

Improvement of Plasma Etching Durability of Positive Working Resist by Copolymerization, Blending, and Crosslinking

NOBUO UENO, YASUNORI DOI and KAZUYUKI SUGITA,
*Department of Image Science and Technology, Faculty of
Engineering, Chiba University, Yayoi-cho, Chiba 260, Japan* and
SHIGERU SASAKI and SHIRO NAGATA, *Central Research
Laboratories, Kuraray Co., Ltd., Aoeyama, Sakazu,
Kurashiki 710, Japan*

Synopsis

The plasma etching durability of O_2 and CCl_4 was investigated for copolymer and polymer blend of poly(methyl methacrylate) (PMMA) and poly(α -methylstyrene) (PMSt) as a function of MSt content. Further, the effects of crosslinking on plasma etching were studied by incorporating *N*-methylolated methacrylamide into the copolymer as a crosslinkable site during prebaking. The plasma-etching resistance of PMMA was largely improved by incorporating or adding only a small amount of MSt. Especially in the case of the CCl_4 plasma etching, the copolymer and the polymer blend with 10 mol% of MSt showed etching resistance as great as that of PMSt homopolymer. Stabilization of the polymers against the plasma etching can be explained by the sponge effect, the energy migration followed by the quenching by the phenyl ring. The polymer blend offered similar etching resistance as the copolymer, indicating an effective occurrence of the energy migration between the polymer chains. Etching resistance was also improved by crosslinking, also due to the enhancement of the sponge effect.

INTRODUCTION

Traditional work in developing organic resist has been devoted mainly to improving its lithographic sensitivity to ionizing radiations. The recent continuing trend in shrinking microelectronic-device size requires new resists with (a) high dry-etching resistance and (b) high resolution as well as (c) high sensitivity. It has been known, however, that increase in the plasma-etching resistance is often accompanied by a serious reduction in the chain scission efficiency, which results in decrease of the sensitivity of positive-working resists. For example, it was reported by Taylor and Wolf¹ that dry-etching resistance and sensitivity were contradicting properties, since there was a linear relationship between O_2 plasma-etching rate and Gs value, the efficiency of chain scission per 100 eV of absorbed high energy radiation. A similar relationship between the dry-etching rate and sensitivity was also presented by Harada et al.² We note here that these relationships were derived from the studies on one-component resist systems composed of degradable linear homopolymers, and do not deny the possibility to realize excellent resist systems

which have both properties, if the development of the resist polymer is performed by copolymerization, blending, and precrosslinking.

It has been known empirically that dry-etching resistance can be improved by incorporating or adding aromatic moiety into the undurable resist polymers.³⁻⁵ This improvement is considered to be due to the quenching of the electronic energy by the aromatic groups. The quenching mechanism was theoretically investigated by Tsuda and his coworkers using isolated benzene molecule as a model system.^{6,7} The plausibility of their model system in discussing the quenching mechanism in the polymer is supported by the fact that benzene moiety conserves its molecular nature even in the polymer solid to which benzene ring is chemically bonded.^{8,9} From an intuitive point of view, however, it seems that the effective quenching of the electronic energy introduced into the polymer chains reduces the Gs value as well as the plasma-etching rate even for the copolymer system which contains aromatic moieties as the quencher, because the aromatic moieties may also quench the energy introduced by the high energy radiation. Therefore, the basic method to overcome the conflict in the positive working resists is (i) to use the energy dependence of the "sponge effect"¹⁰ and (ii) to enlarge the difference of the solubility between the irradiated and unirradiated area in getting high sensitivity of the durable polymer by a strong developing condition. The former method (i) involves the application of so called "site-selective reaction" or "energy-selective reaction"¹¹ and the energy dependences of the migration length and/or the energy transfer probability of the electronic excitations. In this case, we expect different stabilization effects of the polymer against the electronic energies introduced by the plasma and high energy radiations. Therefore, the polymer system which has larger migration length for the energies introduced by the plasma than those by the electron beam of high energy would offer high plasma etching resistance with little loss of the sensitivity by introducing a small amount of the quenching moiety into the polymer system. On the other hand, the latter method was used successfully by Harada et al. in sensitizing poly(phenyl methacrylate) by copolymerization with methacrylic acid as cross-linking sites (Φ -Mac).²

There are many works which aimed at improving plasma-etching resistance of a sensitive polymer by adding or incorporating aromatic compounds as the quencher.¹²⁻¹⁵ Among these it is interesting to note that the addition of as little as 20% 3-chlorostyrene into poly(glycidyl methacrylate) results in a twofold improvement in O₂ plasma-etching resistance,¹⁴ although the system works as a negative resist. Further, as we have reported briefly in the previous report on the copolymers and polymer blends of poly(methyl methacrylate) (PMMA) and poly(α -methylstyrene) (PMSt), that polymer systems containing 30-50 mol% MSt were as durable as PMSt homopolymer against O₂ plasma, while the sensitivities were around the averaged value of PMMA and PMSt.¹⁵ These experimental data suggest that mechanism (i) plays an important role in improving plasma-etching resistance. The determination of the plasma-etching rate as a function of the amount of the quencher will provide a basic understanding of the process of plasma etching and of how to design an excellent high-performance resist polymer.

In this study we selected PMMA and PMSt which are typical examples of low plasma-etching resistance and long plasma-etching durable resist of poor

sensitivity, respectively, and prepared various copolymers and polymer blends of these polymers. The O_2 and CCl_4 plasma-etching rates were measured as a function of the composition in the copolymer and the polymer blend. Further, the effect of crosslinking on the etching rate was investigated by incorporating *N*-methylolated methacrylamide into the copolymer as a crosslinkable site during prebaking.

The results demonstrate that the plasma-etching resistance of PMMA can be increased drastically by incorporating only a small amount of MSt which acts as the quencher and that the degree of improvement of the resistance depends highly on the etching gas, indicating the effective occurrence of the energy-dependent "sponge effect" in these polymer systems.

EXPERIMENT

Preparation of Resist Polymers

Poly(α -methylstyrene) (PMSt) was prepared by cationic polymerization in CH_2Cl_2 at $-78^\circ C$ with BF_3OEt_2 as a catalyst. Poly(α -methylstyrene-co-methyl methacrylate) (PMSt-MMA) and poly(methyl methacrylate) homopolymer (PMMA-1) were prepared by emulsion polymerization at $80^\circ C$ with $K_2S_2O_8$ as an initiator. These polymers were fractionated from a toluene or a tetrahydrofuran/methanol system. Poly(α -methylstyrene-co-methyl methacrylate-co-*N*-methylolated methacrylamide) (PMSt-MMA-MAAm, T37-1.2, T37-1.7 and T38-2.9) was prepared by emulsion polymerization of α -methylstyrene, methyl methacrylate, and methacrylamide at $80^\circ C$ with $K_2S_2O_8$ as an initiator and *N* methylolation in tetrahydrofuran with a formaldehyde solution in *n*-butanol in the presence of maleic anhydride, and fractionation from a tetrahydrofuran/hexane system. PMSt-MMA-MAAm (T23-1.2) was prepared by emulsion polymerization at $80^\circ C$, fractionation from a tetrahydrofuran/hexane system, and then methylolation. Further, various polymer blends were prepared as described in Table I.

The copolymerization ratio in moles of these polymers was estimated by elementary analysis, M_n and M_w were by GPC and T_g was by DSC. The polymer data are summarized in Table I and the molecular structures are shown in Figure 1.

Besides the above polymer systems, a commercial resist OEER-1000 (Tokyo Ohka CO., Ltd.) (PMMA-2) and a commercial polystyrene (Koso Kagaku Co., Ltd.) (PSt) were used as controls.

Film Preparation and Thickness Measurement

The resist films were prepared by spin-coating at about 2800 rpm from toluene solutions on copper-evaporated glass plates. The films without MAAm were prebaked in an air-circulating oven at $180^\circ C$ for 20 min, and those containing MAAm were prebaked at $200^\circ C$ for 60 min. After the latter prebaking, no thickness reduction of the films was observed after dipping in a developer, due to the effective thermal crosslinking of MAAm units incorporated in the polymer chain.¹⁷

The phase separation of the coated films, especially the films of polymer blends, was carefully investigated with a scanning electron microscope before

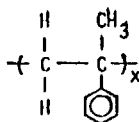
TABLE I
 Summary of Polymer Data

Polymer	MSt : MMA : MAAm (mol)	$\bar{M}_w (10^4)$	\bar{M}_w/\bar{M}_n	T_g (°C)	T_c (°C) ^a
PMMA-1	0 : 100 : 0	55.6	3.42	105	164
PMMA-2	0 : 100 : 0	57.0	4.54	105	164
PMSt					
(P-1)	100 : 0 : 0	1.2	1.11		61
(P-4)	100 : 0 : 0	3.9	1.08		61
(P-8)	100 : 0 : 0	8.1	1.15		61
(P-19)	100 : 0 : 0	19.2	1.09		61
(P-35)	100 : 0 : 0	34.8	2.52	173	61
(P-59)	100 : 0 : 0	59.3	2.44	173	61
PSt		22.4	5.16	100	150
PMSt-MMA					
(C-10)	10 : 90 : 0	36.8	2.73	134	
(C-21)	21 : 79 : 0	31.9	2.14	152	
(C-39)	39 : 61 : 0	64.5	1.90	157	
(C-44)	44 : 56 : 0	37.4	1.69	170	
PMSt & PMMA					
(B-10)	10 : 90 : 0	blend of PMMA-1 and P-35			
(B-21)	21 : 79 : 0	blend of C-10 and P-35			
(B-39)	39 : 61 : 0	blend of C-10 and P-35			
(B-44)	44 : 56 : 0	blend of C-10 and P-35			
(B-80)	80 : 20 : 0	blend of C-10 and P-35			
PMSt & PMMA					
(B39-1)	39 : 61 : 0	blend of C-10 and P-1			
(B39-4)	39 : 61 : 0	blend of C-10 and P-4			
(B39-8)	39 : 61 : 0	blend of C-10 and P-8			
(B39-19)	39 : 61 : 0	blend of C-10 and P-19			
(B39-35)	39 : 61 : 0	blend of C-10 and P-35			
(B39-59)	39 : 61 : 0	blend of C-10 and P-59			
PMSt-MMA-MAAm					
(T23-1.2)	23.3 : 75.5 : 1.2	30.3	2.16		
(T37-1.2)	37.0 : 61.9 : 1.2	40.8	2.11	158	
(T38-2.9)	37.5 : 59.6 : 2.9	33.5	2.56	164	

^a Cited from Ref. 16.

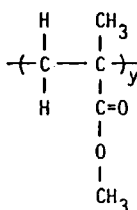
 α -Methylstyrene

[MSt]



Methyl methacrylate

[MMA]



Methylolated methacrylamide

[MAAm]

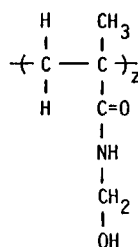


Fig. 1. Molecular structure of polymers.

and after plasma etching, and the topography of the surface resulting from the phase separation¹⁸ was not observed within the estimated resolution ($\sim 300 \text{ \AA}$) of the microscope. Thus we concluded that uniform films were obtained even for the polymer blends without the phase separation.

The etching depth and the initial film thickness were measured with a multiple-interference microscope (Nikon Surface Finish Microscope) after evaporating aluminum thin film onto the surface of the resist film in order to increase the accuracy of the thickness measurements. The initial film thickness was 4000–8000 \AA .

Plasma Etching of Resists

The plasma-etching apparatus was shown in the previous report.¹⁵ The etching of resists was carried out in the stainless steel chamber separated from the glow discharge region by a multichannel orifice (MCO), a bundle of glass tubings of 3 mm inner diameter and 100 mm long (for O_2 plasma etching), or by a stainless steel mesh of 37% light transmittance and $0.15 \times 0.15 \text{ mm}$ opening (for CCl_4 plasma etching). The etching gas was introduced into the quartz chamber, discharged at 300 W by a 13.56 MHz power supply (Nippon Koshuha Co., Ltd. SKN-05P), and excited species were introduced into the etching chamber through MCO (O_2) or the mesh (CCl_4). The pressure in the etching chamber was maintained at 0.05 Torr for O_2 plasma etching and 0.02 Torr for CCl_4 plasma etching, respectively. These were monitored with a Pirani gauge calibrated by a Macleod gauge.

The specimen was exposed to the stream of the excited species through a thin copper or stainless steel mask with small holes. In the present etching, we found no loading effect on the etching rate even for PMMA which showed the largest etching rate in the resists investigated. The etching rate was small under the present conditions, and accordingly the temperature rise of the resist film during etching was found to be small. Thus the precise temperature control of the etching could be realized.

The contribution of ionic species to the etching was studied by applying various dc potentials to the specimen holder, and was found to be negligible. We believe that the present etching was performed mainly by neutral species.

Determination of the Etching Rate

In this experimental set-up, the plasma etching would include the direct etching of the resist by photons emitted from the discharge area.^{19–22} Generally, the rate of the thickness reduction of the resist by the photoetching becomes smaller with increase in the etching time.^{19,22} In the present plasma etching, however, a linear relationship was observed between the etching depth and the etching time, independent of the initial film thickness, and the etching depth increased at a constant rate until it reached the initial thickness as long as the resist temperature was kept constant. A few examples are shown in Figure 2. Therefore, we neglected the effect of the photoetching on the present results, and the plasma-etching rate was determined as the slope of the depth versus etching time plot. In the calculation of the etching rate and the activation energy from the results, we used the method of least squares.

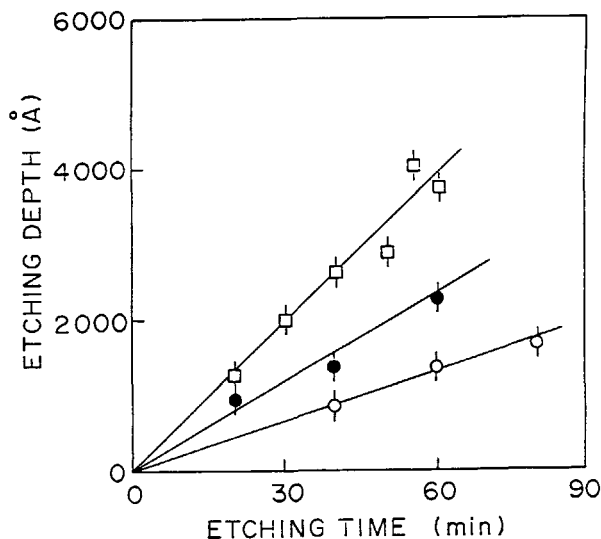


Fig. 2. O_2 plasma etching depth vs. etching time; Copolymer (C-10) at 90°C ; (●) Polymer blend (B-10) at 70°C ; (○) Polymer blend (B-10) at 36°C .

RESULTS AND DISCUSSION

Effects of Molecular Weight on the Plasma Etching

We first show the molecular weight dependence of the O_2 and CCl_4 plasma-etching rates using PMSt homopolymers (P-1 ~ P-59) and polymer blends (B39-1 ~ B39-59) in Figures 3 and 4. As can be seen, there is no remarkable difference in the etching rate in the M_w range of $2 \times 10^5 \sim 6 \times 10^5$ for either O_2 and CCl_4 etching. Such independence of the etching rate of the molecular weight was also observed for PMMA in CF_4/O_2 plasma etching by Harada.²³ This is because the scission susceptibility is not a function of molecular weight.²⁴ In the following discussion, we will neglect the effects of the difference of the molecular weight on the etching rate.

Plasma Etching of Binary Systems

The temperature dependence of the O_2 plasma-etching rate is shown by the Arrhenius plot in Figure 5 for the copolymers and the polymer blends, together with their homopolymers and PSt for comparison. For all polymers, the etching rate increases with temperature, and accelerated abruptly above the bend point which appeared at $70\text{--}85^\circ\text{C}$. The bend points and the activation energies are summarized in Table II.

The Arrhenius plots for the CCl_4 plasma-etching rate are shown in Figure 6. As in the case of the O_2 plasma etching, the etching rate was accelerated above the bend point, and it appears at similar temperature range as the case of the O_2 plasma etching. The activation energies for the CCl_4 plasma etching were found to be larger than those for the O_2 etching.

The bend points are compared with T_g and the ceiling temperature (T_c) in Table II. Harada²³ and Tsuda²⁵ reported that the bend point was associated with T_g at which molecular mobility of polymers increases. However, no

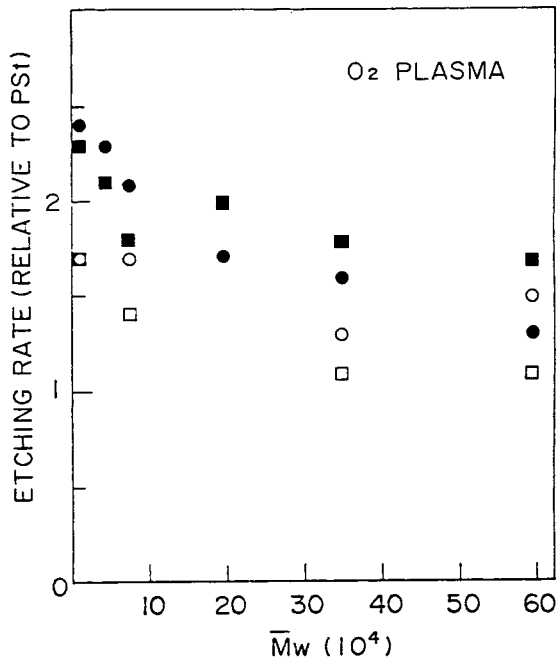


Fig. 3. Molecular weight dependence of O₂ plasma-etching rate: (□) PMSt homopolymer at 70°C; (○) PMSt homopolymer at 40°C; (■) Polymer blend B39 at 70°C; (●) Polymer blend B39 at 40°C.

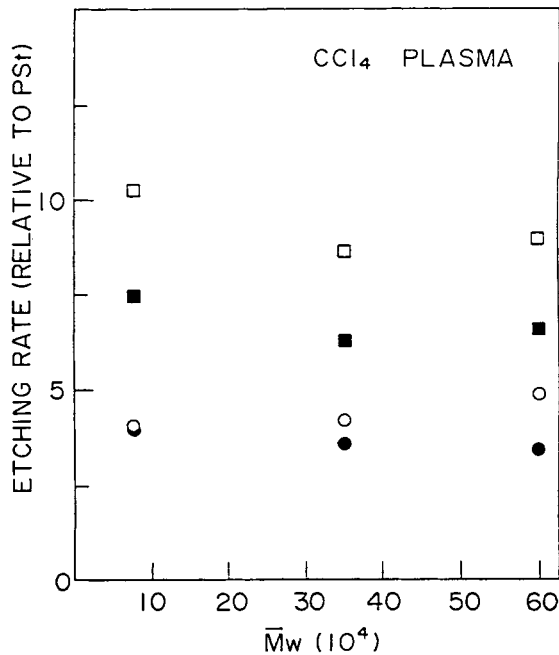


Fig. 4. Molecular weight dependence of CCl₄ plasma-etching rate: (□) PMSt homopolymer at 70°C; (○) PMSt homopolymer at 40°C; (■) Polymer blend B39 at 70°C; (●) Polymer blend B39 at 40°C.

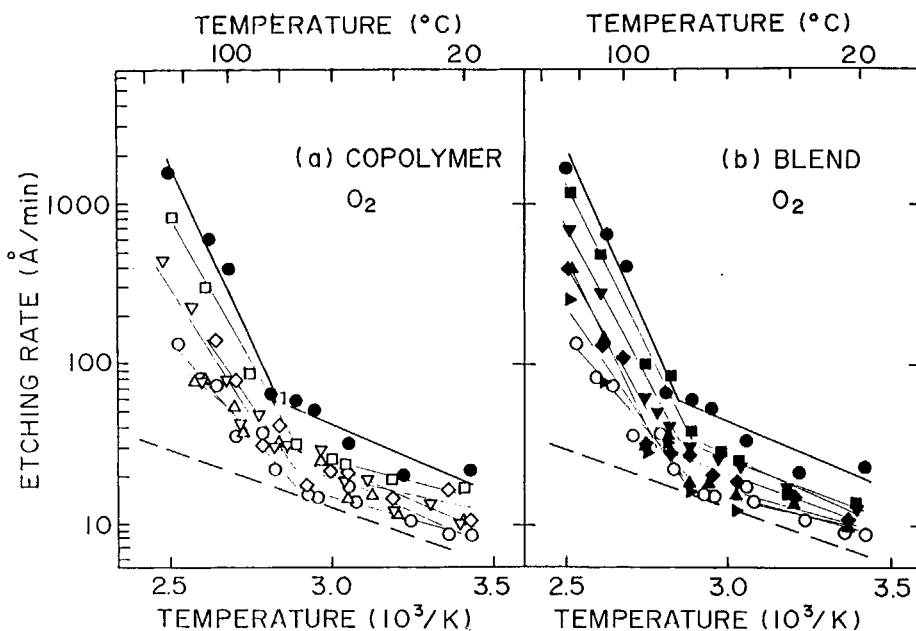


Fig. 5. Arrhenius plot of O_2 plasma-etching rates for binary systems: (●) PMMA-2; (□) C-10; (▽) C-21; (◇) C-39; (△) C-44; (■) B-10; (▼) B-21; (◆) B-39; (▲) B-44; (▴) B-80; (○) P-35 (PMSt); (---) PSt.

systematic correspondence was found between them in our results. Further, the bend points had no correlation to T_c .

As seen in Figures 5 and 6, PMSt is durable as PSt below the bend point. In the case of the CCl_4 etching, on the other hand, one can expect that PMSt becomes more durable than PSt below $20^\circ C$ on account of large activation energy (E_a). Similar to PMSt, the copolymers and the polymer blends show fairly large E_a and thus have great durability at lower temperature. These results clearly indicate that lowering the substrate temperature reduces the etching rate, thereby increasing the etching resistance of the organic resists. We mention here the Ballantyne et al. could etch silicon in a CF_4/O_2 plasma to form a fiducial pattern of $3.8 \mu m$ deep using poly(butene-1-sulfone) (PBS), a well known unendurable resist, as a dry-etch mask by maintaining the temperature of the substrate below $15^\circ C$.²⁶

Effects of Copolymerization and Blending on the Plasma Etching

As shown in the previous section, both copolymers and polymer blends had fairly long durability in the O_2 and CCl_4 plasma etching in comparison with PMMA. Therefore, the etching rates were plotted as a function of the MST content in weight and in mol, and they are shown in Figures 7 and 8 for the O_2 and CCl_4 plasma etching, respectively. In the figures, the etching rate calculated by assuming additivity²⁷ of those of PMMA and PMSt are also shown. In the case of the O_2 plasma etching, it is seen that the durability of the

TABLE II
The Bend Points and the Activation Energies in the Plasma Etching

Polymer	Bend Points (°C)	E _a (Kcal/mol) ^a	T _g (°C)	T _c (°C)	
PMMA-2	80	3.9	105	164	
O ₂ plasma	PMSt-MMA (C-10)	70	2.3	134	
	(C-21)	85	3.9	152	
	(C-39)	75	1.9	157	
	(C-44)	80	4.2	170	
	PMSt & PMMA (B-10)	70	4.0		
	(B-21)	80	3.5		
	(B-39)	85	3.4		
	(B-44)	75	2.5		
	(B-80)	75	2.0		
	PMSt (P-35)	75	2.6	173	61
PSt	— ^b	3.2	100	150	
CCl ₄ plasma	PMMA-2	80	4.0	105	164
	PMSt-MMA (C-10)	80	9.3	134	
	(C-21)	75	6.7	152	
	(C-39)	70	5.8	157	
	(C-44)	70	6.9	170	
	PMSt-PMMA (B-10)	75	8.7		
	(B-21)	75	7.8		
	(B-39)	65	7.0		
	(B-44)	60	4.9		
	(B-80)	60	5.7		
	PMSt (P-35)	65	11.5	173	61
	PSt	85	4.2	100	150
	PMSt-MMA-MAAm (T23-1.2) ^c	60	3.3	158	
	(T37-1.2) ^c	60	4.0	164	
uncrosslinked (T37-1.2)	75	4.4			
(T38-2.9) ^c	60	1.7			

^aActivation energy below the bend point.

^bThe bend point was not detected below 160°C.

^cThermally crosslinked by the prebaking.

copolymers and the polymer blends is larger than the calculated value based on the simple additivity of the durability of the homopolymers. Further, such a trend can be found out more drastically for the CCl₄ plasma etching. Although the error in determining etching rate was typically 30–50% for low etching rate region and about 20% for high etching rate region, these results were observed repeatedly. The copolymer and the polymer blend containing only 10% of MSt show durability similar to PMSt in the CCl₄ plasma etching. In other words, the addition of only 10% of PMSt into PMMA results in about a sixfold improvement in the CCl₄ plasma-etching durability of PMMA. It is interesting to note that both the copolymer and the polymer blend showed similar dependence of the etching rate on the MSt content. This finding reveals that the energy migration or transfer takes place effectively between the polymer chains, followed by the quenching at the phenyl ring.

We have shown that the copolymer and the polymer blend with 10% MSt were 2–4 times more sensitive to electron beam when MIBK was used as a

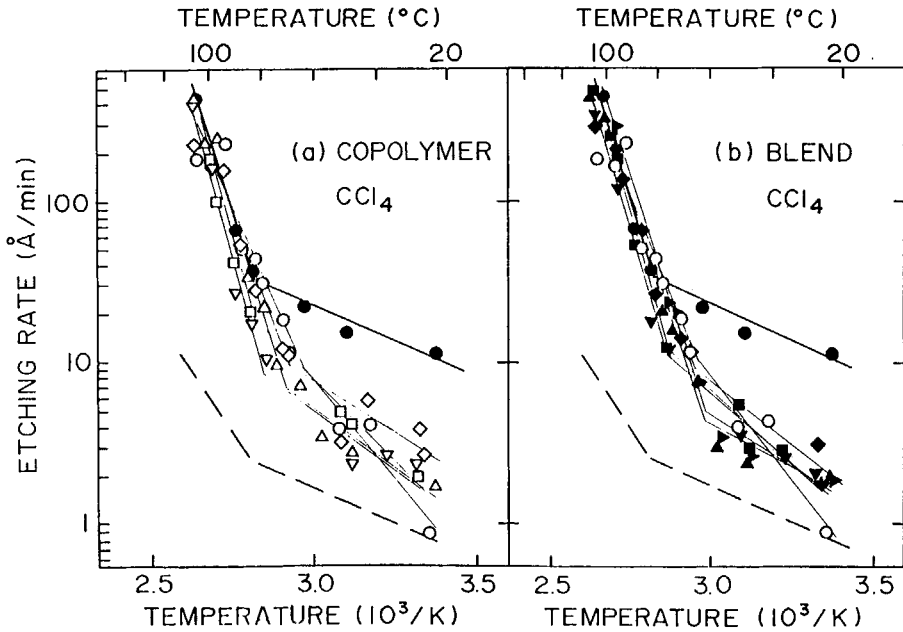


Fig. 6. Arrhenius plot of CCl_4 plasma-etching rates for binary systems: (●) PMMA-2; (□) C-10; (▽) C-21; (◇) C-39; (△) C-44; (■) B-10; (▼) B-21; (◆) B-39; (▲) B-44; (►) B-80; (○) P-35 (PMSt); (---) PSt.

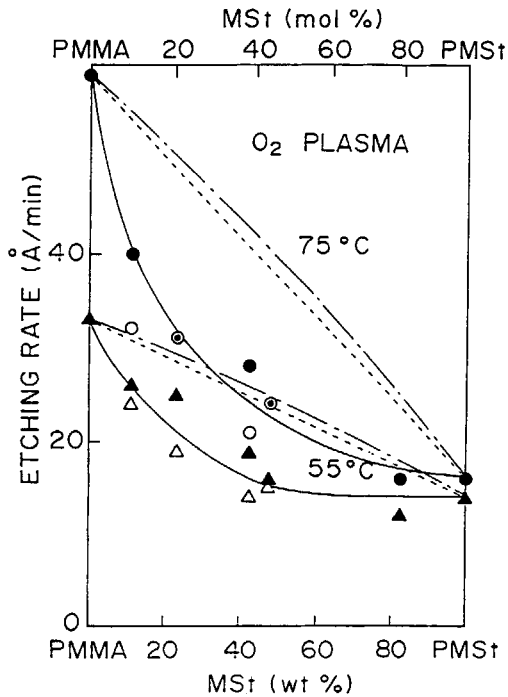


Fig. 7. Effect of composition on O_2 plasma-etching rate: (●) Polymer blend at 75°C ; (○) Copolymer at 75°C ; (▲) Polymer blend at 55°C ; (△) Copolymer at 55°C . Broken and chain lines indicate wt% and mol% additivity of the etching rates of the homopolymers, respectively (see text).

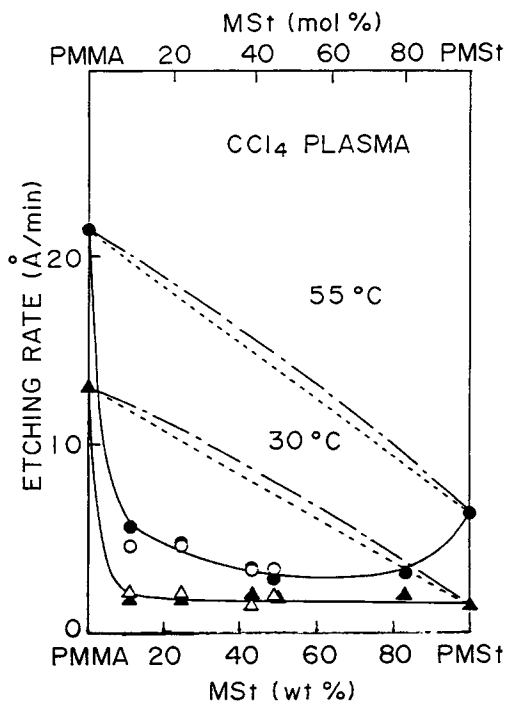


Fig. 8. Effect of composition on CCl_4 plasma-etching rate: (●) Polymer blend at 55°C; (○) Copolymer at 55°C; (▲) Polymer blend at 30°C; (△) Copolymer at 30°C. Broken and chain lines indicate wt% and mol% additivity of the etching rates of the homopolymers, respectively (see text).

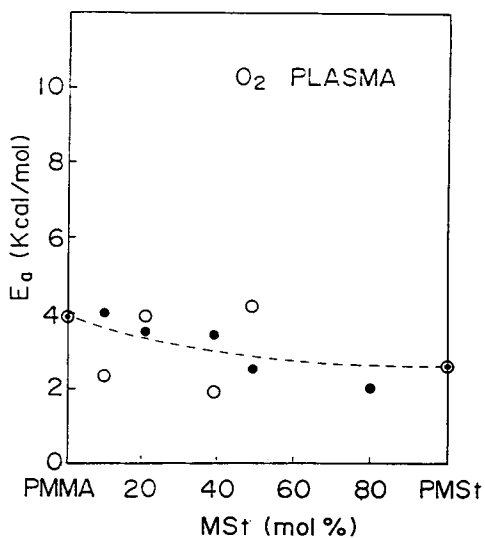


Fig. 9. Effect of composition on the activation energy below the bend point in O_2 plasma etching: (●) Polymer blend; (○) Copolymer.

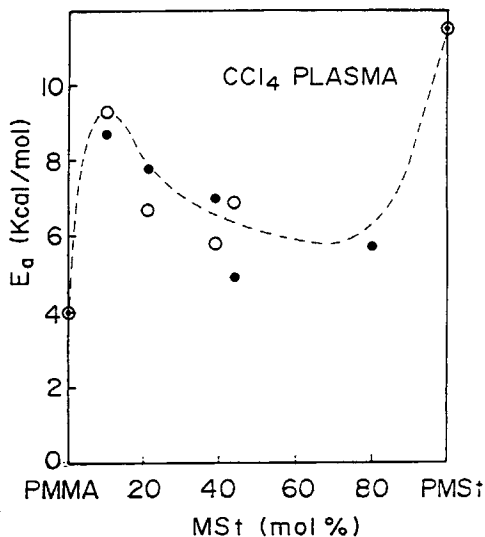


Fig. 10. Effect of composition on the activation energy below the bend point in CCl_4 plasma etching: (●) Polymer blend; (O) copolymer.

developer in comparison with PMMA developed in the usual manner.¹⁵ Thus the enhancement in both the durability and the sensitivity could be realized by copolymerization and blending. We do point out that by introducing aromatic moieties as an electronic energy quencher and by choosing the etching temperature we can obtain a new resist of both large dry-etching resistance and high sensitivity, which have been considered contradicting properties.

Figures 9 and 10 show the activation energies of the O_2 and CCl_4 plasma etching as a function of the MSt content for the temperature below the bend point. In the case of the O_2 plasma etching, the activation energy tends to decrease monotonically with MSt content, whereas in the CCl_4 plasma etching it shows an interesting behavior as seen in Figure 10. Although the origin of the difference between the MSt content dependencies of the activation energy in the O_2 and CCl_4 plasma etching is not clear at present, it would be necessary to take into account the migration or diffusion of the etchant into the resist as well as the migration and transfer of the electronic energies introduced into the chain. In fact, the penetration of reactive hot atoms into solid was observed by Taylor et al. for the reaction of nitrogen with silicon.²⁸

Plasma Etching of Ternary Systems and the Effects of Crosslinking

The results of the plasma etching for the binary systems indicate the effective occurrence of the "sponge effect"^{10,13,29} in these systems. The important point of the "sponge effect" is that the electronic energies introduced into the polymer chain should migrate effectively to the phenyl ring followed by the quenching. The results for the copolymers and the polymer blends indicate that such an energy migration takes place not only along the polymer chain but also among the chain. Therefore, it is interesting to study the effects

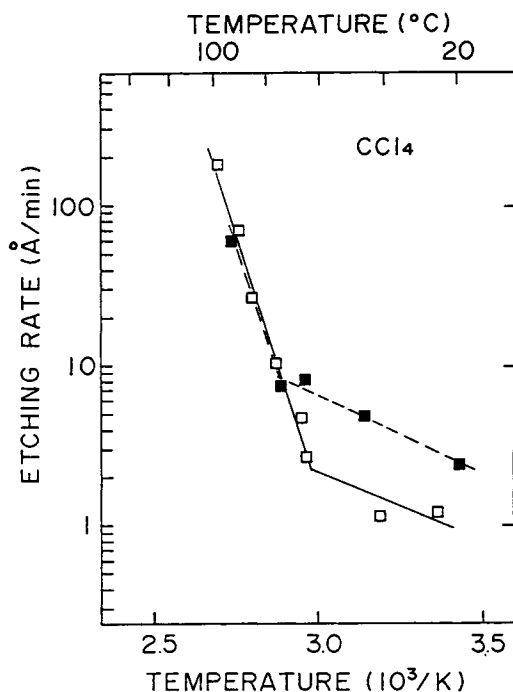


Fig. 11. Effect of crosslinking on CCl_4 plasma-etching rate: (■) Uncrosslinked T37-1.2; (□) Crosslinked T37-1.2.

of crosslinking of the chain on the plasma-etching resistance, since the crosslinking changes the molecular packing in the polymer solid and we can thereby expect the increase of the energy migration length.

Figure 11 shows the effects of the crosslinking on the CCl_4 plasma-etching rate of T37-1.2 polymer which was prebaked at 180°C for 20 min and at 200°C for 40 min. Under the former prebaking condition the crosslinking did not take place, whereas the polymer chains crosslinked during the latter prebaking.^{17,30} The result clearly demonstrates that low-density crosslinking can reduce the etching rate below the bend point. This is attributable to the increased migration length of the electronic energy due to the crosslinking. In Figure 12, we compare the results for crosslinked T23-1.2, T37-1.2, and T38-2.9 with those for linear C-21 and C-39 which contain similar amounts of MSt and MMA as the crosslinked polymers and show similar etching rate as uncrosslinked T37-1.2 below 60°C . The result for PSt is also shown for comparison. The bend points and the activation energies for these terpolymers are shown in Table II. It is seen that the loosely crosslinked ternary systems, T23-1.2, T37-1.2, and T38-2.9, provide the CCl_4 plasma-etching resistance as large as PSt below the bend point, indicating an effectiveness of the crosslinking in enhancing the plasma-etching resistance.

Our recent study on the electron-beam sensitivity of the ternary systems indicated that there was only a slight loss of sensitivity in comparison with that of PMMA and their sensitivity became higher when they were developed under stronger conditions.³⁰ Accordingly, it is concluded that the contradicting properties in the positive working resist of degradable polymer, the

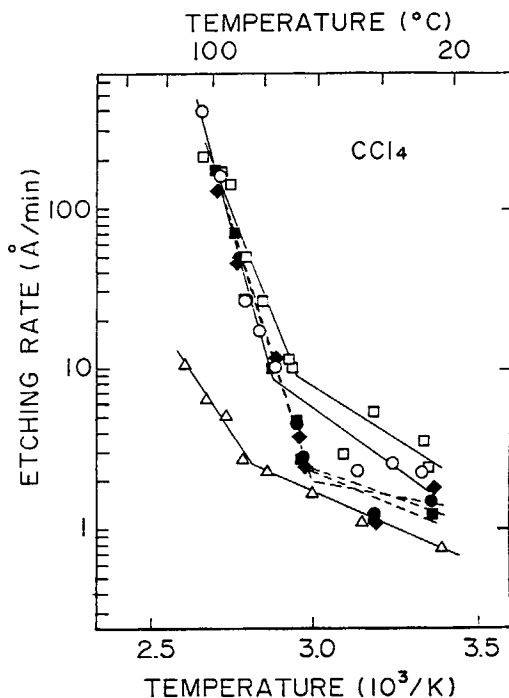


Fig. 12. Comparison of CCl_4 plasma etching characteristics of copolymers and crosslinked ternary systems: (O) C-21; (□) C-39; (●) T23-1.2; (■) T37-1.2; (◆) T38-2.9; (Δ) Pst.

dry-etching resistance, and the sensitivity, can be both improvable by the use of (i) the energy dependence of the "sponge effect" in the polymer solid and (ii) the enhanced difference of the solubility between the exposed and unexposed area with force developer. The former is very attractive in developing new resist polymers. However, it is necessary to study the "sponge effect" on the Gs value as well as on the plasma etching in order to clarify the role of the energy-dependent "sponge effect" in the stabilization of polymers.

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