, b = broad.

TABLE 3. NMR Spectral Characteristics of Homopolymers and Copolymer<sup>a</sup>

No.	Compound	$\delta$ , ppm						
		$\alpha$ -CH <sub>3</sub>	-CH <sub>2</sub> -	-CH-	-OCH <sub>3</sub>	Aromatic	Ar-OH	
1	MMA-2H-4-AB-0	1.83	1.80	-	3.10	-	-	
		1.00	2.10	-	3.55(s)			
		1.30			4.00			
2	MMA-2H-4-AB-3	1.0	1.90	2.65	3.10	8.60 <sup>b</sup>	7.95	
		1.20	2.60		3.50(s)	7.10		
		1.50			4.00	7.50		
3	MMA-2H-4-AB-6	-	2.00	2.90	-	6.60 <sup>b</sup>	7.95	
			2.30			7.10		
						7.40		

<sup>a</sup>High-resolution (90 MHz) <sup>1</sup>H NMR spectra recorded in CDCl<sub>3</sub>.<sup>b</sup>Multiplet, (s) strong.

Determination of Reactivity Ratios

In order to estimate the reactivity ratios  $r_1$  and  $r_2$  (where  $r_1$  refers to 2H-4-AB,  $r_2$  to MMA), four methods, viz., Joshi and Joshi (JJ) [17], Mayo and Lewis (ML) [18], Fineman and Ross (FR) [19], and Kelen and Tüdös (KT) [20], were employed. Only the JJ method is described here in detail.

Joshi and Joshi [17] presented a nongraphical linear least-squares analysis of  $r_1$  and  $r_2$  which is derived analytically from the intersecting multiple lines of the copolymer composition equation in the form due to Mayo and Lewis [18]. The equations obtained by them are

$$r_1^{\circ} = \frac{\left[ \sum \frac{1}{1+m_i^2} \cdot \sum \frac{m_i C_i}{1+m_i^2} \right] - \left[ \sum \frac{m_i}{1+m_i^2} \cdot \sum \frac{C_i}{1+m_i^2} \right]}{\left[ \sum \frac{m_i}{1+m_i} \right]^2 - \left[ \sum \frac{1}{1+m_i^2} \cdot \sum \frac{m_i^2}{1+m_i^2} \right]}, \quad (5)$$

$$r_2^{\circ} = \frac{\left[ \sum \frac{m_i}{1+m_i^2} \cdot \sum \frac{m_i C_i}{1+m_i^2} \right] - \left[ \sum \frac{m_i^2}{1+m_i^2} \cdot \sum \frac{C_i}{1+m_i^2} \right]}{\left[ \sum \frac{m_i}{1+m_i^2} \right]^2 - \left[ \sum \frac{1}{1+m_i^2} \cdot \sum \frac{m_i^2}{1+m_i^2} \right]}, \quad (6)$$

where  $m_i = F^2/f$  and  $C_i = F(1/(f-1))$ ,  $F$  being the mole ratio of monomers in the feed and  $f$  the mole ratio of monomers in the copolymer. Our values of  $F$  and  $f$  are given in Table 4, and the final values obtained for  $r_1$  and  $r_2$  by solution of Eqs. (5) and (6) from IR are 2.52 and 0.89, respectively, and from NMR are 2.53 and 0.90, respectively.

The results obtained by the other three methods agree quite closely with the above results.

Viscometric Study

Viscometric results are tabulated in Table 5. The  $[\eta]$  values were obtained by extrapolating  $\eta_{sp}/C$  to zero concentration. The Huggins' constant  $K_H$  was found from the equation

TABLE 4. Mole Ratios in Feed and Copolymer<sup>a</sup>

No.		M <sub>1</sub> -M <sub>2</sub> System		M <sub>2</sub> -M <sub>1</sub> System	
		F	f	F	f
1	MMA-2H-4-AB-1 <sup>b</sup>	4.00	8.95	0.25	0.11
2	MMA-2H-4-AB-2	2.33	5.03	0.43	0.20
3	MMA-2H-4-AB-3	1.00	1.89	1.00	0.53
4	MMA-2H-4-AB-4	0.43	0.67	2.33	0.48
5	MMA-2H-4-AB-5	0.25	0.35	4.00	2.86
6	MMA-2H-4-AB-1 <sup>c</sup>	4.00	9.00	0.25	0.11
7	MMA-2H-4-AB-2	2.33	5.02	0.43	0.20
8	MMA-2H-4-AB-3	1.00	1.87	1.00	0.53
9	MMA-2H-4-AB-4	0.43	0.68	2.33	1.47
10	MMA-2H-AB-5	0.25	0.34	4.00	2.90

<sup>a</sup>M<sub>1</sub> is 2H-4-AB and M<sub>2</sub> is MMA.

<sup>b</sup>Data based on copolymer composition by IR analysis.

<sup>c</sup>Data based on copolymer composition by NMR analysis.

$$\eta_{sp}/C = [\eta] + K_H[\eta]^2 C.$$

The data clearly indicate that the value of  $K_H$  is affected by the composition of the copolymer and that the change is not uniform with all solvents. The value of  $K_H$  can be helpful in understanding the nature of the copolymer.

For random azeotropic copolymers,  $K_H$  is found to be lower than in the parent homopolymers [21]; this is found to be true also for block copolymers, where the value of  $K_H$  reaches a minimum at about 0.5 mol fraction [22]. For the copolymers other than the above two types, the decrease of  $K_H$  is not uniform as was found in the present system. This suggests that the copolymers prepared are other than random azeotropic and block copolymers.

### Thermal Studies

The glass-transition temperatures ( $T_g$ ) were determined from DSC traces (Fig. 3). The  $T_g$  of the homopolymers, poly(MMA) and

TABLE 5. Huggins Constant ( $K_H$ ) and Intrinsic Viscosity  $[\eta]$  for MMA-2H-4-AB Copolymers at 30°C

Compound	Methyl ethyl ketone		Dimethylformamide		Chloroform	
	$[\eta]$ , dL/g	$K_H$	$[\eta]$ , dL/g	$K_H$	$[\eta]$ , dL/g	$K_H$
MMA-2H-4-AB-0	0.16	0.35	0.35	0.42	0.36	0.39
MMA-2H-4-AB-1	0.17	0.39	0.37	0.31	0.36	0.24
MMA-2H-4-AB-2	0.18	0.38	0.38	0.31	0.36	0.41
MMA-2H-4-AB-3	0.20	0.41	0.26	0.32	0.30	0.15
MMA-2H-4-AB-4	0.14	0.60	0.25	0.61	0.24	0.28
MMA-2H-4-AB-5	0.14	0.83	0.21	0.63	0.23	0.37
MMA-2H-4-AB-6	0.13	0.91	0.20	0.65	0.21	0.39

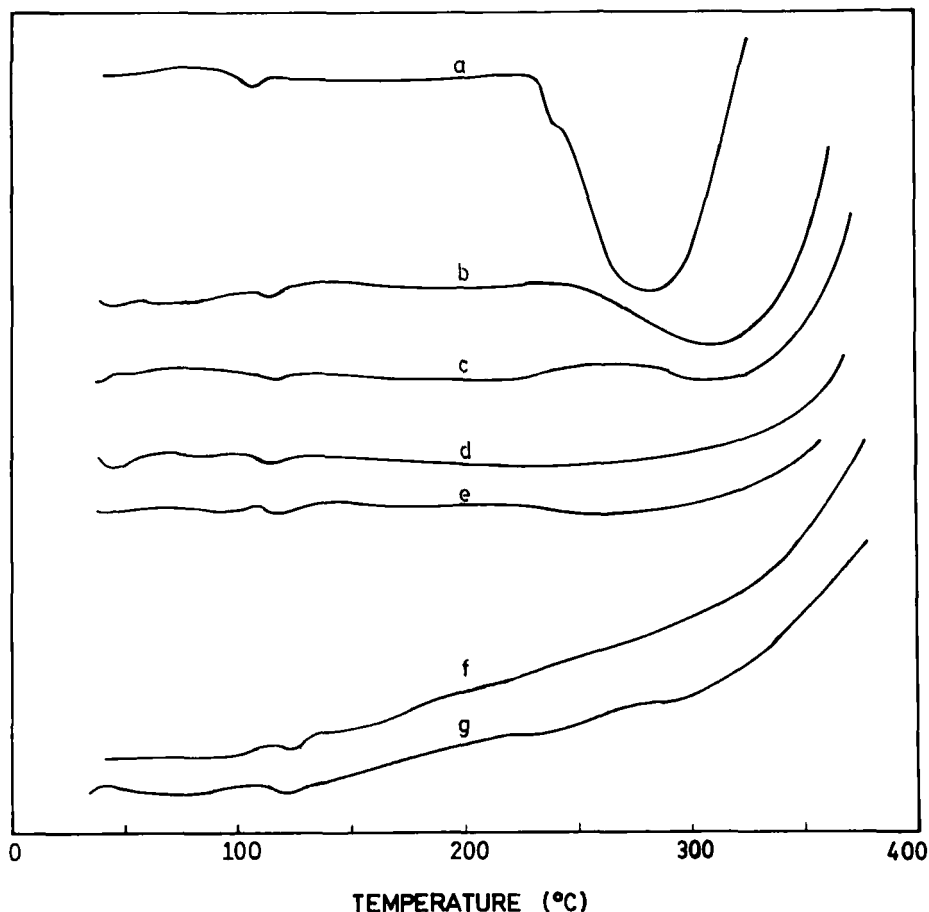


FIG. 3. DSC thermograms of copolymers in air. Heating rate,  $10^{\circ}\text{C}/\text{min}$ . a: MMA/2H-4-AB-0; b: MMA/2H-4-AB-1; c: MMA/2H-4-AB-2; d: MMA/2H-4-AB-3; e: MMA/2H-4-AB-4; f: MMA/2H-4-AB-5; and g: MMA/2H-4-AB-6.

poly(2H-4-AB), are  $105$  and  $122^{\circ}\text{C}$ , respectively. The transition observed in the temperature range  $100$  to  $122^{\circ}\text{C}$  for the copolymers is due to the glass transition.

It follows clearly from Fig. 3 and Table 6 that there is a marked increase in  $T_g$  with increasing 2H-4-AB content in the copolymer.

This is in accordance with the observations of Bailey [11] for styrene/2,4-dihydroxy-4'-vinylbenzophenone copolymers. A slight loss in

TABLE 6. Glass-Transition Temperature ( $T_g$ ), Initial Decomposition Temperature (IDT), and Kinetic Parameters

Copolymer	$T_g$ , °C	IDT, °C	Percentage weight loss at temperature, °C						Order of reaction n	Energy of activation E, kcal/mol
			300	350	400	500	600	600		
MMA-2H-4-AB-0	105	260	21.0	65.0	85.5	100	-	-	1.0	53.0
MMA-2H-4-AB-1	112	268	10.5	38.0	70.5	94.0	-	-	-	-
MMA-2H-4-AB-2	115	272	8.0	28.5	64.0	84.0	100	100	1.6	62.1
MMA-2H-4-AB-3	118	274	6.5	18.0	53.5	76.5	100	100	1.8	65.3
MMA-2H-4-AB-4	120	277	5.0	14.5	48.0	70.0	99.0	99.0	1.9	66.0
MMA-2H-4-AB-5	121	279	4.0	12.0	46.5	68.0	99.0	99.0	2.0	66.5
MMA-2H-4-AB-6	122	280	3.0	11.0	46.0	66.0	99.0	99.0	2.0	66.7



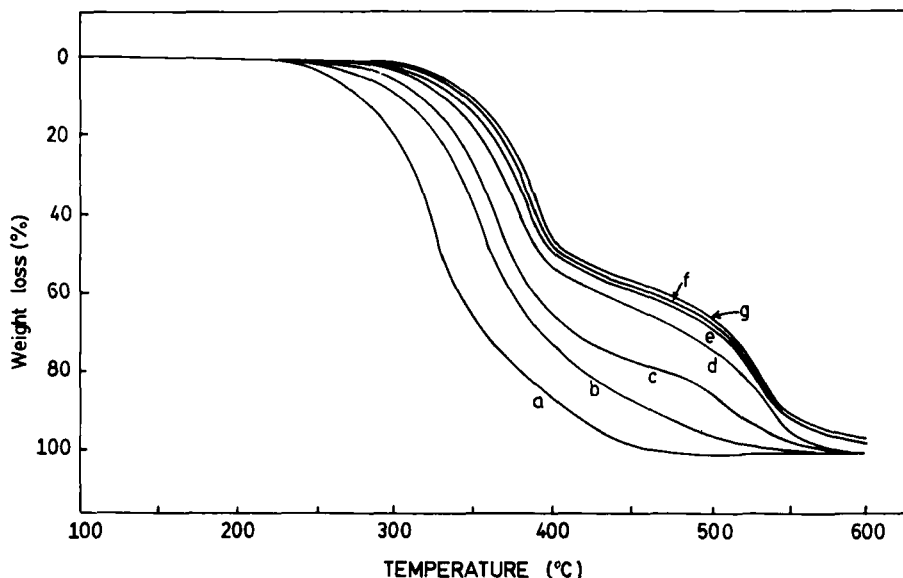


FIG. 4. TGA traces of copolymers in air. Heating rate,  $8.5^{\circ}\text{C}/\text{min}$ . a: MMA/2H-4-AB-0; b: MMA/2H-4-AB-1; c: MMA/2H-4-AB-2; d: MMA/2H-4-AB-3; e: MMA/2H-4-AB-4; f: MMA/2H-4-AB-5; and g: MMA/2H-4-AB-6.

chain flexibility may occur as a result of association of the 2-hydroxybenzophenone units in the poly(MMA) matrix. The rigidity in copolymer chains might be expected to increase with increasing 2-hydroxybenzophenone content because of steric hindrance imposed by the 2-hydroxybenzophenone unit.

Thermogravimetric analysis (TGA) data are shown Table 6 and Fig. 4. From the values of IDT it is evident that the thermal stability of the copolymers increase markedly as the 2H-4-AB content increases. The thermal decomposition of poly(MMA) in air commences around  $260^{\circ}\text{C}$  while that of poly(2H-4-AB) begins around  $280^{\circ}\text{C}$ . The rate of decomposition is very fast up to about  $400^{\circ}\text{C}$ . The weight loss decreases as the MMA content decreases because MMA contains a quaternary carbon atom which is highly susceptible to thermal decomposition. In each case, decomposition takes place in two stages, as is evident from Fig. 4. The first rapid stage of decomposition may be due to bond rupture and volatilization of low molecular weight fragments produced during decomposition. The second slow stage of decomposition suggests increased thermal stability, probably due to the presence of  $-\text{OH}$  groups in the side chain which forms crosslinks during heating.

The energy of activation ( $E$ ) and order of reaction ( $n$ ) were evaluated from TGA thermograms by the method of Anderson and Freeman [23] and are reported in Table 6. The energy of activation increases as the 2H-4-AB content increases, as expected from the crosslinking ability of pendant benzophenone units.

## ACKNOWLEDGMENTS

The authors thank Professor R. P. Patel, Head, Department of Chemistry, for providing necessary facilities. One of us (M. P.) is grateful to the University Grants Commission New Delhi, for providing a Junior Research Fellowship.

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Received October 2, 1985

Revision received December 28, 1985