

Copolymers of Chosen Alkyl Methacrylates with *N*-Phenylmaleimide and *N*-(4-Halogenphenyl)maleimides: A UV-Aging Study

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ABSTRACT: Homopolymers and copolymers of ethyl and butyl methacrylates with *N*-phenylmaleimide, *N*-(4-chlorophenyl)maleimide, and *N*-(4-bromophenyl)maleimide were synthesized by free-radical bulk polymerization with benzoyl peroxide as the initiator. The content of imide in the copolymers was about 5–10 or 7.5 wt %. The homopolymers and copolymers were irradiated with ultraviolet (UV) light in a climatic test chamber for various periods to study their aging behavior. After 100, 250, and 500 h, the structure, thermal stability, chemical resistance, and some physicomechanical properties were examined. The influence of UV radiation time on structure and the investigated properties of the homopolymers and copolymers were studied. The experimental results indicate that all investigated copolymers were resistant to UV radiation after 500 h. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3244–3250, 2001

Key words: copolymerization; ethyl methacrylate; butyl methacrylate; *N*-phenylmaleimide; *N*-(4-chlorophenyl)maleimide; *N*-(4-bromophenyl)maleimide; aging investigation on UV radiation; thermal stability; chemical resistance; physicomechanical properties

INTRODUCTION

The use of maleimides in copolymerization with alkyl methacrylates (MAs) gives the possibility of the synthesis of copolymers with higher thermal strength, and in addition, copolymers containing *N*-(monohalogenphenyl)maleimides are also less flammable. During recent years, many publications have appeared that describe the chemical modification of various vinyl polymers, such as those of styrene, alkyl acrylates or MAs, vinyl acetate, vinyl chloride, vinylidene chloride, and butadiene, by the addition of *N*-substituted maleimides (*N*-aryl or *N*-alkyl-aryl) and *N*-(monohalogenphenyl) maleimides.^{1–15}

It is known that the structure and physical properties of polymers change with time. These changes during aging are mainly related to external factors, such as temperature, light, humidity, oxygen (photooxidation), and chemically aggressive media, acting on the polymer. Also, manufacturing processes influence the aging of polymers. Although the properties of alkyl MA polymers, especially poly(methyl methacrylate)s, and their copolymers with various maleimides have been widely reported in the literature,^{1–15} few references appear to the properties of the copolymers after exposure to ultraviolet (UV) radiation.

This article reports an aging investigation of the UV radiation of homopolymers and copolymers of ethyl methacrylate (EtMA) and butyl methacrylate (ButMA) with *N*-phenylmaleimide (*N*-PhMI), *N*-(4-chlorophenyl)maleimide [*N*-(4-ClPh)MI], and *N*-(4-bromophenyl)maleimide [*N*-(4-BrPh)MI].

The copolymers [EtMA-*N*-PhMI, ButMA-*N*-PhMI, EtMA-*N*-(4-ClPh)MI, ButMA-*N*-(4-ClPh)MI, EtMA-*N*-(4-BrPh)MI, and ButMA-*N*-(4-BrPh)MI] were obtained by free-radical bulk copolymerization with benzoyl peroxide (BP) as the initiator. The nominal content of suitable imide in each copolymer was about 5–10 or 7.5 wt %. The aging effects on the homopolymers and copolymers of UV radiation at 100, 250, and 500 h were studied. After each time, the structure, thermal stability, chemical resistance, and some physico-mechanical properties were examined. The influence of UV radiation time on structure and the investigated properties of the homopolymers and copolymers were defined. The experimental results showed that all copolymers were resistant to UV radiation after 500 h.

EXPERIMENTAL

Monomers

EtMA, Pure (Fluka A.G., Basel, Switzerland)

EtMA was separated from an inhibitor in a standard manner¹⁵ and dried over anhydrous magnesium sulfate and then distilled under reduced pressure just before use (refractive index $n_D^{20} = 1.4140$, density $d_4^{20} = 0.9110$ g/cm³).

ButMA, Pure (Chemical Works, Oświęcim, Poland)

ButMA was purified in the same manner as EtMA ($n_D^{20} = 1.4231$, $d_4^{20} = 0.8936$ g/cm³).

N-PhMI and N-(4-Halogenphenyl)maleimides

N-PhMI and *N*-(4-halogenphenyl)maleimides were prepared in the same manner as other maleimides,^{8,11–15} that is, by the reaction of maleic anhydride with aniline, 4-chloroaniline or 4-bromoaniline, respectively, followed by dehydrocyclization of the resulting maleamic acid. All the reactions were carried out in acetone with acetic anhydride and a small amount of sodium acetate as dehydrating agents, which greatly increased the reaction rate. The monomers were recrystallized from different organic solvents, and the structures were confirmed by the measurement of the melting point (mp) and by elemental, infrared (IR), and ¹H-NMR analysis.

N-PhMI

N-PhMI was recrystallized from CCl₄ (mp = 90–91°C):

ELEM. ANAL. Calcd for *N*-PhMI: C, 69.36%; H, 4.07%, N, 8.09%. Found: C, 68.99%, H, 3.98%, N, 8.10%.

N-(4-ClPh)MI

N-(4-ClPh)MI was recrystallized from ethanol (mp = 108–109°C):

ELEM. ANAL. Calcd for *N*-(4-ClPh)MI: C, 57.83%; H, 2.89%; N, 6.75%. Found: C, 59.78%; H, 2.88%; N, 6.81%.

N-(4-BrPh)MI

N-(4-BrPh)MI was recrystallized from CH₂Cl₂ (mp = 110–111°C):

ELEM. ANAL. Calcd for *N*-(4-BrPh)MI: C, 47.65%; H, 2.40%; N, 5.56%. Found: C, 48.06%, H, 2.49%, N, 5.72%.

BP

Pure-grade BP (Argon, Łódź, Poland), with 86.5% assay,¹⁶ was used as supplied.

Reagents and Solvents

The reagents were maleic anhydride, aniline, 4-chloroaniline, 4-bromoaniline, acetic anhydride, and sodium acetate. The solvents, benzene, methylene chloride, ethanol, tetrachloromethane, acetone, ethyl acetate, methanol, acetic acid, hydrochloric acid, sulfuric acid, nitric acid (concentrated or diluted solution), and sodium hydroxide (10 and 40% aqueous solutions), were all analytical-grade reagents.

Copolymerization

The copolymers EtMA-*N*-PhMI, ButMA-*N*-PhMI, EtMA-*N*-(4-ClPh)MI, ButMA-*N*-(4-ClPh)MI, EtMA-*N*-(4-BrPh)MI, and ButMA-*N*-(4-BrPh)MI were obtained by free-radical copolymerization with 0.3 wt % BP as the initiator. Under the same conditions, homopolymers of MAs were obtained as a reference. The bulk copolymerization was carried out in glass tubes, which were heated in a water thermostat and held at different temperatures and times (60°C for 22 h, 70°C for 24 h, and 80°C for 24 h). Then, the ampules were transferred to an oven, and the heating was continued: at 90°C for 23 h, at 100°C for 24 h, and at 100°C for 20 h. The copolymers were cooled at a rate of 10°C/h. The nominal content of suitable imide in each copolymer was about 5–10 or 7.5 wt %. The MA

Table I Composition and Elemental Analysis of the Homopolymers and Copolymers of Alkyl MAs with Imides

Homopolymer and Copolymer	Sample Number	Composition of the Copolymer		Elemental Analysis (%) ^a		
		Alkyl MA	Imide	N	C	H
EtMA/ <i>N</i> -PhMI	1	100	—	—	—	—
	2	95	5	0.48	61.21	8.52
	3	90	10	0.76	63.83	8.81
EtMA/ <i>N</i> -(4-ClPh)MI	4	95	5	1.16	64.36	8.71
	5	90	10	1.32	64.04	8.48
EtMA/ <i>N</i> -(4-BrPh)MI	6	95	5	1.54	64.38	8.50
	7	92.5	7.5	1.66	64.67	8.67
BuMA/ <i>N</i> -PhMI	8	100	—	—	—	—
	9	95	5	1.13	64.20	8.58
	10	90	10	0.84	65.80	8.92
ButMA/ <i>N</i> -(4-ClPh)MI	11	95	5	1.56	68.17	9.43
	12	90	10	1.63	68.20	9.32
ButMA/ <i>N</i> -(4-BrPh)MI	13	95	5	1.49	69.61	9.99
	14	92.5	7.5	1.48	68.71	9.89

^a Average values from the two designates.

homopolymers were obtained in the same way. The compositions of copolymers and elemental analyses are presented in Table I.

Weather Resistance

The UV-aging study was carried out for the homopolymers and copolymers of EtMA and ButMA with *N*-PhMI, *N*-(4-ClPh)MI, and *N*-(4-BrPh)MI, where each contained about 5–10 or 7.5 wt % suitable imide. The homopolymers and copolymers in the forms of disks (diameter ~ 30 mm, thickness ~ 5 mm) and sheets (thickness = 2–3 mm) were placed in a climatic test chamber (3001 type, Feutron, Greiz, Germany) at a temperature of 40°C and a relative humidity of 60% and were irradiated with UV light (the transmitted light was in the 325–400-nm range with $\lambda_{\text{max}} = 366$ nm) for periods of 100, 250, and 500 h. After 100, 250, and 500 h, the structure, thermal stability, chemical resistance, and some physicomechanical properties were measured. The results are presented in Tables II and III.

Measurements

IR spectra were taken with a PARAGON 1000 Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer, Beaconsfield, England) on KBr pellets and on the film (thickness = 2–3 mm).

¹H-NMR (CDCl₃) spectra for maleimides recorded in δ units were obtained with a BS 587 A spectrometer (Brno, Czechoslovakia) at a frequency of 80 MHz.

Elemental analysis was carried out with an EA 1108 elemental analyzer (Carbo Erba, Milan, Italy).

Investigation of the Copolymers

Thermal Strength

Thermal studies were carried out with an OD-102 derivatograph (Budapest, Hungary) for the powdered homopolymers and copolymers, which contained about 5–10 or 7.5 wt % suitable imide. The measurements were taken in the temperature range 20–1000°C at a heating rate of 10°C/min in an inert (argon) atmosphere, with sample weights of 20–50 mg. The sensitivity of the instrument was 1/20 for DTA (differential thermal analysis) and 1/10 for DTG (differential thermal gravimetry). Thermal studies were also carried out with Madorsky's method¹⁷ in an oxidizing (air) atmosphere for the homopolymers and copolymers, which contained about 5–10 or 7.5 wt % suitable imide, in the temperature range 100–400°C, with sample weights of 20–50 mg.

Glass-Transition Temperature (T_g)

The T_g measurements of the homopolymers and copolymers were carried out with a Höppler con-

Table II T_{di} , T_{d50} , T_{max} for the Homopolymers and Copolymers of Alkyl MAs with Imides, Determined by Dynamic Method in Argon and by Static in Air^a

Sample Number	T_{di} (°C)		T_{d50} (°C)		T_{max} (°C)		T_{d50} (°C) ^a	
	BUV	AUV500	BUV	AUV500	BUV	AUV500	BUV	AUV500
1	205	190	280	265	330	320	320	310
2	210	200	290	275	340	335	330	320
3	210	200	354	340	350	350	350	330
4	210	210	339	310	342	345	340	335
5	212	210	358	345	360	350	365	350
6	210	205	310	305	342	342	330	330
7	215	210	320	310	350	350	350	335
8	195	190	245	250	250	270	260	260
9	220	215	310	300	352	350	335	330
10	240	238	235	330	360	355	345	335
11	220	215	310	310	352	350	310	305
12	240	235	340	360	360	360	320	315
13	220	210	315	300	350	345	340	330
14	225	215	315	305	340	330	325	320

BUV = the values before UV irradiation; AUV500 = the values after 500 h of UV irradiation.

^a The composition of the homopolymer and copolymers is presented in Table I.

sistometer (VEB Prüfgeräte-Werk, type 0481, Medingen, Germany). The load was 0.5 kg.

Softening Temperature

The softening temperature was measured by the Vicat test with a R δ Caest-Torino apparatus (Torino, Italy). The measurements were carried

out for the copolymers in the form of disks (diameter ~ 30 mm, thickness ~ 5 mm) with a load of 49 N at a heating rate of 50°C/h.

Brinnell Hardness

The measurements were made with a Brinnell tester (HPK 746, Feinmechanik, Ralf Kögel, En-

Table III Some Physical Properties of the Homopolymers and Copolymers of Alkyl MAs with Imides

Sample Numbers	T_g (°C)			Vicat (°C)			Brinnell (10 ⁴ N/m ²)		
	BUV	AUV250	AUV500	BUV	AUV250	AUV500	BUV	AUV250	AUV500
1	81	80	84	83 ± 2	74 ± 2	75 ± 2	915	905	831
2	84	88	88	83 ± 2	73 ± 2	77 ± 2	910	900	866
3	86	94	94	83 ± 2	82 ± 2	83 ± 2	940	955	888
4	87	86	84	83 ± 2	76 ± 2	78 ± 2	680	899	768
5	90	90	88	86 ± 2	80 ± 2	82 ± 2	766	899	879
6	72.5	78	82	82 ± 2	73 ± 2	73 ± 2	709	851	840
7	82.5	90	88	85 ± 2	78 ± 2	78 ± 2	746	877	942
8	30	40	44	40 ± 2	42 ± 2	39 ± 2	70	70	77
9	32	44	50	46 ± 2	45 ± 2	45 ± 2	290	291	285
10	35	56	54	52 ± 2	51 ± 2	51 ± 2	355?	360	366
11	40	42	50	48 ± 2	44 ± 2	43 ± 2	137	182	132
12	45	48	52	52 ± 2	50 ± 2	49 ± 2	276	256	253
13	49	44	44	45 ± 2	43 ± 2	44 ± 2	123	173	104
14	55	50	48	46 ± 2	47 ± 2	46 ± 2	170	301	170

The composition of homo- and copolymers is presented in Table I. BUV = the values before UV irradiation; AUV250 = the values after 250 h of UV irradiation; AUV500 = the values after 500 h of UV irradiation.

gelsdorf, Germany) for homopolymers and copolymers. The samples were in the form of disks (diameter ~ 30 mm, thickness ~ 5 mm). The hardness (H_k ; kg/cm²) was calculated from the formula $H_k = F/d\pi h$, where F is the load in kilograms, d is the diameter of the probe ball in centimeters, and h is the depth of the cavity in centimeters. All of the previous measurements were made for the copolymers, which contained about 5–10 or 7.5 wt % suitable imide.

Chemical Resistance

The chemical resistance of the homopolymers and copolymers was studied according to the procedure required by a Polish standard.¹⁸ The following organic solvents, inorganic acids, and alkali were used: acetone, benzene, 1,4-dioxane, methanol, chloroform, acetic acid, aqueous hydrochloric acid, nitric acid, sulfuric acid (concentrated or diluted aqueous solutions), and sodium hydroxide (10 and 40% aqueous solutions). Samples of the copolymers were immersed in each agent for 7 days. Changes in sample appearances were recorded.

RESULTS AND DISCUSSION

The copolymers [EtMA-*N*-PhMI, ButMA-*N*-PhMI, EtMA-*N*-(4-ClPh)MI, ButMA-*N*-(4-ClPh)MI, EtMA-*N*-(4-BrPh)MI, and ButMA-*N*-(4-BrPh)MI] were obtained by free-radical bulk copolymerization with 0.3 wt % BP as the initiator. Each copolymer contained about 5–10 wt % suitable imide. In some copolymers the highest amount of imide was 7.5 wt % due to small solubility of the monomer in methacrylate (cf. Table I). The compositions of the homopolymers and copolymers of EtMA and ButMA with *N*-PhMI, *N*-(4-ClPh)MI, and *N*-(4-BrPh)MI are shown in Table I. The polymerization was carried out at such temperatures until the comonomers converted to solid resins. The homopolymers and copolymers were in the form of hard (EtMA) or soft (ButMA) transparent resins. The copolymers were yellowish because of the presence of imide. Elemental and IR analyses of the products were carried out. The results of the elemental analyses are also shown in Table I. The IR spectra of the copolymers were characterized by the intense absorption bands of MAs and maleimides (Fig. 1). In

no IR spectra was an absorption band for C=C in the range of 1640–1660 cm⁻¹ observed.

The aging effects of UV radiation on the homopolymers and copolymers at 100, 250, and 500 h were studied. After each time, the structure, thermal stability, chemical resistance, and some physicomechanical properties were measured. The structure of the homopolymers and copolymers was studied by FTIR analysis. In Figure 1, the IR spectrum of the EtMA-*N*-(4-BrPh)MI copolymer before UV irradiation is shown. The next bands, in ranges of 2954–2980 cm⁻¹ (for the group Ar—H), 1711.0–1725.5 cm⁻¹ (for the group C—O), 1465.1–1493.6 cm⁻¹ (for the aromatic ring —Ar), 1385.0–1448.7 cm⁻¹ (for the group —OH), and 1142.6–1171.0 cm⁻¹ (for the group —CN) were observed. It is well known that acrylic polymers such as poly(methyl methacrylate) have excellent resistance to photooxidation.¹⁹ All the IR spectra before and after 100, 250, and 500 h of UV irradiation were the same. No degradation changes were observed. The obtained homopolymers and copolymers showed good stabilization against photooxidation.

The thermal analyses of the homopolymers and copolymers were conducted by dynamic and static methods with various criteria as measures of stability. The thermal strength for all copolymers, which contained about 5–10 or 7.5 wt % imide, was studied by a dynamic method with an OD-102 derivatograph in an inert (argon) atmosphere. The thermal stability was indicated as the temperature at the initial (5%) weight loss of the sample (T_{di}), the temperature at 50% weight loss of the sample (T_{d50}), and the temperature at the maximum decomposition rate (T_{max}). The data, T_{di} , T_{d50} , and T_{max} , for the homopolymers and copolymers before and after 500 h of UV irradiation are presented in Table II. We observed certain differences in T_{di} , T_{d50} , and T_{max} values after 500 h of UV irradiation. For poly(methacrylate)s and some copolymers, these values decreased from 5 to 15°C.

Thermal studies of the copolymers were also conducted by a static (Madorsky's) method.¹⁷ Two series of measurements were carried out for the homopolymers and copolymers, which contained about 5–10 or 7.5 wt % imide, in the temperature range 100–400°C. The thermal stability of the homopolymers and copolymers was indicated as T_{d50} . The T_{d50} data for the homopolymers and copolymers before and after 500 h of UV irradiation are shown in Table II. The values of weight loss varied considerably, depending on the copol-

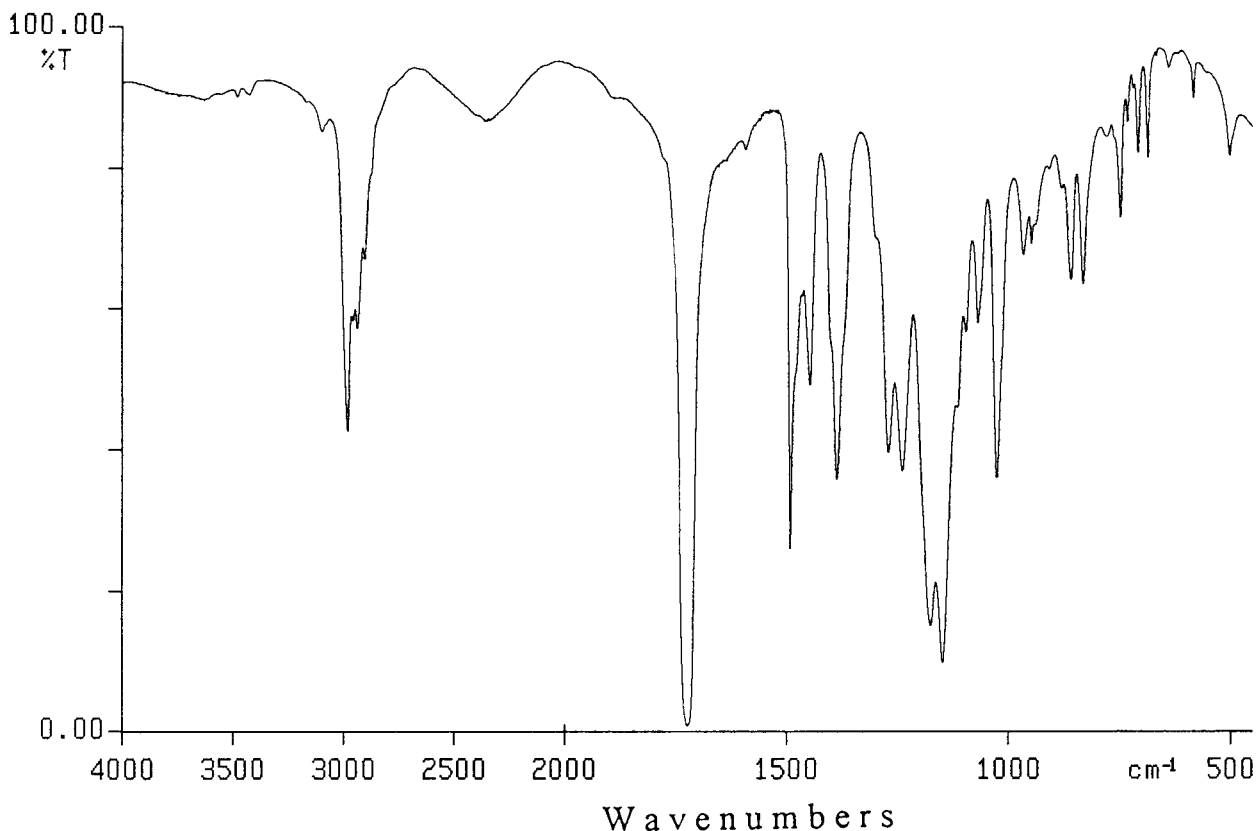


Figure 1 IR spectrum of the EtMA-*N*-(4-BrPh)MI copolymer.

ymer composition. The maximum value of weight loss and the minimum temperature of 50% decomposition (T_{d50}) were observed for the homopolymers. The increase in imide content in the copolymers caused a rise in the T_{d50} values before and after 500 h of UV irradiation, whereas the weight loss decreased. The analysis of the T_{d50} values obtained by dynamic and static methods show that such results confirm the thermal stabilizing influence of imide monomer units on the copolymer strength. Already, 5 wt % imide in the copolymers caused a rise in T_{d50} values from about 10 to 30°C, as measured by both dynamic and static methods. After 500 h of UV irradiation, similar differences in T_{d50} values for all homopolymers and copolymers were observed (Table II).

The thermal stabilizing influence of imide [e.g., *N*-phenyl and *N*-(4-halogenphenyl)maleimide] monomer units on copolymer strength was also confirmed by an investigation of T_g and by the Vicat softening temperature before and after UV irradiation. The measurements of T_g for homopolymers and copolymers, which contained 5–10 or 7.5 wt % suitable imide, were made with

a Höppler consistometer and are listed in Table III. Mean values from three Vicat measurements and from seven Brinnell measurements before and after 500 h of UV irradiation are also presented in Table III. These values show that after 500 h of UV irradiation, T_g was greater from 4 to 10°C for some copolymers and even about 20°C greater for the ButMA-*N*-PhMI copolymer that contained about 10 wt % imide. For poly(methacrylate)s, the values of Vicat softening temperature and Brinnell hardness were the smallest, and for the copolymers, these values were greater, also after 500 h of UV irradiation. The increase of both values was observed if the imide content in the copolymer was greater. A comparison of the obtained values for both kinds of homopolymers and copolymers shows that softening temperature and hardness were greater for the EtMA-imide systems than for the ButMA-imide systems. It is understandable because of a longer group in MA, which influences the stiffening of the polymer chains and causes the decrease of both values. After 500 h of UV irradiation, the Vicat softening point and Brinnell hardness generally were smaller.

Chemical resistance of the homopolymers and copolymers on the action of some organic solvents such as acetone, benzene, 1,4-dioxane, methanol, chloroform, acetic acid, inorganic acids and aqueous alkali:hydrochloric acid, nitric acid, sulfuric acid (concentrated or diluted aqueous solutions), and sodium hydroxide (10 and 40% aqueous solutions) were measured. The investigation of chemical resistance showed that all obtained homopolymers and copolymers were more or less dissolved in the solvents before and after UV radiation. In general, they were only swollen. All copolymers were not resistant to the action of concentrated sulfuric acid, but they were resistant to the action of aqueous hydrochloric acid and nitric acid. Good resistance to the action of 10% aqueous solutions of hydrochloric acid, nitric acid, and sulfuric acid as well as to 10 and 40% aqueous solutions of sodium hydroxide after 500 h of UV irradiation was observed.

CONCLUSIONS

The experimental results indicate that all the investigated copolymers [EtMA-*N*-PhMI, ButMA-*N*-PhMI, EtMA-*N*-(4-ClPh)MI, ButMA-*N*-(4-ClPh)MI, EtMA-*N*-(4-BrPh)MI, and ButMA-*N*-(4-BrPh)MI], which contained about 5, 7.5, and 10 wt % suitable imide, were generally resistant to UV radiation after 500 h. However, an increase in T_g values after 500 h of UV irradiation was observed. This was checked by the structural (IR), thermal, chemical, and some physicochemical properties of the homopolymers and copolymers.

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