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Theoretical calculations of sensitivity of deprotection reactions for acrylic polymers for 193 nm lithography

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The reaction energy of deprotection reactions, density of the reaction site, glass transition temperature, gas permeability, density and relative permittivity of photoresists of poly($TCDA_5$–RMA_3–MAA_2) and poly($TCDMACOOR_4$–$TCDMACOOH_6$) with various protection groups were calculated. The most-enhanced exothermicity was calculated for protection groups containing an ethoxyethyl group as compared to the other protection groups: tetrahydropyranyl, tricyclodecanyl and *tert*-butyl. For the ethoxyethyl protection groups, a good correlation was found between the experimental sensitivity and the calculated values of the relative permittivity and the glass transition temperature of the polymers. This indicates that calculating these properties of polymers can provide a quick way to identify polymers having a high sensitivity for ArF lithography.

The wavelength of light used in photolithography is getting shorter in an attempt to realize smaller and smaller semiconductor devices. In line with this trend, development of photolithography at a wavelength of 193 nm using the ArF excimer laser will be used to make devices that will appear in the beginning of the next century.[1,2] For photoresist materials at this wavelength, a wide variety of acrylic polymers with alicyclic features are now being examined, because the conventional Novolac and/or polyvinylphenol polymers are not sufficiently transparent at a wavelength of 193 nm.[3–17] Acrylic ester functionality is introduced to the polymer as a protecting group, and this ester unit decomposes to carboxylic acid in the presence of acid photochemically generated, thus exhibiting a lithographic performance.

It has been reported that characteristics of these photoresist materials, such as sensitivity (or dose) and dissolution rate, differ depending on the protection group introduced to the photoresist polymer.[14–17] However, no detailed theoretical/molecular orbital studies of factors which control these characteristics have been reported as far as they apply to ArF lithography. We thus decided to carry out theoretical studies of these characteristics. This would hopefully enable us to predict these characteristics with reasonable accuracy and in a shorter time as compared to performing actual experiments, leading to an acceleration of the development of the new lithography process. The property that we chose as a starting point for our theoretical studies is the dependence of sensitivity on the choice of protection group in acrylic polymers, because for this property, a variety of experimental results are already available.[10–17] It should be noted that the sensitivity of ArF photoresists is one of the most important properties to be improved, because, to reduce the damage to glass materials, the intensity of the ArF laser must be reduced as compared to that of the KrF laser used in the conventional lithography process.

Possible factors which govern the dependence of sensitivity are: (1) heat of reaction of the deprotection reaction at the ester unit, (2) van der Waals volume of a segment of polymers, (3) density of polymers, (4) permeability of acids generated in polymers, (5) glass transition temperature (T_g) and (6) relative permittivity (ε) of polymers. We think that the first factor plays an important role if the sensitivity is dominated by the deprotection reaction itself. The other factors are important if the sensitivity is dominated by the diffusion of acid molecules. We note that the second factor represents the density of the reaction sites, *i.e.* the ester units, so that it should correspond to the distance the acid molecules have to diffuse.

Calculations

Heat of reaction for the deprotection reaction at the ether unit of acrylic polymers was calculated by applying the molecular orbital theory both at a semiempirical and an *ab initio* level. For the former, the MNDO Hamiltonian[18] with the PM-3 parameterization[19,20] as implemented in the program MOPAC[21] was applied for the calculations of geometry optimizations and succeeding energy calculations of molecules.

For the latter, local (LDFT) and nonlocal (NLDFT) density functional theory[22–24] was applied by using the program DGAUSS.[25–28] The exchange-correlation potential derived by Vosko, Wilk and Nusair (VWN)[29] was used for the LDFT calculations, whereas for the NLDFT calculations, the Becke exchange functional[30–32] and the Lee–Yang–Parr correlation energy functional[33] were applied. The geometries were fully optimized by applying analytic gradient methods.[34–38] The basis set used for the calculations is of a valence double-ζ+polarization functions quality, called DZVP,[39] having a form of (621/41/1) for the carbon and oxygen atoms and of (41) for the hydrogen atom. The fitting basis set for the electron density and the exchange-correlation potential used in the calculations was in the form of [7/3/3] for the carbon and oxygen atoms and of [4] for the hydrogen atom. The applied numerical grid for the integration was the 'medium" grid in the program DGAUSS. Criteria for the SCF convergence and geometry optimization were those set by the 'medium" options in the program. Thermodynamic correction terms to obtain ΔG_{rxn} in the gas-phase at 25 °C from ΔE_{rxn} were calculated

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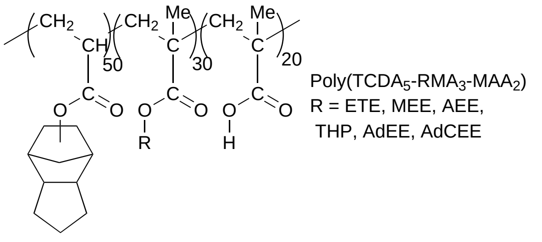
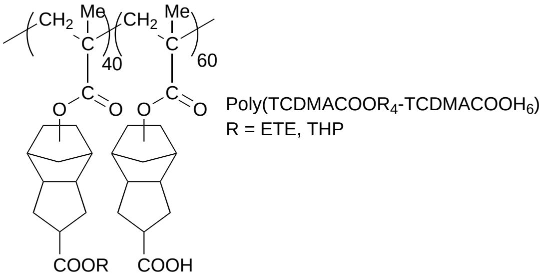
depending on the literature.[40] All of the molecular orbital calculations were done using a Cray J916/12–4096 supercomputer.

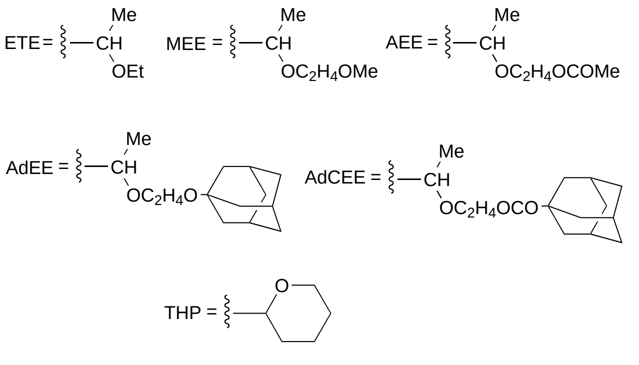
Calculations of the van der Waals volume of a segment of polymers, and the density, permeability, glass transition temperature and relative permittivity of the polymers were performed by applying a graph theoretical treatment of molecular properties,[41–43] as implemented in the 'Synthia' module in the program system POLYMER.[44] All the calculations of this graph theoretical treatment were performed on a COMTEC Solid Impact R-10000 work-station.

Results

Systematic experimental investigations on the sensitivity for ArF lithography have been performed[14–17] for several acrylic polymers with various protection groups.







For the terpolymer, poly(tricyclodecanyl acetate-*co*-methacrylate-*co*-methacrylic acid) [poly($TCDA_5$–RMA_3–MAA_2)], the sensitivity of the polymers with a protection group consisting of ethoxyethyl (ETE), methoxyethoxyethyl (MEE), acetoxyethoxyethyl (AEE), tetrahydropyranyl (THP), adamantyloxyethoxyethyl (AdEE), and adamantylcarbonyloxyethoxyethyl (AdCEE) groups has been reported with the use of triphenylsulfonium triflate (TPS) as a photoacid generator (PAG).[14,15] For the partially protected poly(carbonyltricyclodecanyl methacrylate) [poly($TCDMACOOR_4$–$TCDMACOOH_6$)], the sensitivity for ETE and THP with the use of hydroxysuccinimide tosylate (SIT) as a PAG has been measured.[14,15] The experimental sensitivity of these polymers is summarized in Table 1.[14,15] Experimental parameters for the poly($TCDA_5$–RMA_3–MAA_2) system are not exactly the same as those for the poly($TCDMACOOR_4$–TCDMA-$COOH_6$) system (Table 1),[14,15] so that a direct comparison between the sensitivity for poly($TCDA_5$–RMA_3–MAA_2) and poly($TCDMACOOR_4$–$TCDMACOOH_6$) cannot be made, whereas a comparison of the values for different protection groups for a fixed base polymer can be made. As shown in Table 1, two sets of experimental values are available for the terpolymer, although we note that the order of the sensitivity is the same for the two measurements.

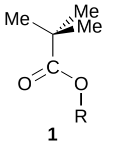
Table 1 Experimental sensitivities reported

protection group	sensitivity (dose)/mJ cm^{-2}		
	Ref. 14	Ref. 14	Ref. 15
	poly($TCDA_5$–RMA_3–MAA_2)		
ETE	1.0[a]		1.4[c]
MEE	1.4[a]		1.6[c]
AEE	0.4[a]		0.8[c]
AdEE	10.0[a]		
AdCEE	4.0[a]		
THP	7.5[a]		3.0[c]
	poly($TCDMACOOR_4$–$TCDMACOOH_6$)		
ETE		6.8[b]	
THP		8.2[b]	

[a]PAG: TPS (1 wt%); pre-baking: 80 °C and 60 s; PEB (post-exposure baking): 60 °C and 60 s for ETE, AEE, MEE, 70 °C and 60 s for THP, 100 °C and 60 s for AdEE and AdCEE; solution for development: TMAH, 0.0476 wt% in water. [b]PAG: SIT (1 wt%); pre-baking: 80 °C and 60 s; PEB: 70 °C and 60 s; solution for development: TMAH, 0.0476 wt% in water. [c]PAG: TPS (1 wt%); pre-baking: 80 °C and 60 s; PEB: 50 °C and 60 s; TMAH, 0.048 wt% in water.

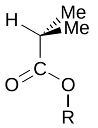
Semiempirical MO and DFT calculations

For our semiempirical MO and DFT calculations, these copolymers are computationally too large for calculations to be done.



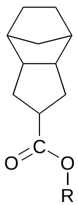
1

R = ETE, AEE, MEE, AdEE,
AdCEE, THP, TCD



2

R = TCD



3

R = ETE, THP

Thus, model compounds **1**–**3** were chosen for the calculations of heat of reaction (ΔH_{rxn}, or ΔG_{rxn}). In order to model deprotection reactions for poly($TCDA_5$–RMA_3–MAA_2), we chose the model molecules **1**, where the polymer chain is terminated by methyl groups. The model molecule **1** was also used for poly($TCDMACOOR_4$–$TCDMACOOH_6$) for the calculations of ΔG_{rxn} (or ΔH_{rxn}) of the deprotection reactions where the tricyclodecanyl group detaches from the polymer main chain. For the possible deprotection reactions of the tricyclodecanyl group detaching from poly($TCDA_5$–RMA_3–MAA_2), the model molecule **2** was used. For deprotection reactions for poly($TCDMACOOR_4$–$TCDMACOOH_6$), where reaction occurs at the ester unit adjacent to the ETE or THP group, the

Table 2 Calculated reaction energy of the hydrolysis reaction [eqn. (1)] in kcal mol^{-1}

R	R′	MNDO/PM-3 ΔH_{rxn} /kcal mol^{-1}	VWN/DZVP $\Delta G_{rxn}{}^{a}$ /kcal mol^{-1}	BLYP/DZVP $\Delta G_{rxn}{}^{a}$ /kcal mol^{-1}
Bu^t	ETE	−11.9	−8.8	−8.8
TCD	ETE	−10.4	−10.1	−11.2
Bu^t	MEE	−8.2	−7.9	−8.5
Bu^t	AEE	−11.4	−9.8	−10.3
Bu^t	AdEE	−11.2	−7.4	−10.7
Bu^t	AdCEE	−11.0	−9.9	−10.8
Bu^t	THP	−11.7	−3.7	−4.4
TCD	THP	−9.4	−5.2	−5.7
Bu^t	Bu^t	−12.3	−2.8	−5.4
Bu^t	TCD	−9.4	0.8	−1.3
Pr^i	TCD	−9.3	−1.9	−3.2

[a] ΔG_{rxn} in the gas-phase at 25 °C.

Table 3 Calculated reaction energy of eqn. (2) in kcal mol^{-1} for model polymer **1**

protecting group	MNDO/PM-3 ΔH_{rxn} /kcal mol^{-1}	VWN/DZVP $\Delta G_{rxn}{}^{a}$ /kcal mol^{-1}	BLYP/DZVP $\Delta G_{rxn}{}^{a}$ /kcal mol^{-1}
ETE	12.8	15.0	−2.0
MEE	14.3	15.5	−0.7
AEE	13.7	14.3	−3.5
AdEE	13.7	12.4	−4.9
AdCEE	14.5	14.8	−4.0
THP	9.6	14.6	−2.4
Bu^t	3.5	16.2	−3.5
TCD	14.7	21.2	2.1

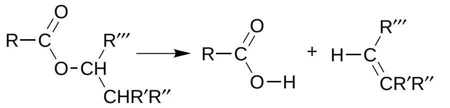
[a] ΔG_{rxn} in the gas-phase at 25 °C.

model molecule **3** was used. We note that because most atoms present in the polymers are sp^3 hybridized, the difference in electronic structure between the polymers and model compounds is not expected to be significant, especially at the ester unit, so that the effect of this modeling on the magnitude of calculated ΔG_{rxn} (or ΔH_{rxn}) is expected to be negligible.

ΔG_{rxn} (or ΔH_{rxn}) values for two reactions of possible relevance to the deprotection reaction in the photoresists were calculated. The calculated ΔG_{rxn} (or ΔH_{rxn}) values for hydrolysis at the ester group[45] present in the polymers catalyzed by an acid [eqn. (1)] are listed in Table 2.

$$\text{R-COO-R}' + H_2O \rightarrow \text{R-COOH} + \text{R}'\text{OH} \qquad (1)$$

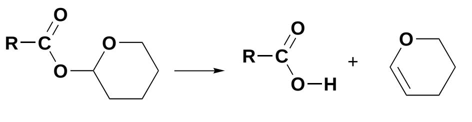
ΔG_{rxn} (or ΔH_{rxn}) values calculated for the other reaction [eqn. (2)] are tabulated in Table 3.



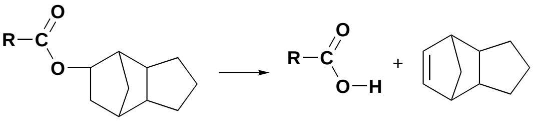
$$\text{R}-\text{C}(=\text{O})-\text{O}-\text{CH}(\text{R}''')-\text{CHR}'\text{R}'' \longrightarrow \text{R}-\text{C}(=\text{O})-\text{O}-\text{H} + \text{H}-\text{C}(\text{R}''')=\text{CR}'\text{R}'' \qquad (2)$$

This is a pyrolysis reaction catalyzed by an acid,[46,47] often referred to as the reaction occurring in the photoresist.[6,48,49] As shown in eqn. (2), the reaction involves a breaking of a O—C bond present in the ester group with formation of a double bond in the protection group.

We note that when the deprotection group is THP or TCD, eqn. (2) should be read as eqn. (3) or eqn. (4), respectively.



(3)



(4)

For the hydrolysis reaction shown in Table 2, the MNDO/PM-3 calculated order of magnitude of the reaction energy does not agree with that at the DFT levels. Furthermore, the reaction energy for the Bu^t group at the MNDO/PM-3 level is calculated to be slightly more exothermic than those for the groups containing an ethoxyethyl unit, which is contrary to experimental results showing lower sensitivity for the Bu^t group than for the THP group and the groups containing an ethoxyethyl unit.[14–17] The VWN/DZVP values are slightly less exothermic than the BLYP/DZVP values. The BLYP/DZVP values for the model compounds **1** and **3** are essentially the same (see the values for R′ = ETE and THP in Table 2). This shows that the reactivity in terms of the hydrolysis reaction should be the same for poly($TCDA_5$–RMA_3–MAA_2) and poly($TCDMACOOR_4$–$TCDMACOOH_6$), if the protection groups present are the same. In the case of R′ = TCD, the BLYP/DZVP values for R = Bu^t and Pr^i are, again, essentially the same, showing that the reactivity in terms of the detachment of the TCD group in poly($TCDA_5$–RMA_3–MAA_2) and poly($TCDMACOOR_4$–$TCDMACOOH_6$) does not differ significantly.

For this reaction, the BLYP/DZVP values of ΔG_{rxn} are calculated to be exothermic, so the reaction is predicted to proceed thermally. The ΔG_{rxn} values of the groups containing an ethoxyethyl group (R′ = ETE, MEE, AEE, AdEE and AdCEE) are essentially the same with an exothermicity of about 8–11 kcal mol^{-1} (1 cal = 4.184 J) at the BLYP/DZVP level. The value for the THP group is calculated to be less exothermic by 4–6 kcal mol^{-1} than that for the groups containing an ethoxyethyl group. The value for the Bu^t group is essentially the same as that for the THP group, and still less exothermic values are calculated for the TCD protection group, so that the general trend of the order of the exothermicity of the calculated values becomes TCD < Bu^t ∼ THP < groups containing an ethoxyethyl group (ETE, MEE, AEE, AdEE and AdCEE). Experimentally, it is known that the TCD group is hardly detached at all, whereas the detachment of the Bu^t group can be observed, although the sensitivity for the Bu^t group is lower than that for the THP group and the groups containing an ethoxyethyl group.[14–17] In addition, as shown in Table 1, the THP group shows a lower sensitivity than that for the groups containing an ethoxyethyl group. Thus, the calculated trend in ΔE_{rxn} is, in general, in agreement with the experimental trend in sensitivity, although it does not account for the difference in the sensitivity for the groups containing an ethoxyethyl group.

For ΔG_{rxn} (or ΔH_{rxn}) of eqn. (2) (Table 3),[50] a similar result for the hydrolysis reaction is obtained; the MNDO/PM-3 calculated order of the magnitude of ΔH_{rxn} does not agree with that at the DFT levels. The reaction energy for the Bu^t group at the MNDO/PM-3 level is calculated to be less endothermic than those for the groups containing an ethoxyethyl unit, which is, again, contrary to experimental results.[14–17] This shows that the semiempirical method does not predict the reaction energy with the necessary accuracy to allow a qualitative discussion. Thus, although the semiempirical MO method has an advantage that it is computationally less expensive than *ab initio* methods, methods with no empirical parameters such as the DFT and *ab initio* MO method must be applied to the prediction of reactivity of deprotection groups in photoresists.

The VWN/DZVP values for eqn. (2) are more endothermic by about 15–20 kcal mol^{-1} than the BLYP/DZVP values, although we note that the order of magnitude of ΔG_{rxn} at the VWN/DZVP level is not different from that at the BLYP/DZVP level. Values for the groups containing an ethoxyethyl group are again essentially the same. In addition, values for the THP and Bu^t groups are essentially the same as those for the groups containing an ethoxyethyl group. The value for the TCD group is calculated to be more endothermic than that for the other groups containing an ethoxyethyl group, which is in agreement with the experimental trend in sensitivity that the TCD group exhibits a lower sensitivity than the other groups.[14–17] These results show that the calculated results do not account for the difference in the sensitivity for the protection groups calculated except for the TCD group.

Results of the graph theoretical treatment

Calculated values of the van der Waals volume, density, glass transition temperature, gas permeability, relative permittivity and density using the graph theoretical treatment are listed in Table 4. In Fig. 1, we plotted experimental sensitivity against the calculated properties for the values for poly($TCDA_5$–RMA_3–MAA_2).

We calculated the van der Waals volume for a segment composed of five TCDA units, three RMA units and two MAA units for poly($TCDA_5$–RMA_3–MAA_2), whereas for poly($TCDMACOOR_4$–$TCDMACOOH_6$), the calculated van der Waals volume corresponds to four TCDMACOOR units and six TCDMACOOH units. We note that this value represents the density of the reaction site, with the larger volume corresponding to a lower density of the reaction site. For the protection groups containing an ethoxyethyl group (ETE, MEE, AEE, AdEE and AdCEE), there is a weak tendency for the sensitivity to be lowered (or the dose to be increased) with an increase in the van der Waals volume for poly($TCDA_5$–RMA_3–MAA_2) [Fig. 1(*a*)]. However, we note that points for the AEE and AdCEE groups are very scattered.

In Fig. 1(*b*), the plot for the density of the polymers for poly($TCDA_5$–RMA_3–MAA_2) is shown. The density of polymers was calculated because this value may represent the magnitude of the free-volume of polymers. However, Fig. 1(*b*) shows no correlation between the experimental sensitivity and the density, with the values for the AEE and AdEE groups being very scattered. Thus, it can be concluded that this value is not related to the sensitivity.

We calculated the gas permeability for nitrogen gas as a parameter which would hopefully represent the mobility of acids in the photoresist and hence dominate the magnitude of the sensitivity. We also calculated oxygen gas permeability, and found that the order was similar to that for nitrogen gas. As shown in Fig. 1(*c*), there is, again, no correlation between the calculated value and the experimental sensitivity for poly($TCDA_5$–RMA_3–MAA_2). It can be concluded that this quantity does not have a significant bearing on the sensitivity, although we note that the mean error for the calculation of this value is reported to be significantly large ($\sim 50\%$; standard deviation).[41–43] Gas permeability is reported to be proportional to the product of the solubility of the gas in the medium and the diffusion coefficient,[51] which may account for the lack of correlation in our results, suggesting that the sensitivity may not simply be described by the product of the two values.

Table 4 Calculated glass transition temperature, gas permeability, relative permittivity and density of the polymers

protection group	van der Waals volume /$cm^3\ mol^{-1}$	density /$g\ cm^{-3}$	T_g /°C	N_2 gas permeability (Dow unit)[a]	relative permittivity
	poly($TCDA_5$–RMA_3–MAA_2)				
ETE	9.8×10^2	1.134	100	6.1×10^2	2.72
MEE	10.1×10^2	1.146	95	6.4×10^2	2.76
AEE	10.5×10^2	1.166	96	4.8×10^2	2.82
AdEE	12.2×10^2	1.157	111	5.7×10^2	2.61
AdCEE	12.6×10^2	1.180	112	4.2×10^2	2.67
THP	9.5×10^2	1.213	119	3.2×10^2	2.66
Bu^t	9.6×10^2	1.119	108	6.9×10^2	2.67
	poly-($TCDMACOOR_4$–$TCDMACOOH_6$)				
ETE	16.6×10^2	1.178	124	3.5×10^2	2.80
THP	16.7×10^2	1.199	138	3.0×10^2	2.78

[a] 1 Dow unit = cm^3 mil/(day × 100 $inches^2$ × atm), where 1 mil = 0.001 inches.

For the glass transition temperature for poly($TCDA_5$–RMA_3–MAA_2), there is a lowering of sensitivity (an increase in dose) with an increase in the glass transition temperature, as established by the plot between the calculated and experimental results as shown in Fig. 1(*d*), although points are somewhat scattered. For poly($TCDMACOOR_4$–$TCDMACOOH_6$), the experimental sensitivity for the ETE group is higher than that for the THP group (Table 1), and the calculated glass transition temperature is higher for the THP group than that for the ETE group. This agrees with the trend in Fig. 1(*d*) found for poly($TCDA_5$–RMA_3–MAA_2).

For relative permittivity, there is a good correlation between the calculated value and the experimental sensitivity for poly($TCDA_5$–RMA_3–MAA_2). It is shown in Fig. 1(*e*) that if the relative permittivity becomes larger, the sensitivity becomes higher (or the dose decreases). For poly($TCDMACOOR_4$–$TCDMACOOH_6$), the relative permittivity for the ETE group is calculated to be larger than that for the THP group, again showing that a larger relative permittivity leads to a higher sensitivity.

Discussion

For the deprotection reaction, the calculated ΔG_{rxn} seems to dominate the experimental sensitivity if the protection group becomes less reactive [ΔG_{rxn} of eqn. (1) > *ca.* -6 kcal mol^{-1}, or ΔG_{rxn} of eqn. (2) > ~ 0 kcal mol^{-1}]. This suggests that, for the TCD protection group, the magnitude of the sensitivity is dominated by the deprotection reaction itself. However, the magnitude of the calculated ΔE_{rxn} does not account for the difference in sensitivity for groups containing an ethoxyethyl group (ETE, MEE, AEE, AdEE and AdCEE groups). For these groups, the reaction energy is calculated to be essentially the same and to be the most exothermic among the groups calculated, suggesting that the rate-determining factor for these compounds is not in the reaction, but is in the diffusion processes. This is supported by the presence of the correlation between the experimental sensitivity and the calculated properties of the van der Waals volume, the relative permittivity and the glass transition temperature, although we note that the correlation with the van der Waals volume was the most scattered among the three.

For the correlation with the relative permittivity, a higher value for the polymer of this quantity is expected to cause a decrease in the value of the pH of the acid molecule, leading to an enhanced quantity of protons (or oxonium ions) formed by the dissociation of the acid molecule. Consequently, the size of chemical species to diffuse becomes smaller, leading to an enhanced degree of diffusion. In addition, transport properties of molecules are known to be related to the solubility of the molecules in the medium.[51] In a previous study on alkali metal cation transport across polymer-supported liquid membranes,[52] it was reported that the experimental Na^+ flux is correlated to the relative permittivity of the liquid membrane solvent. In that study, the Na^+ flux increases with an increase in the relative permittivity, which is consistent with our results.

It has been reported that the dissolution rate of unexposed poly($TCDA_5$–RMA_3–MAA_2) where R = ETE, MEE, AEE, and THP depends on ε_r of the protecting groups, with the more polar protecting groups exhibiting a higher experimental dissolution rate.[14] This means that the presence of protecting groups with low polarity leads to a larger inhibition effect, if we consider the diffusion of the polar solvent TMAH (tetramethylammonium hydroxide) used for the development.[14] A similar situation may hold true for acids diffusing in polymers, leading to a higher sensitivity in more polar media. We note here that for the dissolution rate, the correlation was obtained

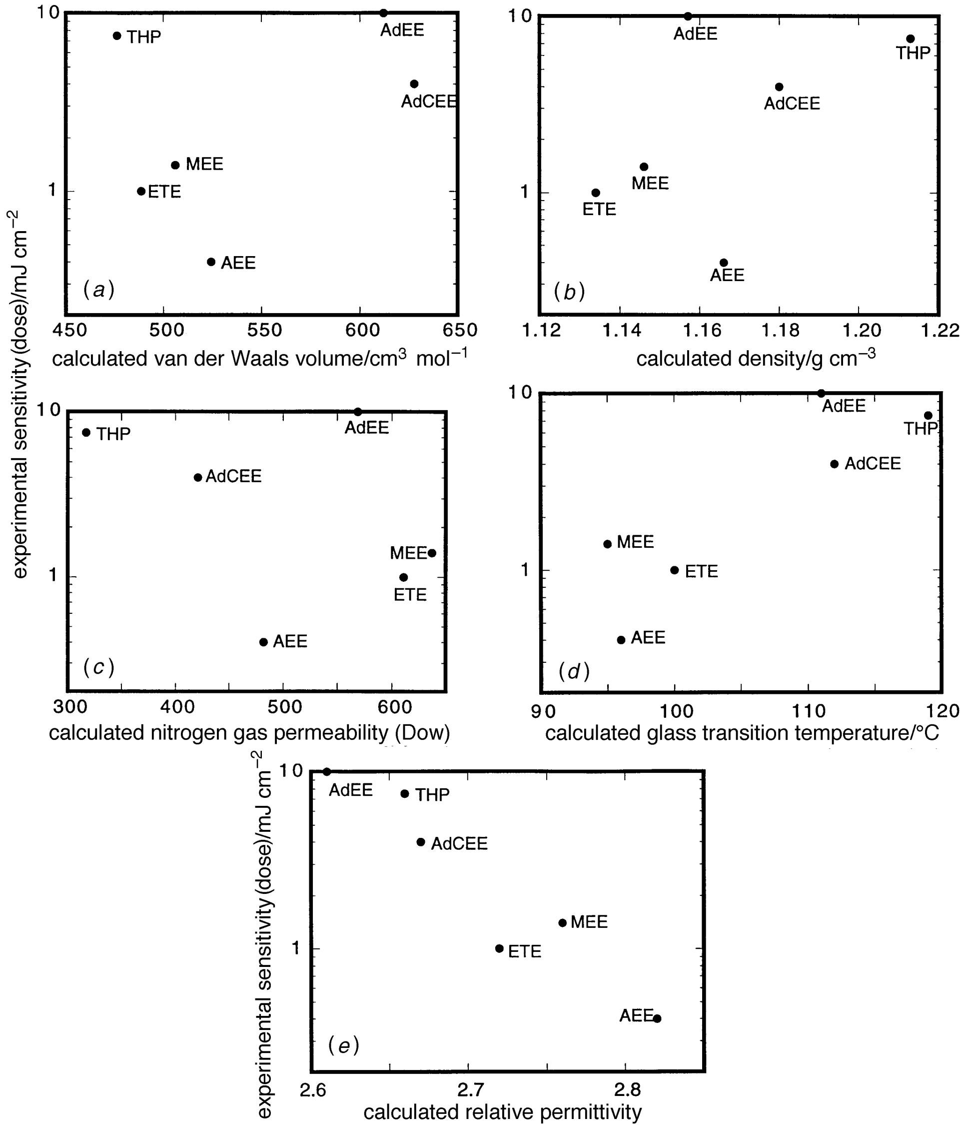


Fig. 1 Plot of the logarithm of the experimental sensitivity against (*a*) van der Waals volume, (*b*) density, (*c*) nitrogen gas permeability, (*d*) calculated glass transition temperature and (*e*) relative permittivity of the polymer

for the relative permittivity of the protection groups, whereas in our study, the correlation for the sensitivity is for the relative permittivity of the polymers. This may indicate that a local relative permittivity plays an important role in the diffusion of the TMAH solvent, whereas for acids, the average relative permittivity of the medium becomes important.

Another correlation found is that of the experimental sensitivity to the calculated glass transition temperature. This correlation is slightly more scattered than that for the relative permittivity. It has been reported[53,54] that the protonic or ionic transport in polymeric membranes is strongly affected by the glass transition temperature, with a higher glass transition temperature leading to a higher conductivity. This is consistent with the correlation we obtained. We further note that the diffusion of molecules larger than a diatomic gas is known to be related to the polymer dynamics of segmental mobility[55] which could be represented by the glass transition temperature for a set of polymers having the same or a similar main-chain structure.

Another possible explanation to account for the difference in sensitivity for the groups containing an ethoxyethyl unit can be extracted from Fig. 1(*a*); there is a weak tendency for the sensitivity to be lowered (the dose to be increased) with an increase in the van der Waals volume, if we ignore the point for THP in Fig. 1(*a*), because the calculated ΔG_{rxn} of THP was different from that of the protection groups containing an ethoxyethyl group. This means that when the density of the reaction site decreases, the sensitivity becomes lower. However, the correlation for this case is much more scattered than the other cases which are shown in Figs. 1(*d*) and (*e*), so that the density of the reaction site may not be the dominant factor in controlling the sensitivity.

Thus, although it is not clear which value is the dominant factor in controlling the sensitivity, it can be concluded that the sensitivity is not dominated by the reaction alone, but is mainly dominated by the values related to the property of diffusion for the polymers with the protecting groups containing an ethoxyethyl unit.

For the THP and Bu^t groups, the calculated ΔG_{rxn} for eqn. (1) is less exothermic than that for the groups containing an ethoxyethyl group, which is consistent with the experimental trend of a lower sensitivity of the THP and Bu^t groups than that of the groups containing an ethoxyethyl group. On the other hand, for the case of eqn. (2), the calculated ΔG_{rxn} values for the THP and Bu^t groups are essentially the same as those for the groups containing an ethoxyethyl group. However, the calculated relative permittivity for the THP and Bu^t groups is smaller, and the glass transition temperature is higher than that for the ETE, MEE and AEE groups containing an ethoxyethyl group, which is, again, inconsistent with the experimental trend. Thus, for the THP and Bu^t protecting groups, our calculated results do not clarify the dominant factor in controlling the sensitivity, suggesting that a balance between the reaction and the diffusion process plays an important role for these groups. We further note that the calculated density for the THP and Bu^t groups does not account for their lower sensitivity than the ETE, MEE and AEE groups, because the value for the THP and Bu^t groups is smaller than that for the ETE, MEE and AEE groups.

Conclusion

We found a correlation between the experimental sensitivity and the calculated values of the glass transition temperature and the relative permittivity for the photoresists of poly(TCDA$_5$–RMA$_3$–MAA$_2$) and poly(TCDMACOOR$_4$–TCDMACOOH$_6$) for protecting groups whose $\Delta G_{\rm rxn}$ of the deprotection reaction (eqn. (2)] is more than about 0 kcal mol^{-1} [or $\Delta G_{\rm rxn}$ of eqn. (1)> *ca.* -6 kcal mol^{-1}]. If the reaction is more endothermic than this value, the experimental sensitivity is found to be controlled by the magnitude of $\Delta G_{\rm rxn}$. These results show that the balance between the two processes of reaction and diffusion dominates the dependence of the experimental sensitivity on the choice of the protecting group.

It is further suggested that calculating the relative permittivity and glass transition temperature of the polymers, in addition to calculating $\Delta G_{\rm rxn}$ of the deprotection reactions, has the potential to provide a quick way to identify polymers having a high sensitivity for ArF lithography.

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