Preparation and Characterization of a High Molecular Weight UV-Stabilizer Based on a Derivative of 2,4-Dihydroxybenzophenone and Its Application in Polymer Materials

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ABSTRACT: In this study, a polymerizable UV-stabilizer, 2-hydroxy-4-(3-methacryloxy-2-hydroxylpropoxy)benzophenone (BPMA), was synthesized using 2,4-dihydroxybenzophenone (UV-0) and glycidyl methacrylate (GMA). It was copolymerized with methyl methacrylate (MMA) to prepare poly(MMA-*co*-BPMA) by emulsion polymerization. The composition and characteristics of poly(MMA-*co*-BPMA) were determined by using proton nuclear magnetic resonance (^{1}H-NMR), gel permeation chromatography (GPC), and ultraviolet-visible absorption spectroscopy (UV–vis). Further, the obtained poly(MMA-*co*-BPMA) was used as a high molecular weight UV-stabilizer and was blended with PVC to prepare PVC/poly(MMA-*co*-BPMA) films. These films were presented under UV light, using PVC film as standard substance. Insoluble substance, GPC, and color difference were used to characterize UV degradation. The results show that poly(MMA-*co*-BPMA) is an effective high molecular weight UV-stabilizer. To detect the migration of poly(MMA-*co*-BPMA), water extraction and heat migration test were used to accelerate the movement of poly(MMA-*co*-BPMA). As a reference, these tests were also carried out on PVC/UV-0 film. The results show that poly(MMA-*co*-BPMA) has very small migration, while nearly 80% UV-0 migrated out from the plastic matrix after the experiments. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2203–2211, 2006

Key words: 2,4-dihydroxybenzophenone; polymerizable; UV-stabilizer; degradation

INTRODUCTION

Ultraviolet light stabilizers are used widely in plastics, cosmetics, and films. The main purpose of UV-stabilizer is to prevent polymers from photodegradation or photocrosslinking caused by ultraviolet light presented in sunlight and artificial light source.

Ultraviolet light stabilizers are divided into inorganic UV-stabilizers, organic UV-stabilizers, and other kinds. Inorganic UV-stabilizers, such as iron oxide, titanium oxide, chromic oxide, and carbon black, usually cannot evenly distribute in the plastic substrate so much as incompatible with the polymer matrix. The final effects depend on the particle size and concentration.[1] These drawbacks limit the application of inorganic UV-stabilizers. Organic UV-stabilizers, generally with small molecular weight, include fluorescent compounds, phenyl-ester of benzoic acid, hydroxyl-benzophenone, benzotriazoles, etc. In the addition of these stabilizers to plastic materials, problems such as migration, incompatibility, volatility, and solvent extraction will inevitably occur. It leads to a strong diminution of the materials' utilization. To resolve such problems, many approaches have been developed, such as preparing reactive UV-stabilizer,[2–11] introducing compatible side chains, or chemically anchoring of the additive to the polymer backbone,[12–15] etc. Among these methods, preparing high molecular weight UV-stabilizer is a highlight because, for most of the polymer materials, blending is the first choice to enhance their UV-resistance. Meanwhile, different high molecular weight UV-stabilizers can be prepared by the copolymerization of a reactive UV-stabilizer with other monomers. In this point, it is very convenient to ameliorate the compatibility between UV-stabilizer and plastic matrix by preparing suitable high molecular weight UV-stabilizer.

In this study, we prepared a polymerizable UV-stabilizer 2-hydroxy-4-(3-methacryloxy-2-hydroxyl-propoxy)benzophenone (BPMA), and then, it was copolymerized with methyl methacrylate (MMA) to get a high molecular weight UV-stabilizer poly(MMA-*co*-BPMA). In consideration of the efficiency of poly(MMA-*co*-BPMA) as a UV-stabilizer, we applied
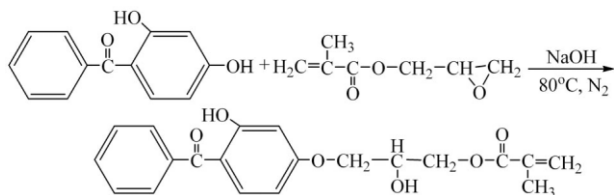
Scheme 1   Synthesis of BPMA by UV-0 and GMA.

PVC as a polymer matrix because PVC is widely used in the world and is easily destroyed by UV light. We investigated the water extraction and heat migration of poly(MMA-*co*-BPMA). The results show that poly(MMA-*co*-BPMA) is an effective high molecular weight UV-stabilizer and it has a lower migration trend than low molecular weight UV-0.

EXPERIMENTAL

Materials

2,4-Dihydroxybenzophenone (purity above 99.5%), provided by Jinchun Meibang Chemical (Wuhan, China), was used as received without further purification. Analytical reagent grade NaOH, tetrahydrofuran (THF), *N,N*-dimethyl formamide (DMF), and cyclohexanone were provided by Kelong Chemical Reagent Factory of China (Chengdu, China). Glycidyl methacrylate was available commercially. Methyl methacrylate (MMA), which was provided by Shanghai Waigang Chemical Factory (Shanghai, China), was distilled before application. Sodium dodecanesulfonate (SDS), azobisisobutyronitrile (AIBN), and potassium persulfate (KPS) were purchased from Wuhan Chemical Reagent Factory (Wuhan, China). PVC was supplied by Yibin Tianyuan Chemical Factory of China (Yibin, China). Water was deionized twice before use.

Synthesis of 2-hydroxy-4-(3-methacryloxy-2-hydroxylpropoxy)benzophenone

2-Hydroxy-4-(3-methacryloxy-2-hydroxylpropoxy)benzophenone (BPMA) was synthesized (Scheme 1) as described in an earlier literature.[16] A mixture of 2,4-dihydroxybenzophenone (UV-0; 0.05 mol) and sodium hydroxide (0.155 g) were added into a 150 mL three-necked round-bottom flask with a stirrer, a refluxing condensation pipe, and a ventilation pipe. To exclude the oxygen gas, the reactor was deaired by vacuum pump and was aerated with nitrogen gas, and then, glycidyl methacrylate (GMA; 0.055 mol) was introduced into the reactor by syringe. The reaction temperature was 80°C, and the reaction time was 5 h. At the end of the reaction, a yellow viscous liquid as coarse product was got. The pure BPMA was got by

column chromatography using thin layer chromatography as monitor, and it was confirmed by ^{1}H-NMR, FTIR, and UV–vis spectroscopy.

Preparation of poly(MMA-*co*-BPMA), PMMA, and PBPMA

Poly(MMA-*co*-BPMA) was obtained through emulsion copolymerization of MMA with BPMA in different molar ratios respectively. The process for preparation of poly(MMA-*co*-BPMA) was shown as follows. First, BPMA (1.8 mmol) was dissolved in MMA (70.8 mmol). The mixture of MMA with BPMA, SDS (0.8 g), and deionized water (40 mL) were placed in a three-necked round-bottom flask equipped with a thermometer, a stirrer, and a refluxing condensation pipe to prepare MMA-BPMA emulsion. KPS (0.032 g) was dissolved in deionized water and then added to the emulsion. The reaction was carried out at 80°C for 3 h. After being coagulated with 5% $CaCl_2$ aqueous solution, poly(MMA-*co*-BPMA) was purified by deionized water with the assistant of centrifugal machine. The final product was dried under 70°C and pulverized to get poly(MMA-*co*-BPMA) powder. PMMA was prepared by the same method without BPMA in the feed, and PBPMA was prepared by solution polymerization in THF using AIBN as initiator at 70°C.

Preparation of PVC/poly(MMA-*co*-BPMA) film, PVC/UV-0 film and PVC film

PVC/poly(MMA-*co*-BPMA) film, PVC/UV-0 film, and PVC film were prepared by the solution casting method.[17] A typical process is stated here. PVC and poly(MMA-*co*-BPMA) were blended together in different molar ratios in 15 mL THF. With the help of a magnetic stirrer, the mixture became homogeneous. Then, it was poured on a 15 cm × 15 cm glass plate to form a 0.5 mm film. The solvent was allowed to evaporate slowly at room temperature. After 24 h, the film was removed from the plate and dried in a vacuum oven at room temperature. PVC/UV-0 film and PVC film were prepared by the same method with different molar ratios of the UV-stabilizer.

UV irradiation of PVC/poly(MMA-*co*-BPMA) film, PVC/UV-0 film, and PVC film

The PVC/poly(MMA-*co*-BPMA), PVC/UV-0 and PVC films were marked before UV irradiation. Then, the films were settled vertically under an artificial antimony–mercury lamplight (500 W) in a self-assemble UV irradiation cabinet. The distance between the polymer and the lamplight was 0.5 m, and the main wavelength range of the antimony–mercury lamplight was between 270 and 400 nm. The irradiation test was

taken at 40°C with air circulating. Samples were removed at different intervals.

Measurement

Spectral study

Before measurement, poly(MMA-*co*-BPMA) was purified by cyclohexanone/methanol system three times and finally dried in vacuum oven at 50°C. Then, both PMMA and poly(MMA-*co*-BPMA) were extracted with deionized water for 7 days in a Soxhlet extractor.

High resolution ^{1}H-NMR spectrum was recorded on a Varian INOVA-400 spectrometer of 400 MHz. Deuterated chloroform was used as solvent and tetramethylsilane was used as internal standard. UV–vis absorption spectra of PMMA and poly(MMA-*co*-BPMA) were measured on a Shimadzu UV-720 spectrophotometer in the range of 200–400 nm, using DMF as solvent.

GPC measurement

PMMA, poly(MMA-*co*-BPMA), PVC/poly(MMA-*co*-BPMA) film, PVC/UV-0 film, and PVC film were characterized by GPC measurement. Samples before irradiation were tested directly, while samples after irradiation were treated by removing the insoluble substance before the test. The molecular weight and its distribution were tested at 35°C using Waters 2410 GPC instrument. THF was used as solvent at a flow rate of 1.0 mL/min, and the instrument was calibrated with standard narrow-molecular weight distribution polystyrene samples.

Determination of color difference of PVC/UV-stabilizer films and PVC film

PVC/poly(MMA-*co*-BPMA) films, PVC/UV-0 films, and PVC film were irradiated under UV light after 0, 48, 96, 144, 192, 240, 288, and 336 h. Unirradiated PVC film was used as reference material. Color differences (ΔE) of all the films were tested by Color Reader CR-10 (Minolta, Japan).

Insoluble substance measurement

The insoluble substance in PVC/poly(MMA-*co*-BPMA), PVC/UV-0, and PVC films were calculated by a same method. A typical process was as follows. First, 0.1 g PVC/poly(MMA-*co*-BPMA) film was dissolved in 25 mL cyclohexanone for 24 h. The weight of a filter paper was measured on an accurate Sartorius balance, and then, the solution was disposed by it. The filter paper with insoluble substance was dried at 80°C in vacuum oven, and the final weight was also measured

by Sartorius balance. The percent of insoluble substance was calculated using eq. (1):

$$\text{Insoluble substance (\%)} = \frac{m_1 - m_0}{0.1} \times 100\% \quad (1)$$

m_0 is the weight (g) of the filter paper, and m_1 is the weight (g) of the filter paper with dried insoluble substance.

### Weight loss by water extraction

The PVC/poly(MMA-*co*-BPMA) films and PVC/UV-0 films were first measured on an accurate Sarorius balance, and then, it was enclosed with a filter paper. The films were extracted by water in a Soxhlet extractor. Samples were taken out at different intervals. The films were dried in vacuum oven at 80°C. The weight was recorded again. The weight loss of the films was calculated using eq. (2):

$$\text{Weight loss (\%)} = \frac{m_0 - m_1}{m_0} \times 100\% \quad (2)$$

m_0 is the film weight (g) before the test, and m_1 is the film weight (g) after water extraction.

Migration test of the UV-stabilizer

The PVC/poly(MMA-*co*-BPMA) films and the PVC/UV-0 films were prepared using solution casting method. To detect the migration significantly, we increased the concentration of UV-stabilizer to 10% in these films. It was tested by using a modified method of ISO/R-183. The diameter of the film was 50 mm, and the thickness of the film was 0.5 mm. Before the test, the weight of the films was exactly measured on a Sartorius balance. The sequence of placement was (from bottom to up) glass plate, filter paper, PVC/UV-stabilizer film, filter paper, glass plate, and heavy substance (5 kg).
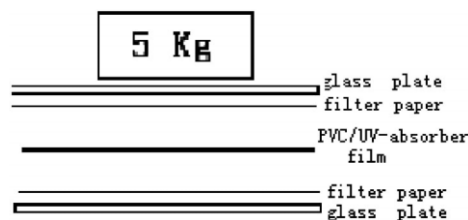
The test was done at (70 ± 2)°C for 72 h. The migration substance was absorbed by rubber or filter paper. The weight loss was calculated as eq. (3):

$$\text{Weight loss (\%)} = \frac{m_0 - m_1}{m_0} \times 100\% \quad (3)$$

TABLE I
Preparation and Characterization of Poly(MMA-co-BPMA) and PMMA

Samples	Mole fraction in feed		Mole fraction in copolymer[a]		Conversion (%)	GPC		
	MMA	BPMA	MMA	BPMA		M_n	M_w	D
PMMA	100	0	100	0	98.5	1.08e6	1.47e6	1.36
P(MMA-co-BPMA)-1	99.54	0.46	99.51	0.49	94.5	1.85e5	6.03e5	3.27
P(MMA-co-BPMA)-2	99.07	0.93	98.78	1.22	93.2	3.87e5	1.27e6	3.29
P(MMA-co-BPMA)-3	98.24	1.76	98.30	1.70	96.5	1.46e6	1.62e6	1.10
P(MMA-co-BPMA)-4	97.62	2.38	97.30	2.70	87.5	1.48e6	1.64e6	1.11

[a] Determined by ^{1}H-NMR spectrum.

m_0 is the film weight (g) before the test, and m_1 is the film weight (g) after heat migration.

RESULTS AND DISCUSSION

Copolymer composition and characterization

The mole fraction in feed, mole fraction in copolymer, conversion and GPC data about PMMA and poly(MMA-co-BPMA) were summarized in Table I. The mole fraction in feed is calculated by starting materials, and the mole fraction in copolymer is determined by ^{1}H-NMR spectrum. As BPMA increased in feed, the mole fraction of BPMA also increased in poly(MMA-co-BPMA), and a little higher concentration was detected. This result shows that BPMA is easy to copolymerize with MMA, and they have a similar reactivity. It is ascribed to the structure of BPMA because a 3-methacryloxy-2-hydroxylpropoxy group existed at 4-position of BPMA. The methacryloxy group is so far away from the benzophenone group that no steric hindrance in the copolymerization. Meanwhile, MMA and BPMA have methacrylate group with high reactivity, and they can easily react with each other to prepare random copolymer.

Nowadays, emulsion polymerization is an effective method in preparing copolymer. Owing to its unique advantages, such as environment friendliness, high reaction rate, and relative simple engineering technology in industrialization, emulsion polymerization was applied in preparing poly(MMA-co-BPMA). The conversion of polymerization is very high as shown in Table I, and it confirms that BPMA and MMA can react with each other easily. This is a better result than solution polymerization,[3,4] which has a low conversion about 10%. The molecular weights of the copolymers are listed in Table I. The M_w values of the random copolymers are about 6.03e5–1.64e6 with polydispersity index (D) between 1.1 and 3.2, and the M_w of PMMA is 1.47e6 with polydispersity index of 1.36.

The chemical structures of poly(MMA-co-BPMA) were characterized by ^{1}H-NMR which is shown in Figure 1. Hydrogen atoms of poly(MMA-co-BPMA) are marked using 1, 2, 3, 4, 5, 6, 7, 8, a, b, c, d. The peaks at $\delta = 7.39–7.49$ ppm are due to aromatic protons, and they belong to $H_{1, 2, 3, 4, 5, 6}$, and the peaks at $\delta = 6.46–6.57$ ppm are also ascribed to aromatic protons $H_{7, 8}$. From Figure 1, it is also realized that peaks
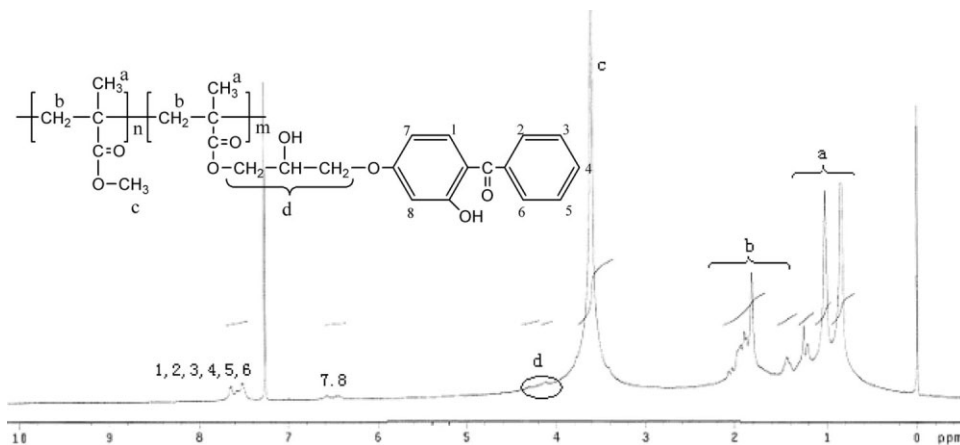

Figure 1 The ^{1}H-NMR spectrum of poly(MMA-co-BPMA).

TABLE II
^{1}H-NMR Characteristics of Homopolymers and Copolymer

Compound	α-CH$_3$		—CH$_2$—		—OCH$_3$	Ar—H		Ar—OH	—CH$_2$—CH—CH$_2$—	
PMMA	0.83	1.00	1.80	1.88	3.58	—		—	—	
	1.20	1.42	1.92	2.05						
Poly (MMA-co-BPMA)	0.84	1.01	1.81	1.89	3.59	6.46	6.57	—[a]	4.11	4.30
	1.25	1.44	1.96	2.06		7.51	7.64			
PBPMA	0.99	1.25	2.00		—	6.33	6.43	12.62	4.04	
	1.40		2.54			7.39	7.49			

[a] The proton of Ar—OH cannot be detected because of its low concentration and low sensitivity.

at about δ = 4.11–4.30 ppm pertaining to five protons of —CH$_2$—CH—CH$_2$— and peaks at about δ = 3.58 ppm are vested to —OCH$_3$. Other peaks at δ = 0.84–1.44 ppm and δ = 1.81–2.06 ppm are ascribed to α-CH$_3$ and —CH$_2$—, respectively.

The ^{1}H-NMR spectrum also helps us in confirming that poly(MMA-co-BPMA) is a copolymer. The important signals and corresponding assignment of PMMA, PBPMA, and poly(MMA-co-BPMA) were listed in Table II. PMMA and poly(MMA-co-BPMA) have the same chemical shifts at α-CH$_3$, —CH$_2$—, and —OCH$_3$. But, when compared with the ^{1}H-NMR spectrum of PBPMA, poly(MMA-co-BPMA) has a higher chemical shift at aromatic proton and —CH$_2$—CH—CH$_2$—. The ^{1}H-NMR spectrum data of aromatic proton in PBPMA are 6.33, 6.43, 7.39, and 7.49, while 6.46, 6.57, 7.51, and 7.64 in poly(MMA-co-BPMA). The chemical shift of —CH$_2$—CH—CH$_2$— in PBPMA is about 4.04, while it is 4.11–4.30 in poly(MMA-co-BPMA). This is ascribed to the different structures of the main chains of PBPMA and poly(MMA-co-BPMA). Benzophenone is an electron-donating group that makes the chemical shift of the neighboring benzophenone group and —CH$_2$—CH—CH$_2$— lower in PBPMA (Scheme 2).

But, in poly(MMA-co-BPMA), this effect is weakened by the -MMA- section. These data help us prove that the structure of poly(MMA-co-BPMA) is a copolymer.

UV-absorbance of poly(MMA-co-bpma)

In this study, the main purpose is to enhance the UV-resistance of poly(MMA-co-BPMA) by bringing the BPMA unit onto to the PMMA chain, and then, poly(MMA-co-BPMA) can be used as a high molecular weight UV-stabilizer. So, it is necessary to characterize the UV-absorbance of poly(MMA-co-BPMA). The UV–vis absorption spectra of poly(MMA-co-BPMA), PBPMA, and PMMA were shown in Figure 2. A peak at 264 nm ascribed to the $n{\rightarrow}\pi^*$ transition of C=O group appears at the curve of PMMA, while the peak is shifted to 261 nm in poly(MMA-co-BPMA) because of the addition of BPMA onto the polymer chains. Other two peaks at 284 and 324 nm ascribed to the $\pi{\rightarrow}\pi^*$ transition and $n{\rightarrow}\pi^*$ transition, respectively, appears at the curve of PBPMA, indicating that 284 and 324 nm are the character peaks of PBPMA. All of the three peaks at 261, 284, and 324 nm appear at poly(MMA-
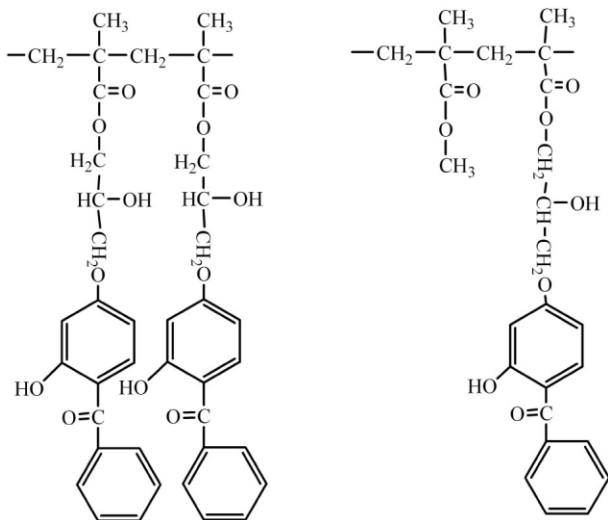
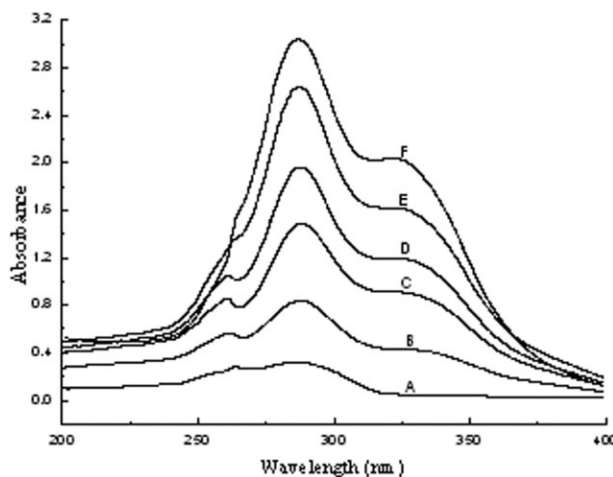**Scheme 2** The main chain structures of PBPMA and poly(MMA-co-BPMA).

Figure 2 The UV–vis absorption spectra of poly(MMA-co-BPMA), PBPMA and PMMA. A: PMMA; B, C, D, E: 0.46, 0.93, 1.76, 2.38% BPMA by mole in poly (MMA-co-BPMA); F: PBPMA) (PBPMA is 0.01% in THF while others are 0.1% in THF by weight).

TABLE III
The Insoluble Substance of PVC/Poly(MMA-co-BPMA), PVC/UV-0, and PVC Films

Samples	UV-stabilizer content (wt %)	Insoluble substance after UV irradiation (%)			
		0 h	48 h	96 h	144 h
PVC	0	0	33.4	47.7	52.4
PVC/UV-0–1	0.3	0	6.7	8.1	11.1
PVC/UV-0–2	0.6	0	5.4	7.4	10.8
PVC/UV-0–3	0.9	0	3.9	5.5	11.9
PVC/UV-0–4	1.2	0	4.2	5.1	8.7
PVC/PMB-1	0.3	0	6.5	7.3	9.0
PVC/PMB-2	0.6	0	6.3	7.8	8.8
PVC/PMB-3	0.9	0	5.0	8.3	10.3
PVC/PMB-4	1.2	0	4.0	6.8	7.7

PMB, poly(MMA-co-BPMA)

co-BPMA). It indicates that when BPMA was copolymerized with MMA in different molar ratios, the BPMA can retain its UV-absorbance, thereby the obtained copolymers have stronger UV-resistance at 284 and 324 nm. This is very useful for protecting poly(MMA-co-BPMA) from UV degradation and is also helpful for using poly(MMA-co-BPMA) as a high molecular weight UV-stabilizer.

Efficiency of poly(MMA-co-BPMA) on protecting polymer materials

Poly(MMA-co-BPMA) is a high molecular weight UV-stabilizer prepared by the copolymerization of MMA and BPMA. In this study, PVC is used as the polymer matrix to determine the efficiency of poly(MMA-co-BPMA) because PVC is widely used and is destroyed by UV light easily. PVC/poly(MMA-co-BPMA) blending films were prepared by adding the poly(MMA-co-BPMA) to the PVC in different molar ratios, and these films were presented under artificial UV light. As a reference material, PVC/UV-0 film and PVC film were also irradiated under UV light. Polymer materials are destroyed by UV-irradiation in two ways: photocrosslinking and photodegradation. In this point, we use percent insoluble substance, molecular weight test, and color difference to determine the UV degradation of PVC.

The insoluble substance of PVC/poly(MMA-co-BPMA), PVC/UV-0, and PVC films after UV-irradia-

tion are listed in Table III. It clearly shows that PVC is easy to crosslink under UV irradiation. After 144 h UV irradiation, the PVC film has 52.4% insoluble substances. However, the insoluble substance of PVC/poly(MMA-co-BPMA) film is only about 7–10%, which is much less than that of PVC film. This result shows that the UV-resistance of PVC is enhanced remarkably by the incorporation of poly(MMA-co-BPMA). Further, the insoluble substance PVC/poly(MMA-co-BPMA) film is near to that of PVC/UV-0 film, indicating that poly(MMA-co-BPMA) is as good as UV-0 in protecting PVC from photocrosslinking.

The efficiency of a UV-stabilizer can not only be detected by insoluble substance, but can also be examined by the molecular weight change. The GPC data of PVC/poly(MMA-co-BPMA) film, PVC/UV-0 film, and PVC film are shown in Table IV. It can be seen that the molecular weight of PVC was changed from 7.03×10^4 to 6.19×10^4 after 326 h UV irradiation. This result shows that PVC is destroyed easily by UV-irradiation. But, the PVC/poly(MMA-co-BPMA) film and PVC/UV-0 film have less decrease in molecular weight. The molecular weight of PVC/poly(MMA-co-BPMA) film is changed from 6.87×10^4 to 7.11×10^4, while that of PVC/UV-0 film is changed from 7.03×10^4 to 6.97×10^4. These results show that both poly(MMA-co-BPMA) and UV-0 are effective UV-stabilizers and poly(MMA-co-BPMA) is more effective than UV-0 because no molecular weight decrease was

TABLE IV
The Molecular Weight and Its Distribution Change after UV-Irradiation

Samples	UV-stabilizer content (wt %)	Unirradiated		Irradiated for 326 h	
		M_n (10^4)	D	M_n (10^4)	D
PVC	0	7.03	1.90	6.19	3.38
PVC/UV-0	0.3	7.03	1.90	6.97	2.23
PVC/PMB	0.3	6.87	1.88	7.11	1.97

PMB, poly(MMA-co-BPMA)

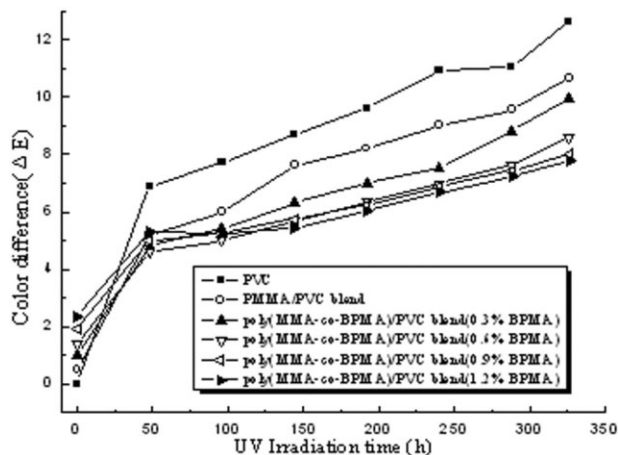**Figure 3** Color difference of PVC, PVC/poly(MMA-*co*-BPMA) blends, and PMMA/PVC blend after UV-irradiation.
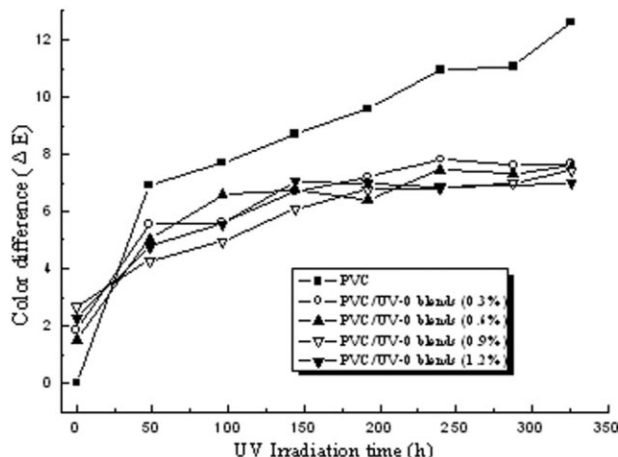

Figure 4 Color difference of PVC and PVC/UV-0 blends after UV-irradiation.

detected in PVC/poly(MMA-*co*-BPMA) film. Before the UV-irradiation, the polydispersity index (*D*) of PVC is 1.90, but after 326 h of UV irradiation, the polydispersity index changes to 3.38. This result shows that the main chain of PVC was destroyed to form small molecular weight part and high molecular weight part by photodegradation and photocrosslinking, respectively, which leads to the polydispersity of PVC broader. However, *D* changes only from 1.88 to 1.97 in PVC/poly(MMA-*co*-BPMA) film. This result shows that the PVC has been protected effectively by poly(MMA-*co*-BPMA). It is better than UV-0 because the change in *D* of PVC/poly(MMA-*co*-BPMA) is smaller than that of PVC/UV-0 film (from 1.90 to 2.23). In one word, poly(MMA-*co*-BPMA) is an effective UV-stabilizer in protecting PVC from UV degradation.

By the accumulation of the UV irradiation time, the color of PVC film changes from transparent to yellow and then changes from yellow to back. The color change of PVC/poly(MMA-*co*-BPMA) and PVC/UV-0 films are also detected during the UV irradiation process. The yellow color is due to the formation of big conjunction carbon–carbon double bond, and the black color is ascribed to the oxidation of PVC. In this point, it is necessary to apply color difference to determine the UV degradation of PVC/poly(MMA-*co*-BPMA) films, PVC/UV-0 films, and PVC film. Figures 3 and 4 show color difference of PVC/poly(MMA-*co*-BPMA) films and PVC/UV-0 films. As a reference material, the color difference of PVC film was also examined in this measurement. Before the UV-irradiation, color difference of PVC/poly(MMA-*co*-BPMA) and PVC/UV-0 films are enhanced as the increasing concentration of UV-stabilizer in the polymer materials because poly(MMA-*co*-BPMA) and UV-0 are yellow substances. After 50 h UV irradiation, the PVC/

poly(MMA-*co*-BPMA) films and PVC/UV-0 films have less color difference than PVC because of the addition of UV-stabilizers. In Figure 3, color difference becomes distinctive after 100 h, exhibiting that the PVC/poly(MMA-*co*-BPMA) films have less color difference. It is also realized that PVC/poly(MMA-*co*-BPMA) films containing 0.6%, 0.9%, and 1.2% BPMA in polymer matrix have the same color difference. This result demonstrates that only 0.6% BPMA contained in PVC/poly(MMA-*co*-BPMA) film can act as an effective UV-stabilizer in protecting PVC from color change. All the measurement results show that poly(MMA-*co*-BPMA) plays as efficient UV-stabilizer in protecting PVC matrix from UV degradation. Its function is no less than the low molecular weight UV-0 (Fig. 4) in protecting PVC from UV degradation.

Migration of high molecular weight UV-stabilizer poly(MMA-*co*-BPMA)

Low molecular weight UV-stabilizer usually migrates from the polymer matrix by solvent, heat, or UV light.
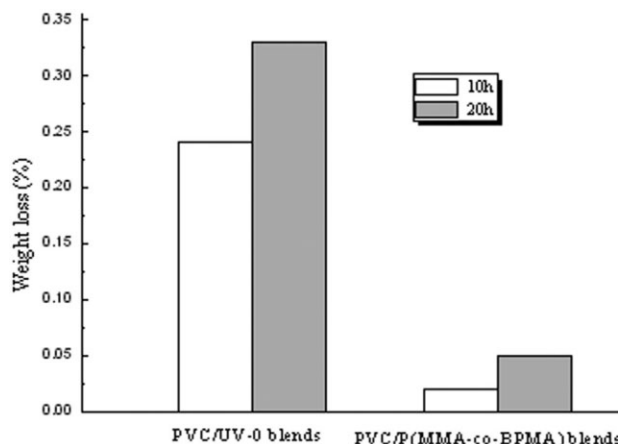

Figure 5 The weight loss of PVC/poly(MMA-*co*-BPMA) and PVC/UV-0 films after water extraction test (1.2% UV-stabilizer in blending).
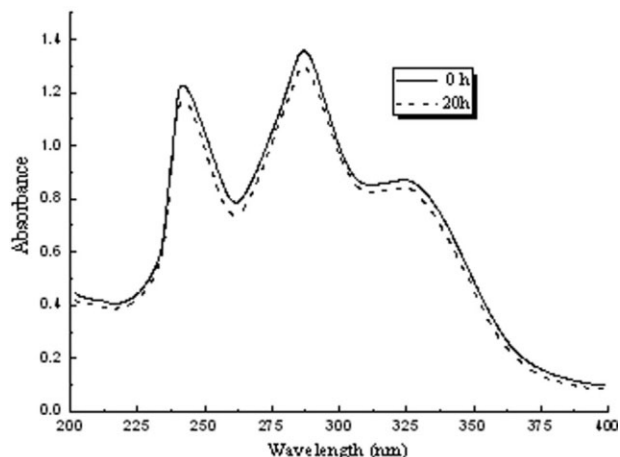
Figure 6 The UV–vis spectra of PVC/poly(MMA-*co*-BPMA) film before and after extraction (0.1% in THF by weight).

Figure 8 The weight loss of PVC/poly(MMA-*co*-BPMA) and PVC/UV-0 films after heat migration test (10% UV-stabilizer in blending).

It will weaken the UV-resistance of polymer materials. The main purpose of preparing high molecular weight UV-stabilizer is to resolve such problems. In this study, poly(MMA-*co*-BPMA) was used as a high molecular weight UV-stabilizer, and UV-0 was used as a small molecular weight stabilizer. Water extraction test and heat migration test were used to determine the migration of the UV-stabilizers. In Figure 5, it shows that the weight loss of PVC/poly(MMA-*co*-BPMA) film (0.05%) is less than that of the PVC/UV-0 film (0.33%) after 20 h water extraction. It indicates that poly(MMA-*co*-BPMA) keeps well in PVC film, while the small molecular weight UV-stabilizer UV-0 has been extracted by water. This is consistent with the UV–vis spectra in Figures 6 and 7. The UV absorbance of PVC/poly(MMA-*co*-BPMA) film changes less than that of PVC/UV-0 film, especially at 284 and 324 nm. All these results indicate that poly(MMA-*co*-
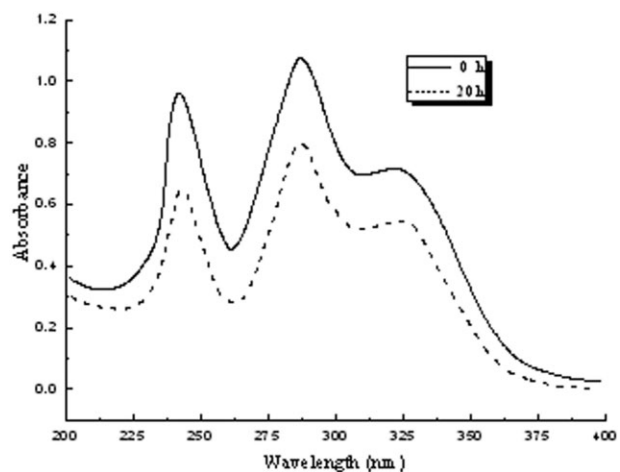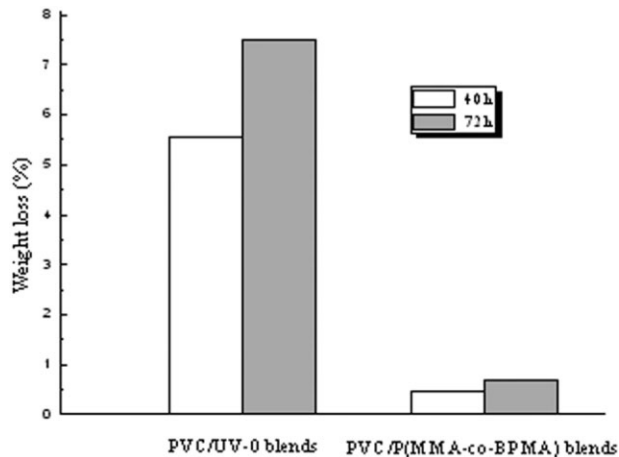
BPMA) is effective in protecting UV-stabilizer from migration.

The heat migration measurement was carried out to test the migration of UV-stabilizer under heat. After heat migration, the PVC/UV-stabilizer films will be lightened because the UV-stabilizer has migrated out of the PVC matrix. In this measurement, crystal powder UV-0 was detected on the surface of PVC/UV-0 films, but was not detected on the surface of PVC/poly(MMA-*co*-BPMA) film. The weight loss of PVC/poly(MMA-*co*-BPMA) film and PVC/UV-0 film are shown in Figure 8. It reveals that the weight loss of PVC/poly(MMA-*co*-BPMA) (0.55%) is much less than that of PVC/UV-0 (7.5%), indicating that poly(MMA-*co*-BPMA) is a more effective UV-stabilizer in protecting UV-stabilizer from migration than UV-0.

CONCLUSIONS

A high molecular weight UV-stabilizer poly(MMA-*co*-BPMA) can be prepared by copolymerization of MMA and BPMA. The migration problems can be resolved by increasing the molecular weight of the UV-stabilizer and the poly(MMA-*co*-BPMA) is effective in protecting PVC from UV degradation and photocrosslinking.

Figure 7 The UV–vis spectra of PVC/UV-0 film before and after extraction (0.1% in THF by weight).

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