

Synthesis and Characterization of Poly[(methyl methacrylate)-*co*-(methacrylic acid)] for a UV-Sensitive Aqueous Base Developable Lithographic Plate

Suda Kiatkamjornwong,¹ Suteera Tessiri²

¹ Department of Imaging and Printing Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

² Multidisciplinary Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

Received 12 October 2001; accepted 5 February 2002

ABSTRACT: Syntheses of the copolymers of methyl methacrylate and methacrylic acid were carried out by free radical chain polymerization in the presence of benzoyl peroxide (BPO) as an initiator. The effects of the monomer ratio and polymerization time on the averaged molecular weights, polydispersity index, and glass transition temperature were investigated. FTIR and NMR were used for functional group characterization, GPC for average molecular weights and the distribution, elemental analysis for CHO content, and DSC for the glass transition temperature. The copolymers were mixed with tripropylene glycol diacrylate (TPGDA) and trimethylol propane ethoxylated triacrylate (TMPEOTA), 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur[®] 1173) and benzophenone (Darocur[®] BP) with anthraquinone for visibility of images. The photosensitive coating was spin-coated onto the anodized aluminum plate on which a thin film was formed. The wet film was then coated with PVA solution as an oxygen barrier layer. The

plate assembled with a control wedge and a black color separation film was exposed to UV radiation at different exposure times. The plate was developed in a dilute alkaline developer. The resulting plate was evaluated for its reproduction properties in terms of surface properties (hydrophilic/hydrophobicity) by contact angle measurement of image/nonimage areas, resolution by microline, tone reproduction, and adhesion tests. The article describes the results of the syntheses, characterizations, and uses of the copolymer as a binder of a negative, lithographic printing plate. The present lithographic printing plate is good for a medium viscosity printing ink to produce medium printing quality on uncoated paper. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1829–1837, 2002

Key words: photopolymerization; copolymerization; lithography; resists; coatings

INTRODUCTION

Photoresist can be prepared by three methods. The first involves crosslinking of a light-sensitive colloid or synthetic polymer by addition of a photosensitizer that causes polymer decomposition to form an active species that insolubilizes the surrounding vehicle or binder. Examples of this system are dichromate/gelatin and azide rubber. Second, polymers with built-in photosensitive groups capable of forming crosslinks between their molecules lower the solubility significantly upon exposure to actinic energy. Poly(vinyl cinnamate) is one of the examples. The third is polymerization producing insolubilization, whereby multifunctional monomers are made to polymerize via actinic radiation with/without a photosensitizer/initiator. Chandross et al.¹ studied photosensitive bodies sensitive to ultraviolet radiation and exhibiting excel-

lent contrast of images. The images were formed from a base-soluble polymer of poly(methyl methacrylate-*co*-methacrylic acid) mixed with base-insoluble compounds of *o,o'*-dinitrobenzyl esters. The base-insoluble esters decomposed upon irradiation to form base soluble entities in the irradiated regions. These irradiated portions were then soluble in basic solutions that developed desired images with good contrast to give a positive imaging process. It is the purpose of the present research to synthesize a base copolymer of methyl methacrylate and methacrylic acid used as a binder for multifunctional monomers to produce a negative, lithographic printing plate. We formulated a plate-coating chemistry for a negative working plate incorporation of the newly synthesized binder, multifunctional acrylate monomers, a pigment for image visibility, and a coating promoter.

PROCEDURE

Syntheses of poly[(methyl methacrylate)-*co*-(methacrylic acid)]

Methyl methacrylate (MMA) supplied from Eternal Resin Co., Ltd., Bangkok, Thailand) was purified by

Correspondence to: S. Kiatkamjornwong (ksuda@chula.ac.th).

TABLE I
Effect of Monomer Ratio of Methyl Methacrylate
and Methacrylic Acid on Polymer Properties

Run No.	MMA %	MAA %	T_g °C	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
T16-90	90	10	116	128,000	52,000	2.5
T16-80	80	20	140	129,000	58,000	2.2
T16-70	70	30	163	128,000	69,000	1.9
T16-60	60	40	156	123,000	72,000	1.7
T16-50	50	50	171	132,000	62,000	2.1

In isopropyl alcohol 75% w w⁻¹ monomer concentration 25% w w⁻¹, benzoyl peroxide 1% w w⁻¹, reaction temperature 70°C, agitation rate 295 rpm.

the conventional alkaline method and passed through an activated aluminum oxide column. Methacrylic acid (MAA) was from Mitsui Specialty Chemicals Co., Ltd., Bangkok. The MMA was also purified by the same method mentioned above. The copolymerizations of MMA and MAA were carried out in a 500-cm³ round-bottom flask equipped with a paddle stirrer with an agitation rate of 295 rpm, a reflux condenser, and a thermometer. A mixture of MMA and MAA (130 cm³ of 25% w w⁻¹), mixed with 75% w w⁻¹ isopropyl alcohol (IPA, commercial grade from Merck, Honenbrunn, Germany) was polymerized at 70°C and 1% w w⁻¹ benzoyl peroxide (BPO) initiator (from Merck Co., Ltd., Honenbrunn, Germany), based on the total comonomer concentration. After the desired reaction time had elapsed, the synthesized copolymers were isolated by precipitation in diethyl ether (analytical grade from Labscan Asia Co., Ltd., Bangkok). The pure copolymer was obtained by dissolution in IPA to extract the unreacted monomer and reprecipitation in diethyl ether.

Effect of the monomer ratio

Table I shows the ratios of MMA/MAA for the radical copolymerization in 1% BPO at 70°C with an agitation rate of 295 rpm. The same procedure was carried out as above.

Effect of polymerization time

Table II gives the range of polymerization time of MMA and MAA at the ratio of 70 : 30 in 1% BPO at 70°C with an agitation rate of 295 rpm. The same procedure was carried out as above.

Copolymer characterization

Identification of functional groups by infrared spectroscopy

The functional groups of the copolymers were investigated using Fourier Transform infrared spectroscopy (Perkin-Elmer Infrared Spectrophotometer, model 1760A, USA). The IR disc was prepared by the conventional method.

Identification of functional groups by nuclear magnetic resonance spectroscopy

The ¹³C-NMR spectra of copolymer solution (10–15% w w⁻¹) in d₆-DMSO (d₆-dimethyl sulfoxide) were prepared with a 10-mm probe on an Advance DPX-800 spectrometer (Germany) operated at 400 MHz in the pulsed FT-mode with wide-band modulated proton decoupling. An internal standard of TMS was employed. The probe temperature under experiment conditions was 25°C.

Elemental analysis

The C, H, and O compositions in these copolymers were analyzed by an Elemental Analyzer (Perkin-Elmer PE2400 Series II, USA).

Molecular weight averages and their distribution

A sample was weighed accurately to 0.005 g in a test tube containing 5 cm³ of tetrahydrofuran (THF), then sealed with aluminum foil and paraffin film. After the sample dissolution was completed, the solution was filtered through a membrane filter with a pore size of 5 μm in a 5-cm³ volumetric flask. A WATERS gel

TABLE II
Effect of Polymerization Time of Methyl Methacrylate and Methacrylic Acid (70:30)
on Polymer Properties

Run No.	Time h	T_g °C	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n	Element composition		
						%C	%H	%O
T05	5	158	78,000	36,900	2.1	—	—	—
T07	7	165	66,700	35,000	1.9	—	—	—
T13	13	167	79,000	35,000	2.2	57.986	8.007	34.007
T16	16	163	128,000	69,000	1.9	58.199	8.159	33.042
T24	24	153	70,000	36,700	1.9	—	—	—

MMA:MA = 70:30 in 1% benzoyl peroxide at 295 rpm.

TABLE III
Composition of the Photosensitive Coating Material for Offset Printing Plate

Photosensitive material	Content, % by weight
MMA/MAA copolymer 30% in IPA/MEK 1:1	58.3
TPGDA	21.0
TMPEOTA	12.2
Darocur® 1173	4.3
Darocur® BP	3.9
Anthraquinone	0.3

permeation chromatograph (GPC 510, USA), was equipped with a series of four Ultrastaygel columns having nominal exclusion limits of 10^3 , 10^4 , 10^5 , and 10^6 , respectively. An injection of 100 μL ($1 \times 10^{-1} \text{ cm}^3$) of the filtered solution was given to the GPC at a controlled temperature of 35°C. The GPC was equipped with a differential refractometer, using THF as an eluent with a flow rate of $0.7 \text{ cm}^3 \text{ min}^{-1}$. The \overline{M}_w , \overline{M}_n , and a polydispersity index ($\overline{M}_w/\overline{M}_n$) were analyzed by MAXIMA software for GPC by comparing with the standard calibration curves of a polystyrene standard having an \overline{M}_w range from 2.98×10^3 to 2.08×10^7 .

Thermal properties of the copolymers

The samples were prepared by drying at 60°C to a constant weight. Glass transition temperatures of the copolymers were measured using a differential scanning calorimeter (NETZSCH DSC 200 from Selb/Bavaria, Germany) programmed at a heating rate of $20^\circ\text{C min}^{-1}$.

Plate coating

A typical recipe of photosensitive materials for a negative coating chemistry was formulated as shown in Table III. The viscosity of the solution was measured by a Brookfield viscometer (model RVT, with a small sample adapter and a spindle number 14) at 25°C under various shear rates of 1, 2, 4, 8, and 20 s^{-1} . The viscosity was calculated by multiplying by 0.4 for the set revolutions of 2.5, 5, 10, 20, and 50 rpm, respectively.

The photosensitive coating was coated onto an anodized aluminum substrate by spin coating (Able Co., Ltd.) so that a smooth film was formed. The film was overcoated with 2% poly(vinyl alcohol) or PVA205 solution (Siam Resin & Chemical Co., Ltd., Bangkok) as an oxygen barrier. The plate was air blown dry (Casiko 500, Peoples Republic of China) in a safelight room.

Evaluation of the coating for a lithographic printing plate

The coated aluminum plates were assembled with a control step wedge and exposed to UV radiation (Ta Shiang Machine Co., Ltd., Model TS-VPPPF 32 SP-2, Taiwan) at different exposure times. They were then developed in an aqueous base developer (1 : 5 dilution of Fuji Film Developer DN-3C, Tokyo, Japan). The plates were then washed with tap water and dried. The qualities of the images were then characterized for resolution and tone reproduction.

Surface properties

To investigate the hydrophilic–hydrophobic properties of the resulting plate, a Contact Angle Meter (FACE Kyowa Interface Science Co., Ltd., Model CA-A, Tokyo, Japan) was used to measure the contact angles of a diluted fountain solution (Anchor, CA), and oleic acid on both the image areas and nonimage area. Five measurements were made on each image and nonimage area of one plate to obtain an accurate average.

Image characteristics

Dot characteristics were examined using an image analyzer (Lusex-F software Program of Nireco QJ 8500 coupled with Olympus SZH10). Dot characteristics of the original film and the resulting plate were compared.

Dot gain

Percentage dot areas of the original film and the reproduced dots at 40, 50, and 60% dot area were evaluated by the same image analyzer and a densitometer (MacBeth, USA).

Adhesion test

A pressure-sensitive tape (3 M 610 or equivalent, St. Paul, MN) was pressed onto the coating surface or solid areas of the printing plate. The tape was pulled straightly and peeled off. The amount of the peeled-off coating was evaluated according to ASTM D 3359-97.

Printing experiment

The plate was gummed or coated with gum Arabic solution (Fuji GU-7, Fuji Photo Film Co., Ltd., Tokyo, Japan) during storage. Before printing, the plate was wiped off with a moist sponge to remove the gum Arabic. The plate was then covered with the fountain solution (20 to 30 cm^3). An inking rubber roller was rolled on a patch of ink (Panorama Sheetfed Ink,

TABLE IV
Comparison of the Reactivity by Rate Constants and Termination Mode of MMA and MAA

Monomer	$k_p(\text{M}^{-1} \text{s}^{-1})$	$k_t^{1/2}(\text{M}^{-1} \text{s}^{-1})$	$k_p/k_t^{1/2} (\text{M}^{-1} \text{s}^{-1})^{1/2}$	Percentage of termination	
				Disproportionation	Combination
MMA	705	3.24	390	79	21
MAA	670	4.41	320	<79 ^a	>21

k_p , k_t are the rate constants of propagation and termination, respectively.

^aAn approximate value.

PPR-1, Magenta, A.S. Ink & Chemical Bank Co., Ltd., Korea) to obtain a full coverage of ink. The ink on the inking roller was then applied to the moist plate. The ink was transferred to the image areas while the non-image areas remained noninked. A piece of uncoated paper was then covering over the plate and a clean roller was placed on the back of the paper. It was rolled gently over the paper. The images were then transferred to the paper. The prints were then evaluated to compare with the original dot areas.

RESULTS AND DISCUSSION

As mentioned above, the parameters under study are the monomer ratio and polymerization time. The resulting products are solid and relatively hydrophilic. We must keep them away from moisture. We investigated the functional groups first to ensure the occurrence of copolymers by IR followed by further confirmation by ¹³C-NMR.

From the IR peaks of the copolymers of MMA and MAA, the following peaks were found. The broad peak at 3591 cm⁻¹ indicates the OH stretching; the weak peak at 2955 cm⁻¹, and the strong peaks at 1490, 1455, and 1389 cm⁻¹ represent the C—H bending of CH₃ and CH₂; the strong peak at 1733 cm⁻¹ and the weak peak at 1673 cm⁻¹ are for the C=O ester and acid, respectively. Another strong peak at 1152 cm⁻¹ indicates the C—O stretching of the ester group. To confirm the carbon positions of the copolymers of MMA and MAA, the assignments of the following chemical shifts confirmed the existence of the MMA-MAA copolymer: The chemical shifts at 17.9 ppm for —CH₃ carbon, at 45 for tertiary carbon (>C<), at 52 for the methoxy carbon (—OCH₃), at 55 for methylene carbon (—CH₂), at 177.61 to 178.5 for the carbonyl carbon of MMA and at 180.2 for the carbonyl carbon of MAA are found.

Effect of MMA : MAA ratio on the glass transition temperature and molecular weights and their distribution

Table I shows the effect of MMA : MAA ratios on the glass transition temperatures of the copolymers. Varying the monomer ratio has a direct impact on the glass transition temperatures of the resulting copolymers.

The T_g of poly(methyl methacrylate) or PMMA is 115°C and that poly(methacrylic acid) or PMAA is 230°C.² The synthesized copolymers have the T_g values in between at 116.1°C, which is close to the T_g of PMMA (115°C) at a 90 : 10 ratio of MMA : MAA. Likewise, when the monomer ratio is 50 : 50, the T_g value is in the middle range (171°C). Comparing the two polymers, the moiety of PMMA is a rather flexible segment, while the MAA portion is a hard and glassy segment. Because there is only one glass transition temperature of the copolymer, we can thus state that the resulting material is a random copolymer of MMA and MAA.

Regarding the average molecular weights and polydispersity index, the weight-average molecular weights for all the monomer ratios are relatively constant. The number-average molecular weight of the copolymers increased with increasing ratios of MAA. The polydispersity index is rather broad (1.9 to 2.7). Because this polymerization is carried out in solution, accessibility of the monomer to the precursor radicals is diffusion controlled phenomenon. The reactivity ratios of the MMA monomer (r_1) and MAA (r_2) are 0.78 and 0.33, respectively.³ Table IV shows the comparison of reactivity by rate constants of MMA and MAA. Based on $k_p/k_t^{1/2}$ ratio⁴ between the MMA and MAA in Table IV, one can see that more MMA units are added in the polymer chains. The high molecular weights of the copolymer could be obtained because the ratio of $k_p/k_t^{1/2}$ is relatively high. The k_p and k_t are the rate constants for propagation and termination stages. The greater reactivity of MMA results in its being incorporated preferentially in the first-formed copolymer. As the reaction proceeds the feed material is lacking in the MMA monomer, while the copolymer becomes progressively enriched in MAA at the later stage, because MMA has been used up earlier.

The copolymer undergoes the greater disproportionation as shown in Table IV. The percentage of disproportionation termination of MMA or chain transfer to the polymer by hydrogen radical abstraction is higher than that of MAA because the beta hydrogen and the steric hindrance of the methyl group obstruct the incoming MMA monomers and the growing PMMA chains. Considering the transfer reactions among the reactive ingredients and the result-

ing polymers, we found that chain transfer to the polymer is significant. Chain transfer constant to PMAA and PMMA at 60°C are 7.7×10^{-1} to 1.28, and 1×10^{-5} to 3.6×10^{-2} , respectively, depending on the type of solvent.⁵ Regardless of both monomer concentrations, PMMA always has a higher average molecular weight.

Effect of polymerization time on the glass transition temperature and molecular weights and their distributions

Table II shows the effects of the polymerization time (5, 7, 13, 16, and 24 h) on glass transition temperatures and the molecular weights and weight distributions of the copolymers. Most of the average molecular weights increased with polymerization time, and after 16-h polymerization, both average molecular weight and T_g decreased. Elemental analysis for C, H, and O for 13- and 16-h polymerization is also given in Table II. The result indicates that the variation of reaction time insignificantly affects the CHO composition of the copolymers.

The role of the reaction time is to allow more conversion of the monomer to the growing chains of both monomers. Because the termination of both monomers favors disproportionation, an excessively long reaction time may accentuate the extent of disproportionation relative to combination. The half-life for BPO⁶ and the high content of MMA are also important determinants of the ratio of disproportionation to combination. Because its half-life is 7.3 h at 70°C in benzene solution, the second half of the thermal initiator then started to work during the polymerization period (16 h) to give more radicals. Generally, a longer polymerization time allows the radicals or growing chain radicals to diffuse to encounter each other and terminate themselves. Longer polymerization times additionally increase the yield of the final product. Agreement between the reaction time, molecular weights, and glass transition temperature was found. According to Table II, the longer reaction time produced higher molecular weight polymers and a higher glass transition temperature. However, too long a polymerization time enhances the chain transfer to polymers. This led to the decreased \bar{M}_w at the long reaction time of 24 h.

Plate coating

Table III shows the composition of the photosensitive coating materials for an offset printing plate. The MMA/MAA (70 : 30) copolymer solution of 30% in a mixed solvent of isopropyl alcohol/methyl ethyl ketone (1 : 1) was used. This polymeric binder is good for incorporating other ingredients for exposure to a UV source. Selection of the polymeric binder is one of the

most important parameters in a plate-coating formulation. Rigid and hard or soft and flexible monomers can be copolymerized to form the polymer backbone. The influence of different monomers on the resulting film properties is very significant. In this research, we chose MMA and MAA as the polymerizing monomers for preparing the polymer binder. MMA tends to yield films with good exterior durability, hardness, and stain and water resistance. MAA usually yields films with good hardness, and solvent and grease resistance. In addition, the proportion of one monomer in the copolymer directly influences the T_g of the copolymer binder. The glass transition temperatures of the copolymers currently used are in the range of 150 to 167°C. Most coating films require a compromise of properties, and thus they can be obtained by copolymerization of more than one type of monomer.

The mechanical properties required from a cured coating include hardness, flexibility, adhesion, abrasion resistance, strength, durability, scratch resistance, and toughness. Many of these properties are interrelated and primarily depend on the following.⁶ The chemical structure of the prepolymer, the molecular weight of the prepolymer, the functionality of the diluent, and the nature of the crosslinked network.

Reactive diluents

Monomers or reactive diluents present in the radiation-curing systems perform the primary functions of fluidizing agents and viscosity control agents. More importantly, they behave as crosslinking agents to increase or decrease the crosslinking density of the polymeric network and modify the final product. Because the monomers participate in the curing process by copolymerizing with the unsaturations in the oligomers or prepolymer, they can have a great influence either on the cure kinetics and photoresponse rate or on the properties of the coating. These are mainly on mechanical properties (film hardness, flexibility, and adhesion) or chemical resistance. Increase in the crosslinking density of the cured film can enhance the hardness of a coating. Increasing the functionality of the reactive diluents is the normal practice for achieving such a property. The low irritancy multifunctional monomers of tripropylene glycol diacrylate (TPGDA) and trimethylol propane ethoxylated triacrylate (TMPEOTA) are suitable for controlling hardness and flexibility of the cured film. As the monomer functionality was increased, the photopolymerization developed much faster and stopped faster as well because a high initial concentration of the reactive group was used up faster and depleted earlier. Gelation was observed faster, which limited the extent of photopolymerization of the crosslinked polymer. Such a fast reaction leads to a dilemma: fast curing is considered appropriate for economic reasons, but the film stability is

also reduced because it contains a substantial amount of unreacted double bonds. Upon room-temperature photopolymerization, the system passed through the glass transition isothermally; the mobility of the unreacted double bonds was strongly reduced. Nevertheless, diffusion of the free monomers still proceeded to transport to the reactive sites via chain transfer for the reduced reaction rate and increased segmental mobility.

The use of a prepolymer with components having high glass transition temperatures also helps to enhance film hardness. The more rigid the prepolymer and the higher the crosslinking density, the harder the cured film. TPGDA increases the film hardness while TMPEOTA induces film flexibility. The TPGDA-to-TMPEOTA ratio of 21 to 12 is the selected concentration for the current formulation, because the molar concentration of the monomers in the system determines its influence on the film properties because the former gives more film flexibility and printability.

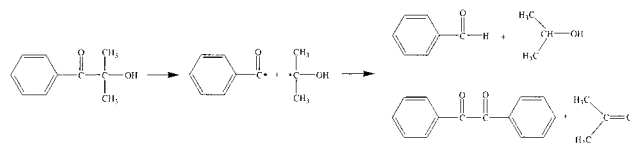
Photoinitiating system

Both TPGDA and TMPEOTA contain diacrylate (two positions of δ bonds) and triacrylate (three positions of δ bonds) functionality, respectively, which are sensitive to UV radiation. The higher the acrylate functionality, the greater the UV sensitivity. The photopolymerization is enhanced by the presence of photoinitiators. Although the unsaturated vinyl acrylated monomer can self-polymerize under UV irradiation, its rate of curing is far too slow for industrial applications. In this work, a photoinitiator package was used to enhance the UV curing speed. Norrish type I initiator, 2-hydroxy-2-methyl-1-phenyl-propan-1-one (or 2-hydroxy-2-methylpropiophenone, HIPK) or Darocur[®] 1173, was used along with the Norrish type II initiator, benzophenone (BP) or Darocur[®] BP. Photoinitiators are generally divided into two classes according to the cleavage mechanism [as shown in eqs. (1) and (2)] by which the initiating radicals are formed. Darocur[®] 1173 undergoes a unimolecular reaction [see eq. (1)] and dissociates to yield an aromatic carbonyl compound containing suitable substituents, which facilitate a direct photofragmentation, thereby producing two radicals per one cleavage. The aromatic carbonyl moiety acts as the chromophoric group. Depending on the nature of the functional group and its location in the molecule relative to the carbonyl group, the fragmentation can take place at a bond adjacent to the carbonyl group (α -cleavage), at a bond in the β -position.⁸ The HIPK does not have aromatic substituents in the hydroxyl alkyl moiety, which basically prevents the formation of chromophoric compounds, leading to a nonyellowing, clear coating. For the BP photoinitiator, hydrogen abstraction by the excited initiator and photoinduced electron transfer is fol-

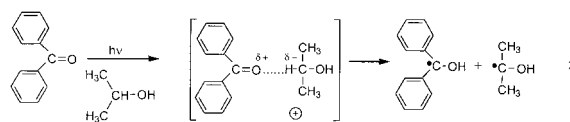
lowed by fragmentation. A typical hydrogen abstraction process is the reaction of excited ketones with hydrogen donors, such as alcohols (IPA in the present study). Upon excitation of the ketone to its $n\pi^*$ triplet state, an electron is promoted from the nonbonding n orbital on oxygen to an antibonding π orbital, which is delocalized over the aromatic π system; thus, it gives rise to the excited stated oxygen to become more electrophilic. The partial positive charge on an oxygen atom can then interact with the electron-rich C—H bond adjacent to the heteroatom, resulting in hydrogen abstraction as shown in Reaction (2).⁸

A combination of HIPK [type I, in Reaction (1)] and BP [type II, in Reaction (2)] photoinitiators is superior to using either one alone for UV curing in air. The type I photoinitiator can furnish the primary radicals, which deplete with the oxygen in the system. The type II photoinitiator (BP) induces the photosensitized decomposition of a cophotoinitiator via the corresponding initiation mechanism. Therefore, in practice, the mixtures of both photoinitiators are often used to obtain a synergistic effect.⁹ After coating the coating formulation on an aluminum plate, PVA solution was overcoated to prevent oxygen from the air from inhibiting the surface curing, because oxygen is a radical scavenger whose inhibition effect is very great (a very high Z value of 33,000 for MMA) at 70°C.¹⁰

The coating system was irradiated to UV radiation, the exposed areas were initiated by the normal radical chain polymerization to result in the image areas, composed of the network of MMA/MAA crosslinked by TPGDA or TMPEATA. The unexposed areas were remained unchanged to become the nonimage areas. As the polymerization proceeded, the viscosity of the irradiated areas increased steadily to yield a solid, highly crosslinked polymer film, in which the segmental mobility was severely restricted. The reaction proceeds further in this phase, although probability of the polymer radicals encountering the unreacted acrylate double bonds was sharply reduced until all the mobile and accessible reactive groups had been consumed to form an insoluble network.



Reaction 1



Reaction 2

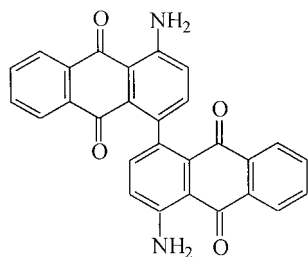


Figure 1 Chemical structure of anthraquinone.

Pigment additive

Upon UV irradiation, the photopolymerization of the photosensitive system took place to completion; the images formed on the plate could not be easily viewed. A suitable pigment, which does not interfere with the working conditions of the ingredients and UV chemistry, should be added to enhance the contrast between the image and nonimage areas. Anthraquinone (Ciba® Oracet Red BG, Ciba Specialty Chemicals, Bangkok) was found to be compatible with the chemical components and UV chemistry. The final plate after UV exposure and development in 1 : 5 dilution of Fuji Film Developer DN-3C (aqueous base alkaline developer) had red-colored images with clear nonimage areas of aluminum substrate. The anthraquinone structure, shown in Figure 1, is relatively polar, because the two amine groups and the four oxygen atoms of the ketone parts are compatible with the carboxylate group of the MAA chains.

Evaluation of hydrophilic and hydrophobic properties of the plate

The viscosity of the plates (T9–13, T8–16, T10–5, and T6–15) leads to non-Newtonian at low shear rates, which becomes Newtonian at high shear rates. It implies that the coating chemistry is shear thinning or pseudoplasticity, which is the general property of lithographic plate coating chemistry. When increasing the shear rate on the plate coating, the viscosity decreases. The working viscosity for the plate coating is in a range of 4.4 Pa s at a shear rate of 8 s⁻¹.

Basically, a lithographic plate is a planographic printing plate where the image areas and nonimage areas are on the same level. Chemically, the image areas accept oil or ink, whereas the nonimage areas accept water or fountain solution. The difference between the hydrophilic and hydrophobic properties is very important for the print quality. For the surface wettability of the plates, water, fountain solution, and oleic acid were used as wetting agents for both areas. The average contact angles of five measurements were recorded. Both water and fountain solution give high contact angles (50 to 60 degrees) on the image area, while oleic acid gives lower contact angles (10–18

degrees). The contact angles of fountain solution on the nonimage area are lower than that of water (10 degrees), and oleic acid (40 degrees). Surface tensions of water, oleic acid, and fountain solution are 72.8, 37.3, and 44 mN m⁻¹, respectively. Main compositions of fountain solution are gum Arabic, ethylene glycol, phosphate salts, and weak acid to provide a pH range of 5 to 5.5, which desensitizes the nonimage area when contacting with lithographic ink. The resulting contact angles indicate that the image area is relatively oleophilic or hydrophobic, because the oleic acid contact angles are smaller than those of water on the same surfaces. On the other hand, the nonimage areas are hydrophilic because the contact angles of water are smaller than those measured by oleic acid. Basically, the contact angles of hydrophobic surfaces measured with water are larger than 90°, and for hydrophilic surfaces, they are much smaller than 90°. In our present research, the difference in contact angles is very small. This result can be explained as follows: The polymeric binder is the copolymer of MMA and MAA, which is the base for the coating ingredients to disperse in. The methacrylic acid moiety in the polymer binder is quite hydrophilic, in that water can interact with it through hydrogen bonding. In addition, it can still be wetted by oleic acid, which has the same carboxylic acid functionality. For the aluminum surface having a surface energy of about 360 mN m⁻¹, both liquids can wet the surface more or less depending on their polarity, because both liquids have a smaller surface tension.

Effects of monomer ratio and polymerization time on exposure time and dot reproduction

Based on the coating chemistry, TPGDA and TMPEATA are the crosslinking monomers. Their role in crosslinking can be many folds. First, a crosslinking reaction between TPGDA and TMPEOTA could most probably occur to provide a crosslinking copolymer. Second, crosspolymerization or grafting reaction at the unsaturated chain ends of the polymer binder makes the plate more insoluble and rigid. Third, both of them could self polymerize to produce homopolymers.

The amount of radiation to which the plate is exposed is the principal variable that the plate maker has to adjust to control the image transfer to plate. It is also the most significant factor affecting the basic plate requirements that all plates need a sufficient level of exposure to run the proper chemical reaction, hydrophilicity and hydrophobicity, and an adequate resolution. Figure 2 shows the control step-wedge and dot areas of 38, 47, and 57%. We found in Table V that the higher the exposure times, the higher the percentage dot reproduction. Considering the different dot sizes, all the plates produce dot gain. The most sensitive,

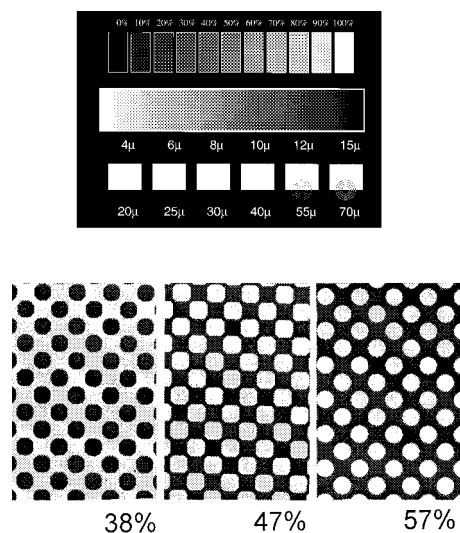


Figure 2 Negative film control wedge (center top), bottom left, 38% square dots; bottom center, 47% square dots, and bottom right, 47% round dots.

reproduction dot gains found at 57% original dot area are from 3 to 20%. Molecular weight effect on dot reproduction quality can be divided into two groups (Table V). Both the low \bar{M}_n and \bar{M}_w range of 35,000–36,900 and 70,000–79,000, respectively, and the higher \bar{M}_n and \bar{M}_w range of 58,000–69,000, and 128,000–133,000, respectively, produce the acceptable ranges of dot reproduction for the lithographic plate. The higher \bar{M}_w copolymer produces somewhat better printing quality (tone reproduction), because the higher binder viscosity reduces the degree of photopolymerization. Even at a longer exposure time, the higher molecular weights yield the same amount of dot reproduction. Although the polymerization time imposes the greater effect on dot gain, the extent is not so significant on plate quality. The longer polymerization time produces a lower molecular weight with many unsaturated bonds at chain ends. Increasing the exposure time can induce more chain end polymerization with TPGDA or TMPEATA. Polydispersity in-

dexes of the copolymer molecular weight are in a close range and do not influence the dot quality of the plate at both low and high molecular weight ranges. Polydispersity index of the binder cannot be used as an indicator for evaluation because it does not give any information about the plate quality.

Exposure time and resolution

Table VI shows the effects of the monomer ratio and polymerization time on exposure time and plate resolution. As the longer reaction time of this type of termination yields the higher chain transfer, or slightly lower averaged molecular weights require a longer exposure time to obtain the same level of resolution. On the contrary, the copolymer with a higher MMA concentration or having lower molecular weight produces a better plate resolution at the same exposure time because of the lower extent of photocopolymerization. Importantly, \bar{M}_n is a more effective indicator of the resolution trend than \bar{M}_w , because the lower \bar{M}_n produces the thinner Microline width. Nonetheless, all the plates have a rather poor resolution compared with the standard commercial plates.

Evaluation of printing quality

A pressure-sensitive tape was applied to test the strength of the coating. The tape did not remove much coating from the plate surface according to ASTM D3359-97. The results show that the photosensitive coating has a good adhesion to the aluminum substrate. The film forming properties of the copolymer of MMA and MAA are so strong that it can withstand the viscous ink from back trapping of both polymer coating and ink. For printing, the plate was first covered with the fountain solution (20 or 30 cm³) on a small plate for desensitizing the nonimage areas. The ink was applied later. Although the contact angles indicate that both image and nonimage areas could be wetted by both fountain solution and oil, excess emul-

TABLE V
Effect of Monomer Ratio and Polymerization Time on Dot Reproduction

Type	Binder property			Exposure time, s	Dot reproduction (%) from the original percentage dot of		
	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n		38	47	57
T05	78,000	36,900	2.1	64	40	52	64
T13	66,700	35,000	2.2	98	40	52	63
T24	70,000	36,700	1.9	105	56	64	77
T16-50	133,000	62,000	2.1	105	44	55	67
T16-70	128,000	69,000	1.9	125	42	54	67
T16-80	129,000	58,000	2.2	105	40	49	60

T05, T13, and T24 indicate different polymerization times of 5, 13, and 24 h, respectively, for a MMA-MAA ratio of 70 : 80. T16-50, T16-70, and T16-80 denote the polymerization time of 16 h with MMA-MAA ratios of 50 : 50, 70 : 80, and 80 : 20, respectively.

TABLE VI
Effect of Monomer Ratio and Polymerization Time on Plate Resolution

Type	Binder property			Microline width (μm)	
	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n	for exposure time, s	at complete circle ^a
T05	78,000	36,900	2.1	91	25
				98	25
T13	66,700	35,000	1.9	91	25
				98	30
				105	30
T16-70	128,000	69,000	1.9	91	40
				105	40
T16-80	129,000	58,000	2.2	91	55
				105	55

T05 and T13 indicate different polymerization times of 5, and 13 h, respectively, for the MMA: MAA ratios of 70 : 30. T16-70 and T16-80 denote the polymerization time of 16 h with the MMA: MAA ratios of 70 : 30 and 80 : 20, respectively.

^a Complete microlines are obtained when the half-positive and half-negative lines appear and join in a complete circle.

sification of oil-in water on the nonimage areas and water-in-oil on the image areas were not found. The equilibrium emulsification on both areas prevents scumming and tinting on the nonimage and image areas, respectively. The prints so obtained have good contrast between the image and nonimage areas. Neither scumming nor tinting was observed from 10 prints tested. The image areas had adequate ink densities, depending on the tonal range, while the nonimage areas were clean and paper white.

We, therefore, can state that the copolymer of MMA and MAA currently synthesized with the proposed ingredients is a good polymeric binder and promotes the surface properties for a negatively lithographic plate developable by an aqueous alkaline developer.

CONCLUSIONS

The syntheses of the copolymers of methyl methacrylate and methacrylic acid were carried out by free radical polymerization for preparing an ultraviolet light sensitive coating, which is developable with an aqueous-based alkaline developer. The monomer ratio of MMA and MAA and the polymerization time were the parameters investigated. The averaged molecular weights for this type of plate were in the range of 80,000 to 130,000 for \bar{M}_w and 40,000 to 70,000 for \bar{M}_n . The \bar{M}_n , not the \bar{M}_w of the copolymer has a pronounced effect on the plate quality. The copolymers have glass transition temperatures in the range of 158 to 164°C. Multifunctional monomers of TPGDA and TMPEOTA functioned well as the crosslinking monomers with photoinitiators of Darocur[®] 1173 and Darocur[®] BP upon UV irradiation, indicated by the insolubility of the exposed areas. The plate coating chemistry, which was developed by the aqueous alkaline

developer, performed well as the lithographic surface printing material on which fountain solution can differentiate the image area and nonimage area. The copolymer of MMA and MAA currently synthesized with the proposed ingredients is thus a good polymeric binder and promotes the surface properties for a negative, lithographic plate developable by an aqueous alkaline developer.

References

- Chandross, E.; Reichmanis, E.; Wilkins, C.W., Jr. U.S. Pat. 4,666,820 (1987).
- Andrews, R. J.; Grulke, E. A. In *Polymer Handbook*; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; John Wiley & Sons: New York, 1999, p. II 232, 4th ed.
- Greenley, R. Z. In *Polymer Handbook*; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; John Wiley & Sons: New York, 1999, p. VI 203, 4th ed.
- Kamachi, M.; Yamada, B. In *Polymer Handbook*; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; John Wiley & Sons: New York, 1999, p. II 82, 4th ed.
- Ueda, A.; Nagai, S. In *Polymer Handbook*; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; John Wiley & Sons: New York, 1999, p. II/100, 4th ed.
- Odian, G. *Principles of Polymerization*; John Wiley & Sons, 1991, p. 215, 3rd ed.
- Dufour, P.; Knight, R.E.; Pincus, A.; Skelhore, G. G.; Tanihata, T. *Chemistry and Technology of UV and EB Formulation for Coating, Ink and Paints*, Vol. 4. Formulation. Sita Technology: London, 1991, p. 34.
- Dietliker, K. K. *Chemistry and Technology of UV and EB Formulation for Coating, Ink and Paints*. Vol. 3. Photoinitiators for Free Radical and Cationic Polymerization. Sita Technology: London, 1991, p. 70.
- Fouassier, J. P.; Rabek, S. F. *Radiation Curing in Polymer Science and Technology*, Vol. II. Photoinitiating System. Elsevier Science: London, 1991, p. 245.
- Odian, G. *Principles of Polymerization*; John Wiley & Sons: New York, 1991, p. 263, 3rd ed.