

Synthesis and Photosensitivity of Acryloylmorpholine Copolymers with a Pendant (Meth)acryloyl Group

Atsuyuki Ninomiya,¹ Hikoji Yoshimura²

¹ Resource and Environmental Technology Group, Metropolitan Industrial Technology Research Institute, 3-13-10 Nishigaoka, Kita-ku, Tokyo 115-8586, Japan

² Director, Amco Enterprises Inc., 3-27-401 Shibuya, 4-chome, Shibuya-ku, Tokyo 150, Japan

Received 2 November 2000; accepted 20 March 2002

ABSTRACT: We have developed new photopolymers that have superior waterproof properties and that can easily interact with polyfunctional acrylate compounds, thus serving as hydrophobic photocrosslinking reagents. Acryloylmorpholine monomers whose homopolymers were less moisture absorbing than the usual water-soluble polymers but were still water soluble to a good degree, were copolymerized with other acryloyl monomers. We then introduced the photosensitive (meth)acryloyl group to side chains of the resulting polymers. Among six copolymers examined, the copolymers composed of acryloyl morpholine, hydroxy-

ethyl acrylate, ethyl, or methyl methacrylate, and methacryloyl isocyanate were found to have nicely balanced hydrophilicity and waterproof properties, in addition to good compatibility with hydrophobic photocrosslinking reagents. The composite polymers thus obtained were confirmed to be promising photopolymers usable even in a highly humid environment. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 684–692, 2003

Key words: compatibility; photopolymerization; water-soluble polymers

INTRODUCTION

Many synthetic photopolymers^{1–4} have been developed since Minsk's (Kodak) polyvinylcinnamate.⁵ We have reported on the photosensitivity and other properties of several new photopolymers having the cinnamoyl,⁶ azido,⁷ or acryloyl⁸ group. Recently, we have been studying hydrophilic photopolymers that include the acryloyl group. There are many types of useful hydrophilic photopolymers, including bichromates,⁹ diazos,¹⁰ and stylbazoliums.¹¹ Nevertheless, there are fewer useful hydrophilic photopolymers than hydrophobic photopolymers. We have previously investigated some new water-soluble azido photopolymers¹² in an attempt to determine whether any of them have properties similar to those of the above existing products. To augment our previous investigation, in the present study we selected acryloylmorpholine (AM) as our starting material to develop hydrophilic (water-soluble) acrylate photopolymers (WAPs). Although poly(acryloylmorpholine) (PAM), a homopolymer of AM, is very hydrophilic, a dried PAM film is incohesive, hard, and less moisture absorbing than are the usual water-soluble polymers. Because the common hydrophilic photopolymers are usually very moisture absorbing, offset printing plates

that utilize these photopolymers tend to absorb moisture from the air, making them difficult to use in a highly humid atmosphere, for example, during the Japanese rainy season. It has, therefore, been our intent to develop a new hydrophilic but water-resistant photopolymer utilizing PAM's favorable properties. In addition, we have expected this photopolymer to have an affinity with hydrophobic photocrosslinking reagents, for example, acrylate-type polyfunctional monomers, which are usually incompatible with general hydrophilic photopolymers. When we want to use a water-soluble photopolymer, we must usually add water-soluble or at least hydrophilic photocrosslinking reagents. Although there are such hydrophilic reagents, including bichromate compounds, diazo resins, and others, very few are available. It would, therefore, be profitable to develop a hydrophilic photopolymer that is compatible with the widely available hydrophobic photocrosslinking reagents. In this study, we selected DPCA-60 (a hexaacrylate of a caprolactone-modified dipentaerythritol) as a representative hydrophobic photocrosslinking reagent, and we examined whether it could be mixed with our newly synthesized WAPs. [DPCA did not quite dissolve in 100% water, but it dissolved easily in 100% dioxane (DO) of organic solvent.] It is a basic characteristic of our polymers that their main chain and side chains are composed of an AM copolymer and acryloyl polymers, respectively. We synthesized these polymers in two steps, by first copolymerizing AM with other acryloyl-type monomers and then intro-

Correspondence to: A. Ninomiya (Atsuyuki.Ninomiya@iri.metro.tokyo.jp).

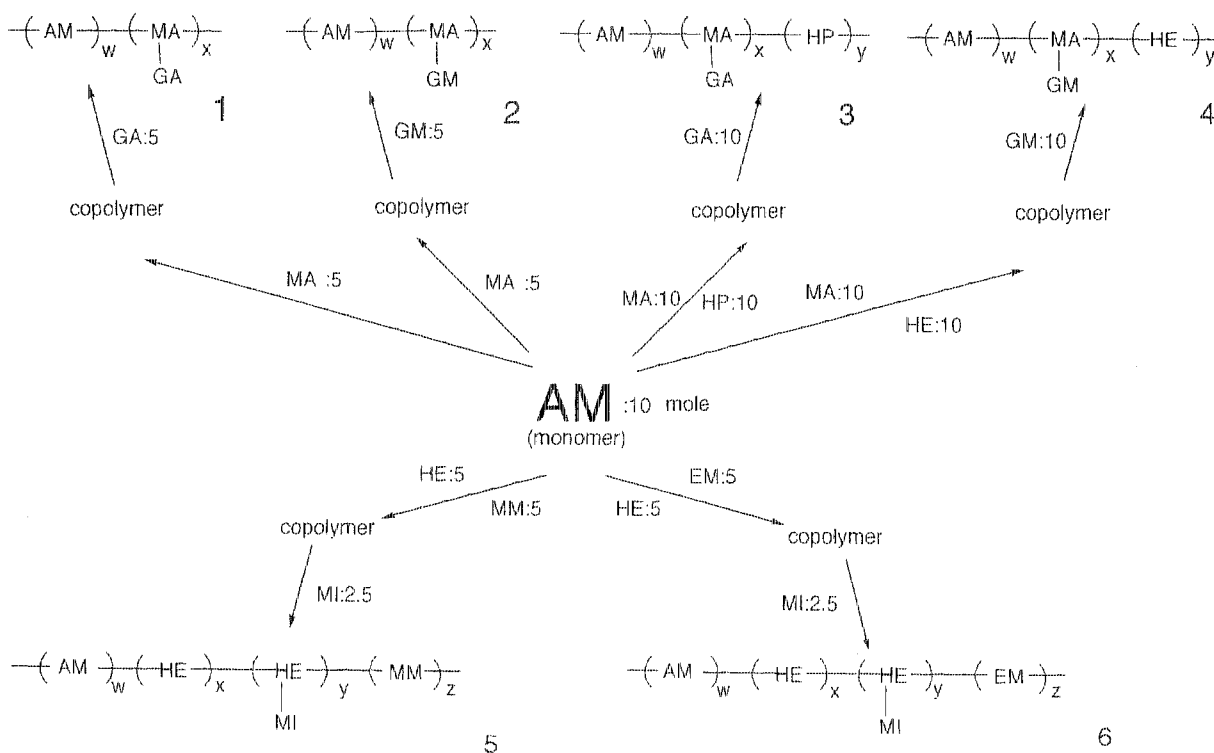


Figure 1 Conceptual figure of the synthetic process and composition (composition: in molar basis) of the newly synthesized photopolymers.

ducing (meth)acryloyl groups to the side chains of the copolymer using glycidyl acrylate (GA), glycidyl methacrylate (GM), or methacryloyl isocyanate (MI). A conceptual representation of the synthetic scheme is given in Figure 1, and the chemical structures of the six newly synthesized polymers are shown in Figure 2. We report here some new results regarding the excellent characteristics of these compounds, especially in relation to the relative degree of water resistance at various humidities and to their photosensitivity as measured by the gray-scale method.

EXPERIMENTAL PROCEDURES

Reagents and analytical instruments

The starting material used was AM available from Kohjin Co., Ltd. (Japan), and the comonomers used were special-grade reagents of 2-hydroxyethyl acrylate (HE), ethyl methacrylate (EM), methyl methacrylate (MM), 2-hydroxypropyl acrylate (HP), methacrylic acid (MA), GA, and GM. We selected comonomers for AM having at least two of the following characteristics: (1) good water solubility; (2) a functional group capable of being introduced to GA, GM, or MI; (3) an affinity for hydrophobic photocrosslinking reagents; (4) anti-skin stimulation.

GA, GM, or MI of a special-grade reagent was introduced to the side chain of the copolymer as a pho-

tosensitive group that was expected to exhibit high photosensitivity. Water was distilled to remove the disinfectant. DO of a special grade was used as received. The following were used without further purification: Azobis-isobutyronitrile (AIBN) and ammonium persulfate (APS) as initiators, α -thioglycerine (TG) as a chain-transfer reagent, ammonium hydroxide (NH_4OH) as a catalyst introducing the photosensitive group, benzoin isopropylether (BIPE) as a photopolymerizing initiator, DPCA as a photocrosslinking reagent, Michler's ketone (MK) as a photosensitizer, hydroquinone (HQ) as a thermal polymerizing inhibitor. We used analytical instruments to determine the structures of the synthesized polymers, including an LC-08 liquid chromatograph (Japan Analytical Industry Co., Ltd.), an LC-6AD high-pressure liquid chromatograph (HPLC) (Shimadzu Co.), an SM-401 ultraviolet (UV) spectroscope (Otsuka Electronics Co., Ltd.), an Ex-400 nuclear magnetic resonance (NMR) spectroscopy (JEOL Ltd.), a System 2000 Fourier transform infrared (FTIR) spectroscopy (Perkin-Elmer Co.), and a JIR-5500 FTIR (JEOL Ltd.). For UV irradiation we used a 501C-250W high-pressure Hg lamp (Ushio Ltd.) whose intensity of illumination was 41.9 mW/cm^2 based on measurement with the UV-M10-S UV Light Measure (an apparatus for measuring the quantity of light; ORC Manufacturing Co. Ltd.).

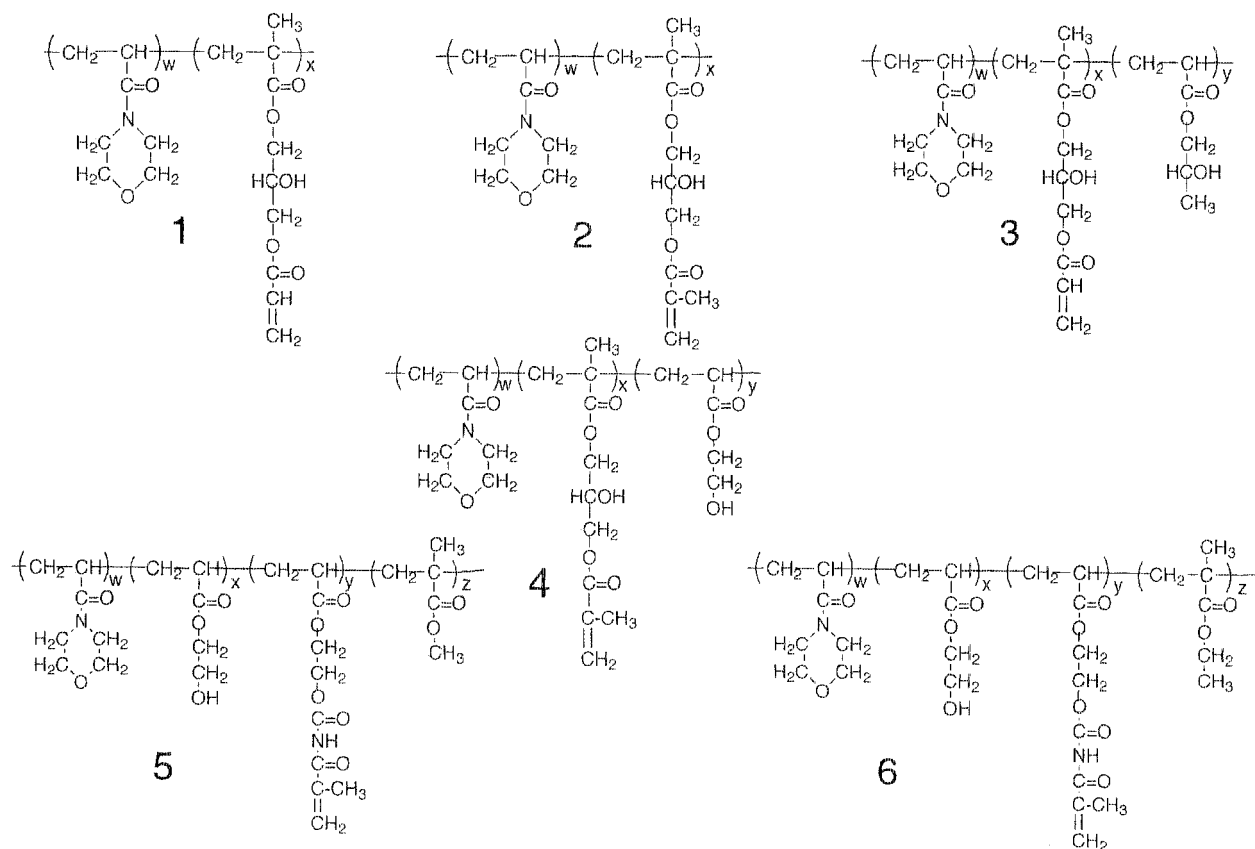


Figure 2 Chemical structures of synthesized photopolymers.

Synthesis of the WAPs

The synthetic processes for 1, 2, 3, 4, 5, and 6, shown in Figure 1, differed slightly from one another. As many parts of the processes were similar, however, we have described the standard process below. We placed the starting materials shown in Table I, into a 300-mL flask with a reflux condenser and thermometer. We then mixed these materials thoroughly at room temperature. Letting N_2 gas flow into the flask soaking in the oil bath, we stirred the mixture for 1 h at 60°C, 2 h at 70°C, 1 h at 90°C, and finally 2 h at the reflux temperature of the solvent (101.4°C). The product was homogeneous and transparent in the flask. Here we stopped

the experiment and removed the solution (~10 g) for analysis. The HPLC spectra revealed that all the monomers had disappeared and been converted into copolymers. The 1H -NMR spectra showed that the composition of the copolymers was almost consistent with the theoretical value. We then, as a second step, placed this solution (50 g), containing the synthesized copolymers, into another 100-mL flask with the other necessary ingredients shown in Table II, and mixed them at room temperature under N_2 atmosphere for 4–5 h to achieve glycidylation or urethanization. Consequently, we obtained a homogeneous and light yellow-brown transparent solution containing the final

TABLE I
The First Step in the Synthesis of the Copolymer of Acryloylmorpholine (g)

	AM	HE	EM	MM	HP	MA	DO	H ₂ O	AIBN	APS	TG
1	45.0	—	—	—	—	15.0	—	240.0	—	0.24	1.2
2	22.5	—	—	—	—	7.5	—	120.0	—	0.12	0.6
3	23.7	—	—	—	21.8	14.5	50.0	240.0	—	0.24	1.2
4	24.7	20.3	—	—	—	15.0	50.0	240.0	—	0.24	1.2
5	28.2	11.6	11.4	—	—	—	51.2	—	1.54	—	2.2
6	33.8	13.9	—	12.0	—	—	59.8	—	1.79	—	2.6

AM, acryloyl morpholine; HE, 2-hydroxyethyl acrylate; EM, ethyl methacrylate; MM, methyl methacrylate; HP, 2-hydroxypropyl acrylate; MA, methacrylic acid; DO, dioxane; AIBN, azobis-isobutyl nitrile; APS, ammonium persulfate; TG, thioglycerine.

TABLE II
Introduction of (Meth) acryloyloxy Group into the Copolymer (the Second Step) (g)

	A*	MI	GA	GM	NH ₄ OH	HQ	DO
1	80.0	—	7.77	—	4.2	0.005	—
2	50.0	—	—	4.15	4.2	0.005	—
3	100.0	—	6.2	—	8.4	0.010	—
4	100.0	—	—	7.0	8.4	0.010	—
5	40.0	2.32	—	—	—	0.005	13.5
6	40.0	2.39	—	—	—	0.005	2.4

A*: Solution containing the copolymer synthesized with the materials in the Table I. MI, methacryloyl isocyanate; GA, glycidyl acrylate; GM, glycidyl methacrylate, NH₄ OH: hydroxy ammonium; HQ, hydroquinone.

six compounds. All the compounds (1–6) were precipitated with excess ethanol (liquid), and the precipitates were then dissolved with the smallest quantity of a mixed good solvent (water 1 : dioxane 1 by weight). We followed this process three times for each compound. We used hydrophobic AIBN as the catalyst for copolymerization in the case of compounds 5 and 6. In another case, we used hydrophilic APS that could be dissolved in water. APS is believed to disturb the introduction of a photoreactive group to the side chain of a copolymer. We were able to check the remaining APS qualitatively based on whether a drop of this solution showed a violet color when placed on KI starch paper. If the color did not change, then the appreciable amount of APS was no longer present due to decomposition. In the synthesis of 5 and 6, the reaction between the OH group of the copolymer's side chain and the isocyanate group of MI was so quick that it could be carried out with no catalyst at room temperature in N₂ atmosphere. In contrast, the synthesis of 1, 2, 3, and 4 was carried out using NH₄OH as a catalyst at reflux temperature in N₂ atmosphere for 4–5 h.

Measurement of moisture absorption

Several different conditions in terms of humidity were set up, and the moisture absorption of each compound was measured in each of these atmospheres to investigate the water resistance of each WAP. With a rotary spin-coater, a flat coat of each WAP (solvent : water–dioxane, 1 : 1) was spread onto a glass plate (30 × 30 × 3 mm) to a thickness of 30 μm. After being kept in a draft at room temperature for several hours, the plates were placed in a dry box at 40°C for a few hours. They were then preserved at 23°C in a desiccator in which the inner humidity was kept constant using the method described below. We measured the weight of each sample before and after preservation, w_1 and w_2 , respectively. Preservation continued until w_2 became constant. The percentage of moisture absorption (k_n , %) was calculated according to eq. (1).

$$k_n(\%) = [(w_2 - w_1)/w_1] \times 100 \quad (1)$$

The humidity in the desiccator was set as follows. A solution (400–1000 g) of sulfonic acid and distilled water was poured into the bottom of a brown desiccator, and the samples were placed on the upper-middle plate (210 mm) of the desiccator apart from the solution at 23°C. By changing the concentration of H₂SO₄ aq. in the range of 20–50 wt %, we obtained various relative humidities. The humidity was measured with a digital hygrometer (CTH-170) inside the desiccator, and the values obtained were 35, 56, 74, and 88%. This experiment was done in the air conditioning room (23°C, humidity: 50%).

Measurement of water solubility

The WAP samples were powdered, and their sizes were made as even as possible to obtain accurate results. After these samples (0.1 g) were accurately weighed, they were placed into a mixed solution (water and dioxane) and kept at rest after being stirred by an ultrasound wave stirrer for 30 s. If the samples remained insoluble, they were stirred using the method described below for 24 h. The WAP sample, solvent (20 mL), and stirring rod (diam. 8 × 20 mm) were set into a flat-bottomed flask (diam. 30 × 200 mm) with reflux condenser that was soaked into the silicone oil in a water bath (BM-41: diam. 210 × 70 mm) with a stirring rod (diam. 8 × 40 mm) on the magnetic stirrer (Mag-Mixer:MD-81; Yamato Scientific Co., Ltd. 300 × 300 × 170 mm). Both stirring rods were rotating at 150 revolutions/min as controlled by the Mag-Mixer. This experiment was done in an air-conditioned room, as described above also. The percentages of water in relation to dioxane were set respectively, to 0, 33, 50, 67, and 100 wt %. We calculated the solubility parameters (δ_m)¹³ of five mixed solvents applying eq. (2) to investigate WAP's solubility in detail and found them to be 10.0, 12.1, 13.5, 15.5, and 24.2 (cal/cm³)^{1/2} in the case of 23°C.

$$\delta_m = \sum(\delta f_i) = \sum(E_i f_i / V_i) \quad (2)$$

where δ_i is the solubility parameter of solvent i ; f_i is the volume fraction of solvent i ; E_i is the molar evap-

oration energy (kcal/g) of solvent i ; and V_i is the molar volume (mL/mol) of solvent i .

After keeping these five solutions at temperatures of 23°C, we investigated the solubility of each compound (sometimes their insoluble portions were weighed using a digital balance). The following five levels of solubility were established:

1. Level 4: the entire quantity was dissolved within 4 h.
2. Level 3: the entire quantity was dissolved within 24 h.
3. Level 2: most of the sample was dissolved (> ~50 wt %), but a small portion of it had swelled or remained insoluble after 24 h.
4. Level 1: a small portion of the sample was dissolved (< ~50 wt %), but most of it remained insoluble or had swelled after 24 h.
5. Level 0: the entire quantity remained insoluble after 24 h.

Measurement of photosensitivity

Keeping in mind the results obtained above, we mixed the photosensitive compounds, including a photocrosslinking reagent and a photosensitizer, with our synthesized photopolymers (1–6). These photopolymer composites were dissolved homogeneously in the mixed solvent using an ultrasound wave stirrer and were coated onto glass plates using the rotary coater. They were then dried for 24 h in a vacuum box at 40°C after drying naturally in a draft. The thickness of the films dried on the glass plates was ~30 μm . All of this experiment was performed in the dark. The dried films were then covered with negative film (Kodak step tablet No. 2) and irradiated by a Hg UV lamp under various conditions. Photosensitive components (1'–6') containing the WAPs were irradiated in air, but the 6' was irradiated in a vacuum or in flowing O_2 gas in addition to in air, in the same manner reported¹³ previously, with a vacuum line and a gas cylinder. After irradiation, the films were developed in tap water for 1 min and then rinsed in methanol for 2 min. After the films dried, their photosensitivity was measured by determining where the developed images began to appear under the step tablet.

RESULTS AND DISCUSSION

Structural analysis of synthesized WAPs

The peak positions of the newly synthesized compounds 1, 2, 3, 4, 5, and 6 were ascertained by IR and NMR spectra. The NMR spectra of 6(WAP) were shown in Figure 3 as representative results for each of the six.

For reference, we show them of PAM by the numerical values measured as follows.

PAM

$^1\text{H-NMR}$ δ = 3.90–3.30 (broad, CH_2 ; morpholine group), 2.80–2.55 (CH; main chain); δ = 1.90–1.55 (CH_2 ; main chain); $^{13}\text{C-NMR}$ δ = 174.8, 67.2, 46.7, 43.2, 36.8, 35.3; IR (neat) 2959, 2911, 2849, 1640, 1631, 1461, 1440, 1359, 1300, 1267, 1234, 1113, 1068, 1031, 871, 842, 573 cm^{-1} .

The composition of the copolymers shown in Figures 1 and 2 can be verified by calculating the proton integration of the NMR spectra; accordingly, the compositions of the newly synthesized WAPs 1–6 are shown in Table III. As shown, we were actually able to obtain two-component copolymers (1 and 2), three-component copolymers (3 and 4), and four-component copolymers (5 and 6) with exactly the same compositions as the charged ones. The yields for 5 and 6 were somewhat better than those for the other compounds, possibly because the quantity of solvent required for the synthesis of 5 and 6 was less than that needed for the other compounds, due to the good solubility of the starting materials. Our results also show that 5 and 6 were more sensitive to the quality of the solvent used in the synthesis. As shown in Table IV, several physical values of the WAPs (1–6) were almost the same as those of PAM, including the average molecular weight (M_w), the absorption maximum (λ_{max}), and the estimated molecular absorption coefficient (ϵ_{max}) of the UV spectra.

Moisture absorption

The degrees of moisture absorption of 1–6 are shown in Figures 4 and 5. The moisture absorption of three well-known water-soluble polymers was also measured under the same conditions. These polymers were poly(vinylalcohol) (PVA, polymerization degree: ~500, saponification degree: ~85%) and poly(vinylpyrrolidone) (PVP, molecular weight: ~160,000), as commonly used water-soluble polymers, and poly(sodium acrylate) (PSA, polymerization degree: 2700–7500), as one of the most water-soluble polymers. The data for copolymers 1 and 2 showed that replacement of GA with GM provided negligible change in moisture absorption. A comparison of the data for copolymers 1–4 indicated that incorporation of HP or HE in the AM, corresponding to copolymers 3 and 4, caused an appreciable increase in moisture absorption. Figures 4 and 5 also revealed that, if a comonomer, MM or EM, was added to give hydrophobicity to the copolymers, the waterproof property remarkably improved, as shown by the plots for copolymers 5 and 6. In copolymers 5 and 6, MI was used as a reagent to introduce acryloyl groups onto side chains, although

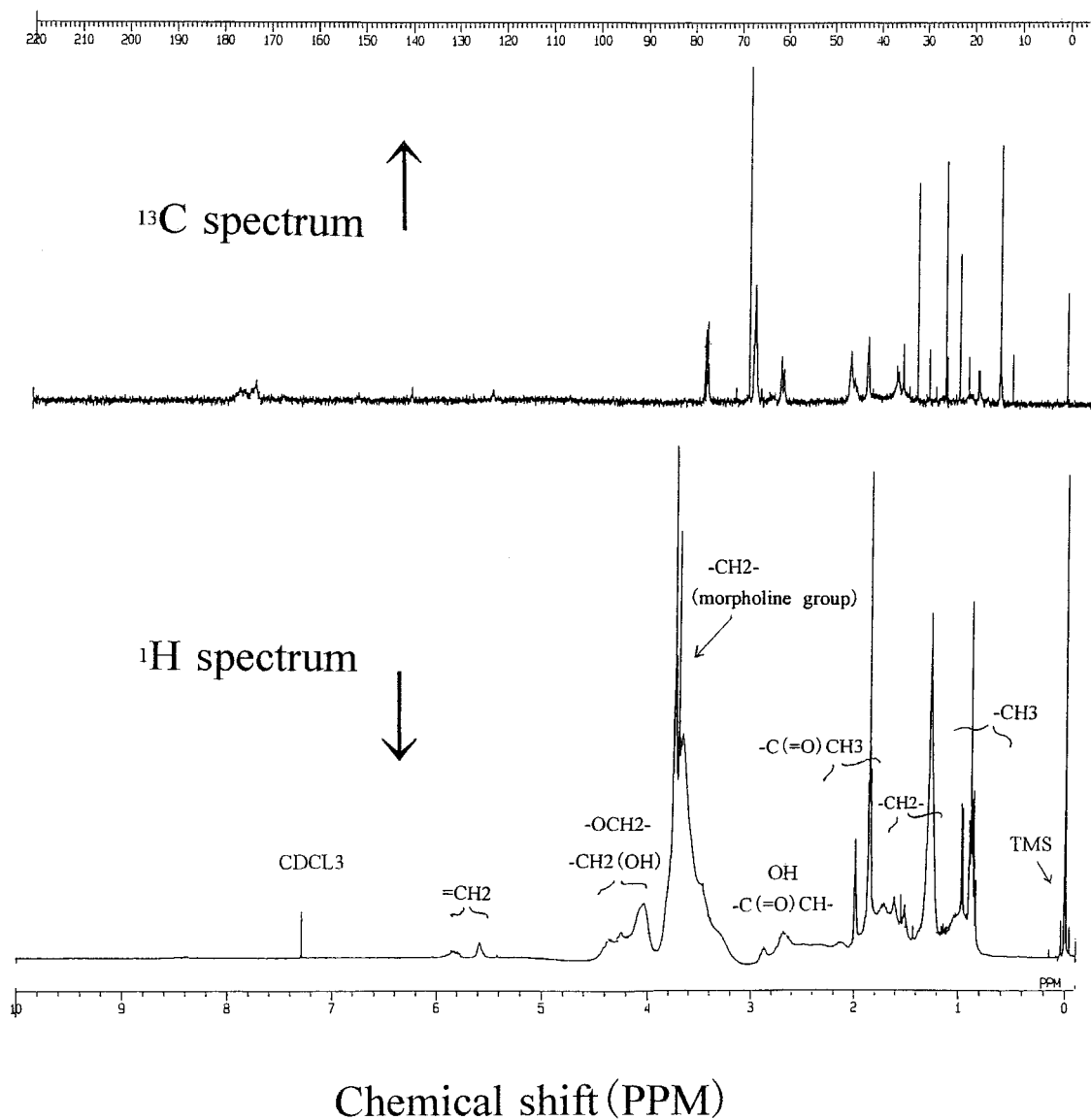


Figure 3 The NMR spectra of 6 (WAP).

GA or GM was used in copolymers 1–4 for the same purpose. The superiority of copolymers 5 and 6 over other copolymers in terms of their waterproof property might be partially attributed to the difference in the acryloyl group-introducing reagents. As shown in Figures 4 and 5, the degrees of moisture absorption for compounds 5 and 6 were smaller than that for PVA,

while those of compounds 3 and 4 were larger. As the curve for PAM almost overlaps with that of PVA, the degrees of moisture absorption of the two seem to be very similar. PVP and PSA, however, showed higher degrees of moisture absorption than did any of the newly synthesized 1–6 polymers. We concluded,

TABLE III
The Experimental Values of Polymer Composition

	w	x	y	z
1	0.64	0.36		
2	0.64	0.36		
3	0.33	0.33	0.33	
4	0.33	0.33	0.33	
5	0.50	0.13	0.13	0.25
6	0.50	0.13	0.13	0.25

TABLE IV
Characteristics of Synthesized 1–6

	Yield (%)	$M_n (\times 10^5)$	λ_{\max} (nm)	ϵ_{\max}
1	45.4	1.79	237	46.2
2	48.9	1.78	237	39.0
3	58.2	1.39	236	37.3
4	42.3	1.65	236	21.3
5	88.5	1.76	236	26.8
6	84.1	1.94	236	30.9
PAM	91.4	1.71	239	31.8

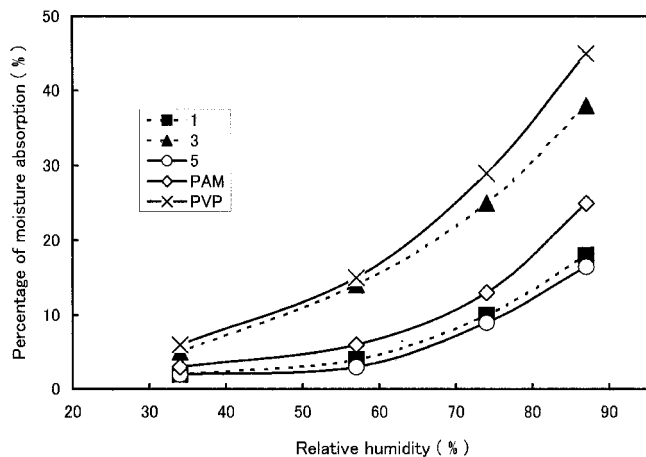


Figure 4 Relation between relative humidity and percentage of moisture absorption of various polymers.

therefore, that 1–6 are more waterproof than PVP and PSA, in the order of 5,6 > 1,2 > 3,4. In addition, 5 and 6 were found to be more waterproof than the copolymers whose fraction (w) of acryloylmorpholine was 0.9 in the structures of 1 and 2 (Fig. 1).

Water solubility

Figures 6 and 7 show the samples' degrees of water solubility. Samples with similar chemical structures showed similar degrees of solubility in the solvents. In combinations of 1 and 2, 3 and 4, and 5 and 6, similar solubilities were observed in the solvents composed of water and 1,4-dioxane in various ratios. Only 5 and 6 could be dissolved to 100% dioxane at Level 4, and any other samples either could not be dissolved or dissolved at most to Level 1. We can easily predict that the larger the percentage of AM in a copolymer, the less soluble in dioxane the copolymer will be. This is because PAM cannot be dissolved in any solvent other than water or dimethylformamide (DMF). An inverse

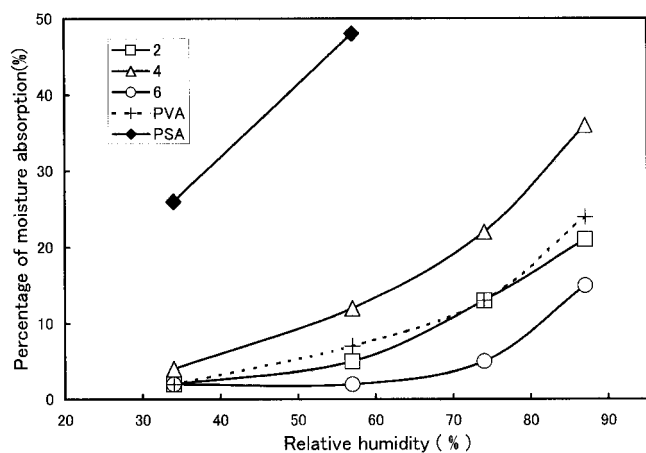


Figure 5 Relation between relative humidity and percentage of moisture absorption of various polymers.

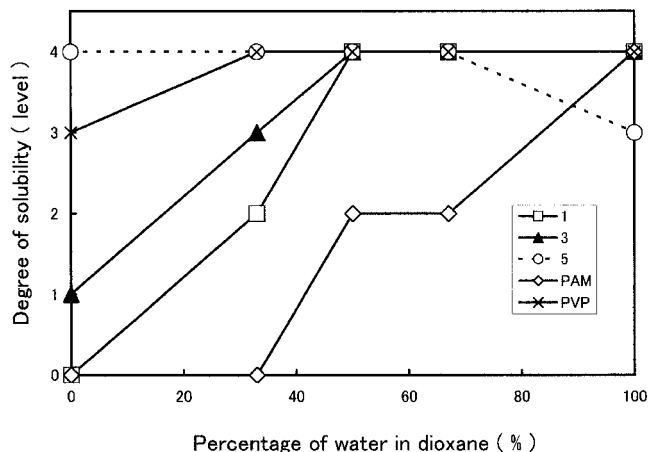


Figure 6 Relation between percentage of water in dioxane and degree of solubility of various polymers at 23°C. [The figures in the parentheses show the solubility parameter: (cal/cm³)^{1/2}.]

result was obtained for 3 and 4, however, showing poorer solubility in 100% dioxane than that of 5 and 6, although the former copolymerized with AM at a smaller ratio than the latter. We, therefore, suggest that 3 and 4 possess both hydrophilic and nonhydrophobic groups in their comonomer portion, whereas 5 and 6 possess hydrophobic groups. Namely, 3 and 4 possess more of the OH group than 5 and 6 do. We believe that this explains why 5 and 6 show poorer solubility in 100% water than do 3 and 4. All samples other than 5 and 6 dissolved easily in pure water at Level 4, but PVA (except PSA) showed the least solubility when water was used as the cosolvent with dioxane. The other highly water-soluble PSA did not dissolve in the mixed solvent, even in that containing only 1/3 dioxane. Although PVA showed a higher solubility in the mixed solvent than PSA did, it was

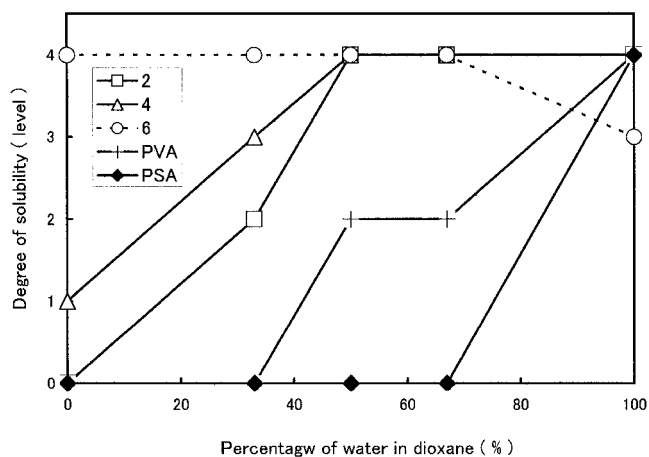


Figure 7 Relation between percentage of water in dioxane and degree of solubility of various polymers at 23°C. [The figures in the parentheses show the solubility parameter: (cal/cm³)^{1/2}.]

TABLE V
Photosensitive Compounds Using 1-6 (g)

	WAP (1 ~ 6)	DPCA	BIPE	MK	PVP	AM	H ₂ O	DO	DMF
1' & 2'	0.4	0.30	0.06	0.002	0.4	0.2	3.0	3.0	1.0
3' & 4'	0.4	0.30	0.06	0.002	0.4	0.2	2.0	2.0	1.0
5' & 6'	1.0	0.30	0.06	0.002	—	—	—	5, 0	—

WAP (1-6), water-soluble acrylate photopolymer; DPCA, hexaacrylate of caprolactone modified dipentaerythrytol; BIPE, benzoin isopropylether; MK, michler's ketone; PVP, polyvinylpyrrolidone; DMF, dimethylformamide.

less hydrophobic than 1-6. PVP, however, was found to be a convenient polymer, having the double function of hydrophilicity and hydrophobicity as related to solubility. This is one reason why PVP is often used as an additive in photopolymer compounds in printing. In the present experiment, it was found that 1'-6' (photopolymer compounds) are all hydrophilic, and that 1'-4' are especially soluble in water. Of course, in the case of a thin film ($\sim 30 \mu\text{m}$), 5' or 6' could easily be developed with only tap water. Consequently, the order of water solubility among the WAPs appears to be 1, 2, 3, 4 > 5, 6, and the order of solubility in the organic solvent dioxane is 5, 6 > 3, 4 > 1, 2. This solution being not regular¹⁴ as mentioned by Hildebrand,¹⁵ we cannot discuss the solubility parameter theoretically, but we can say that with the solubility parameter of water being $24.2 (\text{cal}/\text{cm}^3)^{1/2} (23^\circ\text{C})$, those of 5 and 6 are close to that of dioxane (10.0) and those of 1-4 are between that of 5 or 6 and 24.2. Based on our investigation, we conclude that the solubility parameter would be affected by the percentage of AM in a copolymer and a hydrophilicity or hydrophobicity in the comonomer portion. We also examined the solubility of 5 and 6 at various temperatures, i.e., 5, 20, 35, etc. (data not shown) in 100% water and confirmed that the higher the temperature, the higher the solubility. For example, 5 and 6 exhibited Level 4 solubility in 100% water at 35°C.

Photosensitivity

The strong hydrophobic photocrosslinking reagent DPCA was not miscible with hydrophilic polymers in general. When 1-6 were mixed with DPCA and solvent to measure the relative photosensitivity according to the gray-scale method, however, separation did not occur, at first. We found, however, that, after drying, their films did show some slight separation, except with 5 and 6. Therefore, as in the usual method, PVP was added as a binder to each WAP, except in the case of 5 and 6; in addition, AM was added to stop the decrease in photosensitivity, and dimethylformamide (DMF) was added to solubilize these mixtures. The percentages of these additives were determined in the usual way. As a result, photopolymer compounds 1'-6' were prepared as shown in Table V. When a photopolymer compound is used in a photomechanical

process, it must generally be insolubilized at least at the fourth step (transmission degree: ~ 0.32) of the gray-scale step tablet No. 2 (Kodak) with a 3-min UV exposure, although the time required to insolubilize is changed by the thickness of the film coating. The film thickness of $\sim 30 \mu\text{m}$ used in this experiment is suitable for screen-printing. The result is shown in Figure 8 and Figure 9. It is due to the similar chemical structures of the WAPs that the combinations of 1' and 2', 3' and 4', and 5' and 6' showed the same photosensitivity. We investigated the effect of oxygen only for 6' irradiated in the various atmospheres, and it was consequently found that atmosphere affected photosensitivity in the order of vacuum > air > oxygen (Fig. 9). Consequently, we were able to confirm that 6' is an acrylate-type photopolymer that is affected by oxygen's light-quenching properties. The resolving power in this experiment was worsened in proportion to the oxygen concentrations in the atmosphere; consequently, when a sample was irradiated in a 100% oxygen atmosphere, the developed images frequently could not be easily distinguished. We hypothesize that the oxygen coupled with 6', and we are now investigating the resulting structure. As an example, the absolute photosensitivity of 6' was calculated by the following equation, taking into consideration that an illumination quality (I) of 1 min's irradiation was found to be $2.43 \text{ J}/\text{cm}^2$ by the UV light measure, and the film of 6' was insolubilized under the fourth step

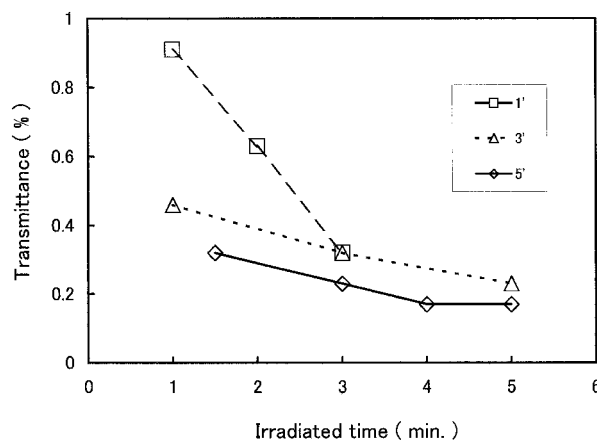


Figure 8 Relation between irradiated time in air and transmittance of step tablet where sample began to insolubilize.

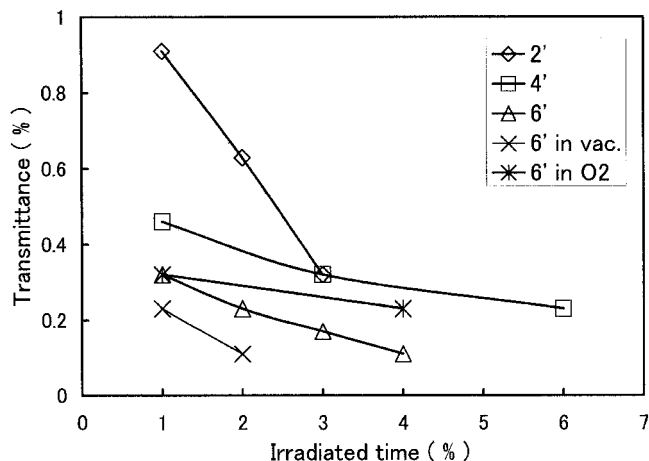


Figure 9 Relation between irradiated time in air and transmittance of step tablet where sample began to insolubilize.

(transmission degree: $T \sim 0.32$) of the Kodak step tablet No. 2.

$$S_0 \leq I \times T \quad (3)$$

Therefore, 6' might at least have better absolute photosensitivity (S_0) above 0.78 J/cm^2 . This level of photosensitivity is satisfactory considering that the thickness of the samples being measured was $\sim 30 \mu\text{m}$, which is thick enough for general use in the printing field. Photocrosslinking images were not obtained when PVA, PVP, or PEG having the same components as 1'–4' was used, as shown in Table V. When the AM fraction in the polymer was too large ($> \sim 2/3$) or too small ($< \sim 1/3$), we found that an adequate photocrosslinking image could not be obtained due to bad homogeneity. From the results described above, however, we were able to conclude that the degree of photosensitivity for 1'–6' was 5', 6' $>$ 3', 4' $>$ 1', 2'. When we consider these results and the affinities for DPCA, we believe that the practical photosensitivity for 1–6 is the same order as that just mentioned, 5, 6 $>$ 3, 4 $>$ 1, 2.

CONCLUSIONS

Photopolymers 1–6 were newly synthesized in order to develop acrylate-type photopolymers possessing greater waterproof properties than the usual water-soluble polymers, a level of hydrophilicity that allows them to be developed by water, and a degree of hydrophobicity sufficient to give them an affinity with DPCA. We investigated those properties of these new photopolymers, and the following results were obtained.

1. Waterproof property (antimoisture absorption) was in the order of 5, 6 $>$ 1, 2 $>$ 3, 4. This result

means that increases of a fraction of AM in the copolymer increased this property, but the existence of a hydrophobic comonomer (MM, etc.) greatly affected the waterproof property.

2. Hydrophilicity (water solubility) was in the order of 1, 2, 3, 4 $>$ 5, 6, and the degree of solubility in 100% dioxane was in the order of 5, 6 $>$ 3, 4 $>$ 1, 2 at 23°C . We might be able to say that the solubility parameters of 5 and 6 are close to that of dioxane [$10.0 \text{ (cal/cm}^3)^{1/2}$] and those of 1–4 are between those of 5 or 6 and water [$24.2 \text{ (cal/cm}^3)^{1/2}$]. The solubility parameter appears to be affected by the percentage of AM in a copolymer and a hydrophilicity or hydrophobicity in the comonomer portion.
3. Photosensitivity was in the order of 5, 6 $>$ 3, 4 $>$ 1, 2. This means that the compatibility (hydrophobicity) of WAPs with DPCA and the solubility (hydrophilicity) of them in the developing process affect photosensitivity delicately and synergistically.

Based on all of the results described above, we found that 5 and 6 are the most suitable photopolymers for our purposes.

The authors are greatly indebted to Professor, Dr. Haruma Kawaguchi of Keio University for his helpful discussion and suggestions.

References

1. Aikawa, S.; Tasaka, S.; Zhang, X.; Inagaki, N. *J Appl Polym Sci* 2000, 76, 1741.
2. Chappelow, C. C.; Pinzino, C. S.; Jeang, L.; Harris, C. D.; Holder, A. J.; Eick, J. D. *J Appl Polym Sci* 2000, 76, 1715.
3. Feng, K.; Tsushima, M.; Matsumoto, T.; Kurosaki, T. *J Polym Sci Part A Polym Chem* 1998, 36, 685.
4. Itoh, H.; Kameyama, A.; Nishikubo, T. *J Polym Sci Part A Polym Chem* 1997, 35, 3217.
5. Minsk, L. M.; Smith, J. G.; Van Deusen, W. P.; Wright, J. F. *J Appl Polym Sci* 1959, 2, 302.
6. Ninomiya, A.; Nishiwaki, T.; Anda, K. *Bull Jpn Soc Print Sci Technol (in Japanese)* 1983, 2, 47.
7. Ninomiya, A.; Nishiwaki, T.; Anda, K.; Yokozawa, Y. *Bull Jpn Soc Print Sci Technol (in Japanese)* 1987, 4, 326.
8. Ninomiya, A.; Sindo, Y. *Tokyo-toritu Kogyo Gijutu Senta Kenkyu Hokoku (in Japanese)* 1996, 25, 87.
9. Duncalf, B.; Dunn, A. S. *J Appl Polym Sci* 1964, 8, 1763.
10. Huisgen, R. *Angew Chem* 1948, 67, 328.
11. Borden, D. G.; Williams, J. L. R. *Macromol Chem* 1977, 178, 3035.
12. Ninomiya, A.; Usui, M. *Bull Jpn Soc Print Sci Technol (in Japanese)* 1991, 4, 270.
13. Ninomiya, A.; Nishiwaki, T.; Anda, K.; Shinoda, T. *Bull Jpn Soc Print Sci Tech (in Japanese)* 1978, 2, 47.
14. Hildebrand, J. H.; Scott, R. L. *Regular Solutions*; Prentice-Hall: Englewood Cliffs, NJ, 1962.
15. Hildebrand, J. H.; Scott, R. L. *The Solubility of Non-Electrolyte*; Reinhold: New York, 1950.