

Radical Polymerization of New Functional Monomers: Mono- and Dimethacryloyl Isocyanate Containing Bisphenol-A and Its Derivatives

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SYNOPSIS

New functional monomers mono- and dimethacryloyl isocyanate containing bisphenol-A were prepared on reaction of methacryloyl isocyanate (MAI) with bisphenol-A (BPA) and its derivatives at low temperature. The monomers thus obtained were characterized with IR, UV, and ^1H - and ^{13}C -NMR spectra. Radical polymerization of mono- and dimethacryloyl isocyanate containing bisphenol-A and its derivatives was studied in terms of the rate of polymerization, solvent effect, copolymerization, thermal properties, and kinetic measurements of photocrosslinking. Polar solvents such as DMSO and NMP were found to slow the polymerization. Copolymerization of BPA-MAI (M_1) with MMA (M_2) in DMF was studied at 90°C. The monomer reactivity ratio was calculated to be $r_1 = 0.17$ and $r_2 = 1.34$ according to the method of Fineman-Ross. Functional polymers containing the allyl group were successfully modified and photocrosslinked on irradiation in the presence of benzoin isopropyl ether. The photocrosslinking process follows second-order kinetics. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Methacryloyl isocyanate (MAI) is a new heterofunctional monomer that has a polymerizable double bond and a highly reactive acyl isocyanate group in the same molecule.¹⁻⁸ Either end group of the molecule may be reacted independently, leaving the other function available for subsequent reactions. The possible uses for MAI fall into four categories: (1) Vinyl-functionalized derivatives can be made by reacting the acylisocyanate group to monofunctional reagents. (2) Polyacylisocyanate resins can be made by polymerizing the methacryl group. (3) Vinyl-functionalized resins can be made by reacting the acylisocyanate group to polyfunctional molecules. (4) Heterocyclic compounds can be made by cycloaddition reactions with dienophiles or dipolarophiles such as hetero-Diels-Alder reactions of MAI with enamines or vinyl ethers.⁹ Functional polymers have become increasingly important because of their

diverse applications such as polymeric reagents and crosslinking resins. Functional monomer/polymer systems derived from acrylates and methacrylates are used extensively, e.g., in adhesives and coatings.

Methacryloyl isocyanate (MAI) may be reacted with alcohols or amines, leaving the vinyl bond for radical polymerization. New functional monomers mono- and dimethacryloyl isocyanate containing bisphenol-A (BPA) were prepared by the reaction of MAI with BPA and its derivatives at low temperature. In the present article, we describe the results of radical polymerization of BPA-MAI and BPA-dimethacryloyl isocyanate (DMAI) in terms of polymerization, solvent effect, copolymerization, polymer modification, thermal properties, and photocrosslinking kinetics.

EXPERIMENTAL

Reagents

Methacryloyl isocyanate (MAI) (Nippon Paint Co.) was prepared from methacrylamide and oxalyl

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chloride^{2,10-12} and purified on distillation at reduced pressure (45°C/6000 Pa) (literature,¹¹ 52–53°C/5200 Pa). Bisphenol-A [2,2-bis(4-hydroxy)phenyl]propane was purified by recrystallization from toluene; mp 156°C. Bisphenol-A derivatives of five kinds such as bis[4-(β-hydroxyethoxy)phenyl]propane (HEPA), bis[4-(β-hydroxy(iso)propoxy)phenyl]propane (HPPA), 3,3',5,5'-tetrabromobisphenol A (TBBPA), bishydroxyethyl ether of TBBPA (TBHEPA), and bishydroxypropyl ether of TBBPA (TBHPPA) were prepared as previously reported.^{13,14} The solvents were purified according to standard methods.

Monomer Preparation

Preparation of Methacryloyl Isocyanate Containing Bisphenol-A (BPA-MAI)

Bisphenol-A (120 g, 0.53 mol) and ethyl acetate (240 mL) were charged into a flask (1 L) equipped with stirrer and thermometer under argon. The mixture was stirred to a homogeneous solution at 0°C. Methacryloyl isocyanate (MAI) (61.3 g, 0.55 mol) was added dropwise for 3 h. After completion of the addition, the mixture was stirred for 3 h. The solution was distilled in a vacuum. The residue was poured into benzene in a blender to precipitate a white solid. The solution was filtered to remove the white solid, and the filtrate was distilled in a vacuum. After the solvent distillation, 143 g of the product

Table I ¹H-NMR Data of BPA-MAI (in DMSO-*d*₆)

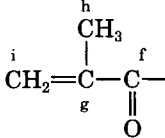

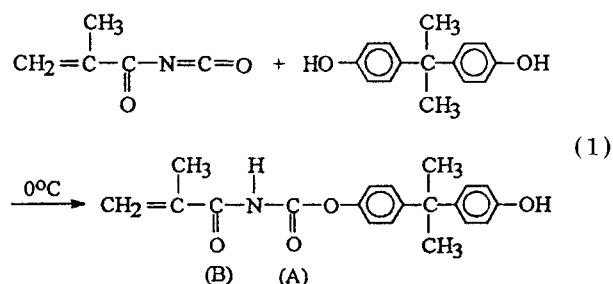
Proton	Chemical Shift δ (ppm)
	1.82
—NH	10.99
=CH ₂	5.66, 5.96
	6.66, 6.98, 7.06, 7.22
—OH	9.17
H ₃ C—C—CH ₃	1.52

Table II ¹³C-NMR Data of BPA-MAI (in DMSO-*d*₆)

Carbon	Chemical Shift δ (ppm)
a, a'	140.3
b, b'	128.4
c, c'	121.7, 121.9
d, d'	148.8, 149.1
e	119.7
f	167.2
g	140.2
h	18.4
i	123.0
j	43.0
k	31.0

was obtained. The yield was about 80%. BPA-MAI was characterized with IR, UV, ¹H-NMR (Table I), and ¹³C-NMR (Table II) spectra. The solubility of BPA-MAI was tested in various solvents and the results are summarized in Table III. This monomer was soluble in acetone, THF, chloroform, ethylacetate, *n*-butyl acetate, benzene, methanol, ethanol, 1,4-dioxane, and DMSO. However, it was insoluble in *n*-hexane, water, and xylene. The synthesis reaction is given below:



IR (KBr): $\nu_{\text{O-H}}$ (3346), $\nu_{\text{C=O}}$ (A) (1772), $\nu_{\text{C=O}}$ (B) (1698), $\nu_{\text{C=C}}$ (1627), N—H_{str} (3280), CH₃ str. (2964) cm⁻¹. UV (DMSO): $\lambda_{\text{max}} = 274.7$ nm ($\epsilon = 2.03 \times 10^4$ L mol⁻¹ cm⁻¹).

Preparation of Dimethacryloyl Isocyanate Containing Bisphenol-A (BPA-DMAI)

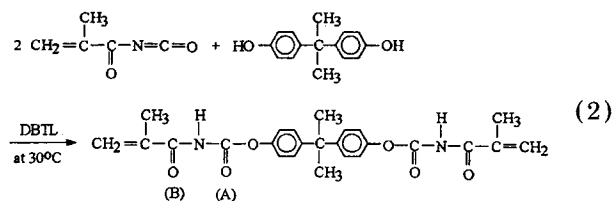
Bisphenol-A (10 g, 0.04 mol) and *n*-butyl acetate (20 mL), in the presence of a dibutyltin dilaurate

Table III Solubility of Mono- and Dimethacryloyl Isocyanate Containing Bisphenol-A and Its Derivatives

Monomer	Solvents ^a												
	<i>n</i> -Hexane	DMSO	Acetone	Methanol	THF	H ₂ O	Chloroform	Ethyl Acetate	<i>n</i> -Butyl Acetate	Benzene	Xylene	Ethanol	1,4-Dioxane
BPA	×	⊙	⊙	⊙	⊙	×	Δ	⊙	⊙	Δ	○	⊙	⊙
BPA-MAI	○	⊙	⊙	⊙	⊙	×	⊙	⊙	⊙	⊙	Δ	⊙	⊙
BPA-DMAI	×	⊙	⊙	⊙	⊙	×	⊙	Δ	Δ	○	×	Δ	Δ
HEPA	○	⊙	⊙	⊙	Δ	×	⊙	⊙	⊙	Δ	○	⊙	⊙
HEPA-MAI	×	⊙	⊙	Δ	×	×	⊙	⊙	⊙	⊙	×	Δ	⊙
HEPA-DMAI	Δ	○	○	Δ	Δ	Δ	○	⊙	⊙	○	○	⊙	×
HPPA	×	Δ	⊙	⊙	⊙	Δ	○	⊙	⊙	⊙	○	⊙	Δ
HPPA-MAI	⊙	Δ	Δ	⊙	×	×	⊙	Δ	Δ	○	○	⊙	○
HPPA-DMAI	×	⊙	⊙	⊙	⊙	×	⊙	⊙	⊙	Δ	○	⊙	⊙
TBBPA	Δ	⊙	⊙	⊙	○	×	⊙	⊙	⊙	⊙	⊙	⊙	⊙
TBBPA-MAI	×	⊙	⊙	⊙	×	⊙	×	⊙	⊙	×	⊙	⊙	⊙
TBBPA-DMAI	⊙	⊙	⊙	⊙	○	⊙	×	⊙	⊙	⊙	⊙	⊙	○
TBHEPA	Δ	⊙	⊙	⊙	×	⊙	×	⊙	⊙	Δ	⊙	⊙	⊙
TBHEPA-MAI	×	⊙	⊙	⊙	⊙	×	×	⊙	⊙	⊙	⊙	⊙	⊙
TBHEPA-DMAI	×	⊙	⊙	⊙	⊙	×	⊙	⊙	⊙	⊙	○	⊙	⊙
TBHPPA	×	⊙	⊙	⊙	⊙	×	⊙	⊙	⊙	⊙	⊙	⊙	⊙
TBHPPA-MAI	×	⊙	⊙	⊙	○	⊙	⊙	⊙	⊙	×	⊙	⊙	⊙
TBHPPA-DMAI	×	⊙	⊙	⊙	×	×	⊙	⊙	⊙	○	○	Δ	Δ

^a (⊙) soluble; (○) partially soluble; (×) insoluble; (Δ) soluble on heating at 60°C.

(DBTL, a few drops) as a catalyst, were charged into a flask (100 mL) equipped with stirrer and thermometer under argon. The mixture was kept at 30°C. Methacryloyl isocyanate (10.7 g, 0.10 mol) was added dropwise for 1 h. After completion of the addition, the mixture was stirred for 6 h. The precipitated product was washed several times with *n*-butyl acetate and then dried under reduced pressure. The yield was about 94.30%; mp 165°C. BPA-DMAI was characterized with IR, UV, ¹H-NMR (Table IV), and ¹³C-NMR (Table V) spectra. The monomer BPA-DMAI was soluble in acetone, THF, chloroform, methanol, 1,4-dioxane, and DMSO, but it was entirely insoluble in *n*-hexane, water, and xylene (Table III). The synthesis reaction is given below:



IR (KBr): $\nu_{\text{C}=\text{O}}$ (A) (1758), $\nu_{\text{C}=\text{O}}$ (B) (1690), $\nu_{\text{C}=\text{C}}$ (1629), $\text{N}-\text{H}_{\text{str}}$ (3266), CH_3_{str} (2960) cm^{-1} . UV (DMSO): $\lambda_{\text{max}} = 279.8 \text{ nm}$ ($\epsilon = 3.05 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$).

Preparation of BPA Derivatives-MAI and BPA Derivatives-DMAI

Bisphenol-A derivatives of five kinds, namely, bis[4-(β -hydroxyethoxy)phenyl]propane (HEPA),

Table IV ¹H-NMR Data of BPA-DMAI (in Acetone-*d*₆)

Proton	Chemical Shift δ (ppm)
	1.96
-NH	9.83
=CH ₂	5.65, 5.98
	7.07, 7.10, 7.27, 7.30
H ₃ C-C-CH ₃	1.68

Table V ¹³C-NMR Data of BPA-DMAI (in DMSO-*d*₆)

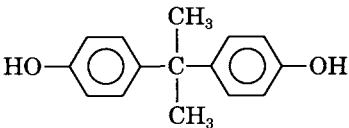
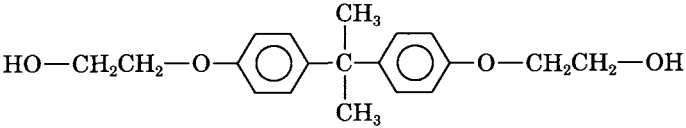
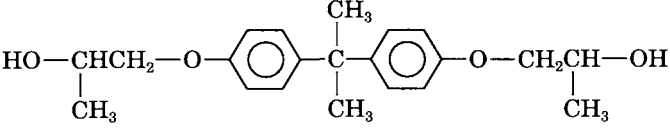
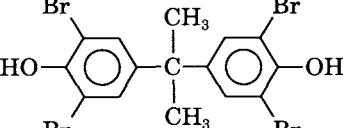
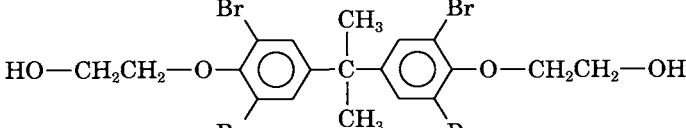
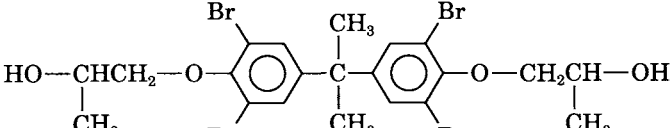
Carbon	Chemical Shift δ (ppm)
a	138.7
b	127.6
c	121.4
d	154.9
e	119.5
f	169.3
g	140.2
h	18.2
i	123.5
j	41.5
k	30.7

bis[4-(β -hydroxy(iso)propoxy)phenyl]propane (HPPA), 3,3',5,5'-tetrabromobisphenol A (TBBPA), bishydroxyethyl ether of TBBPA (TBHEPA), and bishydroxypropyl ether of TBBPA (TBHPPA) were reacted with mono- and dimethacryloyl isocyanate to produce the corresponding new monomers HEPA-MAI, HEPA-DMAI, HPPA-MAI, HPPA-DMAI, TBBPA-MAI, TBBPA-DMAI, TBHEPA-MAI, TBHEPA-DMAI, TBHPPA-MAI, and TBHPPA-DMAI. The same molar ratio and method previously described was used to prepare BPA derivatives-MAI and BPA derivatives-DMAI monomers as described in Table VI, but a suitable solvent for each reaction had to be chosen. A satisfactory solvent had to have a low boiling point and to allow the product to precipitate. Table III also shows the qualitative solubility behavior of various monomers such as BPA derivatives-MAI and BPA derivatives-DMAI. Almost all monomers except HEPA-DMAI were soluble in DMSO, methanol, ethanol, ethyl acetate, and acetone but insoluble in *n*-hexane and water. These new monomers described in Table VII were identified with UV spectra and melting point determinations. The results or IR appear in Table VIII.

Polymerization

The rate of polymerization in various solvents at 60 \pm 0.01°C was determined with a gravimetric method. The gas from an ampule that contained the monomer, solvent, and AIBN was removed several times in a high-vacuum system and the ampule was sealed.

Table VI Structures of BPA Derivatives

BPA Derivative	Structures
BPA	
HEPA	
HPPA	
TBBPA	
TBHEPA	
TBHPPA	

The polymer precipitated with much methanol. THF was used to dissolve the polymer which was reprecipitated with methanol. The purified polymer was dried for about 24 h at 60°C under vacuum and weighed. The rate of photopolymerization at $30 \pm 0.001^\circ\text{C}$ was measured in a vacuum-sealed dilatometer.¹⁵⁻¹⁸

Copolymerization

Copolymerization was undertaken at various mol ratios of BPA-MAI to MMA in DMF at 90°C. BPA-MAI, MMA, AIBN, and DMF were introduced into an ampule (100 mL). The reaction was done in a degassed and sealed tube with constant shaking. The conversion was followed up to 7%. The copolymer products were precipitated with methanol, purified by reprecipitation using THF solution and methanol, dried at 100°C for 24 h under vacuum, and weighed.

Rate of Photocrosslinking with a Gravimetric Method

Films of thickness 0.12 mm were irradiated with a high-pressure mercury vapor lamp (600 W) at a distance 12 cm. Dry films of unsaturated poly(BPA-MAI) were obtained by casting their DMF solution containing benzoin isopropyl ether (3 mass %) and pentaerythritol triacrylate (5 mass %) on a glass surface in the absence of light. Irradiation was carried out under argon at 30°C. The increase of mass of the insoluble fraction with period of irradiation was measured.

Preparation of Unsaturated Poly(BPA-MAI)

The unsaturated poly(BPA-MAI) used in this work was obtained on reacting allyl bromide with the hydroxy side group of poly(BPA-MAI). The content of double bonds in the polymer was determined to

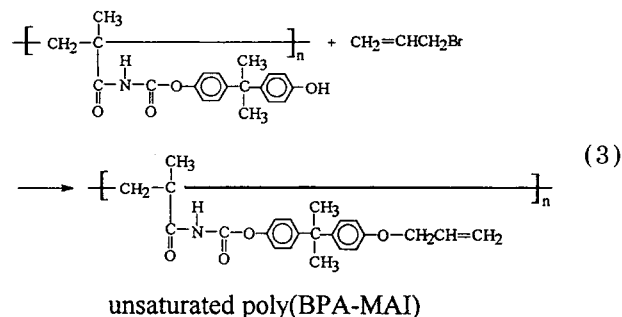
Table VII Reaction Solvent, Yield, State, Melting Point, and UV Absorbance of Mono- and Di-methacryloyl Isocyanate Containing Bisphenol-A and Its Derivatives

Monomer	Solvent ^a	Yield (%)	State ^b	T_m ^c (°C)	λ^d (nm)	$\epsilon \times 10^{-4}$ (L mol ⁻¹ cm ⁻¹)
BPA	—	—	S	156	280.0	9.29
BPA-MAI	Ethyl acetate	80.42	L	—	279.3	1.84
BPA-DMAI	<i>n</i> -Butyl acetate	94.30	S	165	279.8	3.05
HEPA	—	87.55	S	109	278.3	2.79
HEPA-MAI	Acetone	85.41	L	—	278.3	1.87
HEPA-DMAI	Acetone	78.54	S	92	277.0	1.68
HPPA	—	79.84	L	—	276.5	2.51
HEPPA-MAI	THF	83.29	L	—	278.3	2.81
HPPA-DMAI	THF	80.20	L	—	277.0	3.26
TBBPA	—	85.25	S	178	288.2	5.20
TBBPA-MAI	Benzene	84.32	L	—	276.3	0.87
TBBPA-DMAI	Chloroform	75.37	S	85	288.2	4.77
TBHEPA	—	85.78	S	98	280.3	1.49
TBHEPA-MAI	Chloroform	88.79	L	—	279.0	0.49
TBHEPA-DMAI	Acetone	80.26	L	—	278.7	0.44
TBHPPA	—	87.43	L	—	278.7	2.00
TBHPPA-MAI	Benzene	72.91	L	—	278.3	1.35
TBHPPA-DMAI	Acetone	68.99	L	—	275.4	0.74

^a Solvent was used to synthesize monomer.^b S → solid state; L → liquid state.^c Buchi Model 535 was used.^d UV absorption in DMSO.**Table VIII Wavenumbers of IR Absorption of BPA Derivatives—MAI and DMAI**

Monomer	IR (cm ⁻¹)									
	OH	N—H Str.	C=O (A)	C=O (B)	C=C (vinyl)	N—H	CH ₂ Str.	CH ₃ Str.	C=C (ring)	Br
BPA	3348	—	—	—	—	—	—	2960	1450	—
BPA-MAI	3346	3280	1772	1698	1627	1507	—	2964	1452	—
BPA-DMAI	—	3266	1758	1690	1629	1496	—	2960	1451	—
HEPA	3376	—	—	—	—	—	2932	2966	1449	—
HEPA-MAI	3346	3278	1764	1666	1627	1507	2928	2956	1453	—
HEPA-DMAI	—	3260	1765	1672	1625	1506	2920	2954	1454	—
HPPA	3320	—	—	—	—	—	2920	2960	1455	—
HPPA-MAI	3428	3274	1763	1665	1626	1506	2922	2960	1453	—
HPPA-DMAI	—	3274	1761	1675	1625	1505	2924	2962	1454	—
TBBPA	3472	—	—	—	—	—	—	2978	1468	776
TBBPA-MAI	3440	3275	1766	1667	1627	1499	—	2952	1463	803
TBBPA-DMAI	—	3266	1763	1666	1625	1508	—	2960	1451	800
TBHEPA	3380	—	—	—	—	—	2924	2954	1461	781
TBHEPA-MAI	3433	3276	1767	1666	1626	1507	2920	2954	1461	798
TBHEPA-DMAI	—	3276	1758	1695	1626	1508	2925	2964	1460	800
TBHPPA	3352	—	—	—	—	—	2924	2962	1446	776
TBHPPA-MAI	3428	3283	1765	1666	1625	1505	2926	2964	1448	792
TBHPPA-DMAI	—	3274	1765	1669	1626	1507	2928	2958	1452	798

be $1.45 \times 10^{-2} \text{ mol g}^{-1}$ by titration with potassium permanganate. The unsaturated side groups undergo free-radical polymerization initiated by benzoin isopropyl ether that photodissociates into reactive radicals:



Thermal Analysis

For thermal analysis, we used a Perkin-Elmer thermal mechanical analyzer Model TGS-II. The heating rate at $10^\circ\text{C}/\text{min}$ and a sample mass 5 mg were used.

RESULTS AND DISCUSSION

Solvent Effect on the Rate of Polymerization (R_p)

Rates of polymerization of BPA-MAI in various solvents were determined at 60°C . Inherent viscosities which were measured in DMSO at 30°C are presented in Table IX. The trend of inherent viscosity is consistent with that of the rate of polymerization.

The solvents significantly affect the polymerization. It is observed that polymerization is slower and inherent viscosity is smaller in polar solvents than

in nonpolar solvents. A similar phenomenon was observed in the polymerization of di-*n*-butyl itaconate¹⁹ and monomethacrylic esters containing bisphenol-S.²⁰ Sato et al.¹⁹ reported that the enhanced rate of polymerization in nonpolar solvents is ascribed to the large rate constant (k_p) for propagation. The polymer chain interacts with its solvent. A polar solvent readily interacts with the polymer chain, thus probably resulting in decreasing k_p . As the rate of polymerization is proportional to k_p ,^{15-18,21-25} the solubility parameter (SP) may be used as a rough measure of such an interaction. Figure 1 shows a plot of $\log R_p$ against the SP value of solvents. This result indicates that less polar solvents for the polymerization of BPA-MAI give a large R_p values.

Copolymerization

Copolymerization of BPA-MAI (M_1) and MMA (M_2) was carried out in DMF at 90°C . The variation in feed ratios and the resultant copolymer compositions determined with elemental analysis (% C) were used to evaluate reactivity ratios for the BPA-MAI/MMA copolymer (Table X). The results of elemental analysis of all copolymers have to be corrected by eliminating the amount of water absorbed by the acyl urethane linkage of copolymers. The method of Fineman-Ross was used to determine reactivity ratios at small conversions of the copolymer. Figure 2 is a Fineman-Ross plot used to determine the reactivity ratios for BPA-MAI (M_1) and MMA (M_2). The reactivity ratios, r_1 and r_2 , for the monomer pair M_1 and M_2 , can be determined from

$$F(f-1)/f = r_1(F^2/f) - r_2$$

where $f = d(M_1)/d(M_2)$ and $F = (M_1)/(M_2)$.

Table IX Solvent Effect on the Rate of Polymerization Rate (R_p) of BPA-MAI at 60°C

Solvent	ϵ^a	δ^b [(J cm ⁻³) ^{1/2}]	R_p^c ($10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$)	η_{inh}^d (mL g ⁻¹)
Ethyl acetate	6.02	18.40	1.92	0.30
THF	7.58	18.60	1.77	0.28
Pyridine	12.40	21.88	1.28	0.22
NMP	32.00	23.10	0.94	0.17
DMF	36.10	24.74	0.67	0.13
DMSO	46.68	24.53	0.52	0.11

^a Dielectric constant.

^b Solubility parameter.

^c [BPA-MAI] = 0.25 mol L^{-1} ; [AIBN] = $6.0 \times 10^{-3} \text{ mol L}^{-1}$.

^d Inherent viscosity in DMSO at 30°C .

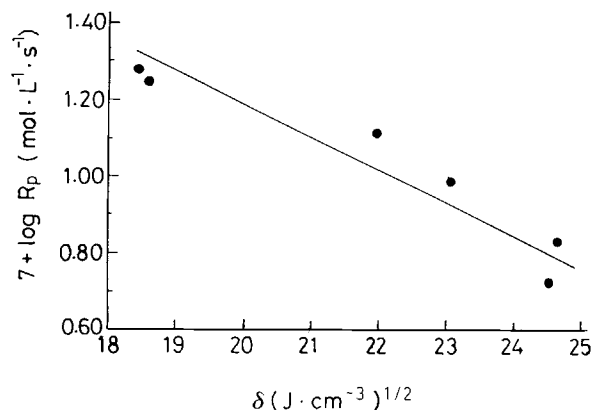


Figure 1 Relationship between rate of polymerization (R_p) for BPA-MAI and the solubility parameter (δ) of solvent.

The reactivity ratio r_1 was determined to be 0.17 from the slope and $r_2 = 1.34$ from the ordinate intercept; hence, $r_1 \times r_2 = 0.23$. These values reveal that MMA shows a higher reactivity than does BPA-MAI irrespective of the kind of propagating ends.

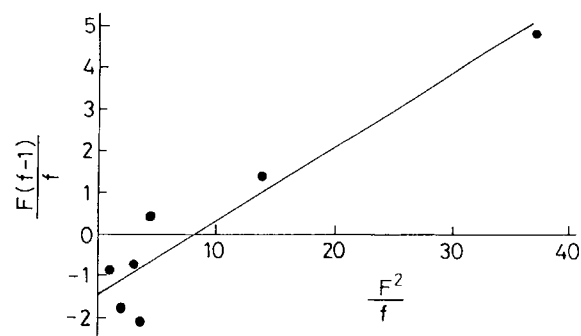


Figure 2 Determination of reactivity ratios for the copolymerization of BPA-MAI with MMA by the method of Fineman-Ross.

In addition, random copolymerization occurs between these different types of monomers. A similar trend of rate of polymerization for various monomers both in photopolymerization and in thermal polymerization is discernible in Table XI. In particular, the rate of thermal polymerization of MMA has been found to be larger than that of BPA-MAI in

Table X Results of Copolymerization of BPA-MAI (M_1) and MMA (M_2) at 90°C

Experiment	Monomer (Mol %)		Elemental Analysis C (Mass % in Copolymer)		Amount of Absorbed Water ^a (%)	M_1 in Copolymer ^c (Mol %)
	M_1	M_2	Calcd	Found		
1	90	10	Calcd	69.71	6.90	68.58
			Found	62.75		
			Corrected ^b	67.40		
2	80	20	Calcd	68.63	6.13	60.70
			Found	62.47		
			Corrected	66.55		
3	70	30	Calcd	67.55	5.42	54.96
			Found	62.36		
			Corrected	65.93		
4	60	40	Calcd	66.47	5.20	40.41
			Found	61.01		
			Corrected	64.36		
5	50	50	Calcd	65.40	5.13	24.93
			Found	59.47		
			Corrected	62.69		
6	40	60	Calcd	64.32	5.00	20.85
			Found	59.14		
			Corrected	62.25		
7	10	90	Calcd	61.08	3.66	9.36
			Found	58.78		
			Corrected	61.01		

^a Amount of absorbed water (%) = [(sample mass at room temperature - sample mass after drying under vacuum at 100°C)/sample mass after drying under vacuum at 100°C] × 100.¹⁴

^b Corrected value = found value/(1 - amount of absorbed water).

^c [AIBN] = 9×10^{-3} mol L⁻¹. Solvent: DMF. Total monomer concentration = 9.38×10^{-1} mol L⁻¹. Total volume = 50 mL.

Table XI Rate of Polymerization of Various Monomers

Monomer	Photopolymerization $R_p/10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}$ ^a	Thermopolymerization $R_p/10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ ^b
BPA-DMAI	17.9	8.21
BPA-MAI	5.81	2.53
MMA	8.86	3.11

^a [Monomer] = 0.2 mol L⁻¹. [1,1'-Azobis(cyclohexanecarbonitrile)] = 6 × 10⁻³ mol L⁻¹. Solvent: DMF. Temperature = 30°C by dilatometer method.

^b [Monomer] = 0.938 mol L⁻¹. [AIBN] = 9 × 10⁻³ mol L⁻¹. Solvent: DMF. Temperature = 90°C by gravimetric method.

DMF with AIBN as the initiator at 90°C. Further, the rate of thermal polymerization of BPA-DMAI was three times that of BPA-MAI. In photopolymerization, the rate of BPA-DMAI was approximately three times that of BPA-MAI and twice that of MMA.

Kinetic Measurement on UV Curing

Photocrosslinking reactions have become increasingly important because of their industrial applications such as for relief printing plates, printed coatings, and printing inks. The unsaturated polymer used in this work was obtained by reacting allyl bromide with the hydroxy side groups of poly(BPA-MAI) [see eq. (3)]. These unsaturated side groups undergo free-radical polymerization by initiation with benzoin isopropyl ether, which photodissociates into two equally reactive radicals.

The results are shown in Table XII. The degree of photocrosslinking increases with duration of irradiation. Figure 3 shows the relationship of 1/(1 - α) and the irradiation period, in which α is the degree of conversion (insoluble fraction). The photocrosslinking process is second order. Similar

results were observed by Sabr Nal, and Smets²⁶ and Liaw and Shen²⁷ for unsaturated polymethacrylic esters and acrylated epoxy resin, respectively. The reaction constant is 1.61 × 10⁻⁵ mol s⁻¹.

TG Curve Characteristics of Poly(BPA-MAI)

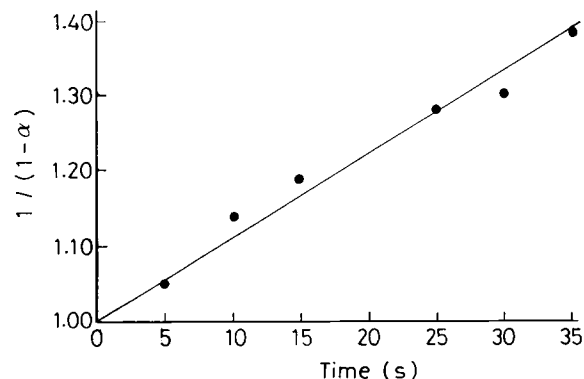
The TG curves for the thermal degradation of a sample (5 mg) of poly(BPA-MAI) are shown in Figure 4 for a heating rate of 10°C/min in a nitrogen atmosphere. The significant observation is that the mass loss in the range 30–100°C is about 3.21%. This effect is probably due to the hygroscopic nature of the samples caused by the acyl urethane groups of poly(BPA-MAI). This fact is consistent with the result of the elemental analysis of the copolymer of BPA-MAI and MMA (*vide supra*). Hence, we conclude that the elemental analysis of the copolymer of BPA-MAI and MMA must be corrected.

The TG curve for poly(BPA-MAI) in a nitrogen atmosphere has two stages and shows two maxima peaks at 248 and 398°C. In the first stage, mass loss starts at 169°C and continues to 335°C with 17.5% mass loss. The second stage (46.0%) is complete by 492°C and shows a maximum rate of mass loss at

Table XII Rate of Crosslinking at 30°C of Poly(BPA-MAI) Carrying Unsaturated Side Groups by Gravimetric Method

Irradiation (s)	Insoluble Fraction Unsaturated [Poly(BPA-MAI)]
5	0.047
10	0.111
15	0.152
25	0.211
30	0.233
35	0.273

^a [Benzoin isopropyl ether] = 3 mass % by polymer. [Pentaerythritol triacrylate] = 5 mass % by polymer.

**Figure 3** Rate of crosslinking as a function of irradiation time, α = degree of conversion (insoluble fraction).

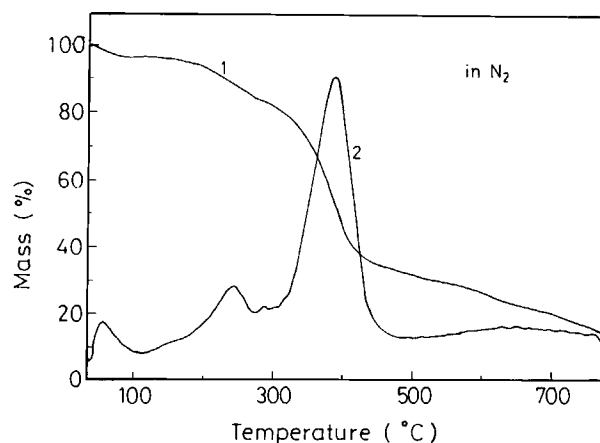


Figure 4 The curves of (1) TGA and (2) DTG obtained in the nitrogen atmosphere of poly(BPA-MAI); heating rate = $10^{\circ}\text{C min}^{-1}$.

398°C as shown by the derivative facility associated with the TG apparatus. The mass fraction remaining at 800°C is 14.86%.

CONCLUSION

New functional monomers derived from MAI and BPA derivatives were successfully prepared. Polar solvents were found to slow the polymerization of BPA-MAI. The monomer reactivity ratios of BPA-MAI (M_1) with MMA (M_2) in DMF at 90°C were calculated to be $r_1 = 0.17$ and $r_2 = 1.34$ by the Fineman and Ross method. The photocrosslinking kinetics of unsaturated poly(BPA-MAI) followed second order. The rate coefficient is $1.61 \times 10^{-5} \text{ mol s}^{-1}$ at 30°C .

We thank the National Science Council of the Republic of China for financial support (Grant NSC 84-2216-E-011-025) and the Nippon Paint Co. Ltd. for supplying the MAI.

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Received July 12, 1995

Accepted August 30, 1995