Positive-Working Photoresists Containing Tetrahydropyranyl Group as an Acid-Labile Polymer for Rainbow Holograms

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Various molecular weights of acid-labile polymers of tetrahydropyranyl methacrylate/3(4)-methylstyrene were evaluated as visible light sensitive positive-type photoresists for their application on rainbow holograms. The experimental results show that diffraction efficiency, S/N ratio and contrast of a reconstructed image from a rainbow hologram were influenced by the average molecular weight (Mn); the copolymer with Mn = $5 - 8 \times 10^4$ gave better results and with a minimum exposure energy of 3.2 mJ/cm^2 using 488 nm laser light. It is possible to be applied to the production of the stamper for embossed holograms by means of using this copolymer.

Journal of Imaging Science and Technology, 44: 74–79 (2000)

Introduction

Holograms enable reproduction of three-dimensional stereoscopic images, and hence have often been used in covers of books, magazines or the like, pop art display, gifts etc., on account of their attractive designability and decorative effect. In particular, embossed type holograms have been used widely for many purposes in recent years because large amount of embossed holograms having durability can be produced inexpensively.[1] Embossed holograms have also been applied in the field of security for such items as credit cards and valuable securities.[2] Among various recording materials, positive-working photoresists are used to fabricate the original relief pattern for the embossed hologram because of their excellent resolution—above 1,000 lines/mm. However, conventional photoresists to record the surface relief recording are of low sensitivity for laser exposure in the visible region, for example the exposure of Shipley MICROPOSIT-1350, requires ca. 600 mJ/cm^2 when an Ar^+ laser emitting 488 nm light is used which demands a very high optical stabilization during the hologram recording.[3] Therefore development of high sensitive materials in the visible region is strongly desired.

A great deal of effort has been made on the improvement of visible light sensitive polymers that belong exclusively to a negative-working type[4] for holography[5] because it is possible to obtain highly sensitive materials that start a chain reaction such as radical polymerization. However, positive-working photoresists are of greater advantage than negative types in terms of the resolution and grating shape (sinusoidal).[6] One of our previous articles deals with the effectiveness of a sensitizer for the decomposition of iodonium salt which generates not only free radicals but also a Brϕnsted acid.[7] This photoacid-generating system has been applied to visible light sensitive positive-working photoresists.[8]

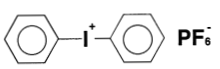
In microlithography applications, tetrahydropyranyl (THP) protecting groups have been studied for chemically amplified resist systems since the 1990s because THP esters and ethers are easily prepared and readily cleaved with heating in the presence of acids.[9] The preparation and deesterification of some polymers substituted with THP ester residues were studied by Kearns and co-workers.[10] Taylar and co-workers have studied the benzyl methacrylate-THP methacrylate copolymer.[11] The THP ether of poly(*p*-hydroxystyrene) was investigated by Sculegel, Hesp and co-workers.[12] The introduction of the THP-group in photosensitive polyimides was applied by Omote and co-workers.[13] Moreover, the introduction of THP-group in photoresists for ArF or KrF eximer laser applications was applied in recent years.[14] Note that these studies aim at developing photoresists sensitive to deep UV light. Moreover, the γ–value of these materials is rising and may generate non-linear noise with usual development conditions which does not affect the result because they are designed for semiconductor manufacturing.

Our previous article revealed that the photogenerated acid acts as catalyst of the thermal cleavage of THP ester group of poly(methacylates) to afford positive-working photoresists.[15] The polymers sensitized with a combination of diphenyliodonium (DPI) hexafluorophosphate (1) with 2-benzoyl-3-(*p*-dimethylaminophenyl)-2-propenenitrile (2) offered the production of

Original manuscript received April 5, 1999

Color plates 11 through 15 are printed in color in the color plate section of this issue, pages 90 and 91.

holographic gratings and rainbow holograms whose maximum diffraction efficiency is ca. 20% for 488 nm light.



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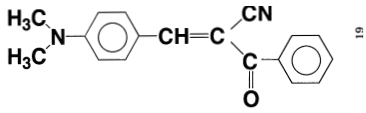

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The exposure energy which gives the maximum diffraction efficiency is approximately 4 mJ/cm^2 while the spatial frequency is 1,200 lines/mm. Through an improved development procedure, we corrected the nonlinear dissolution behavior of the exposed photoresist that caused scattering in the data of holographic characteristics and inhomogeneous development.[16] However, it was impossible to make a good hologram with an aqueous NaOH developer because there was a rough surface aspect in the hologram and a lowering in the diffraction efficiency when a polymer having about 20,000 of number-average molecular weight (Mn) was used as an acid-labile polymer. Thus, it is necessary to investigate the effect of average molecular weight of the polymer on the holographic characteristics of this photoresist system for improving the image quality of rainbow holograms. It is said that the photoresists for preparing the rainbow holograms must have S/N ratio and contrast exceeding more than ca.10, respectively, according to Ref. 17.

This article approaches improvements of S/N ratio and contrast for rainbow holograms and for this purpose the acid-labile polymers of various average molecular weights were prepared and studied. Using the best results, a nickel stamper was prepared from a rainbow hologram made with this photoresist system and applied to the production of embossed holograms.

Experimental

Materials. Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. DPI hexaflorophosphate (1), 2-benzoyl-3-(*p*-dimethylaminophenyl)-2-propenenitrile (2), tetrahydropyranyl methacrylate (THPMA) was prepared by procedures from our preceding article.[15] Commercial 3(4)-methylstyrene (Mst) was distilled under vacuum before use. Aqueous sodium hydroxide (NaOH) developer, obtained from Shipley MICROPOSIT-303A, was used as a developer diluted with ion exchanged water.

Polymerization. Radical polymerization of the methacrylates was carried out in benzene at 60°C with AIBN as the initiator. The mole ratios of Mst as a comonomer of copolymerization were 20% for THPMA monomer. The formed polymer was precipitated in hexane and dried.

Physical Characteristics Measurements. Molecular weights of synthetic copolymers were determined by gel permeation chromatography on a Shimadzu, LC-5A GPC, equipped with shimpack A-805 + A-803 column using THF and polystyrene calibration. The contents of Mst in the copolymers were determined by elemental analyses on a YANACO, CHN corder MT-5.

Preparation of Photosensitive Layer. A solution of 15 wt% the acid-labile polymer in diethylene glycol dimethyl ether (diglyme) was added to DPI salt (1) and the sensitized dye (2). The weight ratio of polymer/DPI salt/sensitizer was 10/2/1. The solution was coated on an anode oxidized aluminium plate (using sensitivity determination) or surface treated glass plate[15] of 5 × 5 inch square size (using preparation of rainbow holograms) with a spin-coater and dried at 80°C for 10 min. This gives about 1 μm thickness layer.

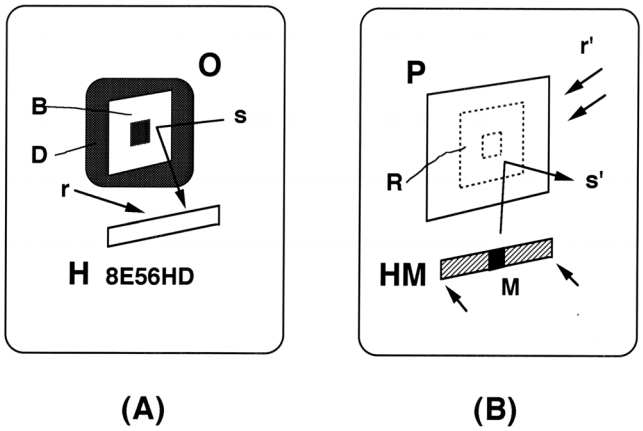


Figure 1. Recording setup for making (A) a Fresnel hologram and (B) a rainbow hologram (**O**, white painted object (**B**, bright area; **D**, dark area) ; **H**, silver halide dry plate; **M**, mask; **P**, photoresist plate; **HM**, master hologram; **s** and **s'**, signal beams; **r** and **r'**, reference beams; **R**, reconstructed image of master hologram).

Sensitivity Determination. The sensitivity was measured by the gray scale method with the use of a step tablet (Kodak 2A), using an expanded beam at 488 nm from an Ar$^+$ laser, a Spectra Physics 2020. The exposed plate was subjected to baking at 110°C for 10 min before development.

Recording of Rainbow Holograms. Figure 1 shows the recording setup a rainbow hologram. The rainbow holograms in the experiment were recorded using the so-called two-step method.[18] In the first step, a Fresnel type master hologram **HM** was recorded on a silver halide dry plate **H** (Agfa 8E56HD) where the dimensions were 1 cm × 10 cm. It should be noted that in the figure, the recorded object shown is the one that is used for the signal to noise (S/N) ratio measurements; it is a painted object with a bright area **B** and a dark area **D**. In the second step, using the image reconstructed from the previously recorded master **HM**, i.e., object beam **s'**, and reference beam **r'**, a rainbow hologram is recorded on a photoresist plate **P** (see Fig. 1). The photoresist plate **P** is located on the reconstructed image **R** path from the master hologram **HM**. The holographic exposure was performed using a Spectra Physics 2030 Ar$^+$ laser emitting 488 nm light. The angle between the object beam **s'** and the reference beam **r'** was set to 35° which means a recording of a hologram with a spatial frequency between 1,000 and 1,300 lines/mm. The exposure range was between 3 and 20 mJ/cm^2 and, after exposure, the photoresist plate was baked at 100°C for 10 min in a saturated moisture atmosphere, wet post-exposure baking (PEB), or at 110°C for 10 min in a dry atmosphere, dry PEB. After PEB, the plate was developed and rinsed with water to obtain the relief type rainbow hologram. A thin metallic film or aluminum was evaporated onto the resist surface of the rainbow hologram as a reflection layer as occasion demands.

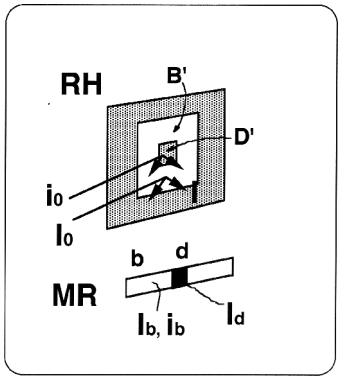


Figure 2. Optical setup for measuring diffraction efficiency [**I/I0**], S/N ratio [**Ib/Id**] and contrast [**Ib/ib**] (**RH**, rainbow hologram (photoresist plate); **MR**, reconstructed image; **B'**, bright area on **RH**; **b**, bright area in **MR**; **D**, dark area on **RH**; **d**, dark area in **MR**].

Evaluation of Rainbow Holograms. A profile of the hologram was observed by atomic force microscopy (AFM) on a SII, SPA-300 system. For the evaluation of the image quality of the rainbow hologram recorded as previously explained,[16] the measurement of the diffraction efficiency, S/N ratio and contrast were performed. For this purpose, the rainbow hologram recorded on a photoresist plate **PH,** is illuminated by the 633 nm emission beam from a He-Ne ion laser, NEC model GLG-5350, in order to measure the light intensity of the conjugated reconstructed image that appeared when the rainbow hologram **PH** was illuminated by the laser beam. In this case the reconstructed image **MR,** is of the same shape of the masked master hologram **MH**. In this article, the diffraction efficiency is defined as the ratio of the intensity **I** of the diffraction light which is collected by two lenses when the laser beam is incident upon the **B'** area of the hologram and intensity **Io** of the incident beam. The S/N ratio is defined as the ratio of the signal and the noise. The signal is defined as the intensity **Ib** measured at point **b** as shown in Fig. 2. Point **b'** is located in the reconstructed mask image **MR** from the **B'** area. The noise is defined as the intensity **Id** measured at point **d**. Point **d** is located between the two apertures of the reconstructed mask image **MR**. The contrast is defined as the ratio of the intensity **Ib** as measured by the point **b** of the reconstructed mask image **MR** and the intensity **ib** as measured **b** of **MR** when the laser beam is incident upon the **D'** area of the hologram.

Preparation of Nickel Stamper. After the gold is evaporated to a thin metallic layer on the photoresist surface of the rainbow hologram to form an electrically conductive layer, the plate was dipped in a metal plating bath which consisted of 45 wt% $Ni(NH_2SO_3)_2$ (Nickel Sulfamate 600, Nikko Metal Plating Co., Ltd.), 0.5 wt% $NiCl_2/6H_2O$ and 3 wt% H_3BO_3 in an aqueous solution. The current density in the bath was set at 40 mA/cm^2. The plate was harvested after 164 h and was washed with ion-exchange water. The metallizing plate obtained was peeled off the glass plate and the remaining resist polymer that remained on the metallizing surface was removed with aqueous alkali and acetone. This gives about 100-150 μm thickness.

Results and Discussion

Polymerization. In general, it is known that the average molecular weight of synthetic polymers in radical polymerization depends on the condition of polymerization, such as amount and varieties of initiator and solvent, and polymerization time.[19] The results of polymerization under various conditions of amount of initiator, the concentration of monomers and polymerization time are shown in Table I.

Solution polymerization was carried out with benzene as a solvent in **Poly. 1-8**. Bulk polymerization was carried out in **Poly. 9-10** for the purpose of obtaining polymers of higher molecular weight. As a result, when the polymerization was carried out in larger amounts of an initiator or smaller amounts of a solvent, the molecular weight for obtaining a polymer become higher. A condition of **Poly. 5** in term of polymerization yield was superior to **Poly. 7** in order to obtain the copolymer having the Mn of about 70,000. When polymerization was allowed to continue in the condition of **Poly. 8**, the Mn of copolymer reached about 140,000. Furthermore, even if the polymerization was carried out on a large scale, the copolymer having respectively similar Mn and the molecular weight distribution (Mn/Mw), can be prepared (**Poly. 4**). The content of Mst in the synthetic copolymers confirmed by elemental analyses, as well as fed monomers, were about 20%.

Sensitivity of Photoresist. The measurement of sensitivity on the results composed of these copolymers containing DPI salt (1) and the sensitizer (2) by means of the gray scale method indicates that an increase in the molecular weight tends to enhance sensitivity shown in Table I. It is considered that the difference in sensitiv-

TABLE I. Acid-labile Copolymer

Poly. No.	Feed in g (wt%)* AIBN	Bz	Reaction time (hr)	Yield (%)	Mn × 10^4	Mw/Mn	Mst content(%)†	Sensitivity‡
1	0.82(3.5)	58.7	9	95	1.39	1.91	16.3	1
2	0.47(2.0)	23.5	9	77	3.69	1.79	20.2	1.4
3	0.24(1.0)	35.2	16	92	5.01	1.89	22.3	2
4	1.1(1.0)	164	16	84	5.47	2.33	—	—
5	0.24(1.0)	23.5	16	96	7.19	2.31	20.0	—
6	0.19(1.0)	23.5	16	98	8.88	1.61	17.5	—
7	0.12(0.8)	23.5	9	35	7.65	1.63	22.0	2
8	0.12(0.5)	23.5	16	93	14.52	1.73	16.1	++§
9	0.59(2.5)	0	4	86	5.98	3.08	18.0	—
10	0.24(1.0)	0	4	66	14.57	2.96	18.8	—

* Fed monomers, except Poly.4; TMPTA / Mst = 20.00g / 3.47g, Poly.4; 95.00g /14.49g, wt%; based on the fed monomers.
† Determined by CHN element analyses.
‡ Determined by a gray-scale method.
§ It was impossible to spin-coat because of high viscosity of this polymer solution.

TABLE II. Evaluation Results under R/S = 4

No.	PEB Condition*	Exposure energy (mJ/cm²)	Diffraction	S/N efficiency (%)	Contrast ratio
		9.0	14.00	1.85	12.69
Poly. 1	dry	7.0	7.15	1.94	15.47
		5.0	6.50	2.18	18.95
		5.0	5.45	2.43	6.42
Poly. 1	wet	4.0	10.30	2.23	4.16
		3.0	8.80	2.07	3.98
		12.0	18.75	16.00	14.63
Poly. 7	dry	9.0	15.50	9.60	6.57
		7.0	16.55	10.87	9.18
		5.0	14.50	6.76	8.69
		5.0	18.10	5.02	5.62
Poly. 7	wet	4.0	15.90	5.77	4.65
		3.0	20.05	4.28	4.67

* dry; 110°C/10 min, wet; Moisture saturated atmosphere 100°C/10 min.

TABLE III Evaluation Results under R/S = 6

No.	PEB condition	Exposure energy (mJ/cm²)	Diffraction efficiency	S/N (%)	Contrast ratio
		20.0	3.02	7.16	33.21
Poly. 3	dry	18.0	3.55	4.80	95.66
		16.0	5.95	8.17	24.87
		14.0	5.36	1.33	36.33
		8.0	4.61	21.63	46.96
Poly. 3	wet	6.0	4.81	17.56	43.02
		4.2	11.50	10.87	20.48
		3.2	6.68	4.73	15.92
		20.0	3.62	4.06	40.25
Poly. 6	dry	16.0	8.18	1.41	160.14
		12.0	2.59	1.46	55.07
		8.0	2.49	8.58	40.95
Poly. 6	wet	6.0	2.14	2.14	12.76
		4.0	5.40	1.67	19.90
		3.2	6.45	1.38	5.59

ity is attributable to the quantity of the carboxylic group in a molecular of the polymer after PEB.

Preparation and Evaluation of Rainbow Holograms. As previously explained, the rainbow holograms of a white painted object **O** were prepared by the 2 step method.[18] The spatial frequency was about 1,260 lines/mm. During recording, the reference-to-signal (R/S) ratio was set between 4 and 8, adjusting the exposure time to optimize the recording conditions of the hologram. After exposure, the photoresist plate was baked at 110°C to accelerate the cleavage of THP group under dry atmosphere conditions—dry PEB, and under moisture-saturated conditions—wet PEB. We examined if the average molecular weight and the PEB conditions have an influence on the holographic characteristics for various the R/S ratios. Table II summarizes the evaluation of rainbow holograms made using **Poly. 1** and **Poly. 7** obtained under the R/S = 4.

The diffraction efficiency and S/N ratio of hologram using **Poly. 7** (Mn; 76,500) were superior to that using **Poly. 1** (Mn; 13,900), that is, the polymer having about 70,000 of Mn gives higher diffraction efficiency and S/N ratio than those having about 10,000 of Mn. By contrast, dry PEB provided better contrast for both polymers although the contrast was lower in **Poly. 1**. The exposure energy which gives the maximum diffraction efficiency under dry PEB was about 3 times lower than for wet PEB. Regarding S/N ratio, wet PEB gives a more noisy image than dry PEB as seen in Table II. The photographs of the holograms made with **Poly. 1** and **Poly. 7** under wet PEB are shown in Plates 11 and 12, respectively (p. 91).

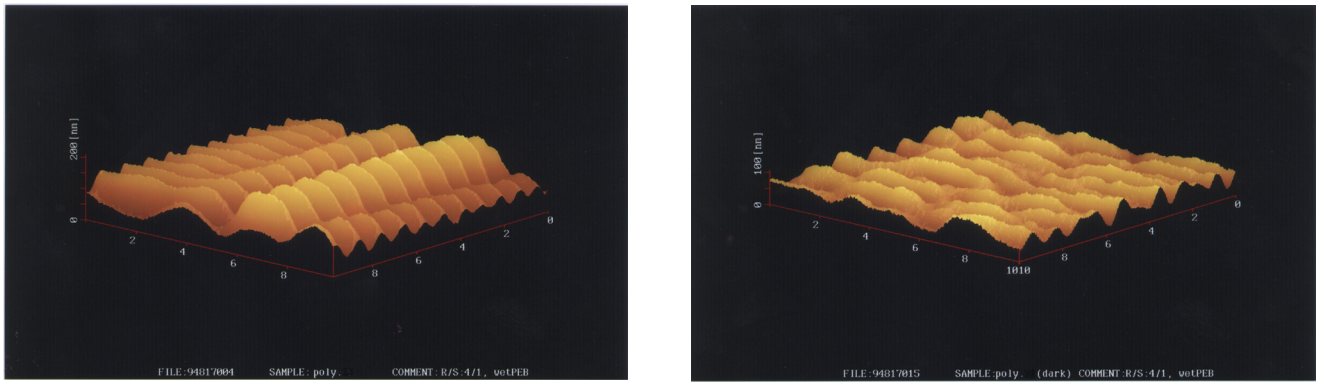
As can be noted in these images, there is a dark area in the hologram made from **Poly. 1** that is observed because of an irregular reflection owing to the roughness of the surface. However, this phenomenon was not observed in **Poly. 7**. It is consider that the dark area, which was not essentially diffracting, was bright, that is, it was impossible to form the relief patterns adequately according to the light interference because hydrolysis of the ester groups in polymer was accelerated with moisture atmosphere and heating and noisy patterns originated. Regarding the S/N ratio, it was lower in **Poly. 1** or **Poly. 7** under wet PEB because the relief surface of the hologram became rough with the strong development conditions achieved under wet PEB and an alkaline developer.

In general, the S/N ratios tend to increase by increasing the R/S ratio during recording, however it decreases in proportion to the diffraction efficiency.[18] Table III shows the evaluation of rainbow holograms obtained under the R/S = 6 as a function of the exposure energy, for **Poly. 3** and **Poly. 6**.

As can be noticed, the S/N ratio and the contrast for R/S = 6 has a higher value under wet PEB than those when R/S = 4 (Table II) though the diffraction efficiency was slightly lower. Good results were obtained at an exposure of 4.2 mJ/cm² for **Poly. 3**, where about 50,000 of

TABLE IV. Evaluation Results under R/S = 8

No.	PEB condition	Exposure energy (mJ/cm²)	Diffraction Efficiency (%)	S/N ratio	Contrast
		8.0	2.22	10.99	32.36
Poly. 6	wet	6.0	1.58	8.89	36.52
		4.0	5.72	3.24	61.48
		3.2	3.52	3.09	26.43
		8.0	5.13	14.01	23.71
Poly. 5	wet	6.0	5.01	12.28	39.12
		4.2	13.19	13.72	26.62
		3.2	4.75	7.98	30.62
Poly. 3	wet	4.0	16.27	9.31	25.30
		3.2	12.97	6.96	16.00
Poly. 4	wet	4.0	15.34	35.22	28.22
Poly. 9	wet	4.0	0.94	3.22	3.85



(a) (b)

Figure 3. Photographs of AFM image of rainbow hologram made from **Poly. 7** under R/S = 4 with dry PEB; (a) bright area, and (b) dark area.

Mn was used. On the other hand, it was impossible to obtain satisfactory results with any polymers of molecular weight under this value with dry PEB except on the contrast. On dry PEB, the exposed area of a relief hologram could not be relieved because of the weak signal beam (R/S = 6) and dry PEB which has weaker development conditions.

Table IV summaries the evaluation of rainbow holograms treated with wet PEB under R/S = 8.

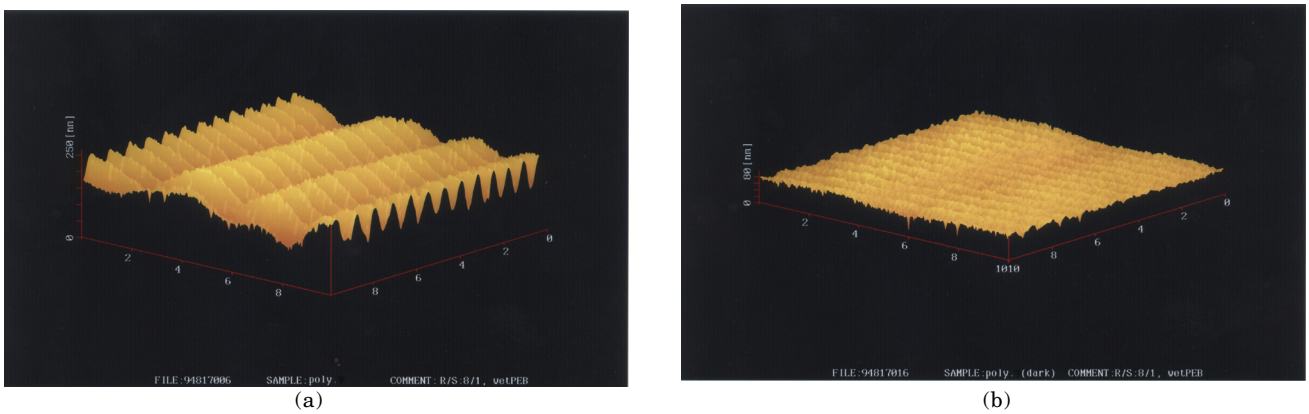
The relationship between the characteristics of making holograms and Mn of the polymers was almost the same as under the R/S = 6; good results were obtained at 4 mJ/cm² using **Poly. 4**. The photograph of this hologram is shown in Plate 13 (p. 92).

Comparing the results using R/S = 8 to 4, the contrast improved—the dark area was not bright. However, it is impossible to obtain a good hologram using wide molecular weight distribution polymer such as synthesized bulk polymerization (**Poly. 9**). Because it was impossible to form the hologram using **Poly. 8** and **Poly. 9**, an experiment concerning **Poly. 10** was not carried out. The AFM images of these holograms are shown in Figs. 3 and 4, respectively.

The bright area **B'** of a rainbow hologram recorded on **Poly. 7** shown in Fig. 3(a), possessed 1,031 grooves in 1 mm, and that recorded on **Poly. 5** and shown in Fig. 4(a) has 1,270 grooves. The depth of both grooves were about 140 nm at the deepest position for R/S = 4 and about 120 nm in R/S = 8. As the rainbow hologram was recorded, the spacing between fringes is regular but not their shapes in a plane diffraction grating. On the other hand, the dark area of hologram **D'** consisted of slightly irregular grooves as can be seen in Fig. 4(b). In addition, it can be seen from Fig. 4(b) that the plane of the dark area **D'** made when R/S = 8 was smoother than that when R/S = 4. It was suggested that the lower contrast was responsible for the existence of grooves that exist in the dark area. The reason of lower S/N ratio could not be proven from the surface form observed by AFM images by comparison of Fig. 3(a) with Fig. 4(a). There is a presumption that the S/N ratio is influenced by homogeneity in neighboring grooves.

Plate 14 (p. 92) shows a photograph of a rainbow hologram and Fig. 5 shows its AFM image made from **Poly. 7** as a master hologram for a nickel stamper.

Preparation of Nickel Stamper. The first stage in producing embossed holograms is to make the surface of the photoresist master electrically conductive by depositing a layer of metal on it, either chemically, such as a silver mirror spray, by nonelectrolytic plating, or by vapor deposition. Following that, the nickel stamper is grown by a standard electroforming process and the final shim is carefully stripped off. The first method was carried out with an industrial silver mirror spray because the THPMA copolymer was dissolved by silver solution contained ammonia. The second method of nonelectrolytic plating with nickel was tried, but the



(a) (b)

Figure 4. Photographs of AFM image of rainbow hologram made from **Poly. 9** under R/S = 8 with wet PEB; (a) bright area, (b) dark area.

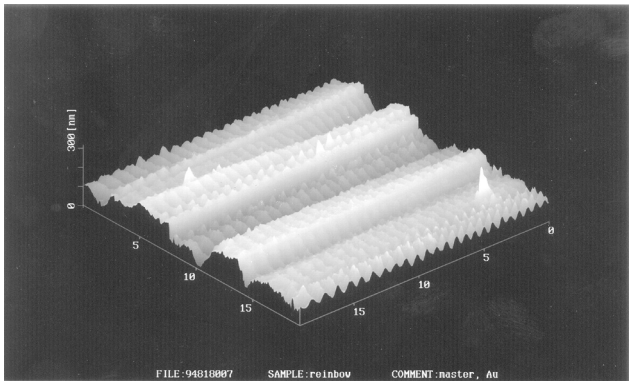


Figure 5. AFM images of rainbow hologram of Plate 14 (p. 92)

copolymer of photoresist was dissolved by the plating solution, too. Therefore, a vapor deposition with gold or nickel was adopted here. The metal plating was carried out with nickel sulfamate bath, and the nickel stampers were reproducibly obtained. Plate 15 (p. 92) shows the nickel stamper of rainbow hologram made with this procedure.

Conclusions

Poly(tetrahydropyranyl methacrylate-co-3(4)-methylstyrene) acts as a positive-working photo-resist for rainbow holograms suitable for exposure by an Ar^+ laser emitting 488 nm light when the polymer is activated with DPI salt and sensitizing dye. Developing properties were improved by controlling the average molecular weight of the acid-labile copolymers. In addition, S/N ratio and the contrast were improved to a value of 35 and 28, respectively, by raising R/S ratio, that is, using a stronger reference beam and developing under a severe condition such as moisture saturated PEB. The photoresist film provided a good profile for relief holograms using the polymer having Mn of 50,000–80,000 and Mw/Mn of about 2.0 under the R/S ratio within the range of 6 and 8.

Acknowledgment. We are deeply indebted to J. Yoshida and T. Nishihara of Toppan Printing Co., LTD., for their considerable assistance with holographic optical arrangements of an assembly, and to T. Ito of Toppan Printing Co., Ltd., for his assistance with experiments concerning the metal plating.

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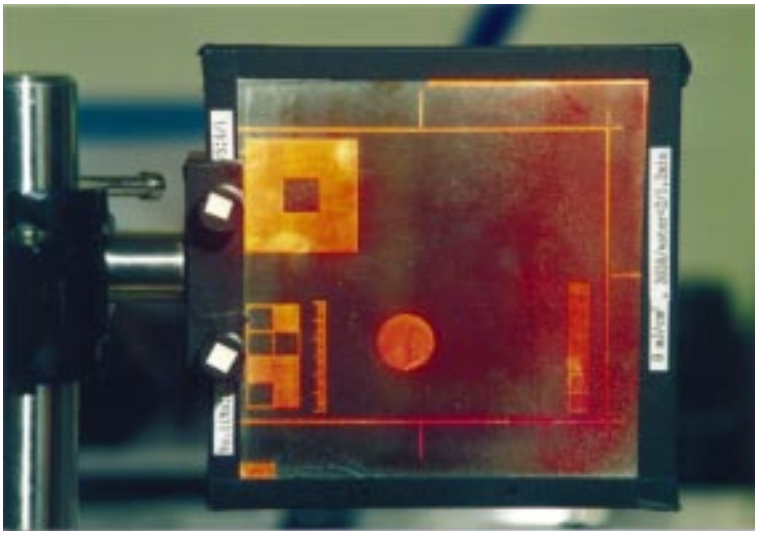
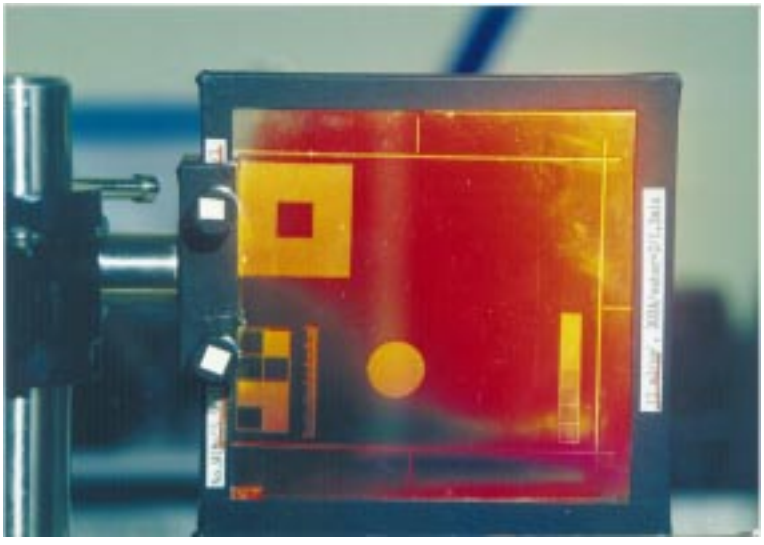
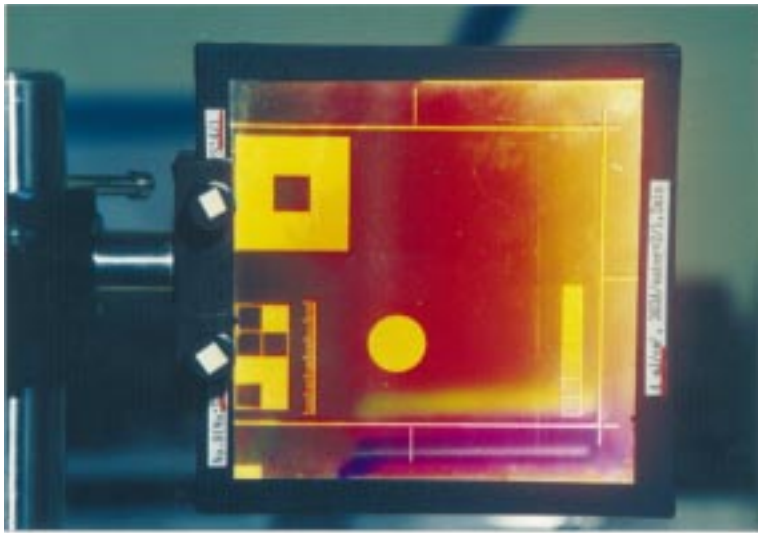


Plate 11. Photograph of a rainbow hologram made from **Poly. 1** under R/S = 4 with dry PEB (Ohe and Ichimura, pp. 74–79).



(a)



(b)

Plate 12. Photographs of a rainbow hologram made from **Poly. 7** under R/S = 4 with (a) dry PEB and (b) wet PEB (Ohe and Ichimura, pp. 74–79).

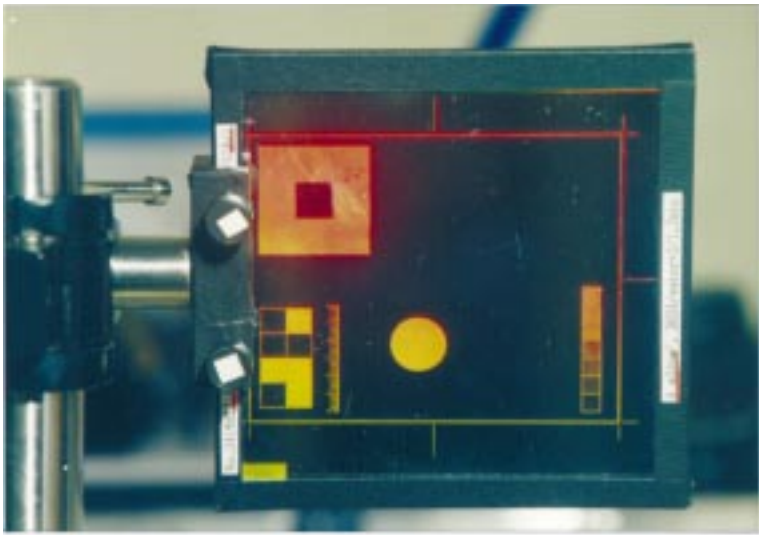


Plate 13. Photograph of a rainbow hologram made from **Poly. 4** under R/S = 8 with wet PEB (Ohe and Ichimura, pp. 74–79).

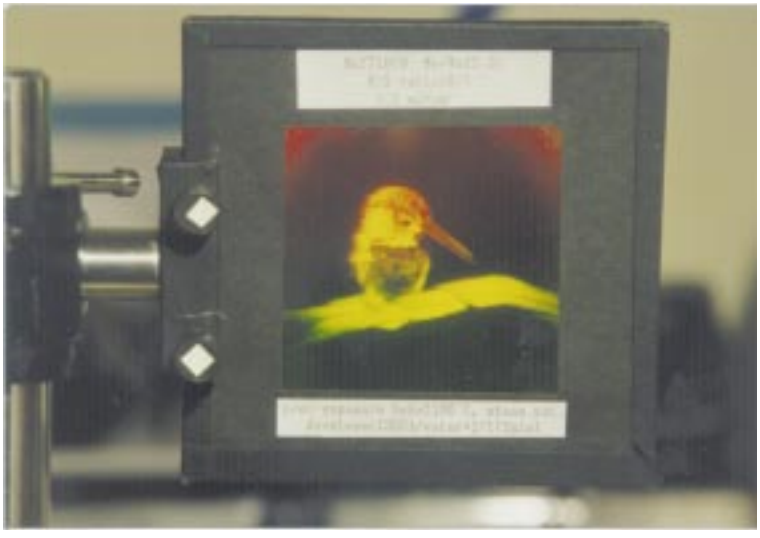


Plate 14. Photographs of a rainbow hologram made from **Poly. 7** (Ohe and Ichimura, pp. 74–79).

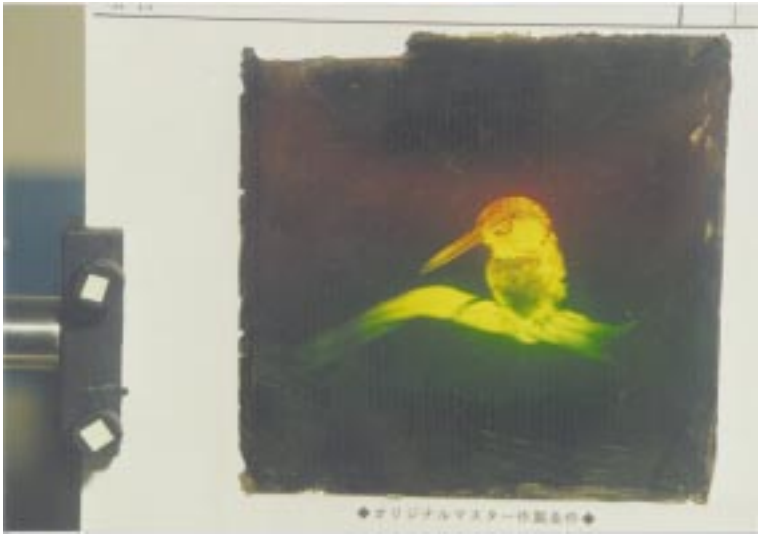


Plate 15. Photograph of nickel stamper of made from rainbow hologram (**Poly. 7**) (Ohe and Ichimura, pp. 74–79).