Stripe Coating with a Coffee-Ring Effect for Color Filter Solutions

Yu-Chih Lin,[1] Yu-Yan Lin,[1] David S. H. Wong,[1] Ta-Jo Liu,[1] Shu-Heng Wen,[2] Kuo-Tung Huang[2]

[1]Department of Chemical Engineering, National Tsing Hua University, Hshin Chu, Taiwan 300, Republic of China
[2]Material and Chemical Lab, Industrial Technology Research Institute, Chu Tong, Taiwan 300, Republic of China

ABSTRACT: The coffee-ring effect of a coated narrow stripe approximately 350 μm wide was examined. The coating solution was based on a new formulation with a specific application for the production of color filters used in liquid-crystal display panels. The basic components of this formulation were color pigments, solvents, and a novel alkali solution resin. The resin was a copolymer consisting of methacrylic acid, hydroxyl ethyl methacrylate, and methyl methacrylate. Three solvents with different boiling points were used: propylene glycol methyl ether acetate, methyl ethyl ketone, and tetrahydrofuran. The formation of a coffee ring on the coated stripe was mainly dependent on the solvent evaporation rate and the acid value of the copolymer. The acid value determined the strength of the hydrogen bonding of the copolymer. Fourier transform infrared analysis revealed that the intramolecular hydrogen bonding of the carbonyl groups of hydroxyl ethyl methacrylate was one of the critical factors affecting the formation of a coffee ring. The other factor was the rate of solvent evaporation. A proper adjustment of the acid value combined with a highly volatile solvent could effectively eliminate the formation of a coffee ring. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1555–1565, 2011

Key words: chain; coatings; FTIR; solution properties; coffee ring; color filter; hydrogen bonding

INTRODUCTION

Liquid-crystal display (LCD) panels appear in many electronic products such as cell phones, digital still cameras, notebook computers, and televisions. A color filter, which provides color images, is one of the key components of an LCD panel. The structure of a color filter can be found in many patents.[1–3] Usually red, green, and blue dots or stripes have to be coated onto a large piece of indium tin oxide (ITO) glass. Conventional technology for producing color filters usually involves the patch coating of red-, green-, and blue-pigment solutions onto large pieces of ITO glass. Processes such as light exposure, etching, and cleaning follow for the creation of red, green, and blue dots or stripes on the glass. The coating and etching are carried out independently for each color, and it takes three cycles to create a piece of a color filter with three color dots or stripes. Normally, 95% of the pigment solution is wasted. Currently, there are several new technologies being developed to replace the conventional technology for the production of color filters. The most popular one is based on ink-jet technology;[4–6] in which small drops of a pigment solution are deposited onto the ITO glass to form dots or stripes. One of the main concerns with stripe forming is that the edges of the created color stripes may not be smooth, and this can jeopardize the color image of the LCD panels. One method for controlling the edge effect is using an open channel or guide to collect the drops from an ink-jet device so that the drops will level off to form a uniform stripe. However, this method of operation can be very tedious.[7,8]

Another potential approach is coating the red, green, and blue stripes directly onto the ITO glass.[9] Because the width of each color stripe is approximately 300 μm, a color filter for a 42-in. LCD TV will need thousands of color stripes. Quality control in terms of the stripe width and cross-sectional shape is critical for the successful development of stripe coating as a replacement for conventional patch coating. In addition, coating solutions used in color stripes consist of many components, including pigments, solvents, binders, and dispersing agents. The quality of a color stripe depends strongly not only on the coating process but also on the drying process of the coating solution.

Previous studies have shown that coffee rings can appear in inkjet-printed dots or stripes. This phenomenon was first observed by Deegan and coworkers,[10–12] and the coffee-ring effect was attributed to the contact-line pinning and an increase in evaporation at the edge of a liquid drop.

Lyon et al.[13] proposed the production of a light-emitting device by an ink-jet deposition technique; two solvents, one with a high boiling point and low solubility and another with a low boiling point and high solubility, were used to adjust the evaporation and then to remove the coffee-ring effect. de Gans and Schubert[14] and de Gans et al.[15] eliminated the coffee ring by printing nonvolatile acetophenone-based inks onto a perfluorinated substrate with different polymers. Park and Moon[16] used a mixture of solvents with colloidal particles to control the deposition of particles on the edges. Van den Berg et al.[17] minimized the appearance of coffee rings with the thermal gelation effect produced by the dispersion of TiO$_2$ particles in a diblock copolymer. Tekin et al.[18] examined the interaction between a solvent [tetrahydrofuran (THF)] and a polymer {poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene]} to control the coffee-ring effect. Lim et al.[19] reported that coffee rings could be removed through the use of solvents of different surface tensions to create a Marangoni flow. Soltman and Subramanian[20] showed that coffee rings could be eliminated through the control of the drop spacing and the temperature of a conducting polymer.

In this article, an experimental study of the coating and drying behaviors of a 350-μm-wide stripe was carried out. Test solutions for making color filters were formulated with different types of solvents and a novel copolymer based on a patent of Huang et al.[21] This new formulation provides superior quality in terms of adhesion and pigment dispersion for color filters. Coffee rings were observed on the stripe. An attempt was made to identify the mechanism of ring formation. A method of eliminating the coffee-ring effect was proposed.

EXPERIMENTAL

Materials

Test fluids for stripe coating were prepared with the same formulation for color filters described in Huang et al.'s patent.[21] The ingredients of this formulation were (1) a pigment, (2) an alkali-soluble resin with a polyaromatic group (a random-type copolymer), (3) a polyfunctional monomer, (4) a photoinitiator, and (5) a solvent.

Our preliminary studies revealed that only two components (the alkali-soluble resin and the solvent) played a major role in the formation of coffee rings. Only these two components were analyzed in this study; the polyfunctional monomer and the photoinitiator were removed from the test coating solutions. A typical alkali-soluble resin is a copolymer consisting of three different types of monomers. The molecular structures of the monomers and the sol-

vents used in this study are presented in Table I. The reactivity ratios of the three monomers are listed in Table I; here r_1 represents the reactivity ratio for each monomer reacting with an identical monomer, whereas r_2 represents the reactivity ratio for one monomer reacting with another monomer. The chance for two monomers to react will be greater with a higher reactivity ratio. Because free-radical reactions are fast, the data for the reactivity ratios indicate that it was most likely for the copolymer to be a random type. The alkali-soluble resin was likely to have the recurring units shown in Figure 1. Each monomer in the resin provided a specific function; methacrylic acid (MAA) was used to adjust the acid value (AV) of the solution, hydroxyl ethyl methacrylate (HEMA) was used to improve the adhesion between the solution and the ITO glass, and methyl methacrylate (MMA) was used to assist the dispersion of the pigments in the solution. A free-radical polymerization process was needed to prepare the resin. Odecyl mercaptan was used as the free-radical initiator, and azobisisobutyronitrile was used as the chain-transfer agent. The ratios of the free-radical initiator and the chain-transfer agent were selected initially to range from 0.5 to 1.50 per mole of the monomers. The polymerization reaction was controlled at 80°C for 16 h in a stirred glass reactor. The molecular weight of the product was measured by gel permeation chromatography and was controlled within 20,000 ± 5000 via the tuning of the weight ratios of the free-radical initiator and the chain-transfer agent to the monomers. Three different solvents were used in the formulation: propylene glycol methyl ether acetate (PGMEA), methyl ethyl ketone (MEK), and THF. The rate of solvent evaporation was measured.

Coating and sample preparation

A stripe-coating system was set up with a nozzle [i.d. = 70 μm (ST215-B) or i.d. = 90 μm (5133CH-B); Nordson Co., Shanghai, China] to deliver a narrow liquid stripe. The nozzle was attached to a supporting device and was pointed vertically downward above a marble platform. A piece of ITO glass was placed onto the marble platform. Once the coating experiment started, the nozzle was lowered to a predetermined position, and the coating solution was delivered through a precision pneumatic pump (Ultra 2400 series, Nordson) and then coated onto the moving ITO glass. The gap between the nozzle and the ITO glass had to be less than 50 μm to deliver a uniform stripe. For each test solution, stripe-coating experiments were repeated at least five times to make sure that the quality of each stripe (i.e., the coating width and the flow rate) was consistent before samples and measurements were

TABLE I
Monomers and Solvents of the Coating Solutions and Monomer Reactivity Ratios

Component	Structure
MAA (Aron Alpha, Toagosei Co., Ltd.)	
HEMA (Aron Alpha, Toagosei Co., Ltd.)	
MMA (Aron Alpha, Toagosei Co., Ltd.)	
PGMEA (Echo Chemical Co., Ltd.; bp = 146°C)	
MEK (Tedia Co., Inc.; bp = 79.6°C)	
THF (Echo Chemical Co., Ltd.; bp = 66°C)	

		Monomer reactivity ratios	
Monomers		r_1	r_2
MMA	MAA	0.209	1.26
MMA	HEMA	0.824	0.630
MAA	HEMA	1.50	0.67

The data were taken from Brandrup and Immergut.[26]

taken. A schematic of the coating loop is shown in Figure 2.

A charged coupling device camera was installed to observe the operation and particularly the variation of the coating width during the coating and drying period. The solvent evaporated very rapidly; there was no liquid movement in the stripe after only a few seconds. The ITO glass with coated stripes was placed into an oven for baking; the baking temperature was higher than 180°C. It usually took more than 40 min to remove the residual solvent in the stripes.
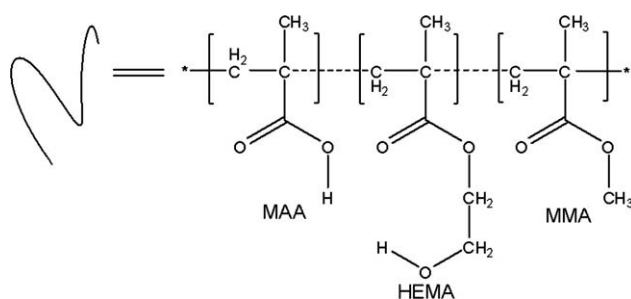

Figure 1 Schematic representation of the recurring unit of the copolymer.

Measurements of the physical properties

All physical properties of the coating solutions presented in Table II were measured under ambient conditions. The surface tension was determined with a surface tensiometer (CBVP-A3, Applied Trentech, Inc., Taipei, Taiwan R.O.C.). Fluid viscosities in the
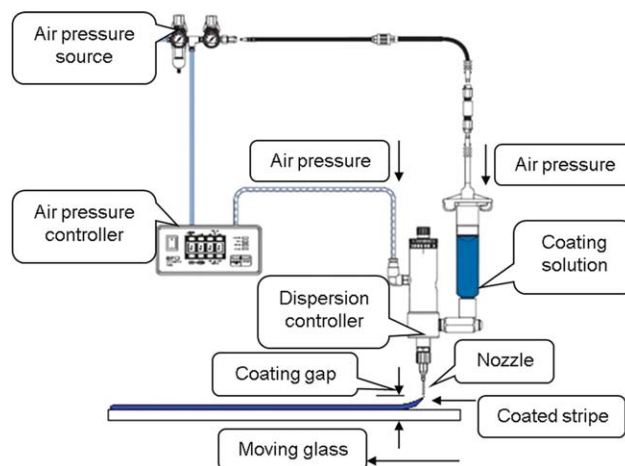

Figure 2 Experimental setup. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

TABLE II
Weight Ratios of the Monomers

	MMA (%)	MAA (%)	HEMA (%)
AV-10	96.56	1.55	1.89
AV-30	89.76	4.61	5.63
AV-80	72.67	12.30	15.03
AV-100	65.78	15.40	18.82
AV-150	48.89	23.00	28.11

low- and high-shear-rate regions were measured with an ARES-LS1 rheometer (TA Instruments, Inc., New Castle, DE, USA) and an LVDV-III+ CP rheometer (Brookfield Products, Inc., Middleboro, MA, USA), respectively. Because of the rapid solvent evaporation, it was not possible to measure the viscosity variations under the condition of continuous solvent evaporation. The contact angle between the coating solution and the ITO glass was measured with a video contact-angle system (AST/VCA-2500XE, AST Products, Inc., MA). The dry coating thickness was determined with a profilometer (Dektak 3ST, Sitek Process Solutions, Inc., CA). Finally, the coffee-ring effect was examined with Fourier transform infrared (FTIR) spectra, which were obtained on a Nicolet Avatar 320 FTIR spectrometer (Taipei, Taiwan) (32 scans at a resolution of 1 cm^{-1} with a KBr disk from 40 to 180°C). The high temperature for FTIR analysis was required for the removal of water and residual solvents so that they would not interfere with the FTIR analysis of the effect of the free hydroxyl groups.

RESULTS AND DISCUSSION

Effects of the parameters

The effects of the compositions of the copolymer and solvents on the coffee-ring formation were first examined. Ten samples were prepared. One of the key parameters in determining the coffee-ring effect was the AV of the solutions; the AV is defined as the mass of potassium hydroxide (mg) required to neutralize 1 g of a chemical substance. The AV is an indication of the strength of hydrogen bonding in solution. AVs for the copolymers under investigation could be varied by the adjustment of the number of carbonyl groups in the monomers. The ratios of HEMA to MAA were fixed for all the samples at different AVs; increasing the contents of the HEMA and MAA monomers and decreasing the contents of the MMA monomer resulted in an increase in AV, and vice versa. Higher AVs seemed to have little effect on the hydrophilicity of the samples, as indicated by the values of the contact angles in Table III, because the solvent contents were approximately 80%; this may be important with respect to the contact angles.

The formation of a coffee ring could be observed visually. Once a stripe was coated, the contact lines on the two edges were pinned. As time progressed, two wave fronts were formed at the central line of the stripe, and they moved toward the two edges of the coated stripe.

The coffee ring was formed within a few seconds, and its shape did not vary much after baking. A typical cross-sectional area of a dried stripe showing the coffee ring is presented in Figure 3. The parameter λ is an indication of the magnitude of the coffee ring:

$$\lambda \equiv \frac{(H_r + H_l)/2}{h} \qquad (1)$$

where H_r and H_l are the maximum heights on the right and left side edges, respectively, and h is the average thickness of the dried film in the central bottom region. More than 50 samples were examined; Table II lists monomer weight ratios for several samples. Ten representative cases are presented in Table III; λ in Table III is the average value of five measurements taken from five coated stripes. The measurements were taken at the same position of the coated stripes. The rate of solvent evaporation could be quantified in terms of the relative volatility, as presented in Table IV. THF had the highest degree of evaporation. Table III shows that λ dropped sharply when AV was reduced from 150 to 30, or the coffee-ring effect was significantly reduced. Comparing the results of samples 4 and 5, we found that adding a pigment to the coating solution had little effect on the coffee ring. The effects of the different solvents can be demonstrated by an examination of the λ values of samples 5–7. The coffee ring disappeared completely in the case of
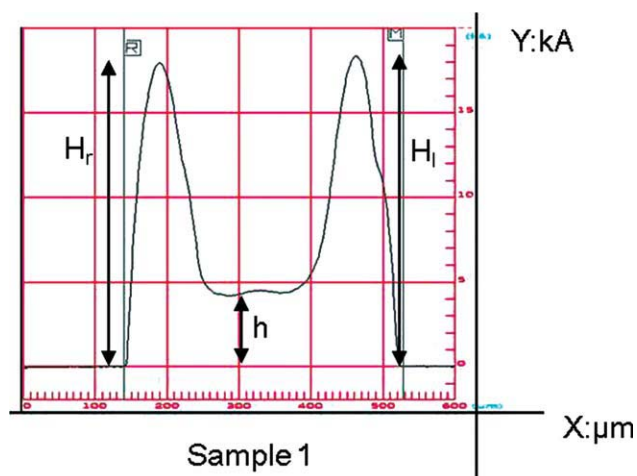

Figure 3 Definition of λ for a coffee ring. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Sample	Component	Solvent	Viscosity (mPa s)	Surface tension (mN/m)	Solid content (%)	Pigment	Contact angle (°)	λ
1	AV-150	PGMEA	10	25.7	9.5	No	20.9	3.5
2	AV-100	PGMEA	11.2	24.8	18	Yes	15.5	3.4
3	AV-100	THF	7.8	26.0	16.2	Yes	15.4	1.4
4	AV-30	PGMEA	14.5	26.1	18.2	No	24.4	1.7
5	AV-30	PGMEA	7.8	26.6	20.1	Yes	14.7	1.4
6	AV-30	PGMEA/MEK = 1	5.5	26.3	20.1	Yes	10.7	1.5
7	AV-30	THF	5.1	26.1	20.8	Yes	23.2	1.0
8	AV-10	PGMEA	6.6	26.6	19.4	Yes	8.9	2.3
9	AV-10	PGMEA/MEK = 1	4.5	26.3	19.3	Yes	<3	1.7
10	AV-10	THF	4.2	27.3	20.0	Yes	23.1	1.1

The values of the contact angles are the averages of the right and left measurements. The viscosity was measured at a shear rate of 30 s^{-1}.

THF at AV = 30. This suggests that using a highly volatile solvent can minimize the appearance of a coffee ring. However, the coffee ring reappeared when AV was further reduced from 30 to 10, as indicated in samples 8–10. A comparison of the three samples suggests that the coffee-ring effect can be minimized with a highly volatile solvent such as THF and through the control of the AV of the coating solution. We found that replacing 50% of PGMEA with the more volatile solvent MEK could reduce the coffee-ring effect, as evidenced by samples 8 and 9 in Table III; however, the effect was less significant in samples 5 and 6. It was reported by de Gans and Schubert[14] that a more volatile solvent may influence the pinning of contact lines, and this is critical for the formation of a coffee ring. We did not find that using a more volatile solvent such as THF changed the pinning of the coating solution to the two edges. Therefore, the mechanisms of coffee-ring formation are different between this study and theirs.

Photographs of some representative cross-sectional areas of samples presented in Table III are shown in Figures 3 and 4. We studied many cases with and without pigment addition and did not find that pigment addition made a significant contribution to the coffee ring. Adding pigment resulted only in rough surfaces between the two edges after drying, as shown in Figure 4. Without the added pigments, the dried film surfaces of samples 1 and 4 were relatively smooth, with added pigments, the surfaces of samples 5, 7, and 10 were quite rough. We did not observe the effect of the solid content on coffee-ring formation. It was difficult to study a solution with a high AV with a solid content higher than 15% because the solution was too viscous for viscosity measurement and coating.

We found that high-temperature baking did not have a significant effect on the coffee ring; only the surface profiles between the two edges were slightly different. The effects of other physical properties of the coating solution on the cause of the coffee ring were also examined. The rheological properties of the coating solutions were measured over a wide range of shear rates; the viscosities of all samples were found to be less than 15 mPa s at moderate shear rates. All the coating solutions in this study exhibited shear-thinning behavior at shear rates higher than 1 s^{-1}.

There is no strong evidence suggesting that the fluid viscosity measured before the coating experiment affected coffee-ring formation significantly. More details on the rheological data and analysis of the coating solution can be found elsewhere.[22] Table III shows that the surface tensions of all samples were very similar. Hence, it would have the same effect, if any, on the formation of the coffee ring.

FTIR analysis

As mentioned earlier, in addition to the solvent evaporation rate, the other key factor controlling

TABLE IV
Relative Volatility of Different Samples

Sample	Average volatility	Solvent
Ethyl acetate (standard)[a]	2.9	
AV-30–PGMEA	0.2	PGMEA
AV-30–PGMEA/MEK	0.65	PGMEA/MEK = 1
AV-30–THF	1.24	THF
AV-10–PGMEA	0.22	PGMEA
AV-10–PGMEA/MEK	0.72	PGMEA/MEK = 1
AV-10–THF	1.34	THF

[a] The volatility of ethyl acetate served as a control for comparison. Details of the measurement procedure can be found in Lin's work.[22]
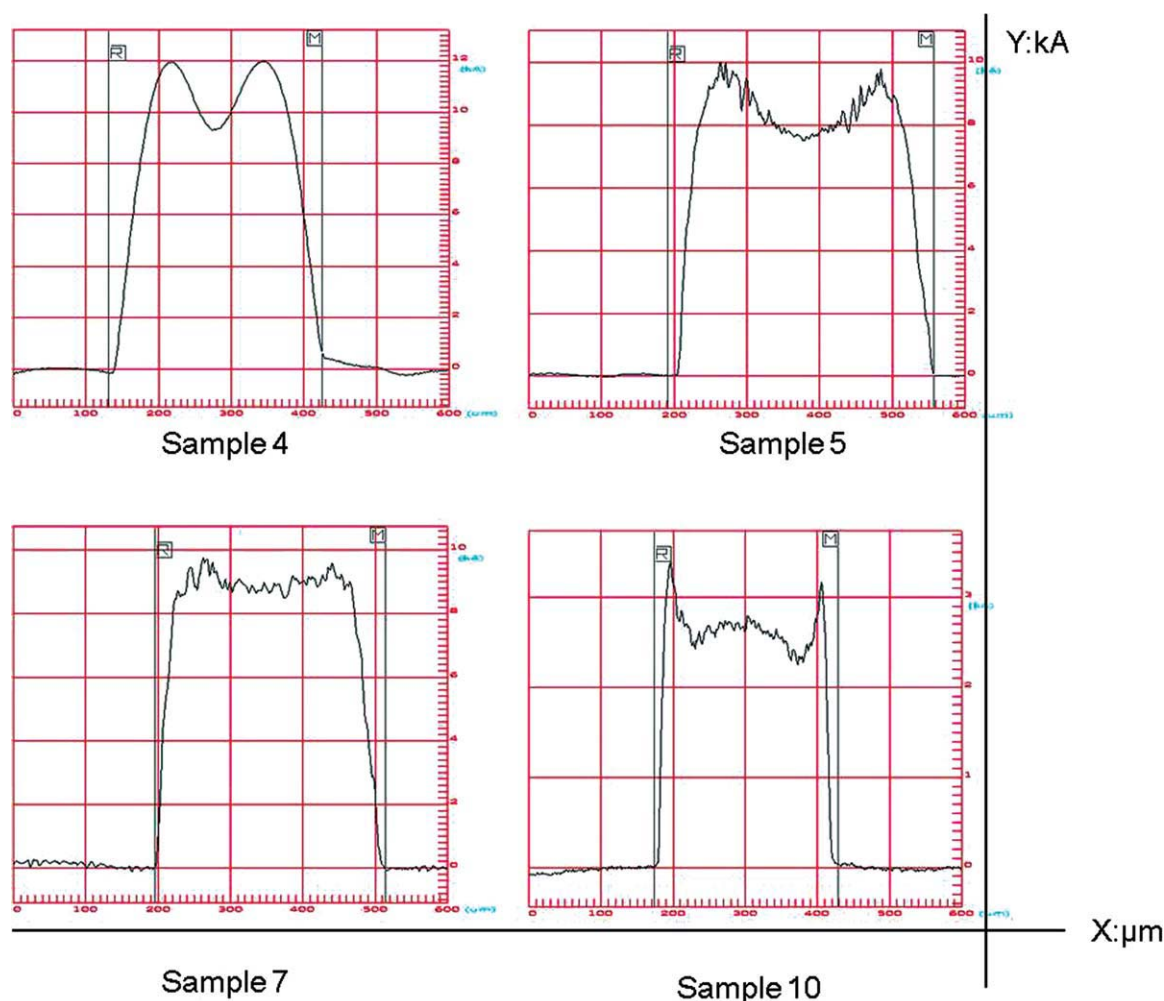
Figure 4 Cross-sectional areas of four coated stripe samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coffee-ring formation is the AV. Because the AV is closely related to the strength of hydrogen bonding, the structure of the copolymer was examined. Figure 1 shows that the effect of hydrogen bonding was mainly contributed by HEMA and MAA units because both units contained carbonyl and hydroxyl groups, whereas MMA had only a carbonyl group. We carried out FTIR analysis to investigate the hydrogen-bonding interaction of HEMA and MAA in the copolymer. A schematic representation of hydrogen bonding from carbonyl and hydroxyl groups of the copolymer is displayed in Figure 5. The stretching bands in the figure were obtained by previous researchers[23–25] who also studied the infrared spectra of free and hydrogen-bonded carbonyl groups of MAA and HEMA as well as the intermolecular and intramolecular hydrogen bonding. The FTIR spectra of copolymers with different AVs are shown in Figure 6. To carry out the FTIR analysis on a quantitative basis, we selected the peaks of carbonyl groups as the base lines for comparison because the contents of the carbonyl groups in the

three monomers were the same. The FTIR spectra in Figure 6(a) indicate that if all the peaks are rearranged to have maximum overlapping, we may observe the variations of the hydroxyl groups. The areas defined in Figure 6(a) were magnified, and the results are shown in Figure 6(b); hydrogen bonding due to free intermolecular or intramolecular interactions of the hydroxyl groups can be clearly observed. With similar approaches, the effects of the AV on the hydrogen bonding associated with hydroxyl groups and carbonyl groups could be identified. The hydrogen bonding associated with hydroxyl groups appeared between 3800 and 2600 cm^{-1}, whereas for carboxyl groups, the range was 1800–1600 cm^{-1}. The curves in these two regions were magnified and are also shown in Figure 6(b,c). Figure 6(b) shows that the variations of the FTIR spectra in the wavelength range of 3600–3200 cm^{-1} were not obvious with the AV increasing. Hence, the effect of hydrogen bonding due to hydroxyl groups on coffee-ring formation may be insignificant. On the other hand, the curves in Figure 6(c) show that as the
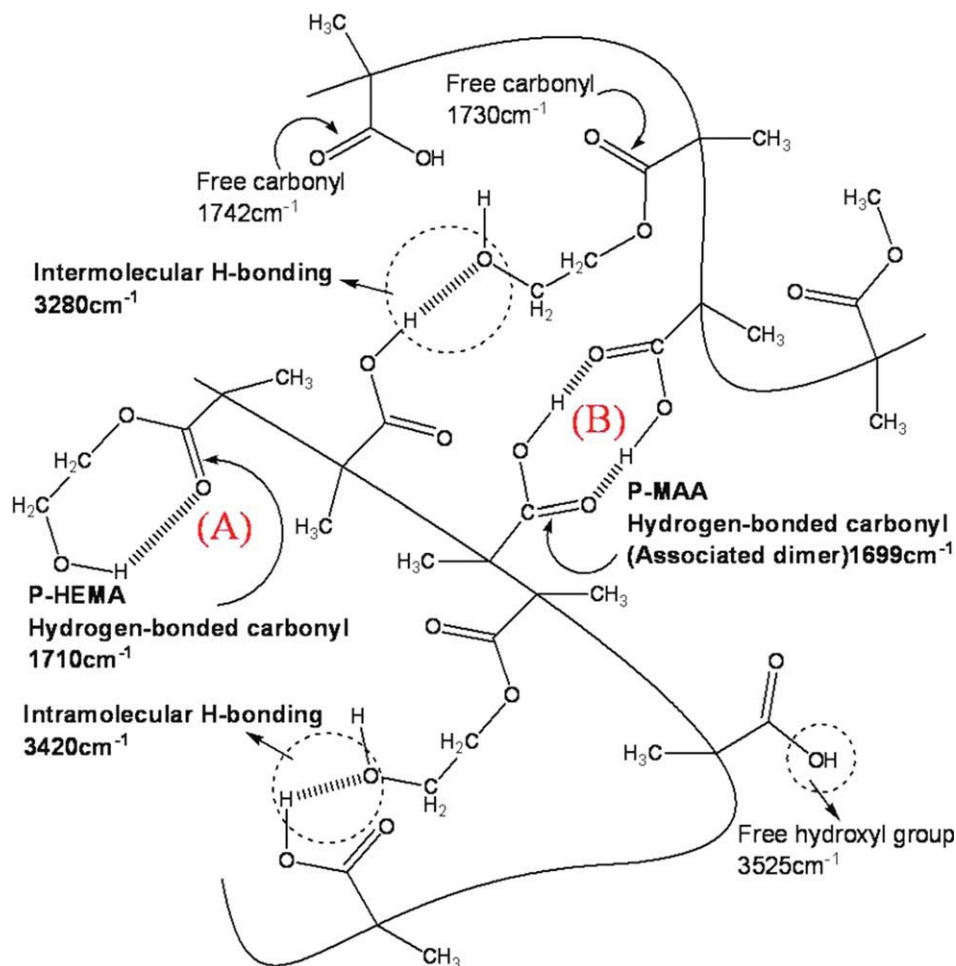
Figure 5 Schematic representation of intramolecular and intermolecular hydrogen bonding and free hydroxyl and carbonyl groups. P-HEMA = hydroxyl ethyl methacrylate in the copolymer; P-MAA = methacrylic acid in the copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

AV increased, the absorbance became stronger and stronger in the region between 1710 and 1690 cm^{-1}, and this suggests a stronger effect of hydrogen bonding of the carbonyl groups of HEMA and the associated dimers of MAA on coffee-ring formation.

A schematic representation of hydrogen bonding of carbonyl groups can be found in Figure 5. The intramolecular hydrogen bonding in HEMA (marked by A in the figure) rather easily forms. It has been reported previously[24,25] that this hydrogen bonding of HEMA is quite stable, and the hydroxyl groups in HEMA are unlikely to form intermolecular bonding with other carbonyl groups unless the carbonyl groups have strong attractive forces [e.g., poly(vinyl pyrrolidone) molecules with N next to C=O]. There were no such carbonyl groups in the solution systems that we analyzed, so the intermolecular hydrogen bonding of HEMA was negligible. On the other hand, for the formation of an associated MAA dimer, two MAA molecules would have to be properly arranged (marked by B in the figure) to form intermolecular bonding. This bonding would not be as easy and stable as the intra-molecular bonding of HEMA. On the basis of the FTIR spectroscopy analysis, it could be concluded that the intramolecular hydrogen bonding associated with the carbonyl groups of HEMA, in comparison with the hydrogen bonding of hydroxyl groups and the intermolecular bonding of MAA, played a dominant role in the formation of the coffee ring as the AV increased. This conclusion can be further quantified in Figure 7, which shows the FTIR spectra and the results of the least-square curve fitting. It is clear that as the AV increased, the absorbance of the hydrogen-bonding carbonyl groups of HEMA also increased, whereas the effects of the AV on other carbonyl groups were not obvious. Because the hydrogen-bonded carbonyl group was stretched and was about 1.5 times longer than the free carbonyl group,[23] the percentage of hydrogen-bonded carbonyl groups (f_b) could be calculated as follows:

$$f_b = \frac{A_b/1.5}{A_b/1.5 + A_f} \tag{2}$$

(a)The carbonyl group is baseline
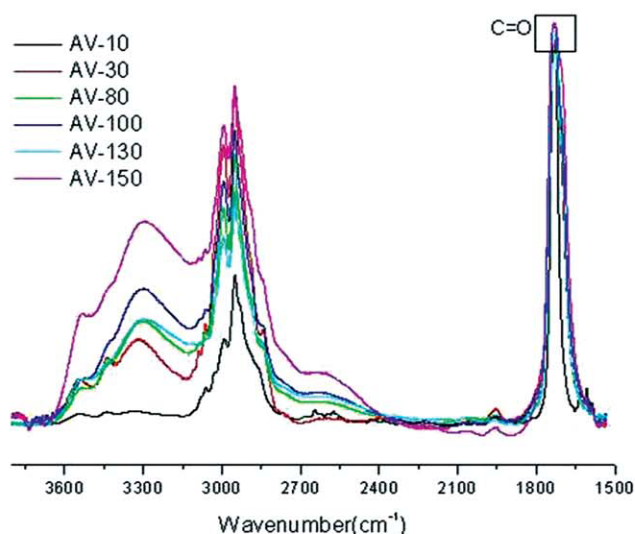
(b)Free, inter, intra -OH
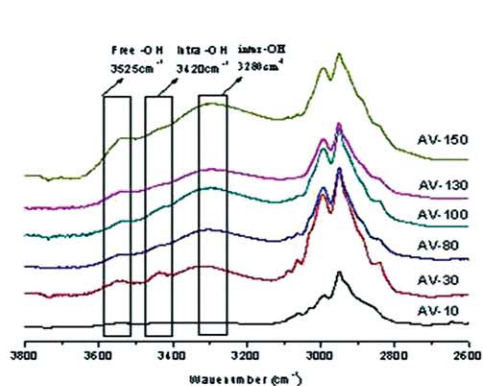
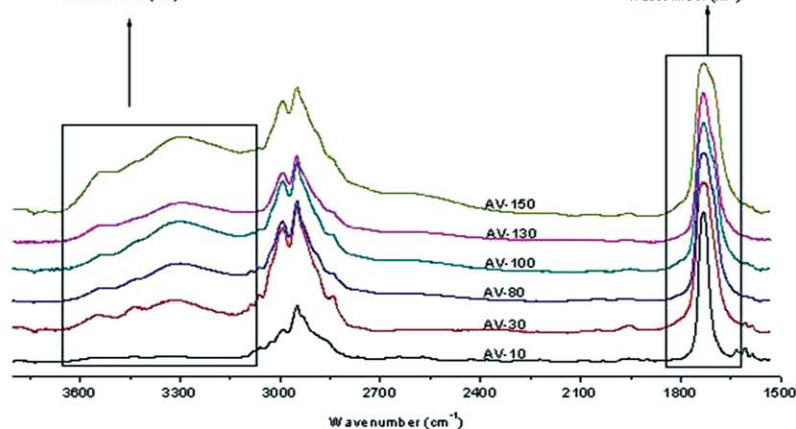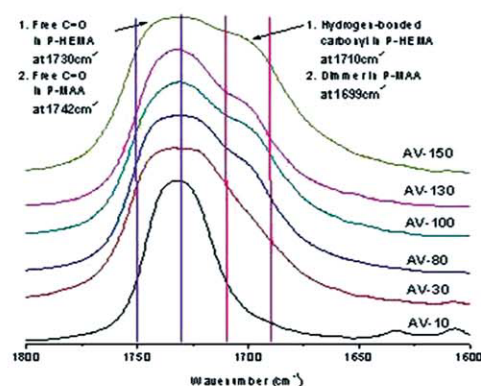## (c)Free and hydrogen bonding C=O

Figure 6 FTIR spectra of copolymers with different AVs: hydrogen bonding and free hydroxyl groups in the region of 3200–3600 cm^{-1} and hydrogen bonding and free carbonyl groups in the region of 1690–1750 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where A_b is the area percentage of hydrogen-bonded carbonyl groups and A_f is the area percentage of free carbonyl groups. Values of f_b based on the data in Figure 8 are listed in Table V. It is apparent that as the AV increased, A_b for hydrogen-bonded car-

bonyl groups in HEMA increased, so f_b also increased.

Deconvolution is possible for the polymer system presented in ref. 25 because the system has only a single hydroxyl group. We had three types of
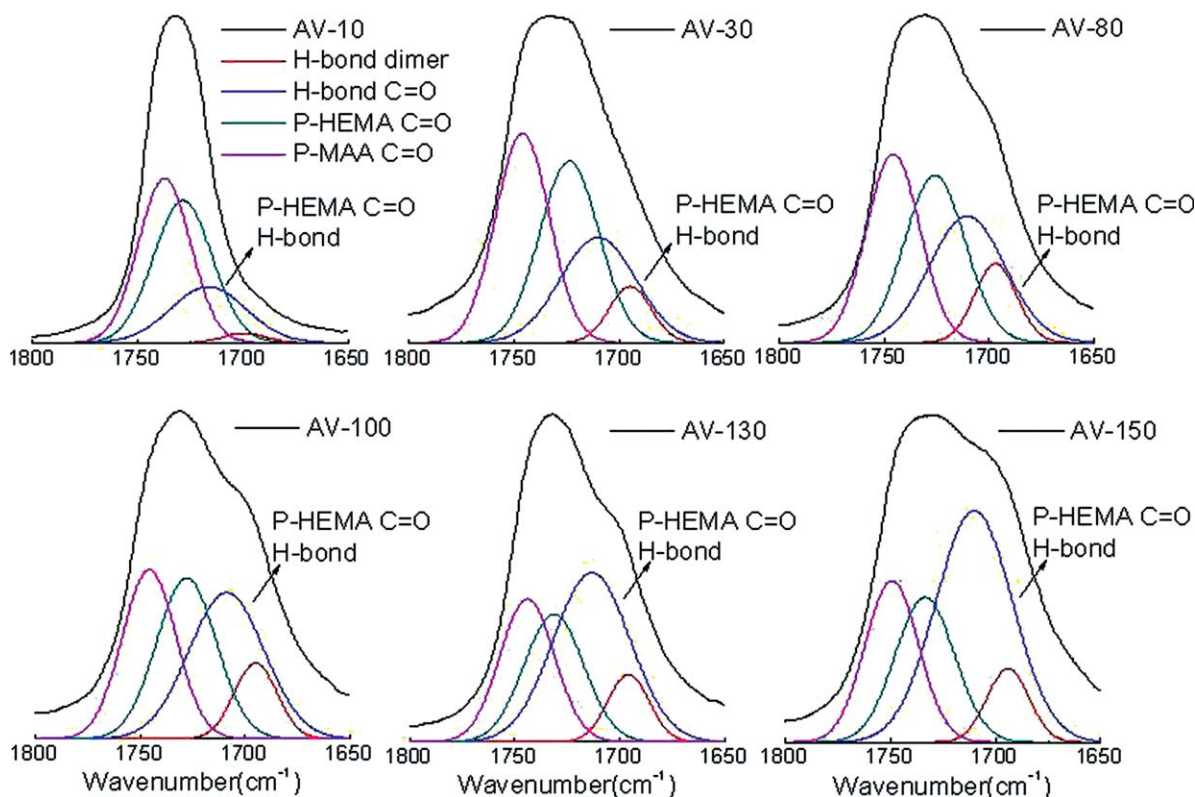
Figure 7 FTIR spectra and curve-fitting results for carbonyl groups with different AVs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

functional groups (—COOH, C=O and OH) in the solutions, and there were many possibilities for the three groups to develop hydrogen bonding with the hydroxyl groups; therefore, it is impossible for us to show the deconvolution results of the hydroxyl groups.

The FTIR spectra for coating solutions with the same AV but different solvents are displayed in Figure 8. The coating stripes were baked at 180°C for the complete removal of the solvents before the FTIR analysis. Some were even baked at 200°C for 30 min to test whether the colors of the stripes were different, and it was found there was no change in the appearance of the samples. Color filters were coated at room temperature and then dried at a temperature lower then 180°C in a real production situation. Therefore, a high-temperature thermal analysis such as thermogravimetric analysis may not be needed, and this may also require an even higher temperature for measurements. Because there is not much difference between the three spectra, we can conclude that the strength of hydrogen bonding was independent of the solvent. However, photographs of the cross-sectional areas of the same coating solutions (Fig. 9) indicate that highly volatile THF was the best solvent for removing coffee rings. Hence, in addition to the AV effect, the rate of solvent evapo-

ration is another key factor influencing the formation of coffee rings.

The mechanism of coffee-ring formation is primarily influenced by two factors: the AV and solvent evaporation. Because the contact lines are pinned at
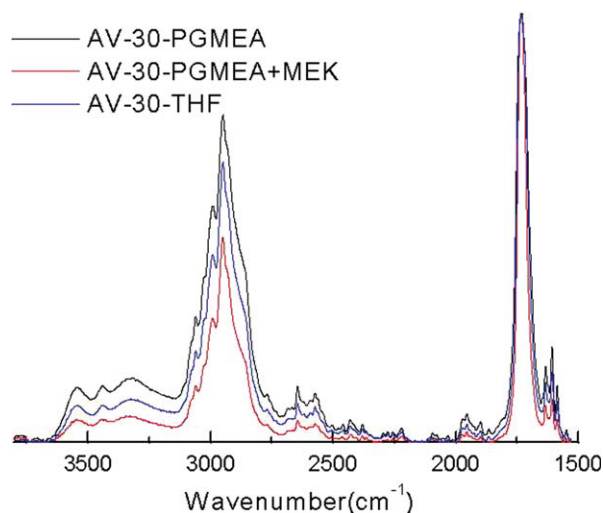

Figure 8 FTIR spectra for different solvent systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE V
Curve-Fitting Results for Carbonyl Groups

| | Carbonyl group of HEMA | | | | | Carbonyl group of MAA | | | |
| | Free | | Hydrogen bond (C=O; intra) | | | Free | | Hydrogen bond (dimer) | |
Polymer	ν (cm^{-1})	A_f (%)	ν (cm^{-1})	A_b (%)	f_b (%)	ν (cm^{-1})	A_f (%)	ν (cm^{-1})	A_b (%)
AV-10	1728	38.7	1716	19.6	25.2	1737	39.8	1699	1.8
AV-30	1723	33.3	1710	24.6	33.0	1745	34.8	1694	7.3
AV-80	1726	30.6	1711	29	38.7	1746	30.4	1697	10
AV-100	1728	29.1	1709	33.4	43.3	1746	27.7	1695	9.8
AV-130	1731	24.4	1713	41.7	53.3	1744	25	1696	8.9
AV-150	1733	22.5	1710	46.7	58	1749	22.7	1694	8.1

the two edges of the coated stripes, the coating solution will move toward the edges. However, a highly volatile solvent will reduce the time allowed for the coating solution to move toward the edges. It was found from the recorded images that the coffee rings formed within a few milliseconds without heating, and there was no evidence of Marangoni flow. On the other hand, the AV affects the strength of hydrogen bonding. The pictorial representation of polymer entanglements shown in Figure 10 can be used to explain the effect of hydrogen bonding. The sketch in Figure 10(a) may represent the situation for the case of AV = 150. As found earlier, the intramolecular hydrogen bonding of the carbonyl groups of HEMA is dominant. Long-chain molecules tend to have self-entanglement, so it becomes easier for the solvent to carry long-chain molecules to the edges and to form a coffee ring. When the AV drops to 30, the sketch in Figure 10(b) implies that both interhydrogen and intrahydrogen bonds are important. The networking of entangled polymers increases the flow resistance for the coating solution moving to the edges. Finally, when the AV is too low, the polymer molecules are widely spread, as represented by the sketch in Figure 10(c) for the case of AV = 10. In this case, hydrogen bonding is weak, and the entanglement of long-chain molecules is loose in the coating solution; this enables the coating solution to move more freely to the edges to form coffee
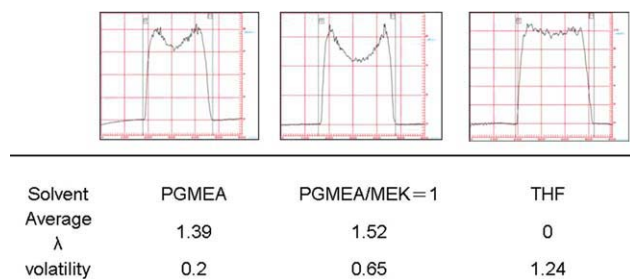
rings. Therefore, hydrogen bonding serves as resistance to solvent movement. The competition of intermolecular and intramolecular bonds determines the strength of solvent flow resistance.
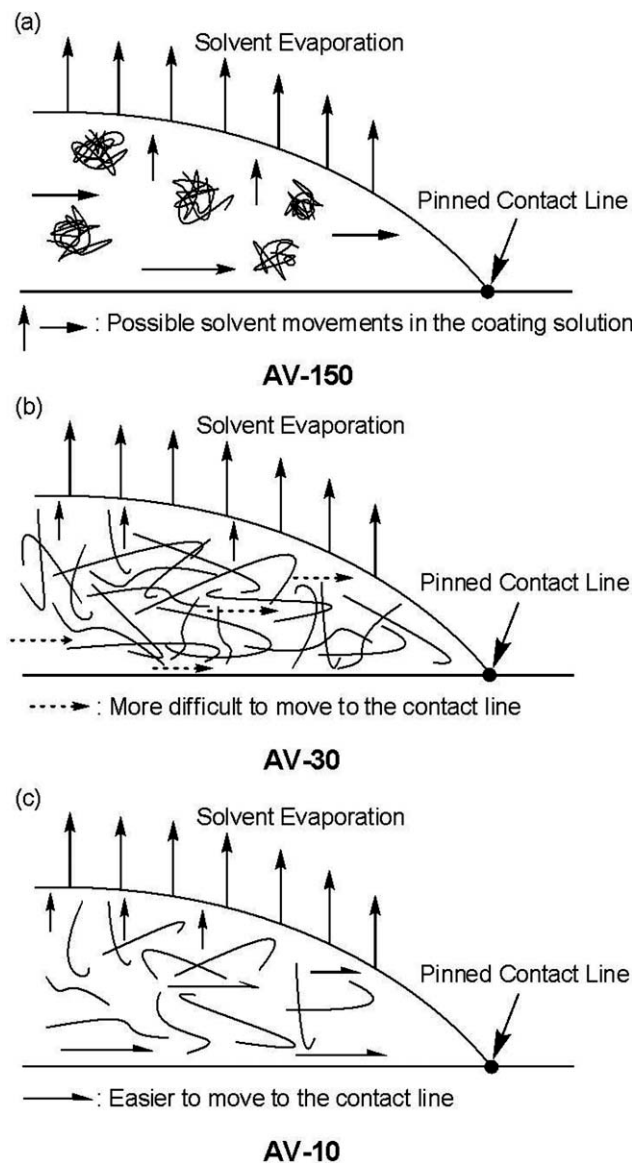
Figure 10 Schematic representations showing the molecular entanglements at different AVs.

Solvent	PGMEA	PGMEA/MEK=1	THF
Average λ	1.39	1.52	0
volatility	0.2	0.65	1.24

Figure 9 Cross-sectional areas for the three solvent systems shown in Figure 8. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

An experimental study examining the quality of a narrow coated stripe with a width of approximately 350 μm was carried out. The coating solution was based on a new patented formulation involving pigments, solvents, and a novel alkali solution resin. The resin was a copolymer of three types of monomers: HEMA, MAA, and MMA. Solvents of different volatilities (PGMEA, MEK, and THF) were used.

Coffee rings were found after the coated stripes were baked and dried. Several factors that could influence the formation of coffee rings were investigated. The effects of pigment addition and the rheological properties of the coating solutions were ruled out, and two critical parameters were identified for coffee-ring formation. These two parameters were the rate of evaporation of the solvents and the AV of the coating solution. It was found that using a highly volatile solvent such as THF and, at the same time, adjusting the AV of the coating solution to some optimum value could effectively eliminate the formation of coffee rings.

FTIR spectroscopy analysis revealed that the strength of intramolecular hydrogen bonding associated with the carbonyl groups of HEMA increased when the AV of the coating solution increased. A proper balance of intermolecular and intramolecular hydrogen bonding in the coating solution could effectively create enough flow resistance to reduce the movement of the solvent to the pinned contact lines and thus minimize the formation of coffee rings. A higher rate of solvent evaporation also helped to reduce ring formation because there was not enough time for long-chain molecules to migrate toward the edges. Therefore, by proper manipulation of the solvents and the AV of the solution, coffee rings can be eliminated or produced for different applications. For example, a coated stripe with a high value of λ may serve as a guide for ink-jet printing of a line with acceptable edge quality. A coated stripe with rings of a sinusoidal shape, as shown in Figure 4 (sample 4), may serve as a good light reflector for certain optical and electronic applications.

References

1. Hiroshi, O. U.S. Pat. 5,317,434 (1994).
2. Zong, F. L. U.S. Pat. 6,271,900 (2001).
3. Yang, T. F.; Sheng, L. P.; Bii, C. C.; Kuo, L. L. U.S. Pat. 6,171,885 (2001).
4. Koo, H. S.; Pan, P. C.; Kawai, T.; Chen, M.; Wu, F. M.; Liu, Y. T.; Chang, S. J. Appl Phys Lett 2006, 88, 111908.
5. Koo, H. S.; Chen, M.; Pan, P. C.; Chou, L. T.; Wu, F. M.; Chan, S. J.; Kawai, T. Displays 2006, 27, 124.
6. Koo, H. S.; Chen, M.; Pan, P. C. Thin Solid Films 2006, 515, 896.
7. Hiroshi, K.; Natsuo, F.; Satoru, K.; Masaharu, S.; Keiji, T.; Tadaaki, K. U.S. Pat. 6,630,274 (2003).
8. Hiroshi, K.; Takao, N.; Tatsuya, S.; Masaru, K.; Sadao, K. U.S. Pat. 5,952,129 (1999).
9. Kokubo, S.; Yoshikawa, T.; Osano, N. Jpn. Pat. JP 2003344642 (2003).
10. Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. Nature 1997, 389, 827.
11. Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. Phys Rev E 2000, 62, 756.
12. Deegan, R. D. Phys Rev E 2000, 61, 475.
13. Lyon, P. J.; Carter, J. C.; Bright, J. C.; Cacheiro, M. W.O. Pat. 02/069119 A1 (2002).
14. de Gans, B. J.; Schubert, U. S. Langmuir 2004, 20, 7789.
15. de Gans, B. J.; Tekin, E.; Schubert, U. S. J Mater Chem 2004, 14, 2627.
16. Park, J.; Moon, J. Langmuir 2006, 22, 3506.
17. van den Berg, A. M. J.; de Laat, A. W. M.; Smith, P. J.; Perelaer, J.; Schubert, U. S. J Mater Chem 2007, 17, 677.
18. Tekin, E.; Holder, E.; Kozodaev, D.; Schubert, U. S. Adv Funct Mater 2007, 17, 277.
19. Lim, J. A.; Lee, W. H.; Lee, H. S.; Lee, J. H.; Park, Y. D.; Cho, K. Adv Funct Mater 2008, 18, 229.
20. Soltman, D.; Subramanian, V. Langmuir 2008, 24, 2224.
21. Huang, K. T.; Chao, S. D.; Cheng, I. J.; Chang, M. H. U.S. Pat. 7,090,062 (2006).
22. Lin, Y. C. M.S. Thesis, National Tsing Hua University, Hsin Chu, Taiwan, 2008.
23. Huang, C. F.; Chang, F. C. Polymer 2003, 44, 2965.
24. Huang, C. F.; Kuo, S. W.; Lin, F. J.; Wang, C. F.; Hung, C. J.; Chang, F. C. Polymer 2006, 47, 7060.
25. Lin, H. C.; Wang, C. F.; Kuo, S. W.; Tung, P. H.; Huang, C. F.; Lin, C. H.; Chang, F. C. J Phys Chem B 2007, 111, 3404.
26. Brandrup, J.; Immergut, E. H. Polymer Handbook, 3rd ed.; Wiley: New York, 1989; Chapter II, p 153.