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Mahendra Patel^a; J. S. Parmar^a; M. R. Patel^a; M. M. Patel^a

^a Department of Chemistry, Sardar Patel University Vallabh, Vidyanagar, India

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SYNTHESIS AND STUDY OF POLYMERIC ULTRAVIOLET ABSORBERS. II

MAHENDRA PATEL, J. S. PARMAR, M. R. PATEL, and M. M. PATEL*

Department of Chemistry
Sardar Patel University
Vallabh Vidyanagar 388120, India

ABSTRACT

Polymeric UV absorbers have been prepared by free-radical solution copolymerization at 75°C of methyl methacrylate and 2-hydroxy-4-methacryloyloxybenzophenone monomers at low conversion (around 10%). The composition of the copolymers was determined by UV, IR, and NMR studies. The molecular weight was estimated by GPC. The reactivity ratios were determined by several methods. Viscosity was used to study the effect of copolymer composition and solvents. The copolymers were also analyzed by TGA and DSC, and DSC was used to study the effect of copolymer composition on T_g .

INTRODUCTION

Polymers carrying the reactive functional groups are of value in a variety of uses. Among these are materials which have ultraviolet absorbing groups attached to the polymer chain [1]. In recent years polyolefin films have been made more stable to atmospheric degradation by incorporating polymerizable 2-hydroxybenzophenones in the main chain [2-4].

*To whom correspondence should be addressed.

Tocker [5] has prepared 2-hydroxy-4-acryloyloxybenzophenone, 2-hydroxy-4-methacryloyloxybenzophenone, and several other similar polymerizable UV-absorbers and has copolymerized them with ethylene to give polymeric UV-absorbers. He found that polyethylene (PE) films (0.1 mm) stabilized with 2-hydroxy-4-methacryloyloxybenzophenone (incorporated as comonomer) were much more resistant to weathering than films stabilized by blending in additives. Tocker [6] reported that repeated toluene extraction of a copolymer of 2-hydroxy-4-methacryloyloxybenzophenone and ethylene did not remove any of the UV stabilizer, and the polymer showed no evidence of exudation. In contrast, PE film stabilized with 2-hydroxy-4-methacryloyloxybenzophenone showed exudation on long-term exposure. Osawa et al. [7] have also prepared polymeric UV-absorbers from 2-hydroxy-4-methacryloyloxybenzophenone and listed their efficiency in PE. They found that in deciding the efficiency of a UV-absorber, its molecular structure is more important than its molecular weight.

We recently reported the synthesis and characterization of UV-absorbers from 2-hydroxy-4-acryloyloxybenzophenone, its homopolymer, and its copolymers with methyl methacrylate [9]. In continuation of this work, the present paper describes the similar study of UV-absorbers prepared from 2-hydroxy-4-methacryloyloxybenzophenone (2H-4MB) and methyl methacrylate (MMA).

EXPERIMENTAL

Materials

Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride in the presence of hydroquinone as inhibitor and was purified by fractional distillation (bp 96°C).

The monomer, 2H-4MB, was prepared by reacting methacryloyl chloride with 2,4-dihydroxybenzophenone in the presence of anhydrous pyridine, as reported earlier [6]. It was recrystallized from ethanol to give pale yellow crystals, mp 77°C.

Methyl methacrylate (MMA) was freed from inhibitor by washing with 5% aqueous NaOH solution, followed by several washings with distilled water, dried over anhydrous sodium sulfate, and distilled. The solvents were purified by recrystallizing twice from chloroform.

Polymerization

Free-radical solution polymerization was adopted for the preparation of two homopolymers and five copolymers of different 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 condenser. Nitrogen gas was bubbled through the contents while they refluxed at 75°C for 1 h. The polymers were precipitated by adding methanol. They were purified by the cyclohexanone/methanol system three times and finally dried in vacuum at 30°C.

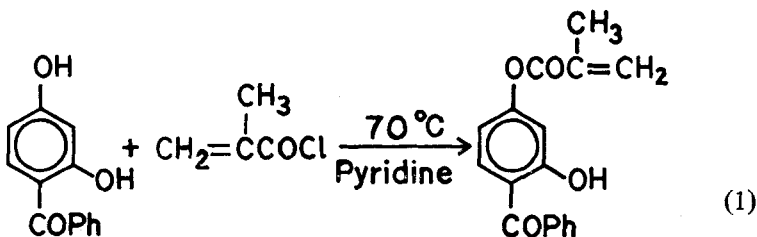
Analysis and Physical Measurements

UV, IR, and NMR spectral analysis, DSC, TGA, and viscometric study of polymers were carried out following the procedures described in an earlier communication [9].

Gel permeation chromatography (GPC) was used to determine the average molecular weights \bar{M}_w and \bar{M}_n . It was calibrated with standard polystyrene samples. The polymers were dissolved in chloroform and analyzed at 30°C.

RESULTS AND DISCUSSION

2-Hydroxy-4-methacryloyloxybenzophenone (2H-4MB) was synthesized from 2,4-dihydroxybenzophenone, which is commercially available, and methacryloylchloride:



There is also the possibility of reaction at the *o*-hydroxyl group, which may give 4-hydroxy-2-methacryloyloxybenzophenone (4H-2MB). Infrared analysis showed the presence of ester absorption at 1740 cm^{-1} and bonded carbonyl at 1625 cm^{-1} , indicating clearly that esterification had taken place on the 4-OH

TABLE 1. Preparation and Copolymer Composition of MMA-2H-4MB Copolymers^a

No.	Copolymer	Mole fraction in the feed		Conversion, %	Mole fraction of 2H-4MB in the copolymer determined by			GPC	
		2H-4MB	MMA		UV	NMR	IR (1620 cm ⁻¹)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$
1	MMA-2H-4MB-0 ^b	0.0	1.0	5.1	0.000	0.000	0.000	1.61	1.19
2	MMA-2H-4MB-1	0.1	0.9	9.2	0.221	0.223	0.220	2.27	1.29
3	MMA-2H-4MB-2	0.2	0.8	9.8	0.369	0.368	0.369	4.36	1.99
4	MMA-2H-4MB-3	0.5	0.5	12.2	0.659	0.661	0.662	5.15	2.26
5	MMA-2H-4MB-4	0.7	0.3	9.6	0.812	0.809	0.809	2.76	1.22
6	MMA-2H-4MB-5	0.8	0.2	10.2	0.873	0.870	0.871	1.92	1.13
7	MMA-2H-4MB6 ^c	1.0	0.0	11.7	1.000	1.000	1.000	—	—

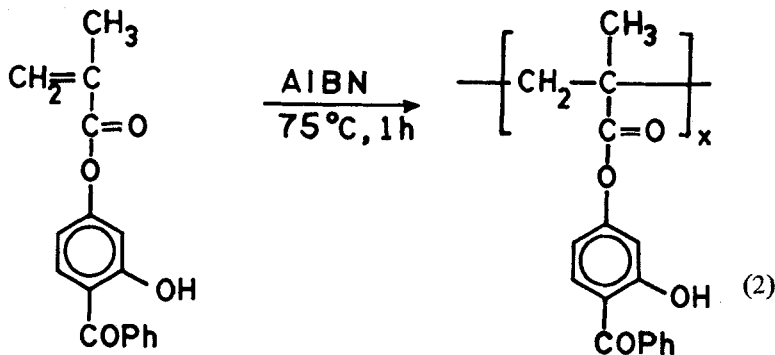
^aPolymerization conditions: Solvent, cyclohexanone (30 mL); initiator, AIBN (60.8 μ mol); temperature, 75 \pm 0.2°C; time, 1.25 h \pm 5 min; low conversion.

^bPMMA.

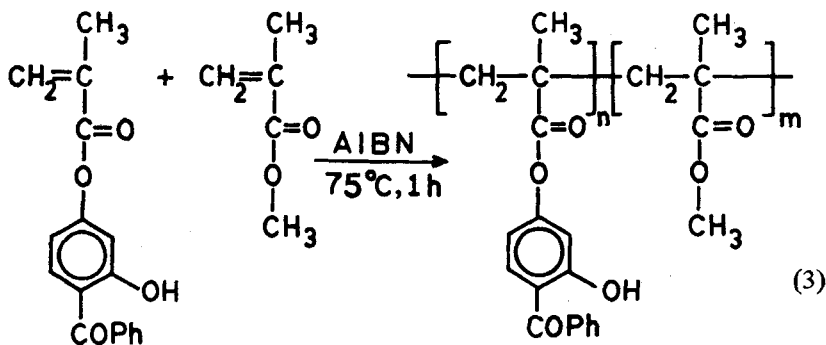
^cPoly(2H-4MB).

position. Ultraviolet analysis also showed strong absorption around 330-340 nm, indicative of *o*-hydroxybenzophenones [6]. The alcoholic solution of the compound gives a violet color with neutral ferric chloride solution. These observations suggest that the compound formed is 2H-4MB and not 4H-2MB.

2H-4MB undergoes homopolymerization to give poly(2H-4MB):



as well as copolymerization with MMA to give a copolymer (MMA-2H-4MB):



Copolymer Composition and Characterization

From the copolymer compositions in Table 1, it can be seen that as 2H-4MB is increased in the feed, the mole fraction of 2H-4MB increases in the copolymer and that the mole fraction of 2H-4MB is higher in the copolymer than in the feed.

The molecular weight of the copolymer increases with the concentration of comonomer, evidently due to a high reactivity ratio and low rate of reac-

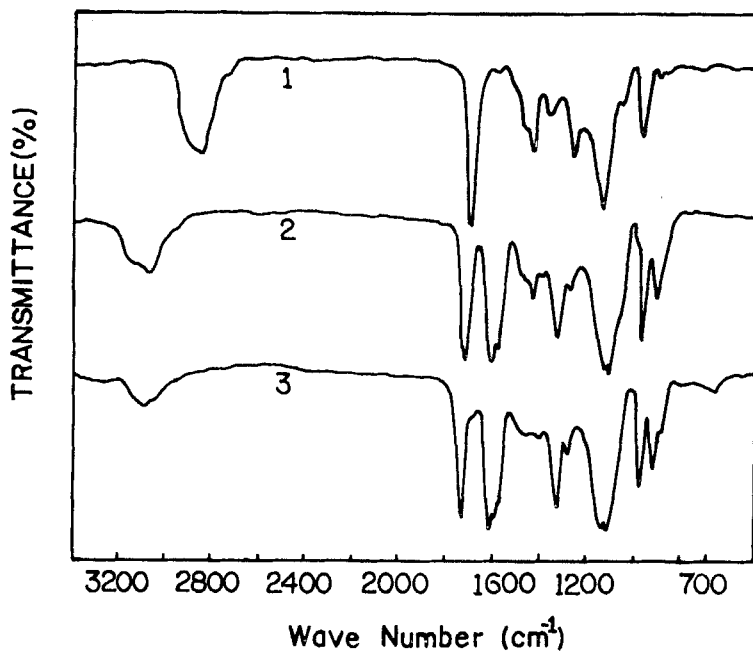


FIG. 1. IR spectra. (1) Poly(MMA), (2) MMA/2H-4MB-4, (3) poly(2H-4MB).

tion of sterically hindered comonomer, which increases the probabilities of propagation and termination by a combination of chain radicals with comonomer ends.

The UV spectrum of 2,4-(OH)₂BP shows one band at 333 nm, due to the $n\rightarrow\pi^*$ transition, and two bands at 290 and 245 nm, due to $\pi\rightarrow\pi^*$ transition [10]. The UV spectra of 2H-4MB and its polymers show only two bands, one at 333 nm ($n\rightarrow\pi^*$) and the second at 270 ($\pi\rightarrow\pi^*$) with a hypsochromic shift. The third band at 245 nm is absent in 2H-4MB as well as in its polymers, indicative of an O-R group in place of OH at the 4-position. The hypsochromic shift agrees with earlier work on the UV-spectra of vinyl polymers [11].

The IR spectra of poly(2H-4MB) and poly(MMA) differ in many respects (Fig. 1). The former has two types of $>C=O$ groups, one due to ester at 1740 cm^{-1} and another due to benzoyl at 1620 cm^{-1} , whereas the latter has only an ester type of $>C=O$ group at 1720 cm^{-1} [12]. Poly(2H-4MB) has phenyl rings in the main chain, shown by 1600 cm^{-1} , which is absent in PMMA. In the case of copolymer, as expected, all three bands are observed.

TABLE 2. NMR Spectral Characteristics of Homopolymers and Copolymer^a

No.	Compound	δ , ppm				
		α -CH ₃	-CH ₂ -	-OCH ₃	Aromatic	Ar-OH
1	MMA-2H-4MB-0	0.83	1.80	3.10	—	—
		1.00	2.10	3.55(s)		
		1.30		4.00		
2	MMA-2H-4MB-4	1.00	2.00	3.10	6.60 ^b	
		1.20	2.20	3.50(s)	7.10	7.95
		1.50		4.00	7.50	
3	MMA-2H-4MB-6	1.00	1.90		6.60 ^b	
		1.20	2.20	—	7.10	7.95
		1.50			7.50	

^aHigh-resolution (90 MHz) ¹H-NMR spectra recorded in CDCl₃. s: strong.
^bMultiplet.

Figure 1 shows the band due to intramolecularly hydrogen-bonded OH at 3000-3200 cm⁻¹. In all these three cases, the presence of tertiary -CH₃ groups is shown by a peak at 980 cm⁻¹. The other bands due to OCH₃ bonding, ν -CH₂ stretching, and -O- ester stretching can also be clearly seen.

The NMR study also helps in the confirmation of the structure of the copolymer. The important signals and corresponding assignments are shown in Table 2 [13].

Determination of Reactivity Ratios

The reactivity ratios r_1 (for 2H-4MB) and r_2 (for MMA) in the present system were estimated by four well-known methods, viz., Joshi and Joshi (JJ) [14], Mayo and Lewis (ML) [15], Fineman and Ross (FR) [16], and Kelen and Tüdös (KT) [17].

The reactivity ratios were determined according to the JJ method as described earlier [9] (Table 3). The r_1 and r_2 based on copolymer compositions determined by IR and NMR analysis agree well with each other. Moreover, the results obtained by the other three methods agree quite closely with the results.

TABLE 3. Reactivity Ratios by the JJ Method [14]

No.	Copolymer	M ₁ -M ₂ System		M ₂ -M ₁ System		<i>r</i> ₁ 2H-4MB	<i>r</i> ₂ MMA
		<i>F</i>	<i>f</i>	<i>F</i>	<i>f</i>		
1	MMA-2H-4MB-1 ^a	4.00	6.73	0.25	0.15		
2	MMA-2H-4MB-2 ^a	2.33	4.25	0.43	0.23		
3	MMA-2H-4MB-3 ^a	1.00	1.96	1.00	0.51	1.613	0.343
4	MMA-2H-4MB-4 ^a	0.25	0.58	4.00	1.71		
5	MMA-2H-4MB-5 ^a	0.11	0.28	9.00	3.54		
1	MMA-2H-4MB1 ^b	4.00	6.71	0.25	0.15		
2	MMA-2H-4MB-2 ^b	2.33	4.25	0.43	0.23		
3	MMA-2H-4MB-3 ^b	1.00	1.95	1.00	0.51	1.609	0.342
4	MMA-2H-4MB-4 ^b	0.25	0.58	4.00	1.72		
5	MMA-2H-4MB-5 ^b	0.11	0.29	9.00	3.49		

^aData based on copolymer composition by IR analysis.

^bData based on copolymer composition by NMR analysis.

The reactivity ratio of 2H-4MB (1.61) is almost five times higher than that of MMA (0.34) in this study.

An attempt was made to correlate the reactivity of the two monomers by computing the Alfrey-Price *Q-e* values [18]. On the basis of methyl methacrylate (*Q* = 0.74 and *e* = 0.40), we calculated the *Q-e* values of 2H-4MB by the equations

$$e_2 = e_1 \pm (-\ln r_1 \cdot r_2)^{1/2} \quad (4)$$

$$Q_2 = Q_1/r_1 \cdot \exp [-e_1(e_1 - e_2)], \quad (5)$$

where *Q*₁ = 0.74 and *e*₁ = 0.40.

Q is a measure of the resonance stabilization of the monomer in copolymerization, and thus the reactivity. The high reactivity of 2H-4MB is reflected by its *Q* value (1.57) which is higher than that of MMA (0.74). Similarly, *e* takes account of polar factors influencing copolymerization. The *e* value of

2H-4AB (1.32) [9] is higher than 2H-4MB (-0.36), in complete agreement with reported e values of similar cases, viz., methyl acrylate (0.60) and methyl methacrylate (0.40), as well as styrene (-0.80) and α -methylstyrene (-1.27) [18].

Viscometric Study

The Huggins constants K_H found from the η_{sp}/c vs c plots are plotted against mole fraction of 2H-4MB in the copolymer (Fig. 2). The curves vary with the solvent power of the solvent used. The solvent power of the three solvents may broadly be arranged in decreasing order as DMF > chloroform > MEK. From the nature of plots it can be seen that K_H does not increase uniformly. This suggests that the copolymers prepared are other than random azeotropic and block copolymers.

Thermal Studies

The DSC traces are shown in Fig. 3. The T_g of poly(MMA) and poly(2H-4MB) are 105 and 143°C, respectively. Figure 3 shows a marked increase in

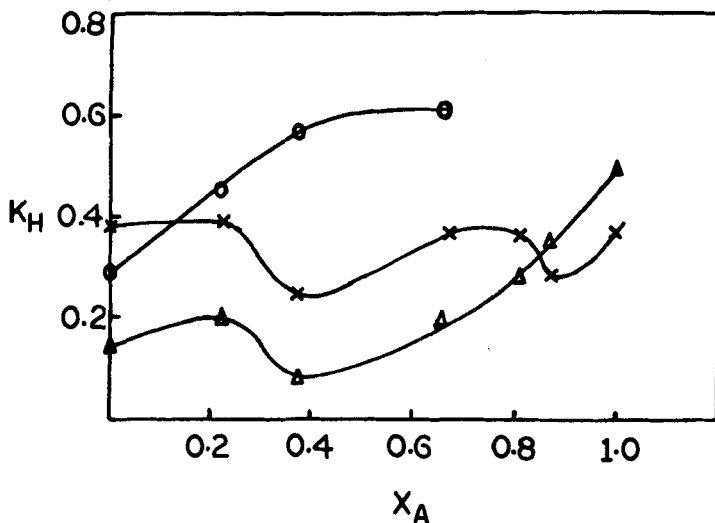


FIG. 2. Plot of Huggins constant (K_H) vs mole fraction of 2H-4MB in copolymer (X_A) in MEK (O), chloroform (X), and DMF (Δ).

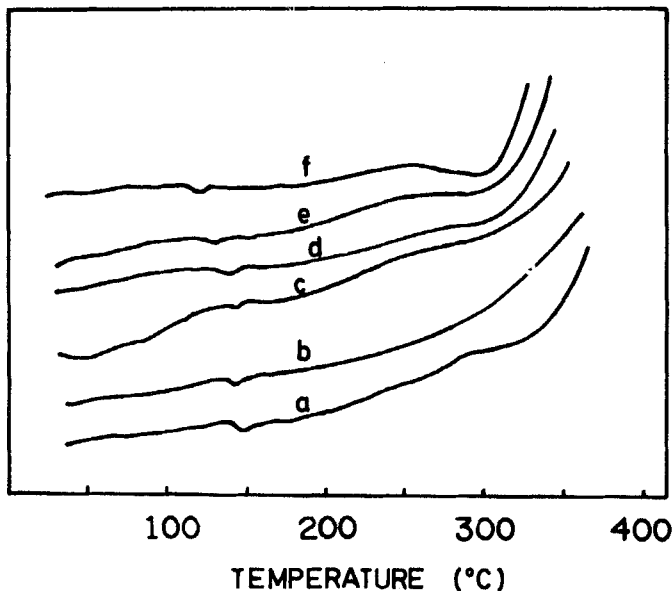


FIG. 3. DSC thermograms of copolymers in air. Heating rate: $10^{\circ}\text{C}/\text{min}$. (a) MMA/2H-4MB-1, (b) MMA/2H-4MB-2, (c) MMA/2H-4MB-3, (d) MMA/2H-4MB-4, (e) MMA/2H-4MB-5, and (f) MMA/2H-4MB-6.

T_g with increasing 2H-4MB content in the copolymer. The rigidity of the copolymer chains might be expected to increase with increasing 2-hydroxybenzophenone content due to steric hindrance.

The T_g 's of copolymers often fit the equations given by Fox [19] and Wood [20], which are based on the assumption that a fixed amount of free volume is associated with each type of monomer unit. The T_g values calculated by these equations and the experimental values [Table 4] agree quite well.

The T_g of poly(2H-4AB) (122°C) is less than that of poly(2H-4MB) (143°C). This suggests that the additional $-\text{CH}_3$ groups on the main chain further reduce the flexibility of the polymer.

Thermogravimetric analysis (TGA) data are shown in Table 4 and Fig. 4. From these data it is evident that the thermal stability of the copolymers increases as the 2H-4MB content increases. The thermograms are almost identical in nature and show only a single stage of decomposition, evidently because

TABLE 4. Glass-Transition Temperature (T_g), Initial Decomposition Temperature (IDT), and Weight Loss Data

Copolymer	T_g , °C		IDT, °C	Percent weight loss at temperature, °C					
	Exp	Calca		300	350	400	500	600	
MMA-2H-4-MB-0	105	—	260	21.0	65.0	85.5	100	—	
MMA-2H-4-MB-1	119	119.05	267	13.0	58.0	76.0	96.5	100	
MMA-2H-4-MB-2	126	125.83	274	9.0	52.0	71.0	91.5	98.0	
MMA-2H-4-MB-3	135	135.40	276	6.0	48.0	66.5	83.0	92.0	
MMA-2H-4-MB-4	139	139.17	281	4.0	45.0	64.0	80.5	93.0	
MMA-2H-4-MB-5	140	140.51	285	3.0	43.0	61.0	78.0	94.0	
MMA-2H-4-MB-6	143	—	285	2.5	42.0	60.0	77.0	94.0	

^aCalculated using relation of Fox [19].

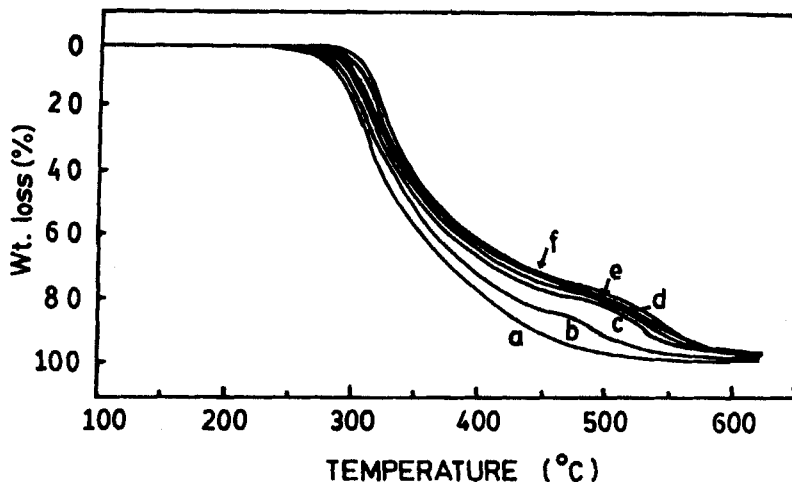


FIG. 4. TGA traces of copolymers in air. Heating rate: $8.5^{\circ}\text{C}/\text{min}$. (a) MMA/2H-4MB-1, (b) MMA/2H-4MB-2, (c) MMA/2H-4MB-3, (d) MMA/2H-4MB-4, (e) MMA/2H-4MB-5, and (f) MMA/2H-4MB-6.

both monomers are of the 1,1-disubstituted vinyl type. The decomposition is rapid for all polymers in the $280\text{--}350^{\circ}\text{C}$ range. This is again due to the presence of alternating tertiary carbon atoms on the main chain. The decomposition continues at a fairly high rate up to 550°C .

CONCLUSIONS

By proper selection of comonomers, useful UV-absorbing polymers with varying amount of UV-absorbing groups (2H-4MB) can be prepared. They have intermediate thermal properties and hence can remain in a blend of homopolymer and copolymer during various applications and can also protect the homopolymer from UV light.

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