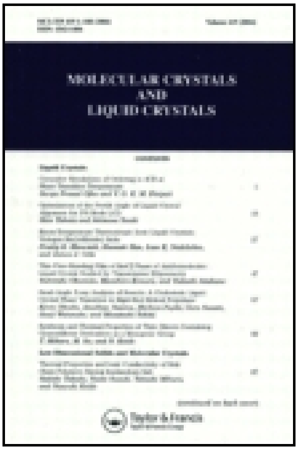


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis of Copolymers Containing Vinylbenzyl Abietate and Their Application as Photocrosslinkable Binder Polymer

Byoung-Woo Park [a] , Woo-Sik Kim [a] , Kwan-Ho Seo [a] , Sang-Woo Kim [b] & Il-Ryon Jeon [c]
[a] Department of Polymer Science, Kyungpook National University, Daegu, Korea
[b] Advanced Display Manufacturing Research Center, Kyungpook National University, Daegu, Korea
[c] Department of Industrial Chem, Kyungil University, Kyungsangbuk-do, Korea

Version of record first published: 31 Jan 2007

To cite this article: Byoung-Woo Park, Woo-Sik Kim, Kwan-Ho Seo, Sang-Woo Kim & Il-Ryon Jeon (2005): Synthesis of Copolymers Containing Vinylbenzyl Abietate and Their Application as Photocrosslinkable Binder Polymer, Molecular Crystals and Liquid Crystals, 443:1, 167-179

To link to this article: http://dx.doi.org/10.1080/15421400500253571

Mol. Cryst. Liq. Cryst., Vol. 443, pp. 167–179, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500253571

Synthesis of Copolymers Containing Vinylbenzyl Abietate and Their Application as Photocrosslinkable Binder Polymer

Byoung-Woo Park
Woo-Sik Kim
Kwan-Ho Seo
Department of Polymer Science, Kyungpook National University, Daegu, Korea

Sang-Woo Kim
Advanced Display Manufacturing Research Center, Kyungpook National University, Daegu, Korea

Il-Ryon Jeon
Department of Industrial Chem, Kyungil University, Kyungsangbuk-do, Korea

Poly(benzylmethacrylate-co-methacrylicacid-co-vinylbenzylabietate) was synthesized by radical polymerization of benzylmethacrylate (BzMA), methacrylic acid (MAA) and vinylbenzyl abietate (VBA) as a photocrosslikable monomer. The composition of the copolymer was measured with ^{1}*H-NMR and FT-IR, and thermal properties and photochemical reaction of copolymers were also investigated. From these results, poly(BzMA-co-MAA-co-VBA) could be applied to binder polymers of color resist for display panel.*

Keywords: binder; copolymer; photocrosslinkable polymer; vinylbenzyl abietate

INTRODUCTION

The display panel has been rapidly developed with increasing use of lap-top computer and generally used in cellular phones, personal

---

This work was supported by grant No.(R12-2002-055-03003-0) from Regional Research Center of the Korea Science & Engineering Foundation.

Address correspondence to Kwan-Ho Seo, Department of Polymer Science, Kyungpook National University, Daegu, 702-701, Korea. E-mail: khseo@knu.ac.kr

computer and most electronic products. It is constituted with liquid crystal display, plasma display panel, electrolumiscent display and so on. Especially, TFT (thin film transistor)-LCD (liquid crystal display) of the excellent resolution has been spotlighted in the field of display to meet the need for miniaturization and economical electric power.

Color filter occupies an important position in the parts and material of the TFT-LCD. In other words, color filter to embody a color for the display is very important part of display panel. It consists of pixels of three primary color (R, G, B) on the substrate using photolithography process.

There are several manufacturing methods for color filter, namely dyeing, pigment-dispersed, printing, electrodeposition [1]. Pigment-dispersed is the most widely applied method in the color filter manufacturing for TFT-LCD [2]. The color resist by radical polymerization consists of acrylic polymers generally used as a binder, polyfunctional monomer, photoinitiators, pigments and solvents [3,4].

In this study, we designed photocrosslinkable binder polymers for simplified color filter by replacing the monomer to play an important role in photoinitiator and binder concurrently [5]. Vinylbenzyl abietate (VBA) has been known as a photosensitive monomer in the latest researches [6,7] and poly(benzylmethacrylate-co-methacrylic acid-co-vinylbenzylabietate) (BMV) were synthesized by the radical polymerization. The thermal stabilities and photochemical reaction properties of BMV were investigated.

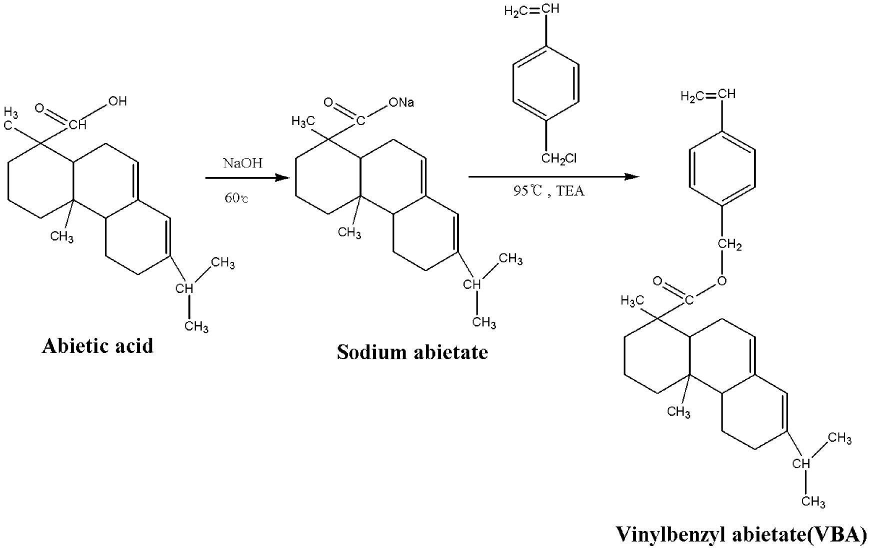
EXPERIMENTAL

Materials

Abietic acids was isolated from crude abietic acid (Aldrich, 70%) using dipenthylamine. 4-Vinylbenzyl chloride (VBC), chlorobenzene were used from Aldrich Chemical Company. Triethylamine (TEA) was purchased from Junsei Chemical Company and purified by distillation. Methacrylic acid benzyl ester (BzMA, 98%, TCI Chemical), methacrylic acid (MAA, 99%, Junsei) were distilled in the presence of hydroquinone under reduced pressure. 1-Methoxy-2-propanol acetate (PGMEA, 99.5%, Aldrich) used without further purification. N,N-Azobisisobutyronitrile (AIBN) of reagent grade was recrystallized from methanol before the use.

Synthesis of Vinylbenzyl Abietate (VBA)

Sodium abietate was prepared as follows [6,7]. Abietic acid (10 g, 33.1 mol) was added to a 10% aqueous solution (20 ml) of sodium

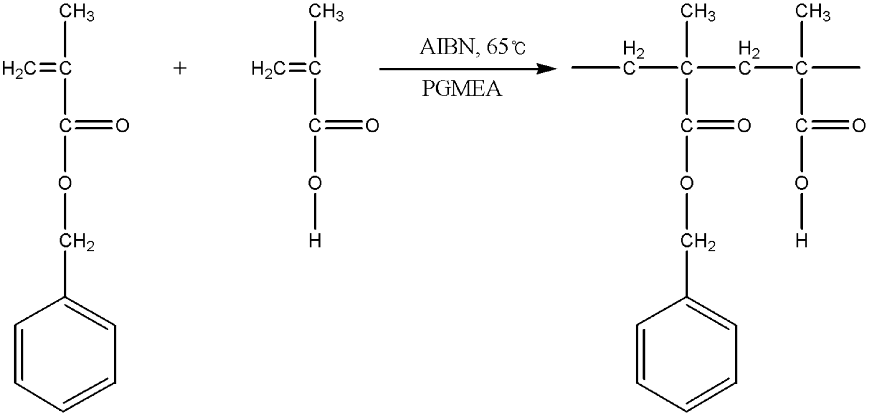


SCHEME 1 Synthesis of VBA.

hydroxide and dissolved by stirring at 60°C for 1 h. The solution was filtered and the filtrate was poured into a large amount of acetone to precipitate sodium abietate. VBA was synthesized according to Scheme 1 by the esterification of a sodium carboxylate with benzyl chloride. VBC (4.6 mL, 0.031 mol), sodium abietate (11.3 g, 0.035 mol), and triethylamine (4.9 mL, 0.035 mol) were put into chlorobenzene (30 mL) including a trace of p-benzoquinone as a polymerization inhibitor. The mixture was stirred at 95°C for 5 h. Most of the unreacted VBC and chlorobenzene in the mixture were eliminated by vacuum distillation. The viscous mixture was added dropwise to a large amount of distilled water to precipitate the product. The product was dried and recrystallized from acetone-distilled water (v/v:2/1). The yield of VBA was 10.2 g (78.7%) with the melting point of 70–72°C.

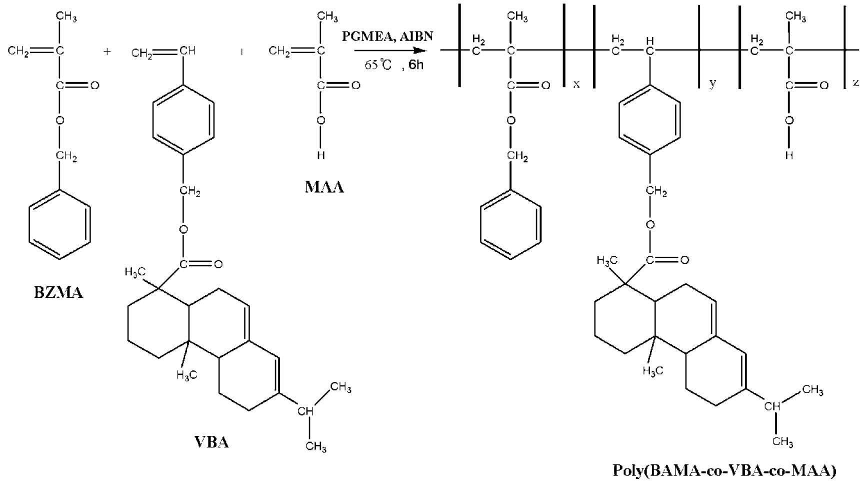
Synthesis of Poly(benzylmethacrylate-co-methacrylic acid) and Poly(benzylmethacrylate-co-methacrylic acid-co-vinylbenzylabietate)

All the copolymers were synthesized by free radical polymerization in sealed ampoules according to Scheme 2 and 3. Monomers and 3 mol%



SCHEME 2 Polymerization of poly(BzMA-co-MAA).

N,N-azobisisobutyronitrile (AIBN) were dissolved in 1-methoxy-2-propanol acetate (PGMEA). Polymerization was performed at 65°C for 6 h. After polymerization, the solution was precipitated into n-hexane. The precipitated copolymers were collected by filtration and washed with n-hexane. After drying under vacuum for 24 h, white powdery material was obtained.



SCHEME 3 Polymerization of poly(BzMA-co-MAA-co-VBA).

Photosensitivity of Poly(BzMA-co-MAA-co-VBA)

For the investigation of photochemical reaction of the poly(BzMA-co-MAA-co-VBA), tetrahydrofuran solutions of the poly(BzMA-co-MAA-co-VBA) were coated on quartz plates with spin coater, and then dried at room temperature. The films were irradiated with a high-pressure mercury lamp (a Shimadzu Model 2401 spectrophotometer) for accumulative times. UV absorbance of these films was measured with a Shimadzu Model 2401 spectrophotometer.

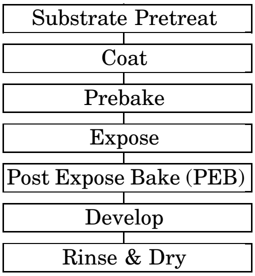
Lithographic Evolution

A binder solution was prepared by dissolving 5 g of poly(BzMA-co-MAA-co-VBA) and 28.33 g of 1-methoxy-2-propanol acetate. The solution was filtered twice through a 0.2 μm membrane filter prior to the application to the silicon substrate. A resist film was prepared by spin coating of photoresist solution on a silicon wafer and baked at 110°C for 5 min to remove residual solvent, and exposed at 254 nm stepper [8]. The exposed film was post-exposure baked at 120°C for 1 min and developed in aqueous 2.38 wt% tetramethylammonium hydroxide (TMAH) solution [9]. The line widths were measured on a Hitachi S-800 CD-SEM and cross-section profiles were obtained by a Hitachi S-8820 SEM. The film forming and lithographic process, and condition of resist solution were summarized in Table 1.

Analysis

Infrared spectra were recorded with a JACO-IR 810 spectrometer by KBr method. ^{1}H NMR spectra were obtained with a Bruker Advanced Digital 400 FT-NMR spectrometer in THF. Ultraviolet spectra were recorded as spin-coated films on quartz plate with a Shimadzu Model

TABLE 1 Manufacturing Procedures and Condition for Resist Solution



Step	Condition
Spin coating	1 step: 500 rpm/15 sec 2 step: 1000 rpm/15 sec 3 step: 1300 rpm/10 sec
Prebake	110°C, 5 min
UV Exposure	365 nm/2000 mJ/cm^2
Post bake	120°C, 1 min
Development	TMAH 2.38 wt%: 2 ∼ 3 min

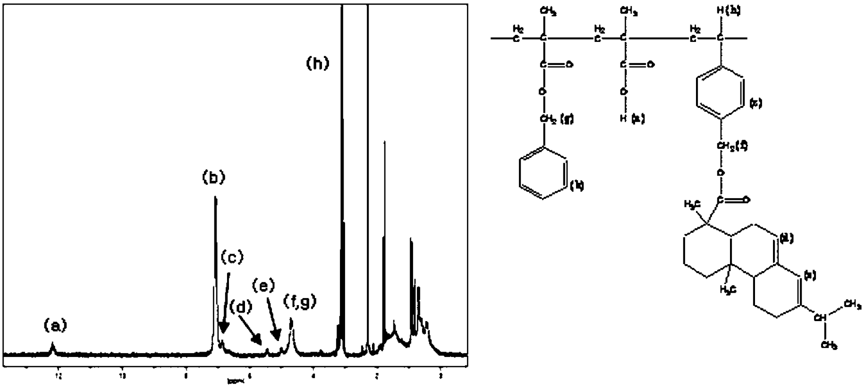


FIGURE 1 ^{1}H-NMR spectra of BMV7330 in THF.

2401 spectrophotometer. The number-average molecular weights (M_n) and the weight-average molecular weights (M_w) of the polymers were measured in THF with a Waters Alliance V2000 gel permeation chromatograph (GPC). The intrinsic viscosities of the polymers were measured in chloroform at 25°C with a Ubbelohde viscometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were obtained on a Dupont 2100 thermal gravimetric analyzer and a Dupont 2000 differential scanning calorimeter. TGA and DSC measurements were made in a nitrogen atmosphere at a heating rate of 10°C min^{-1} and 20°C min^{-1}, respectively.

RESULTS AND DISCUSSION

Synthesis of VBA

The FT-IR spectrum of VBA showed the peak of carbonyl group of the ester at 1718 cm^{-1}. The weak peak at 1629 cm^{-1} can be attributed to

TABLE 2 Feed Ratio of Monomers and GPC Results of Polymers

	Feed, wt%						
	[BzMA]	[MAA]	[VBA]	Yield (%)	M_n	M_w	M_w/M_n
BM73	70	30	–	83	34746	69591	2.003
BM55	50	50	–	87	36106	72746	2.014
BMV7330	70	30	30	88	33647	68319	2.030
BMV5530	50	50	30	85	35377	73298	2.072

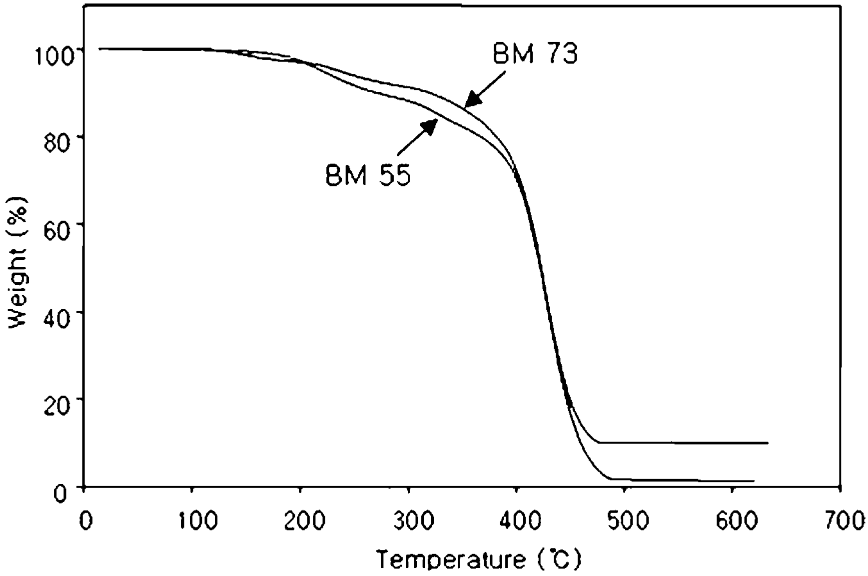


FIGURE 2 TGA thermograms of poly(BzMA-co-MAA).

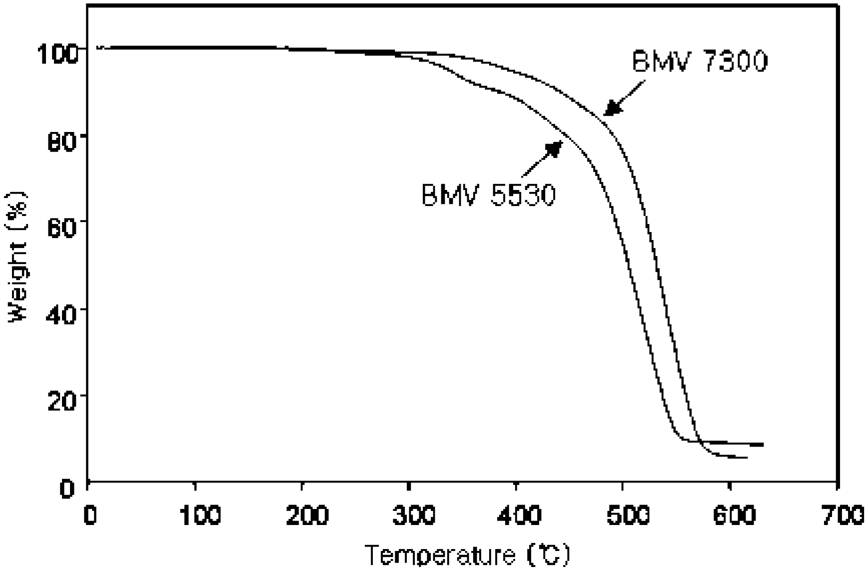


FIGURE 3 TGA thermograms of poly(BzMA-co-MAA-co-VBA).

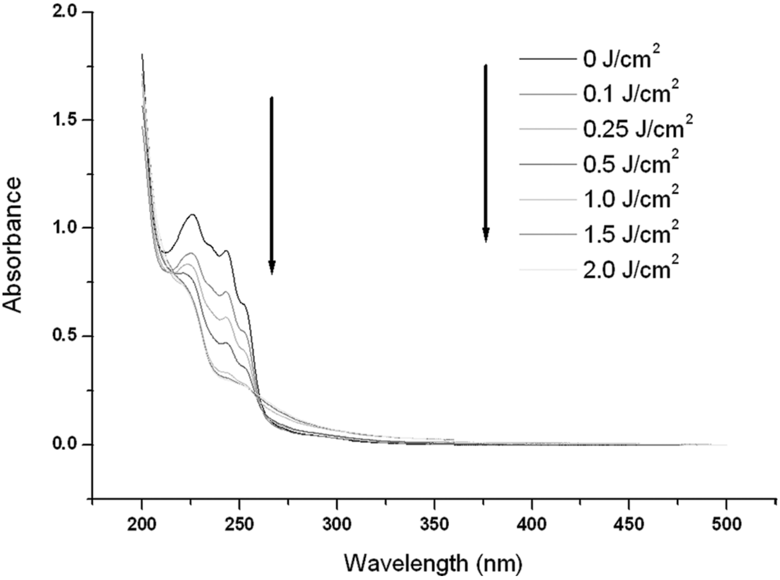


FIGURE 4 Changes in the UV spectral pattern upon irradiation of VBA (Exposure dose = 3 mW/cm^2).

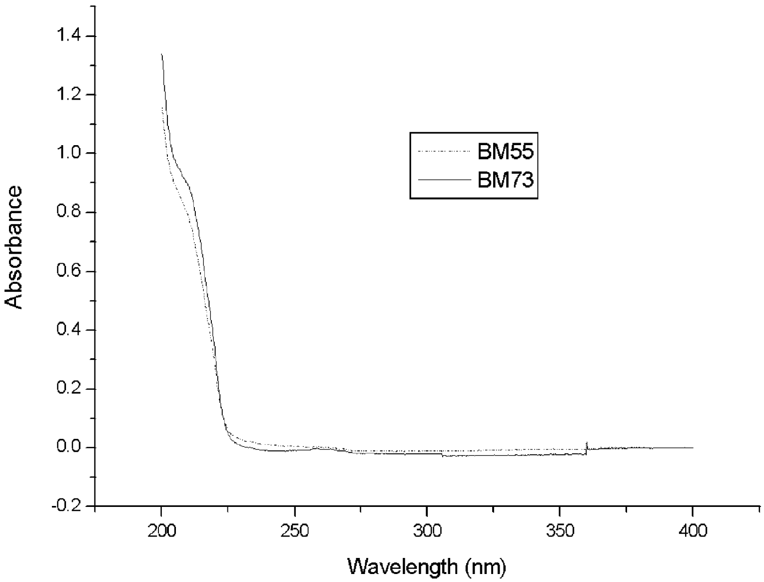


FIGURE 5 Changes in the UV spectral pattern upon irradiation of BM73 and BM55 (Exposure dose = 3 mW/cm^2).

the carbon-carbon double bonds of abietic acid moiety and the weak peak at 1660 cm^{-1} might be due to the vinyl group in VBA [6].

Polymerization

H^1-NMR spectra of poly(BzMA-co-MAA) and poly(BzMA-co-MAA-co-VBA) are shown in Figure 1. Spectrum shows the carbon-carbon double bonds as VBA at 5.41 ppm, 5.87 ppm, and 7.42 ppm. The GPC results of polymers are summarized in Table 2. The number average molecular weight and polydispersity of copolymers were 68,000 $\sim$ 73,000 g/mol and 2.00 $\sim$ 2.07, respectively.

Thermal Properties of Copolymers

TGA thermograms of copolymers are presented in Figure 2 and Figure 3. The onset decomposition temperatures (T_d) are about 170°C in

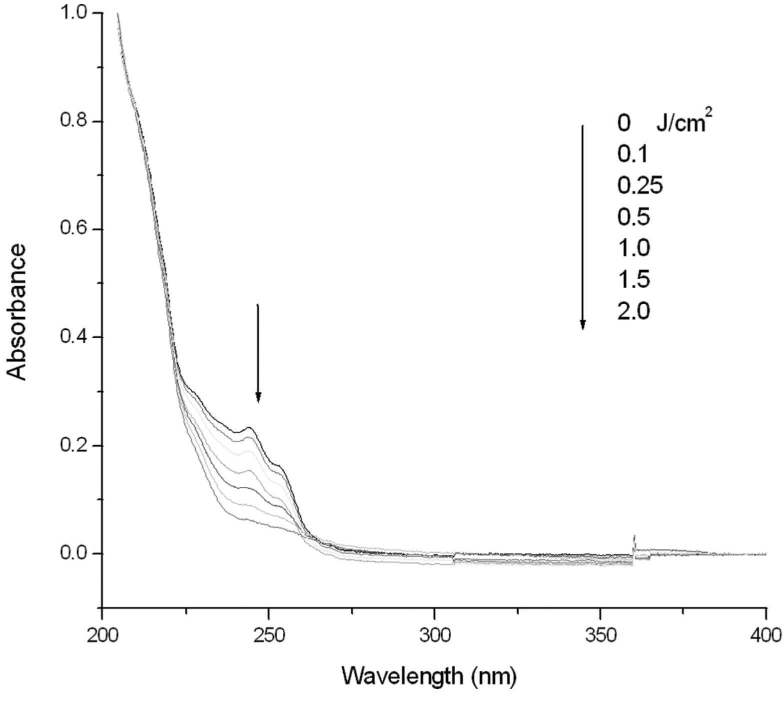


FIGURE 6 Changes in the UV spectral pattern upon irradiation of BMV7330 (Exposure dose = 3 mW/cm^2).

presence of the VBA as a photosensitive monomer and 120℃ in absence of the VBA. The increase of T_d was attributed to the thermal stability of VBA. In addition, BMV7330 shows higher T_d than BMV5530 due to the increasing contents of BzMA , which has been expected to have higher thermal resistance. As a result, it can be expected that the binder polymer has a good thermal resistance during the process for preparing the color filter [10–12].

Photochemical Properties

The changes in the UV spectra of VBA with the respect to the exposure time were shown in Figure 4. The peaks in the range of 234 nm and 243 nm are due to the carbon-carbon double bonds of abietic acid moiety as known, and the peaks are diminished with increasing irradiation times. In Figure 5, the broad peak for poly(BzMA-co-MAA) without VBA was shown . Otherwise, the UV spectra of the poly(BzMA-co-MAA-co-VBA), depicted in Figure 6 and Figure 7,

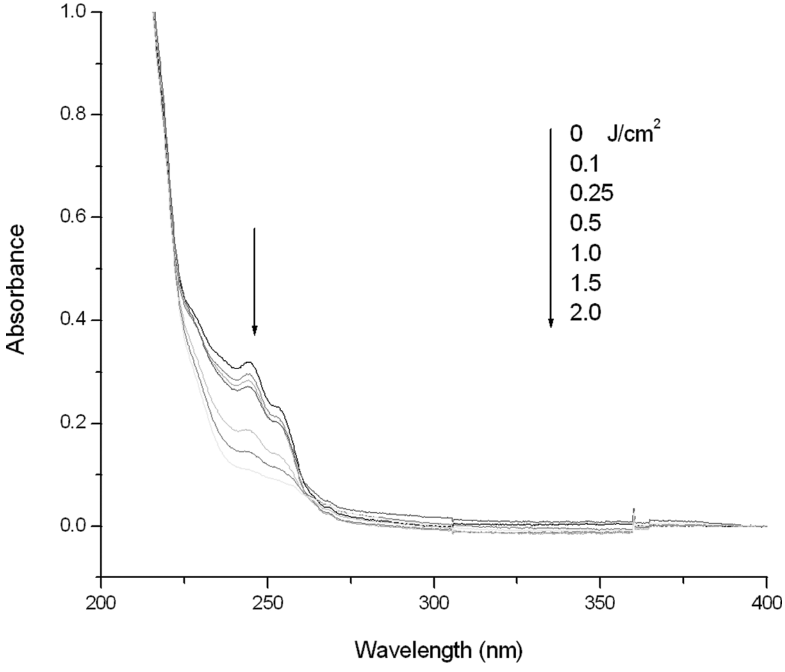


FIGURE 7 Changes in the UV spectral pattern upon irradiation of BMV5530 (Exposure dose = 3 mW/cm^2).

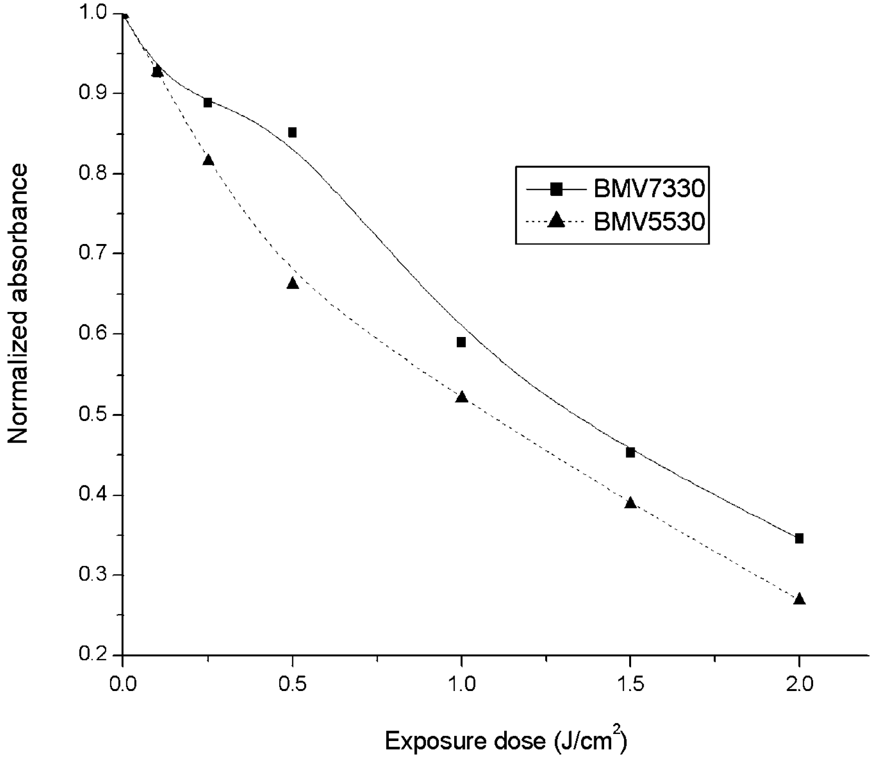


FIGURE 8 Normalized absorbances of BMV7330 and BMV5530.

are similar to the changes of VBA, as shown in Figure 4. From these results, we confirmed that the poly(BzMA-co-MAA-co-VBA) can be crosslinked by the photochemical reaction. In order to show the photochemical reaction as quantity of UV exposure, the standard absorbance in the range of 254 nm as quantity of UV exposure is given Figure 8. This suggests that the poly(BzMA-co-MAA-co-VBA) can be used a binder polymer for photoresist because of its good photochemical reaction [13].

Lithographic Performance

Lithographic evolution was performed on a poly(BzMA-co-MAA-co-VBA) based resist. The scanning electron micrograph for the resist, formulated with BMV7330, was shown in Figure 9. The resist patterns

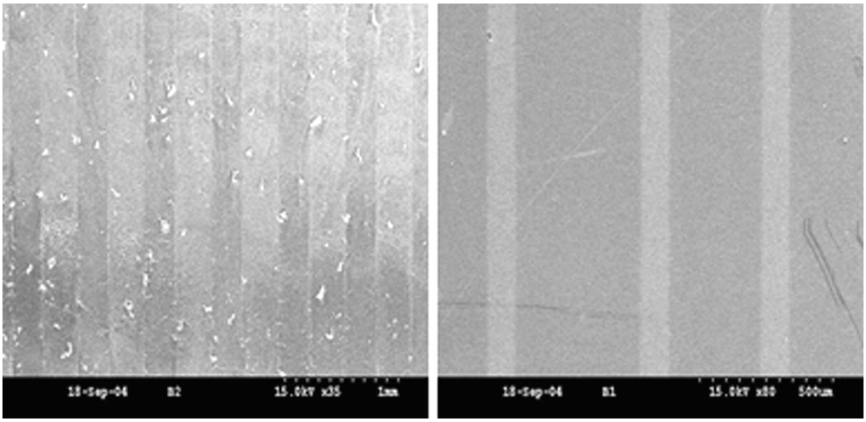


FIGURE 9 Scanning electron micrograph of evolved patterns with BMV5530 based binder.

were obtained at a dose of 2 J/cm^2 using 2.38 wt% TMAH aqueous solution as a developer [14].

CONCLUSION

We designed and synthesized a new type of binder polymer for color filter. Binder polymer of VBA having a photocrosslinkable site with BzMA and MAA were prepared by the radical polymerization. As a result of examination about onset decomposition temperature needed in resist manufacturing process, poly(BzMA-co-MAA-co-VBA) has a thermal stability about 150°C ∼ 170°C. It attributes to a thermal stability of VBA. We confirmed that poly (BzMA-co-MAA-co-VBA) was crosslinked by irradiation. Therefore, it can be a new polymer for the preparation of photocrosslinkable binder polymer. Line and space patterns were obtained using a resist based on the copolymer containing VBA at a dose of 2 J/cm^2 with the standard developer.

REFERENCES

[1] Sabnis, R. W. (1999). *Displays*, *20*, 119.
[2] Auschra, C., Eckstein, E., & Zink, M. (2002). *Prog. Org. Coat.*, *45*, 83.
[3] Kim, J. B., Lee, J. J., & Kang, J. S. (2000). *Polymer*, *41*, 6939.
[4] Lub, J., Broer, D. J., & Witte, P. (2002). *Prog. Org. Coat.*, *45*, 211.
[5] Avci, D. & Mathias, L. J. (2004). *Polymer*, *45*, 1763.

[6] Kim, W. S., Park, L. S., & Seo, K. H. (2003). *Polym. J.*, *35*, 450.
[7] Kim, W. S., Jang, H. S., & Seo, K. H. (2001). *Macromol. Rapid Commun.*, *22*, 825.
[8] Kim, J. B., Yun, H. J., Kwon, Y. G., & Lee, B. W. (2000). *Polymer*, *41*, 8035.
[9] Chisholm, B., Potyrailo, R., Cawse, J., Shaffer, R., Brennan, M., Molaison, C., Whisenhunt, D., Flanagan, B., Olson, D., Akhave, J., Saunders, D., Mehrabi, A., & Licon, M. (2002). *Prog. Org. Coat.*, *45*, 313.
[10] Schlesing, W., Buhk, M., & Osterhold, M. (2004). *Prog. Org. Coat.*, *49*, 197.
[11] Ferbitz, J. & Mormann, W. (2003). *Polymer*, *44*, 527.
[12] Fieberg, A. & Reis, O. (2002). *Prog. Org. Coat.*, *45*, 239.
[13] Balaji, R., Grande, D., & Nanjundan, S. (2004). *Polymer*, *45*, 1089.
[14] Kim, J. B., Kim, J. Y., & Jung, M. H. (1998). *Polymer*, *40*, 243.