Functional Imaging with Chemically Amplified Resists and Organic Molecules

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Chemically amplified resists were tested for preparing universal templates to bind various organic species in micron-scale patterns (functional images). UV exposure and heating of a poly(di-*tert*-butyl fumarate-*co*-styrene):onium salt resist produced alternating areas of nonpolar ester and polar acid/anhydride polymers. Various compounds that were fluorescent dyes or amines could then be placed selectively either into or onto exposed or nonexposed areas, according to the nature of solvents and binding species. The ease and extent of immobilization were found to depend on (i) resist composition, (ii) matrix wettability and permeability by a solvent, and (iii) covalent, ionic, dipole−dipole, or other sorbate−matrix binding interactions.

Introduction

Since their first appearance in the early 1980s, chemically amplified (CA) resists have evolved into a leading-edge patterning technology, capable of resolving sub-quarter-micron features. They were made possible by the development of photosensitive onium salts whose irradiation released strong acid;[1−3] these photoacid generators (PAG) were later combined with acid-sensitive poly(*t*-BOC−OSt).[4−7] Recent developments in CA resist chemistry, irradiation techniques, and process conditions have provided a basis for upcoming mass production of 1−4 Gbit DRAM and other devices with successively smaller critical dimensions.[8−10]

The patternability of microresists also continues to attract attention for several applications other than microelectronics manufacturing. In microoptics, polymer resists have been used to create interconnected channel waveguides and grade coupler elements.[11] The production of optical storage media and liquid-crystal displays (LCD) also involves resist technology. Another nonlithographic example is the creation of array biosensors: subsequent binding of different biomolecules onto a polymer surface has been accomplished employing photodeprotection of hydroxyl groups.[12] Indeed, any application involving micron-scale features can benefit from microresist ideas and technologies.

In microelectronics manufacture and other processes to date, photoresists have usually played only brief (though essential) roles in translating images into an underlying substrate through the following steps: (i) patternwise irradiation of the photosensitive polymer coating; (ii) development of the irradiated polymer into a "relief" image, revealing areas of an underlying (usually inorganic) substrate; (iii) etching or a modifying of the substrate in such denuded areas; (iv) stripping away of the remaining polymer. The substrate surface thus eventually is made to bear an image as areas of contrasting materials, e.g., of insulating vs conducting areas in a circuit pattern.

Alternatively, the polymer coating itself, which has been irradiated and heated to contain a pattern of micron-scale alterations of properties, can be considered a useful structure. Thus, a resist that bears a pattern of altered chemical, physicochemical, and physical properties can be used either directly (e.g., making use of contrasting refractive indexes for waveguiding) or indirectly through its ability to further space-selectively sorb, release, or transport different chemicals of interest. These can be inorganic metal ions and salts, organic nonlinear optical materials, and other dyes, as well as complex biomolecules, oligomers, or even other polymers. With a patterned and functionalized polymer film as product, the etching and stripping steps of the normal microlithographic process are now obviated, though certain areas may be selectively removed by liquid or plasma developers.

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**Scheme 1. Chemical Transformations in a CA
Resist Based on PDBFS**
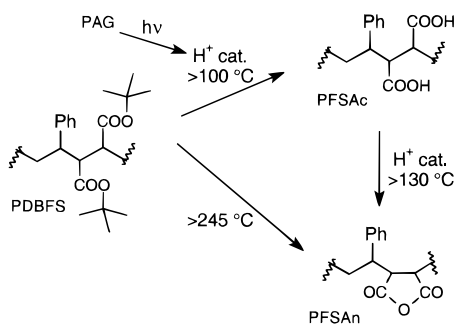
The simplest CA resists consist of a photosensitive catalyst generator and a polymer matrix with catalyst-labile groups. After irradiation, an initial photochemical event—the formation of a small amount of catalyst—is amplified hundreds of times by a cascade of thus-catalyzed reactions of cross-linking, scission, or rearrangement. With their dramatic alterations in structure and reactivity upon small UV doses, deprotection-style CA systems are obviously the first choice for space-selective sorption. The *tert*-butyl ester-based chemistry looks particularly attractive: along with its main function as an acid-labile moiety, this group is also the precursor of highly reactive carboxylic acid groups and, upon further heating, anhydride moieties.

In previous reports we described the formulation of an onium salt with poly(di-*tert*-butyl fumarate-*co*-styrene) (PDBFS) as a good resist for normal (relief-forming) lithography (Scheme 1).[13,14] Its patterning with UV irradiation, followed by heating, produced contrasting areas of the initial PDBFS diester, and newly formed poly(fumaryl-*co*-styrene) acid (PFSAc) or anhydride (PFSAn). Preliminary experiments also showed that various fluorescent dyes could be made to bind to either the protected (PDBFS) or deprotected (PFSAc/An) areas, according to the chosen solvent system, in patterns of 5−10 μm resolution even with a rather rudimentary exposure tool, thus showing the applicability of such resists and processes to achieve space-resolved binding.[13]

A number of articles have presented studies on the creation and application of patterned functionalization of resists with organic and inorganic species. Some reported procedures for microlithography, such as DESIRE,[15] CARL,[16] and a surface (or near-surface) metallization,[17−19] already depend on selective modifications of either irradiated or nonirradiated areas with plasma-resistant inorganic species. Photodirected modifications of polystyrene and poly(3-octylthiophene) have been done with perfluorophenyl azides and fluorescent dyes.[20] Photoinduced grafting of unsaturated molecules

to poly(organophosphazenes) has resulted in structures that were able to immobilize amines, some biomolecules, and metal ions.[21] In the last two examples, relatively large UV doses (in the 1000 mJ/cm^2 range) were needed, because the matrix was modified by direct photoreaction, rather than by a catalytic process (chemical amplification). So far, patterning of organic dyes into CA resists has been briefly reported only from our lab[13,22] and from AT&T labs,[23] where Schilling et al. used a polystyrene with capped phosphonic acid as a template.

Thus, the objective of our research was to explore a variety of ways and conditions to place species of different natures into patterned polymer CA resist systems. This report concerns sorption of organic chemicals from solutions and vapors. A companion report on binding of several metal ions to the same templates of PDBFS:onium salt resist has been published recently.[22]

A set of chemicals for binding was chosen among dyes and amines. Besides the products of dye patterning (e.g., nonlinear optical materials), we were also interested in the process of dye sorption, as can easily be monitored at low concentrations by UV−vis or fluorescence spectroscopies. Amino groups in particular can bind by H-bonding, or ionically, or covalently to acyl moieties. Synthetic dyes and alkylamines could also be models of biomolecules with amino groups, for techniques to place them into desired areas, which is of potential interest for ultramicroscale biochemical analysis or synthesis.

Experimental Section

Chemicals. Hexane, toluene, methanol, *n*-, and 2-propanol were all "glass-distilled" grade from OmniSolv Inc., and *tert*-butyl alcohol was from Baker. Fluorescent dyes (see Scheme 2) rhodamine-6G (R6G), 3-amino-9-fluorenone, 2-aminoanthracene, anthracene, fluorescein, and Brilliant Sulphaflavine came from Aldrich, and fluorescein dibutyrate from Nutritional Biochemicals. Preparations of strongly solvatochromic fluorescent dyes 2-[4-(*N*-methyl-*N*-octylamino)styryl)]pyridine (DAASP-8), its analogue with a C$_{18}$ alkyl tail (DAASP-18), and 4-(5-(*N,N*-dimethylamino)naphthalenesulfonylamido)-1-methylpiperazine (DSMP) were all described previously.[13] Propylene glycol methyl ether acetate (PMA), aqueous ammonia solution (30% NH$_3$/H$_2$O diluted 1:5 with distilled water), and 1,10-diaminodecane, 2- and 4-aminopyridine, and 2,6-diaminopyridine amines were all from Aldrich, "analytical pure" pyridine from BDH, and poly(ethyleneimine) (M_w = 10 kg/mol, 30 wt % in water) from Polysciences.

Photoresist Preparation and Exposure. Di-*tert*-butyl fumarate was prepared from fumaryl chloride and potassium *tert*-butoxide and then polymerized with styrene in toluene by AIBN. The resulting PDBFS was mainly alternating with ca. 45 mol % of fumarate units, M_n = 12 kg/mol, M_w = 20 kg/mol, [η] = 0.08 in chloroform.[13] Photoacid generators (PAG) 4-(phenylthio)phenyldiphenylsulfonium (4TS−SbF$_6$) and triphenylsulfonium (TPS−SbF$_6$) hexafluoroantimonates, and diphenyliodonium triflate (DPI−OTf), were synthesized by known methods.[2]

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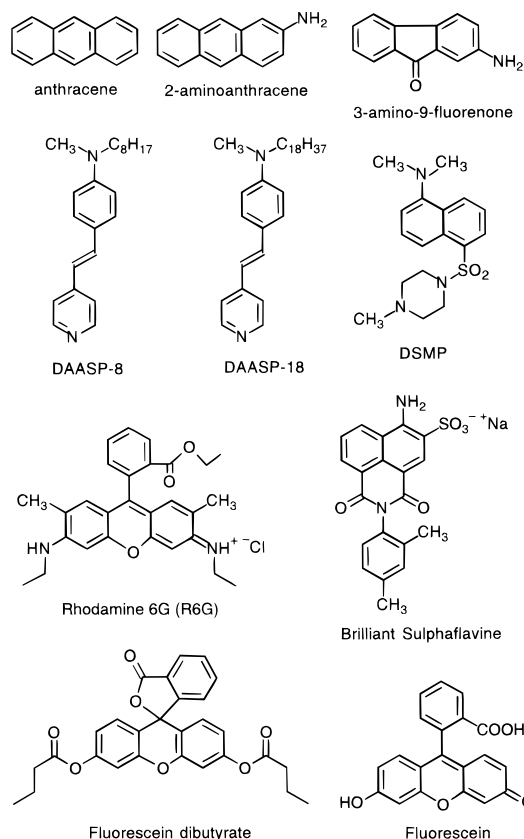(15) Coopmans, F.; Roland, B. *Proc. SPIE* **1986**, *633*, 34.

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Scheme 2. Structures of Fluorescent Dyes

anthracene

2-aminoanthracene

3-amino-9-fluorenone

DAASP-8

DAASP-18

DSMP

Rhodamine 6G (R6G)

Brilliant Sulphaflavine

Fluorescein dibutyrate

Fluorescein

Resist samples were prepared by dissolving 50 mg of PDBFS with 5 mg of an onium salt in 350 mg of redistilled PMA. Because of its slow solubilization, the DPI–OTf salt was first dissolved in one drop of methanol before mixing with the other components. These solutions were filtered through 0.2 μm inorganic membrane filters Anotop-10 (Phenomenex Inc.) and spin-coated onto a substrate at 1000 rpm for 40 s to give 0.8–0.9 μm optically clear films. After postapply bake (PAB) for 60 s at 130–135 °C, the samples were irradiated at 254 nm to 0–100 mJ/cm^2 and then postexposure baked (PEB) at various temperatures and times.

Binding Experiments. Although the resist can perform well at much smaller PAG loading and UV dose,[13] we chose a formulation of PDBFS:4TS–SbF$_6$ 10:1 w:w, a dose of 100 mJ/cm^2, and PAB and PEB both of 130–135 °C for 60 s. These parameters were chosen on the basis of IR results as discussed below.

Thirty milliliter portions of 0.1–0.2 wt % of dye or 1–2 wt % of colorless amine in an appropriate pure or mixed solvent were each placed in a 60 mL beaker. Polymer samples on pieces of Si wafer were immersed into these "functional developing" solutions for 15–30 s with gentle shaking. Samples were then quickly rinsed for 10 s in the same solvent(s) without additives and air-dried before evaluation. To check the stability of binding, the fluorescence of some samples was evaluated both before and after brief then prolonged continued similar rinsing. In most cases we irradiated only half the area of a coated wafer, then processed, treated, and analyzed both irradiated and nonirradiated areas in identical conditions. Thus, contrast (space-selectivity) between exposed and unexposed areas was determined in one run.

Instruments. Using a Headway Research spin-coater, films were applied onto either pieces of Unisil silicon test wafers 3 in. × 330–432 μm N/P ⟨1–1–1⟩, or National Scientific GE 124 polished fused quartz plates 1 in. × 1 in. × $^1/_{16}$ in. (for UV–vis spectrophotometry). The UV source was a Cole-Palmer 9815 Series 100 W UV Hg lamp with a built-in 254 nm narrow-bandwidth filter. Exposures at 254 nm were measured using an Optical Associates OAI P306-001-002 powermeter, and controlled with a timer. PAB and PEB were done on a hot-plate with a surface thermocouple control.
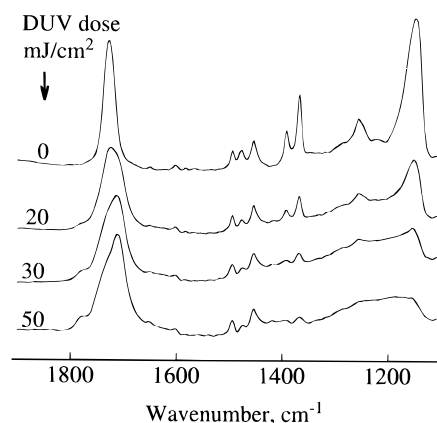

Figure 1. IR spectra of the PDBFS:4TS–SbF$_6$ resist after various deep-UV doses. PAB and PEB for 60 s at 130 °C.

Infrared spectra of coated Si wafers were taken with the IR microscope accessory of a Bruker IF-48 FTIR spectrophotometer in transmission mode. Data were collected at 2 cm^{-1} resolution and converted to graphics by SigmaPlot software from Jandel Scientific. UV–vis spectra were taken on a Shimadzu Spectronic-210UV spectrophotometer. Fluorescence measurements were made with a Spex Model F-112 spectrofluorometer with a 450 W xenon lamp, with the sample surface perpendicular to the incident beam, and the emission detector at 90° for solutions in cuvettes or at 22.5° for solid films. The concentrations of the dyes for the solution fluoroscopy were 1–2 g/L. The spectra were corrected and normalized for comparison. The rough evaluation of dye binding—strong, moderate, weak, absent—was estimated by visual inspection of the samples inside a Spectroline C-4 UV cabinet (Spectronics Corp.) under 365 nm illumination. Solubility of each dye in different solvents—soluble, partially soluble, insoluble—was checked by the apparent fluorescence, color, and turbidity of the solution.

Results and Discussion

IR Study of Catalytic Deprotection. In a previous study[13] we described conditions for relief developing of PDBFS-based resists: (i) PAB for >60 s at 130–140 °C; (ii) exposure to >14 mJ/cm^2 at deep- or mid-near-UV; (iii) PEB for >30 s at >100 °C; (iv) developing in aqueous bases (positive-tone relief image) or in certain organic solvents (negative-tone relief image).

Here though, to understand and optimize the binding species of different natures, more information is required about transformations of the polymer matrix, especially the ester:acid:anhydride ratio after processing under different conditions.

Figure 1 shows a representative set of IR spectra taken from PDBFS:4TS–SbF$_6$ films after different exposures, with PEB for 60 s at 130–135 °C. All peaks characteristic of *tert*-butyl ester, at (in cm^{-1}) 1145 (s, C–O–C, sym), 1254 (m, C–O–C, asym), 1367 and 1392 (m, CH$_3$), 1728 (vs, C=O), 2977 and 3003 (m, CH$_3$), gradually disappeared with increasing UV dose. The accompanying formation of H-bonded carboxylic acid dimers was evident by a detectable shift of the C=O peak to 1708 and by the appearance of the broad hydroxyl band in the 3000–3500 region. The assignment of a new peak at 1745 is less obvious. It can hardly be from intermolecular anhydride, because generally this would show another strong peak above 1800, as in butanoic acid anhydride's 1820 (vs),[24] which was

(24) Pouchert, C. H. *Aldrich Library of FT-IR Spectra*, 1st ed.; Aldrich Inc.: Milwaukee, WI, USA, 1985; Vol. 1–2.

PEB temp
(°C)

25
110
130
150
180

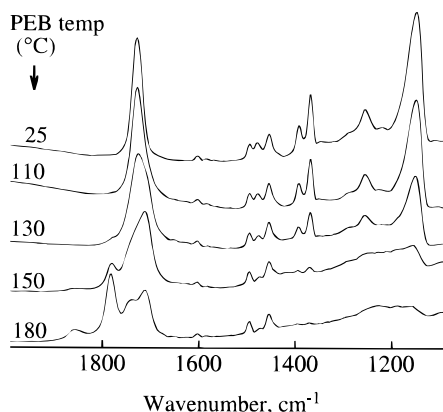1800   1600   1400   1200

Wavenumber, cm⁻¹

Figure 2. IR spectra of the PDBFS:4TS−SbF₆ resist after PEB for 30 s at various temperatures. PAB for 60 s at 130 °C; exposure of 25 mJ/cm² at 254 nm.

clearly lacking here. A second explanation is that this C=O signal also originates from a −COOH, but one that sits in a microenvironment different from that producing the 1708 peak, possibly due to a different type or degree of hydrogen bonding. Indeed, this is probably the reason that the IR spectra of many anhydride-free mono- and dicarboxylic acids show more than one peak in the 1700−1750 region.[24] Working with somewhat similar resists, Ito et al.[25] have assigned their 1740 peak to a "free", non-H-bonded carboxylic acid group. There was no IR evidence of aryl alkyl ketone groups, from theoretically possible Friedel−Crafts acylation side reactions.

As we expected, all processing parameters affected the eventual chemical composition of the irradiated resist. 30 mJ/cm² of deep-UV was enough to remove almost all *tert*-butyl groups after mild PEB. The immediate main products were both kinds of carboxylic acid groups discussed above (1708 and 1745) in comparable amounts, although higher doses gave slightly more of the 1708 signal (Figure 1). IR spectra after a fixed UV dose 25 or 100 mJ/cm², and various PEB, showed that baking longer than 30 s at the same temperature gave little further changes. A more important factor was the PEB temperature (Figure 2). Thus, at 110 °C, deprotection was not complete even after 100 mJ/cm² and 180 s of heating. At 130 and 150 °C, baking gave massive ester deprotection to −COOH. At still higher temperatures (180 °C) and longer times, more and more anhydride was formed. This was evident by a new peak at 1780 together with a small satellite at 1855, consistent with sterically favorable intramolecular cyclic anhydride (compare succinic anhydride at 1790 (s) and 1870 (m), and especially poly(maleic anhydride-*co*-styrene) at 1779 (s) and 1856 (m)).[24] Other side-reactions, such as extrusion of CO or CO₂, might also be possible under conditions of elevated temperatures (>170 °C), oxygen, and acid.[25,26] Thus, we chose an intermediate temperature and time for PEB to largely avoid any such further reactions of deprotected −COOH.

A comparison between our available types of PAG showed this to be another factor affecting the acid: anhydride ratio in the product. At PDBFS:PAG 10:1

w:w loading, and identical PAB, PEB, and deep-UV dose 100 mJ/cm², the amount of anhydride increased in the series 4TS−SbF₆ < TPS−SbF₆ < DPI−OTf. Assuming a complete conversion to photogenerated acid at such a high dose, both TPS−SbF₆ and DPI−OTf release more acid for the same mass, since their molecular masses are lower. Also, the stronger triflic acid from DPI−OTf may better promote eventual dehydration, compared to hexafluoroantimonic acid from 4TS−SbF₆ and TPS− SbF₆. Indeed, elsewhere[27] we have found that triflic acid from DPI−OTf intensively promoted condensation of vicinal carboxylic acid groups, while HSbF₆ from other onium salts was inactive under similar conditions.

Overall, this IR study revealed a range of composition and processing conditions (the "processing window") for maximizing carboxylic acid content. On the basis of these results, we chose the PDBFS:4TS−SbF₆ 10:1 w:w formulation, 100 mJ/cm² exposure, and PAB and PEB for 60 s at 130−135 °C, as standard conditions for binding experiments, at which slight variations of these parameters had little effect on the resist reactions.

Modes for Selective Binding. In CA resists in general, irradiation then heating creates a latent image of altered and unaltered areas. With the PDBFS resist, these areas consist of the nonpolar PDBFS and the highly reactive polar PFSAc/An materials (Scheme 1). We thus considered the following possible mechanisms of selective sorption:

(i) For the PDBFS: treatment with moderately apolar solvents that swell and transport solutes into this nonpolar matrix, to be nonspecifically trapped on drying, without reaction of the polymer's hindered ester groups.

(ii) For the PFSAc/An: similar nonspecific trapping from more polar solvents, along with either ionic interaction or covalent binding of reactive solutes to acid groups and or their covalent binding to anhydride groups.

Moreover, sorption can be made to occur from vapors and nonswelling solvents as well, and either into the bulk or merely onto the surface of a resist area.

Patterning of Dyes. Table 1 presents a summary of the binding experiments with different dyes from various solvent systems; the results are grouped in sets to highlight effects of template, dye, and solvent nature. Having amino or quaternary ammonium groups, some dyes were soluble in pure water, but no sorption was detected from that solvent even into PFSAc, which was not even wetted. The addition of different C1−C4 alcohols to water dramatically increased both the solubility of other dyes and its wetting of the PFSAc surface. Most alcohols improved this wettability after 10−15 vol % alcohol content but above 30−60 vol % of methanol, ethanol, 2-propanol, and *n*-butanol, the PFSAc dissolved. From solutions of intermediate concentrations of these alcohols, we observed strong binding of dyes, but often accompanied by an undesirable swelling of the matrix. An exception was the water:*tert*-butyl alcohol combination, which wetted but did not swell the PFSAc at almost all solvent ratios. The alcohol *tert*-butyl group appears to be sufficiently nonpolar, and its hydroxyl sufficiently hindered, to prevent dissolution of the PFSAc. From the 2:1 v:v water:*tert*-butyl alcohol solution, almost all tested dyes were successfully placed into

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Table 1. Binding of Dyes in PFSAc and PDBFS Materials

PFS	dye	solvent(s)	v:v	dye uptake, comments
acid	R6G	H_2O	pure	no wetting of the film
	R6G	H_2O:methanol	10:5	weak, no film swelling
	R6G	H_2O:methanol	10:10	strong, partial swelling
	R6G	H_2O:methanol	10:20	film dissolved
	R6G	H_2O:*t*-butanol	10:5	strong, no swelling
	DSMP	H_2O:methanol	10:10	strong
	DAASP-8	H_2O:*n*-propanol	10:7	strong
	DAASP-18	H_2O:*t*-butanol	10:10	strong
	fluorescein	H_2O:*t*-butanol	10:5	strong
	3-amino-9-fluorenone	H_2O:*t*-butanol	10:5	strong
	2-aminoanthracene	H_2O:*t*-butanol	10:5	strong
	Brilliant Sulphaflavine	H_2O:*t*-butanol	10:5	strong
	anthracene	H_2O:*n*-propanol	10:7	no binding
ester	DSMP	toluene	pure	film dissolved
	DSMP	hexane:toluene	10:1	strong
	DSMP	hexane[a]	pure	weak, no swelling
	DAASP-18	hexane[a]	pure	weak
	R6G	hexane:toluene	10:1	dye insoluble in solvent
	fluorescein dibutyrate	hexane:toluene	10:1	no binding
	anthracene	hexane:toluene	10:1	no binding
	DAASP-8	hexane	pure	moderate, rinsed off by more hexane
	DAASP-8	hexane:toluene	10:1	strong, stable to hexane

[a] Low solubility of the dye in this solvent.

PFSAc without any detectable adhesion to PDBFS (Table 1). Penetrability of the matrix by water:alcohol mixtures was also easily estimated by IR measurements from treated and semidried samples: additional strong bands at $3000-3500$ cm^{-1} appeared from H-bonded hydroxyl groups of sorbed water and alcohol molecules.

A somewhat similar picture was seen with selective binding into PDBFS. Hexane wetted the PDBFS matrix but did not swell it; however, hexane could not dissolve many dyes with polar groups. Toluene was a good solvent for these dyes but dissolved the PDBFS polymer completely. While a 3:1 v:v mixture of hexane and toluene was still a good solvent for PDBFS, the 10:1 v:v mixture only slightly swelled the PDBFS, trapping any solute there after its evaporation. Though many of the dyes were thus placed selectively in the PDBFS, some, despite being soluble in the solvent mixture, could still not be made to adhere (Table 1).

The nature of the dyes also played an important role here. Most of the dyes employed worked well in both water:alcohol or hexane:toluene mixtures. These dyes possessed amino, pyridinium, ammonium, and carboxy groups (Scheme 2), which provided possibilities of ionic or covalent binding, along with dipole–dipole or other weaker interactions. Some nonpolar dyes, such as anthracene and fluorescein dibutyrate, could not be bound by these methods into either polar PFSAc or nonpolar PDBFS matrixes (Table 1).

We also checked the stabilities of dye-resist solid solutions created in both PFSAc and PDBFS. When binding was done from hexane dye solutions, reimmersion for a few seconds into pure hexane dramatically decreased the intensity of the fluorescence in PDBFS. Further washing in hexane for a few minutes removed dyes completely. As hexane does not swell the polymer, dye molecules had probably been deposited only *onto* the surface and could thus be easily removed afterward. The stability of binding from hexane:toluene solutions was much better: hexane alone could not then remove easily such dye molecules after they had been transported deeply *into* the film.

A prolonged (hours) water rinsing slightly decreased or did not change fluorescence from dyed PFSAc (by
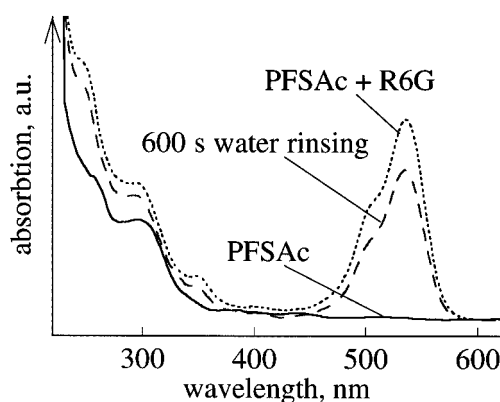

Figure 3. UV–vis spectra of R6G dye in PFSAc.

visual inspection and UV–vis spectroscopy). Even water:alcohol rinsing could not remove all dye, indicating the existence of both weak reversible trapping and strong ionic and/or covalent binding. Figure 3 illustrates this observation for the R6G binding. Nonnormalized UV–vis spectra clearly report the exent of this dye's uptake and the stability of its binding.

Spectrofluorometry of Dyes in the Resist. In addition to straightforward visualization of functional images from binding experiments, some dyes can supply interesting microenvironment information by their fluorescence and UV–vis spectra. In particular, the position and intensity of their fluorescence emission peaks depend on a combination of factors: covalent, ionic, or hydrogen bonding with a matrix, as well as polarity and viscosity of the medium.[28] For example, dansyl dye has been used to monitor solvent amount and interaction in the cross-linked polystyrene matrix.[29] By placing different dyes in either PFSAc or PDBFS, we hoped to understand more about the specific interactions of these polymer matrixes with different functional groups on guest molecules. Thus, these fluorescent dyes served as binding species and "reporters" about binding interactions.

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(29) Shea, K. J.; Sasaki, D. Y.; Stoddard, G. J. *Macromolecules* **1989**, *22*, 1722.
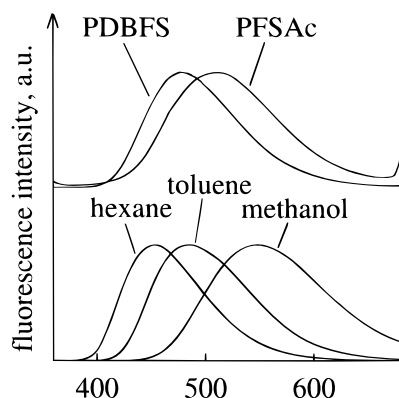
Figure 4. Fluorescence emission spectra of DSMP in different solvents and in PFSAc and PDBFS (offset for convenience). Excitation at 355 nm.

The dyes DAASP-18 and DSMP were chosen for a detailed study as each possess several basic functionalities (Scheme 2). The literature[30] reports the following pK_a values for somewhat similar protonated compounds in water: pyridine 5.25, 4-aminopyridine 9.11, 4-(methylamino)pyridine 9.65, piperazine 9.83, N,N-dimethylaniline 5.15. Effective acidity of the same compounds inside a polymer matrix may deviate from these values. Compared to ion solvation in polar and protic solvents, there is less (if any) stabilization of charged protonated forms in the largely nonpolar polymeric matrix. Thus, some dye "basic" groups may not be fully protonated by polymeric carboxylic acids ($pK_a = 2-5$).

Fluorescence spectra were first taken from solutions of these two dyes in hexane, toluene and methanol, respectively representing nonpolar, intermediate, and polar environments. Both dyes showed strong solvatofluorochromism, with emission peaks shifted to longer wavelengths in the more polar solvents. These spectra were compared with those from dyes in PFSAc (loaded from water:*tert*-butyl alcohol) or PDBFS (loaded from hexane or hexane:toluene). By its emission wavelength, DSMP was able to "report", in a way similar to other dansyl dyes,[29] the following order of polarities for these solvents and polymers: hexane (455 nm), PDBFS (478 nm), toluene (485 nm), PFSAc (510 nm), and methanol (550 nm; Figure 4). Though protonation of the strongly basic piperazine amino nitrogen by the polymeric carboxylic acid was expected from their pK_a values, this probably did not affect fluorescence of the remote dansyl fluorophore. Moreover, in this particular matrix, even in such great excess, carboxylic acid appeared unable to protonate the N,N-dialkylarylamino group (pK_a ca. 5) that is conjugated to the dansyl's electron system, which would have caused complete quenching of the dansyl fluorescense.[29] Thus, this dye can directly report polarity alteration of a resist matrix, irrespective of any change in its pH.

Inside the various media, the DAASP-18 dye showed fluorescence emission peaks at the following positions: hexane 420 nm, toluene 435 nm, methanol 505 nm, and PFSAc 590 nm. The relatively large magnitude of this last value was probably due to additional hydrogen bonding or even complete protonation of this dye's pyridyl ring nitrogen by the acidic matrix. This site is basic enough for such proton transfer because the
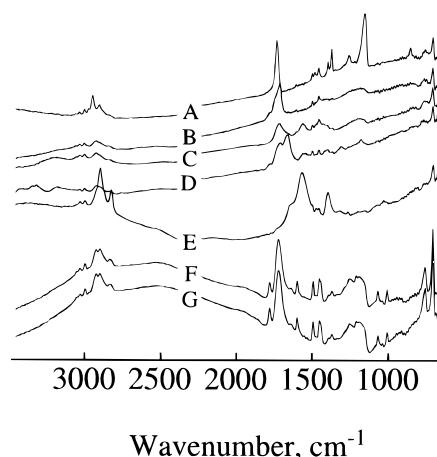
(30) *CRC Handbook of Chemistry and Physics*, 74th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1993; pp 8:43-8:45.

Wavenumber, cm^{-1}

Figure 5. Effect of exposure and functionalization with organic molecules on IR spectra of PDBFS:4TS-SbF$_6$. (A) starting PDBFS resist; (B) deprotected PFSAc form after exposure and PEB; others show (B) after treatment with: (C) ammonia vapors; (D) 1 wt % aqueous solution of 2,6-diaminopyridine; (E) 1 wt % aqueous solution of 1,10-diaminodecane; (F) pyridine vapors for 1 h and (G) for 3 h.

Scheme 3. Simplified Structures of Resist + Amines (Labels A−E as for Figure 5)
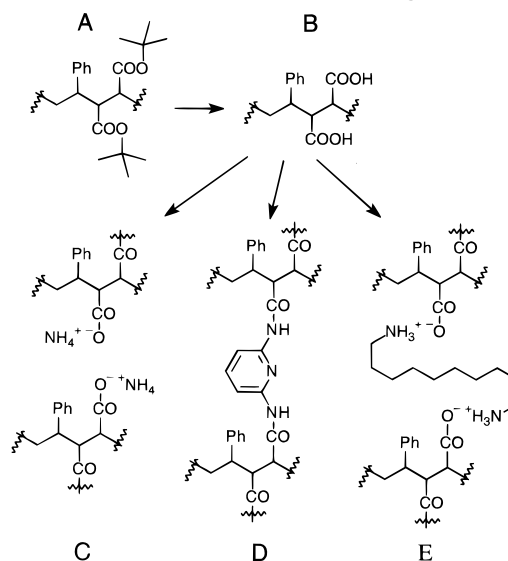
resulting positive charge is stabilized by the lone electron pair on substituent N via extended conjugation, as happens in 4-(N,N-dialkylamino)pyridines (pK_a ca. 9−10). Unlike the piperazine amine nitrogen in DSMP, this basic pyridine nitrogen is part of the fluorophore's conjugation system, and its protonation directly affects the fluorescence peak position. The emission spectrum of DAASP-18 dye in methanol also displayed a shoulder at the same 590−600 nm region, which may be due to hydrogen bonding between the alcohol and the same ring nitrogen.

Binding of Amines. Many biomolecules contain alkyl, aryl, or heterocyclic amino or ammonium group(s), which can be used to immobilize them in an acid- or anhydride-containing matrix. Binding of some model nondye amines was monitored by IR spectroscopy (Figure 5). Some of the proposed resist-amine structures are summarized in Scheme 3.

Functional development was first accomplished with volatile amines from the gas phase. An irradiated and baked PDBFS sample was placed above 5 wt % aqueous

ammonia solution for 120 s. The ammonia vapor was able to deprotonate carboxylic acid groups of the PFSAc, resulting in a decrease of the 1708 peak and appearance of peaks at 1450, 1560, and a broad peak at ca. 3200 (Figure 5, spectrum C) that perfectly matched carboxylate anion and ammonium cation peaks. Further exposure to ammonia vapor rapidly led to complete transformation of acid to salt. Though IR showed some deterioration of PDBFS after more than 600 s of this ammonia vapor treatment, there was a broad time range for transforming only the PFSAc into a water-soluble salt form. By then immersing *in pure water*, ammonia-treated samples of patterned PFSAc and PDBFS gave clean positive-tone relief images, providing an alternative to conventional[13] aqueous base for such development.

Pyridine vapors were also taken up in PFSAc, to a maximum at 1 h, with no further change at 3 h (Figure 5, spectra F and G, by new IR peaks at 1596, 1435, 1010, 750, and 700). However, the polymeric carboxylic acid was not detectably deprotonated by this weaker base (see pK_a values above). Here, a limited uptake was still provided by hydrogen-bonding interactions alone, even when complete proton transfer with ionization seemed to be thermodynamically unfavorable in this polymer matrix.

IR showed PDBFS to be unaffected by various aqueous monoamine solutions. Dilute solutions of monoamines in water did not wet or otherwise affect PFSAc either, while higher concentrations dissolved these areas completely. The critical concentration for such dissolution proved to be ca. 0.5 wt % for ammonium hydroxide, as well as 2- and 4-aminopyridines, which are monobasic compounds toward carboxylic acids. However, diaminopyridine, as well as 1,10-diaminodecane and polyethyleneimine, were all able to form multiple ammonium salts to cross-link carboxylate-bearing polymer without dissolving it (Figure 5, spectra D and E). Along with the salt formation, the presence of amide groups here was also often evident by amide-I and amide-II IR peaks at ca. 1640−1660 and 3100, even without further heating. That PDBFS was not detectably affected by alkylamines implies good contrast for this kind of functional development.

Conclusions

In planning a patterned modification of polymer film (functional development), one must consider the species to bind, the template resist, and its photospeed, along with resolution, contrast, and amount and stability of uptake. The present report creates a basis for a systematic approach to binding a variety of organic species into microscale resist templates. The report's main conclusions are as follows:

For small irradiation doses, the CA chemistry offers the best scope for massive material alteration particulary with (sub)micron resolution. As shown with a CA resist based on PDBFS, transformation of ester to acid groups led to great changes in properties and, thus, to selectivity and contrast in uptake of sorbates between PDBFS and PFSAc. The UV dose and PEB temperature were found to be the main factors controlling the ester:acid:anhydride ratio.

Fast and massive uptake occurs when strong covalent and/or ionic bonds are formed between a solute and a matrix. Various amines were well immobilized selectively within PFSAc areas of patternwise irradiated and heated PDBFS resist. Weaker interactions, e.g., hydrogen bonding, can also be used for a limited sorption of less basic compounds.

For stable binding from solution, the solvent must be (i) able to dissolve a compound to be sorbed, (ii) able to wet and penetrate only one of contrasting areas of a resist, and (iii) unable to dissolve either of these resist areas. For the carboxylic acid matrix, we found the appropriate solvent to be a water:alcohol mixture, while for nonirradiated PDBFS it was a hexane:toluene combination. Yet another way to control wettability is by adjusting pH, as we have reported in a parallel article.[22]

Instant cross-linking by polybasic species (e.g., polyamines or polyvalent ions[22]) is obligatory if the polymer films are not to dissolve as they ionize. On the other hand, pretreatment with gaseous monobasic species, like ammonia, allows positive-tone relief developing of PDBFS-based resists in *pure water*.

Further experiments will explore the image resolutions of the various types of functional development we have here discussed. As in the CARL and other chemical treatments and processes,[16] with careful control of uptake and swelling, one could expect such resolutions to be limited only by the UV exposure technology itself (less than 0.15 μm with modern vacuum-UV tools).

CM960136P