

An *In Situ* Method for Measuring Acid Loss from Polymer Films

CHRIS COENJARTS,¹ JIM CAMERON,² GERD POHLERS,^{1,2} J. C. SCAIANO,¹ ANTHONY ZAMPINI²

¹ Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

² Research and Development Laboratories, Shipley Co., 455 Forest Street, Marlborough, Massachusetts 01752

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ABSTRACT: This article reports an *in situ* approach to studying acid loss from polymer (films of the type used in microlithography). We developed a method which makes use of the dye coumarin 6 (C6) which has absorption characteristics which change dramatically as a result of acid-induced changes in its prototropic forms. Acid loss from polymer films containing C6 is accompanied by its deprotonation, which is signaled by a change in the absorption of the film. This technique provides kinetic data describing acid loss from polymer films. Acid loss is a function of both acid volatilization from sites at the surface of the film as well as diffusional processes within the film. Under controlled conditions, acid loss obeys first-order kinetics, and the half-lives, $\tau_{1/2}$, of acids in phenolic and acrylate polymer films were determined. We studied the effects of temperature, acid structure, polymer structure, and T_g on the $\tau_{1/2}$ values obtained. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1897–1905, 2000

Key words: acid diffusion; acid loss; polymer films; acid sensor

INTRODUCTION

As the feature size in microlithography decreases in response to the demand for increasing miniaturization, problems related to acid diffusion and acid loss become more important. Extensive diffusion of photogenerated acid within a resist can potentially lead to acid loss from the surface of the resist. While acid diffusion can obviously compromise the image quality of a resist, acid loss has also been implicated in the formation of undesirable structures at the surface of both positive and negative resists.^{1–5}

In an attempt to address the issue of acid loss during postexposure bake (PEB) conditions, we

developed an *in situ* method for monitoring acid departure from polymer films. The basis for this method is the dye coumarin 6 (C6) whose utility as an acid sensor in polymer films was demonstrated previously.⁶ The use of acid-sensitive dyes for the purpose of detecting acid in polymer films is well established and many are currently being used in acid-quantification and acid-diffusion studies.^{7–11}

An acid-loss technique based on a spectrophotometric titration of acid containing films was developed by others and used to monitor acid loss from the surface of polyvinylphenol (PVP) films.¹² This technique involves the irradiation of several resist-coated wafers and the actual quantification of the acid involves extraction of each film into a dye-containing solution. It is difficult and tedious to get detailed acid-loss data because multiple extractions are required in order to obtain quality data. Here, we describe an adaptation of this method in which a dye and an acid are incorpo-

Correspondence to: J. C. Scaiano.

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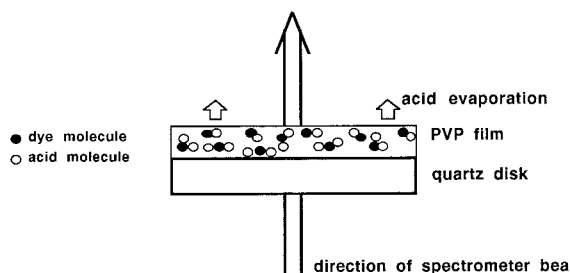


Figure 1 Schematic representation of the setup used to study acid loss from polymer films.

rated into a thin polymer film on a quartz disk and heated in an oven which is mounted in an absorption spectrophotometer, thereby allowing *in situ* absorption measurements. In this way, as acid leaves the film, the absorption of the film changes and well-defined acid loss plots can be obtained. A schematic of the experiment is shown in Figure 1.

To determine the nature of the process which controls the rate of acid loss from polymer films, we compared the kinetics of acid loss obtained using this technique to those obtained using the aforementioned spectrophotometric extraction method as well as a technique designed to measure acid donation between two polymer films.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) (PMMA; average $M_w \sim 120,000$) and poly(acrylic acid) (PAA; average $M_w \sim 2000$) were obtained from Aldrich (Oakville, ON, Canada) and used as received. The various phenolic polymer samples used were obtained from Shipley Co. (Marlborough, MA). Methanesulfonic acid (MSA, 96 g/mol), camphorsulfonic acid (CSA, 232 g/mol), *p*-toluenesulfonic acid monohydrate (TSA, 190 g/mol), and trifluoromethanesulfonic acid (TFA, 150 g/mol) were obtained from Aldrich and used as received. Perfluorooctane sulfonic acid (PFOS, 500 g/mol) was obtained from TCI America (Portland, OR) and used as received. Coumarin 6 (C6) and Rhodamine B Base (Rb) were obtained from Aldrich; the former was recrystallized twice from methanol/dichloromethane. Rb was purified by column chromatography on silica gel (230–400 mesh) using acetone as an eluent.

Preparation of Polymer Films

Thin polymer films were spin-coated at 3000 rpm for 20 s onto 2.5-cm quartz disks using an Integrated Technologies Inc. P-6000 spin coater. The coating solutions were 25 wt % PVP in diglyme, 35% Novolac in diglyme, 15 wt % PMMA in diglyme, and 40 wt % PAA in water. The films were baked at 90°C for 5 min immediately after coating. Typical film thickness was $\sim 1 \mu\text{m}$ for PVP and $\sim 0.7 \mu\text{m}$ for PMMA. The concentrations of the dye, PAG, and acid are given as the concentrations in the solution used for spin coating. When weight percent is also stated, it is given relative to the solids. No attempt was made to determine segregation of the components in these films.

Acid-Loss Experiments

In acid-loss experiments, a stock solution of 0.0075M/1.0 wt % C6 in PVP/diglyme was used. Initial acid concentrations varied from 0.8 to 0.01M. The thermal stability of C6 in a PVP film was established by heating at 170°C for 1 h and noting no appreciable change in the absorption spectrum as measured using a Varian CARY 1E spectrophotometer. The response of the dye to known amounts of acid was determined and used as a calibration curve. Acid-loss studies were performed by placing a quartz disk with a spin-coated film into a small oven which fits in the sample compartment of our absorption spectrophotometer. The oven has small openings on both sides to allow the sample beam of the spectrophotometer to enter the oven, pass through the sample, and reach the detector. A temperature controller wired to the heaters in the oven maintains a constant temperature in the oven via feedback from a thermocouple. An acid-loss experiment involves placing the disk in the preheated oven and acquiring absorption data every 5 s for 1 h. When possible, kinetic analyses were performed on portions of the data obtained after the signal/system had completely stabilized (>600 s). The stabilization period was required to allow the polymer film to reach thermal equilibrium and because of changes in the absorption of the polymer as well as a shift in the acid/base equilibrium between acid and dye which occur at elevated temperatures. The duration of the stabilization period required was determined based on data obtained with films containing either no acid or containing CSA, a relatively slow moving acid (*vide infra*). These absorption changes observed in the initial

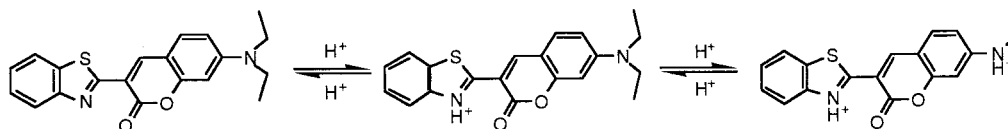


Figure 2 Various prototropic forms of C6.

moments of an experiment, which are unrelated to acid loss, complicate the interpretation of data which is acquired at temperatures different from those used for the creation of calibration curves. To perform a meaningful analysis, only a small portion of the experimental data ($\Delta\text{abs.} \approx 0.05$) is used to extract kinetic information because the response of the dye to small changes in the acid concentration is linear over much of the calibration curves.

Acid-donation Experiments

In acid-donation experiments, a PVP film is spin-coated onto a disk and heated in the usual manner. This is followed by the spin coating of a PAA film onto the PVP film. After spin coating, the second polymer layer, the "sandwich," is again heated in the usual way. The two spin-coating solutions must be mutually incompatible so that the acceptor film is not dissolved during the application of the donor film. A stock solution of 0.0075M/1 wt % C6 in PVP/diglyme was used for the acceptor film. The donor film was made from a solution of 0.2M of the appropriate acid in PAA/water. An acid-donation experiment is performed in the same way as is an acid-loss experiment with the addition of a quartz disk on top of the sandwich, the edges of which are wrapped in Teflon tape to minimize acid escape from the films. Analysis of the data is also performed in the same manner as that used in the acid-loss experiments. The method was described earlier.¹¹

RESULTS AND DISCUSSION

Suitability of C6 as a Probe for Measuring Acid Loss

The structure of the various prototropic forms of C6 and their absorption spectra are shown in Figures 2 and 3, respectively. The absorbance of the monoprotonated form is red-shifted relative to that of the neutral form and that of the diprotonated form is blue-shifted relative to that of the neutral form. The response of C6 to changes in

acid concentration as measured by the absorbance of the monoprotonated form at 533 nm in a PVP film are shown in Figure 4. At low acid concentrations, the ring nitrogen is protonated and the absorbance at 533 nm dominates the spectrum. As the acid concentration increases, the exocyclic nitrogen is protonated as well, and the absorbance at 533 nm decreases.

To be useful in this application, a dye must not only be a thermally stable acid sensor, but must also be a sufficiently weak base so that it does not interfere with acid leaving the film. C6 was used for these acid loss studies because it has two protonation sites of different basicities. It was hypothesized that the monoprotonated form of C6 would be a sufficiently weak base so that deprotonation of the diprotonated form should occur readily. To prove this, we compared the amounts of acid lost from dye-containing films using this method with the amounts lost from films without dye using the aforementioned extraction method. Films containing C6 and MSA were heated and, after cooling to room temperature, the absorbance measured and compared to the calibration curve (Fig. 4) to determine the extent of acid loss. Acid loss from those films without C6 was measured

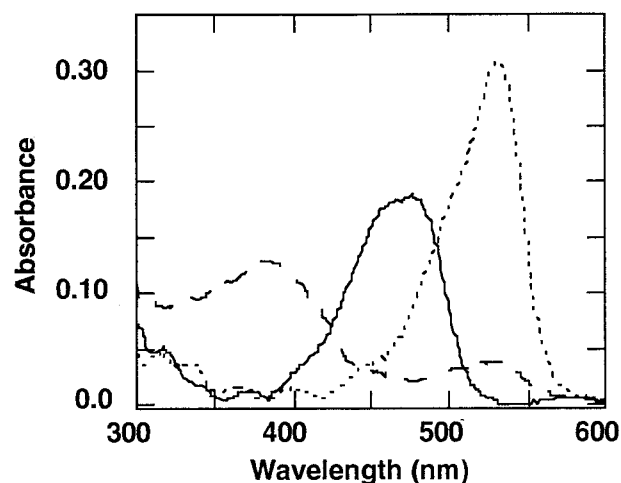


Figure 3 Absorption spectra of the prototropic forms of C6 (0.0075M) with MSA in PVP films: (—) neutral; (···) monoprotonated, (---) diprotonated.

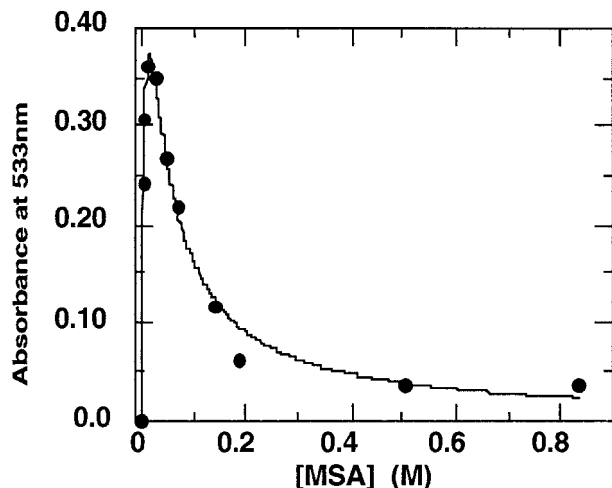


Figure 4 Absorbance of C6 (0.0075M) in PVP film with different concentrations of MSA. The curve fit is based on a consideration of the two basic equilibria of the dye.

via a spectrophotometric titration in which each film is heated and then extracted with a solution containing Rb. It was found that acid loss from a film in which the monoprotonated form of C6 is present is slowed because the dye is anchoring the acid within the film. However, when enough acid is present in the film to allow formation of diprotonated C6, acid loss was much faster, and a close agreement was found between the *in situ* method reported here and the titration method. A direct comparison of MSA loss from PVP films at 130°C as measured by both methods is shown in Figure

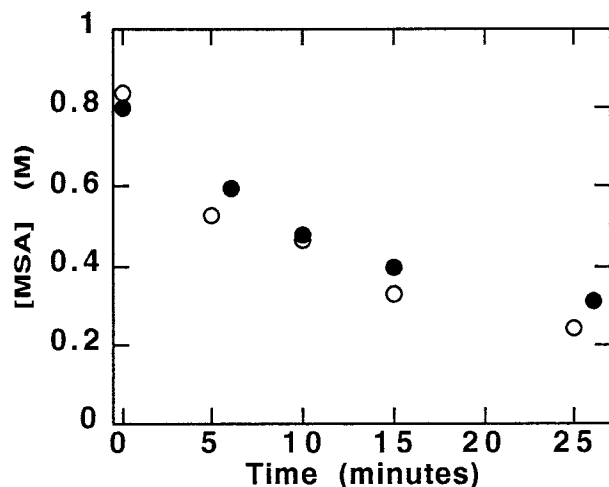


Figure 5 Comparison of the amount of MSA in PVP films after heating at 130°C via (○) the extraction method and (●) the *in situ* method.

5. The deprotonation C6 is facile enough that it does not control the rate of acid loss and, hence, is an adequate probe for studying acid loss. This comparison demonstrates an important point concerning the need for an *in situ* approach to measuring acid loss; a reliable kinetic analysis is impossible with so few data points.

Kinetic Treatment of Acid-Loss Data

For this method to be truly superior to the existing extraction method, the absorbance measurements must be performed *in situ*, while the film is being heated. In this way, many more measurements can be taken and at much shorter intervals so that well-defined plots of acid loss can be generated. The raw data obtained when a film is heated inside the spectrophotometer cannot be directly converted into plots of acid loss by comparison with the calibration curve (Fig. 4) due to absorbance changes which occur upon heating of the film which are due to factors other than acid loss (*vide supra*). Therefore, kinetic analysis of the data is performed only over small changes in acid concentration in which the response of the absorbance of the dye to changes in acid concentration is linear. Comparison with a calibration curve is not required, because over this range changes in the absorbance follow first-order kinetics, as described by the integrated first-order rate law: $A_t = A_i e^{-kt}$. Since acid concentration and absorbance are proportional over the region

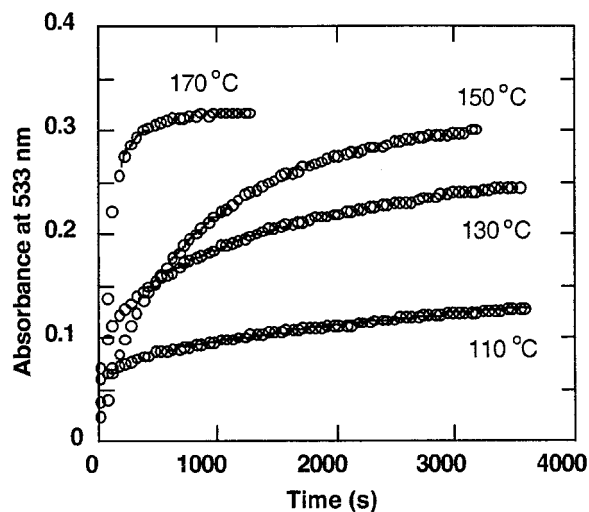


Figure 6 MSA loss from PVP films at different temperatures as measured by the absorbance of C6 at 533 nm: (○) 10% of the experimental data points; (—) first-order kinetic fits.

Table I Half-Lives of MSA in Various Thin Polymer Films

| Polymer | T_g (°C) | Half-Life $\tau_{1/2}$ (min) | | | | | |
|-----------|------------|------------------------------|------|-------|-------|-------|-------|
| | | 70°C | 90°C | 110°C | 130°C | 150°C | 170°C |
| PMMA | 114 | 58 | 10 | 1.4 | <0.5 | <0.5 | <0.5 |
| PVP 1 | 151 | >100 | >100 | 34 | 14 | 9.6 | 1.4 |
| PVP 2 | 167 | >100 | >100 | 41 | 16 | 8.9 | 4.4 |
| PVP 3 | 182 | >100 | >100 | 44 | 24 | 13 | 6.1 |
| Novolac 1 | 80 | >100 | >100 | 15 | 2.3 | 0.6 | <0.5 |
| Novolac 2 | 174 | >100 | >100 | 28 | 18 | 12 | 2.6 |

analyzed, acid loss also follows first-order kinetics. Typical fits for MSA at different temperatures are shown in Figure 6. Since the rate constants obtained are based on the data obtained over a small portion of an experiment, a responsible interpretation requires the assumption that the acid-loss behavior in the first few moments of an experiment and at long time scales is described well by the data at intermediate times.

One of the implications of the fact that acid loss obeys first-order kinetics is that the rate of acid loss is described by the first-order rate law: rate = k [acid]. If required, the first-order rate law can be used to determine the rate of acid loss at acid concentrations more similar to those found in resists.

Kinetics of Acid Loss

The results of experiments using MSA in a variety of different polymers are summarized in Table I, where the acid loss is reported as half-lives, $\tau_{1/2}$, which is the time required to lose half the acid. This quantity is related to the unimolecular rate constant k for acid loss by the relationship $\tau_{1/2} = 0.693/k$.

A consideration of the rate constants which can be extracted from the data in Table I allows for construction of the Arrhenius plot shown in Figure 7. The linearity of the plots obtained indicates that the kinetics for acid loss can be described by the equation $k = Ae^{-Ea/RT}$. The values for the activation energy (Ea) and preexponential factor (A) determined from this plot are shown in Table II. These Arrhenius parameters are clearly determined by a complex interplay of factors (*vide infra*). Given the limited amount of data used to generate these values, they will be interpreted in a qualitative sense only.

The $\tau_{1/2}$ values for a variety of different acids in PVP polymers are summarized in Table III. A thorough consideration of the behavior of acid loss at different temperatures for those acids other than MSA is impossible because most acids do not move appreciable at a wide enough range of temperatures.

Factors Controlling the Kinetics of Acid Loss

To interpret the results of the acid-loss studies, one must establish the nature of the acid-loss process. Clearly, diffusion of acid within the film and volatilization of the acid are both required for acid loss to occur, but the extent to which either process is reflected in the observed kinetics remains to be addressed. Although the kinetics of sorption and desorption of gases and organic vapors in polymer films are controlled entirely by

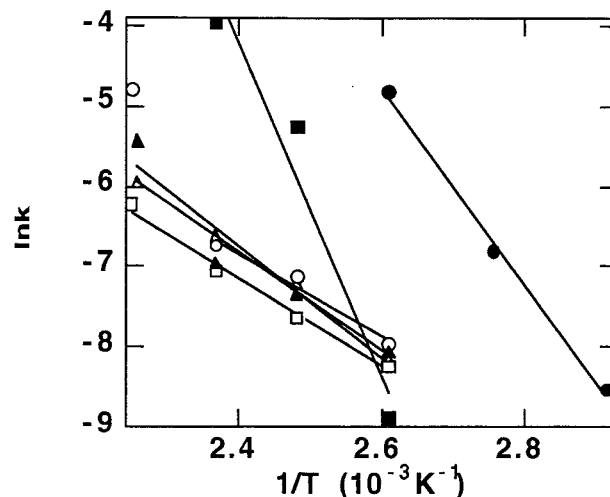


Figure 7 Arrhenius plot for acid loss from thin films of (●) PMMA, (○) PVP1, (△) PVP 2, (□) PVP 3, (■) Novolac 1, (▲) Novolac 2.

Table II Arrhenius Parameters for MSA Loss from Various Thin Polymer Films

| Polymer ^a | Arrhenius Parameters | |
|----------------------|----------------------|-----------------------------|
| | <i>Ea</i> (kJ/mol) | <i>A</i> (s ⁻¹) |
| PMMA | 100 | >10 ¹⁰ |
| PVP 1 | 42 | 10 ² |
| PVP 2 | 51 | 10 ³ |
| PVP 3 | 46 | 10 ² |
| Novolac 1 | 170 | >10 ¹⁰ |
| Novolac 2 | 58 | 10 ⁴ |

^a All measurements were performed at temperatures below the polymer T_g , except for Novolac 1 for which all measurements were performed above the polymer T_g .

diffusion,¹³ one anticipates that evaporation of acids must involve an additional activation barrier.

The fact that acid loss is well described by first-order kinetics suggests that the rate of acid loss from a polymer film is not controlled entirely by diffusion in the film. The rate of acid evaporation from a polymer surface is a process which one would expect to have a simple dependence on acid concentration, whereas diffusion within a polymer film is typically described by more complicated kinetics.¹³

Further evidence that acid loss involves a surface phenomenon is provided by the results of acid-donation experiments, which measure the rate of acid entering a PVP film. The data obtained using the acid-donation technique corresponds to acid entering a dye-containing PVP/acceptor film from a PAA/donor film and protonating the dye. Both the experiment and the kinetic analysis is performed in the same manner as for an acid-loss experiment. However, in this case, the increase in the absorbance of the mono-protonated form is monitored as acid enters the film and protonates the neutral form of the dye. Once again, the data follow first-order kinetics, but gives much faster rate constants than those obtained in the acid-loss studies. That the acid movement again exhibits first-order kinetics suggests control by a surface effect, either in exiting the donor or entering the acceptor film. This is consistent with the fact that if acid loss is governed by some type of surface phenomenon, it should be faster for this approach than in the acid-loss studies because, here, volatilization of the acid is not required. In both studies, the rate of acid diffusion in the PVP films should be the

same, since the composition of the films are the same as well as the temperature. Given that the kinetics observed are not the same, at least one of the methods is not monitoring absorption changes due solely to acid diffusion. The expected relative magnitudes of any surface effects, coupled with the observation that the kinetics for acid loss are slower than for acid donation, effectively eliminate the possibility that diffusion of acid within the film is the only process influencing the observed kinetics.

Experiments using MSA in various polymers were performed to probe the effect of the polymer structure on acid loss and thereby gain further insight into the nature of the acid-loss process. In light of the fact that acid loss ultimately requires both evaporation of the acid and diffusion within the film, it is not surprising that the rate of acid loss increases with increasing temperature. The observed temperature dependence can be rationalized by acknowledging that at higher temperatures a greater proportion of molecules have enough energy to overcome the energy barrier defined by Ea , whatever its specific nature. As such, the PEB temperatures of resists used in industry must be chosen carefully to avoid significant acid loss.

It is clear from the data that when a film of PVP 1 is heated above its T_g of 151°C, to 170°C, the rate of acid loss increases more than is predicted by a consideration of the Arrhenius equation. This is demonstrated by a decrease in the $\tau_{1/2}$ by a factor of 3–4 as compared to films of PVP 2 and 3 for which 170°C is below T_g , as well as by an obvious break in the linearity of the Arrhenius plot (Fig. 7) above the T_g . Analysis of the plot reveals that for all of the PVP polymers the observed Ea for MSA loss is 40–50 kJ/mol and A is about 10²–10³ s⁻¹ when the temperature is below the T_g of the polymer. The observation that acid

Table III Half-Lives of Various Acids in Thin Films of PVP 2

| Acid | Half-Life $\tau_{1/2}$ (min) | | | |
|------|------------------------------|-------|-------|-------|
| | 110°C | 130°C | 150°C | 170°C |
| MSA | 41 | 16 | 8.9 | 4.4 |
| TFA | >100 | 55 | 20 | 8.9 |
| TSA | >100 | >100 | >100 | 61 |
| CSA | >100 | >100 | >100 | 41 |
| PFOS | >100 | >100 | 40 | 19 |

loss is much faster above the T_g of the polymer demonstrates that acid loss is not only a function of properties associated with the acid but also the polymer, specifically, the overall morphology of the polymer, below and above the T_g .

Consideration of results obtained in Novolac films with widely separated T_g 's provides more information concerning the observed T_g effect. Although the Novolacs are not structurally identical, we interpret the differences in the observed rate constants as being due, primarily, to the fact that experiments were performed well above the T_g of Novolac 1 and below that of Novolac 2. The impact of structural features on acid loss will be discussed later. Acid loss from Novolac 1 gives an Ea of 170 kJ/mol and an A of $>10^{10}$ s $^{-1}$ at temperatures above its T_g of 80°C while that from Novolac 2 gives an Ea of 58 kJ/mol and an A of $\sim 10^4$ s $^{-1}$ at temperatures below its T_g of 174°C. The increase in A by several orders of magnitude at temperatures above the polymer T_g dominates over the threefold increase in Ea and results in an overall increase in the $\tau_{1/2}$ values above the T_g .

That acid loss is affected by changes in properties of the polymer suggests that diffusional processes impact the observed kinetics. Moreover, the increased A and Ea observed above the T_g for the acid-loss process is in agreement with results obtained for the diffusion of small molecules within polymers in which diffusion is analyzed as an activated process which is also described by a variation on the Arrhenius equation.¹³ However, given that results from donation experiments suggest that acid loss is not entirely controlled by acid diffusion, we propose that acid loss from polymer films is a function of both diffusion within the polymer and volatilization of the acid.

This result is expected if acid loss from a polymer involves diffusion of acid into sites at the surface which permit escape and is followed by acid volatilization in competition with acid diffusion back into sites within the film.* We define these sites simply as the free regions within a polymer film which are large enough to accommodate an acid molecule. In terms of the Arrhenius

parameter introduced earlier, Ea is a function of the energy barriers required to diffuse within the film as well as that required to leave the polymer surface. More specifically, Ea is a reflection of factors affecting both the ease of diffusion, such as solubility of the diffusant and free volume within the polymer¹³ as well as intrinsic properties of the acid which determine how easily it can be volatilized. The preexponential factor, A , represents the rate at which acid molecules are able to diffuse into sites at the polymer surface which permit escape.

With the aid of this definition of acid loss, one can rationalize the observed T_g effect. Below its T_g , a polymer is restricted to short-range vibrations and rotations, while above the T_g , it experiences more long-range molecular motions and greater rotational freedom. Diffusional studies indicate that this results in either larger or more abundant regions of the free volume within a polymer which are available for occupation by acid molecules upon their diffusion.¹³ The implications on acid loss are obvious: The greater the number of these sites, the greater the rate at which acid can diffuse into these sites and the greater preexponential factor expected for acid loss.

The larger Ea shown for acid loss from Novolac 1 (at temperatures above its T_g) relative to Novolac 2 (at temperatures below its T_g) can also be rationalized in terms of the free volume within a polymer. Diffusion can be described as a series of jumps of the diffusant into vacant sites in the polymer structure. An increase in free volume tends to increase the distance between these sites and thereby increases the jump length required for diffusion; a larger jump involves a greater activation barrier. Above the T_g , the rate of increase of the free volume within a polymer with temperature changes and an increase in activation energy is the result.¹³

The importance of the polymer T_g to the rates of acid loss is relevant to the choice of PEB conditions used for resists as well as the choice of polymer used for the resist. For example, a longer PEB at temperatures below T_g may prove more effective in reducing acid loss than a shorter PEB at temperatures above T_g .

The differences in the kinetics of MSA loss observed for the various PVP and PMMA films is interpreted to be due to structural differences since the data were obtained at temperatures below the T_g 's of each polymer. The Ea and A for PMMA are 100 kJ/mol and $>10^{10}$ s $^{-1}$, respec-

* We draw analogy between the diffusion of acid into and out of sites at the surface followed by acid evaporation to the "steady-state hypothesis" of classical kinetics in which a pre-equilibrium is established prior to formation of the final product. Under these conditions, the experimentally observed rate constant is a function of all the rate constants for the individual processes. Therefore, in these acid-loss experiments, the observed rate constants are functions of both diffusional processes and acid evaporation. See ref. 14.

tively. These values are larger than are the values found for the PVP films. Upon switching the polymer from PVP to PMMA, again the increase in A dominates the increase in Ea and results in an overall decrease in the $\tau_{1/2}$ values.

The bulk of the phenolic groups as well as the H-bonding interactions between phenolic groups on different polymer chains reduces the availability of the free volume within the polymer for acid occupation.¹³ The less bulky PMMA and its weaker interaction between adjacent polymer chains allows for more free volume available for acid occupation and a larger A value is the result.

The larger Ea found for PMMA relative to PVP is due to a variety of factors: These include the aforementioned effect of the free volume on the Ea values which arises from the differing interactions between polymer chains as well as the solubility of the acid. The solubility of acids in these polymers is increased with increasing basicity of the polymers. The basicity of the oxygens in the ester functionality of PMMA is stronger than that of the phenolic oxygens in PVPs. The more extensive protonation of PMMA than of PVP by acid is demonstrated by the fact that higher concentrations of acid are required to fully protonate C6 in a PMMA film. The solvation of acid in PMMA is aided by an ionic interaction between the protonated ester group and the conjugate base of the acid. In phenolic polymers, the interaction between the acid and the polymer is limited to dipole-dipole interactions and hydrogen bonding. Clearly, the stronger the interaction between the acid and the dye, the greater the Ea for diffusion. Based on these results, in addition to the microlithographic requirements placed on polymers, one should consider the structure of the polymer as it pertains to its basicity as well as the bulk of and interaction between functional groups in order to minimize acid loss.

The $\tau_{1/2}$ values were determined for a variety of different acids in PVP polymers in order to identify the role played by the acid structure in the acid loss. The most obvious conclusion one can draw from the data in Table III is that under the conditions commonly used for PEBs in industry (90–130°C, ~60 s) loss of most acids is minimal. However, since most of the acid lost is presumably from regions near the surface of the film, even loss of small amounts result in formation of undesirable surface features in a developed resist, for example, T-topping in a positive resist and rounding in a negative resist.

The data in Table IV show that the trend in $\tau_{1/2}$ values is MSA < TFA < PFOS < TSA < CSA. Upon further examination of the data, the most dominant trend, with the exception of PFOS, is that low molecular weight acids leave the film more rapidly than do heavier ones. MSA leaves the film two to four times faster than does TFA despite their boiling points of 167°C/10 mmHg and ~45°C/10 mmHg, respectively. Under these conditions, molecular weight is a better measure of volatility than is the boiling point since boiling points are, in part, a reflection of the strength of interactions between acid molecules, which is of limited relevance when they are dispersed throughout a polymer. Not surprisingly, the observed trend in $\tau_{1/2}$ values with molecular weights of acids has a coinciding trend for molecular volumes of acids. The size of a diffusant is very important to diffusional processes as it is relevant to the ease of occupation of vacant sites in the polymer.¹³ To reduce the potential for acid loss during PEB, one should use a PAG which generates an acid that is both large and heavy.

Of all the acids studied, PFOS has by far the largest molecular weight, yet its $\tau_{1/2}$ in a PVP film is intermediate to that of TFA and TSA. This result is attributed to weak solvation interactions between the organic polymer and the highly fluorinated acid molecule which render them incompatible. This interpretation is supported by the observation that the quality of the films obtained was poor when high PFOS concentrations were used in the spin-coating solution. Additional support for this conclusion comes from results of experiments aimed at determining the spatial distribution of photoacid generators within photoresists, which indicate significant aggregation of highly fluorinated photoacid generators.¹⁵ This effect is presumably due to the same lack of strong interaction evident between the polymer and the PFOS which allows it to leave the film so rapidly. This result is especially significant because highly fluorinated acids such as PFOS are commonly used in microlithographic applications. The extensive fluorination increases the acid strength considerably, and in the case of PFOS, the large size was originally expected to reduce acid diffusion and loss. This strategy may be misguided since it may result in an acid which is poorly solvated in a resist and may phase-separate, allowing it to leave the film quickly.

Given that the strength of the interaction between the acid and a PVP polymer plays a role in determining the rate at which acid leaves a film,

one might suspect that the stronger acids will be retained by the film more strongly than all the weaker ones due to an increased potential for protonation of the phenolic functionality. Although it is difficult to extract this information from the data given the presence of the more dominant trends previously described, the strongest acids, TFA and PFOS, are among the fastest to leave the films. It would appear then that acid strength is not the dominant issue in acid loss from PVP films. Preliminary experiments also suggest that the casting solvent does not control the rate of acid loss.[†]

CONCLUSIONS

We have presented here results from a new *in situ* technique for measuring acid loss from polymer films. This technique allows for quick and convenient determination of $\tau_{1/2}$ values of acids and has proven useful for probing the effects of PEB conditions, as well as polymer and acid structure on acid loss. While temperature has the most dominant effect on the rate of acid loss, the size of the acid as well as both the acid and polymer structures, as they pertain to the interaction between the polymer and the acid, are also key factors in determining the $\tau_{1/2}$ values of acids in polymer films. The increased free volume generated in polymers above the T_g acts to increase the rate of acid loss. The bulk of and interaction between phenolic groups of PVP and Novolac polymers tends to slow acid loss relative to PMMA films.

It is clear that to minimize acid loss from resists during PEBs, the choice of polymer and photoacid generator must be done carefully. This technique may prove useful for screening polymer/photoacid generator formulations as industry introduces new resists for use at 193 nm.

[†]Preliminary results using ethyl lactate as a casting solvent gave similar results to those obtained using diglyme as the casting solvent. While this suggests that acid loss is unaffected by the solvent, one must acknowledge that under the experimental conditions employed here the bulk of the solvent has probably evaporated prior of the acid-loss of the acid-loss data.

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