

# Dissolution Rates of Poly(Methyl Methacrylate) Films in Mixed Solvents\*

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## Synopsis

A laser interferometer has been used to measure *in situ* the dissolution rates of thin films of poly(methyl methacrylate) (PMMA). The most significant finding is that addition of small amounts of a low-molecular weight nonsolvent can increase the rate obtained with a higher molecular weight solvent. In this study, silicon wafers were coated with polymer (about 1  $\mu\text{m}$  thick) and annealed at 155°C for 1 h. The dissolution rates were measured at 17.5, 22.5, and 27.5°C. All the mixtures contained methyl ethyl ketone (MEK) (2-butanone), as the major component. The minor component was water, methanol, ethanol, 1-propanol, 2-propanol, or ethylene glycol. Water and methanol showed the greatest effects. Both were able to increase the dissolution rate as much as two-fold. All the mixtures exhibit the same activation energy (25 kcal/mol) despite their wide differences in dissolution rate.

## INTRODUCTION

The dissolving of polymers by active solvents is of central importance in the fabrication of integrated circuits. Generally, a process of discrimination is involved since a pattern is to be established between areas which have been irradiated to various degrees by photons, ions, or electrons. One class of operations is that of positive-working, electron-beam resists. In this category, thin (about 1  $\mu\text{m}$ ) polymer films are exposed to a pattern of electrons (20–50 kv) which selectively degrade polymer according to a preset program. It is vital that the degraded polymer be removed, usually in a liquid bath, without dissolving or even swelling the unexposed film. The unexposed film then acts as a temporary mask (a resist) during subsequent processes which etch, dope, metallize, or otherwise treat the exposed areas of the substrate. In this way, circuit elements are placed on the surface of a silicon chip. The same process is used to make optical masks for UV-sensitive films. In this latter case, the electron-beam resist pattern allows selective etching of chromium from an otherwise transparent substrate.

It is obvious that the rate at which polymer is removed is an important parameter in automated manufacturing lines. In many cases, the utility of a polymer system hinges directly on the solvent action during dissolution. Often, the solvent is a mixture selected on the assumption that dissolution characteristics are additive. In the present study, it is shown that additivity is an unwarranted assumption when solvents of different molecular volumes and different polarities are considered.

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## EXPERIMENTAL

Silicon wafers (3-in. diameter with a thin oxide coating) were spin-coated with films of poly(methyl methacrylate) (PMMA) at 1500 rpm for 60 s using a Headway Research Model EC-101D Spinner. The coated wafers were baked 1h at 155°C. Dissolution rates were measured by interferometry using an He-Ne laser beam reflected from the wafer surface. The sample, usually a portion of a wafer rather than a whole one, could be immersed rapidly in the solvent so there was little uncertainty about the starting time of the dissolving process. The solvent was maintained at a constant temperature by a tempering coil and a magnetic stirrer.

About 4 or 5 sinusoidal oscillations take place during the removal of the film so changes in rate can be seen clearly as the polymer dissolves. When some exposed films are tested, the dissolution rate (DR) does increase because the lower layers of polymer nearest the wafer surface have actually been exposed to more electrons than the upper layers. This is due to the phenomenon of backscattering in which electrons which have passed through the polymer film reenter after being partially reflected by the substrate.

The interferometric method is based on the classical equations of reflection of light from two parallel surfaces.<sup>1,2</sup> The period of oscillation is a function of the indices of refraction of the solvent, polymer, and wafer as well as the wavelength of the light. Liquid mixtures were made up on a % basis. The reagent-grade alcohols (Table I) were used on an as-received basis.

## RESULTS AND DISCUSSION

### *Effect of Water on Dissolution Rate*

The dissolution rate of PMMA-1 (Table I) was measured in mixtures of water in 2-butanone (MEK) about to the solubility limit which is 9% water by weight. Water is not a solvent for PMMA, so that the assumption of additivity would lead one to think that dissolution rate would drop as water content increases. In fact, up to a concentration of 6%, water increases DR reaching almost double the DR in MEK alone (Fig. 1). The addition of water does make MEK a poorer solvent in the thermodynamic sense. Even at 6% water, thin residual films are seen on the surface of the water.

The residual films dissolve completely when allowed to remain in the solvent mixture for an extended period (11 min at 17.5°C). The films were not uniform in texture. It is speculated that these films are the final gel layer that has formed during the dissolution process. Despite this evidence that the mixture is a poor solvent, the fact remains that the major part of the film is removed more rapidly by the mixture than by the MEK alone.

### **Effect of Alcohols**

Alcohols also are nonsolvents for PMMA. The smallest alcohol, methanol, shows the greatest enhancement effect (Fig. 2). At 27°C, the rate is doubled by the presence of 20% methanol in the MEK. Ethanol shows a maximum

TABLE I  
Materials Used in Dissolution Measurements

Polymer		
19-C1		
1. KTI Chemicals, Sunnyvale, CA	$M_n = 320 \times 10^3$ , $M_w/M_n = 1.60$	
2. Free-radical polymerization	$M_n = 36 \times 10^3$ , $M_w/M_n = 1.51$	
3. Free-radical polymerization	$M_n = 29 \times 10^3$ , $M_w/M_n = 1.60$	
Solvents		
	Formula wt	Boiling temp (°C)
Methyl ethyl ketone (MEK) (2-butanone)	72.11	79.6
Methanol	32.04	65.0
1-Propanol	60.1	97.1
2-Propanol	60.1	82.4
Ethylene glycol	62.1	198

increase in DR of only about 12%. Higher alcohols only decrease the DR. A rationalization for the behavior can be found in the contrasting dependence of thermodynamic interaction and diffusion on various molecular parameters. The thermodynamic interaction can be correlated through the three components of the solubility parameter. These reflect the polar  $\delta_p$ , nonpolar  $\delta_d$ , and hydrogen-bonding  $\delta_H$  components. The overall solubility

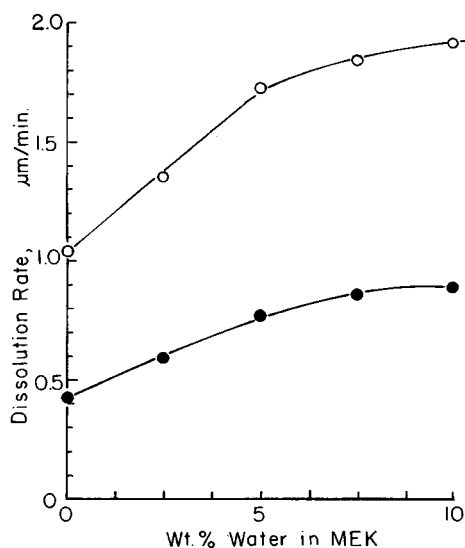


Fig. 1. Dissolution rate (DR) for PMMA in methyl ethyl ketone (2-butanone) with various amounts of water at 27.5°C.  $M_n$ : (●)  $320 \times 10^3$ ; (○)  $36 \times 10^3$ .

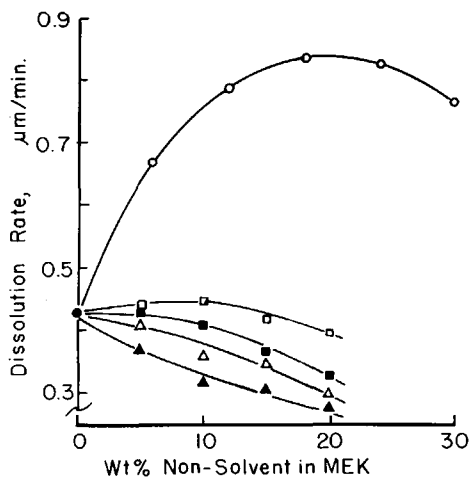


Fig. 2. Dissolution rates for PMMA in MEK at 27.5°C with addition of methanol (○), ethanol (□), 2-propanol (■), 1-propanol (△), and ethylene glycol (▲).

parameter, the square root of the cohesive energy density, has been separated into these three components for many liquids<sup>3</sup>:

$$\delta^2 = \delta_p^2 + \delta_d^2 + \delta_H^2 \quad (1)$$

A plot for PMMA in a number of solvents on the basis of the three components can be made simply on the basis of observed solubility or swelling (Fig. 3 and 4 and Table II). MEK is reasonably centered among other solvents in the plot whereas the alcohols and water are quite distant. If the argument is made that addition of alcohol moves the mixture to a better thermodynamic position, one should compare the effects of methanol and *n*-propanol. Each alcohol should move the solubility parameter in the same direction.

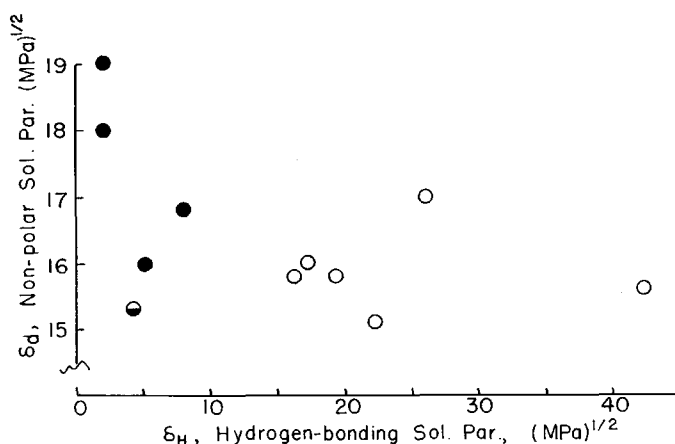


Fig. 3. Solubility map for PMMA on  $\delta_d$ - $\delta_H$  plane: The (●) solubility only for low-molecular-weight PMMA; (●) solubility for both high- and low-molecular-weight PMMA; (○) no solubility. Solvents are identified in Table II.

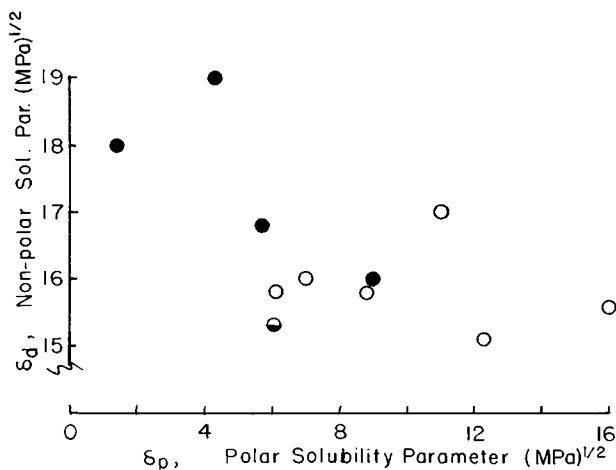


Fig. 4. Solubility map for PMMA on  $\delta_d$ - $\delta_p$  plane. The definitions for symbols are the same as in Figure 3.

From the thermodynamic point of view, a small amount of methanol should be as effective as a larger amount of propanol since the difference in solubility parameters between alcohol and MEK is greater for methanol. The observed effect on dissolution rate is quite the opposite. A small amount of propanol makes a poor mixture for dissolving PMMA whereas any amount of methanol up to 6% only makes the polymer dissolve faster. Thus, it would seem clear that the acceleration of DR is not due to thermodynamic "goodness" but to some diffusional (kinetic, dynamic) property. The diffusion coefficient itself is indeed strongly dependent on molecular size. The Wilke-Chang correlation is an expression of this dependence for liquid-phase coefficients.<sup>4</sup> According to this equation, the liquid diffusivity should be inversely proportional to the cube root of the solute's molar volume.

The enhancement of the DR by water or methanol can be thought of as a "plasticization" effect. The idea is not original. Long and Thompson<sup>5</sup> found

TABLE II  
Solubility Parameters<sup>3</sup>

	Volume (cm <sup>3</sup> /mol)	Solubility parameter [(MPa) <sup>1/2</sup> ]			
		$\delta_d$ non-polar	$\delta_p$ polar	$\delta_H$ H bonding	$\delta$ total
Toluene	106.8	18.0	1.4	2.0	18.2
Chlorobenzene	102.1	19.0	4.3	2.0	19.6
Tetrahydrofuran	81.7	16.8	5.7	8.0	19.4
MEK	90.1	16.0	9.0	5.1	19.0
MIBK	125.8	15.3	6.1	4.1	17.0
Methanol	40.7	15.1	12.3	22.3	29.6
Ethanol	58.5	15.8	8.8	19.4	26.5
1-Propanol	75.2	16.0	6.8	17.4	24.5
2-Propanol	76.8	15.8	6.1	16.4	23.5
Ethylene glycol	55.8	17.0	11.0	26.0	32.9
Water	18.0	15.6	16.0	42.3	47.8

the swelling rate of poly(vinyl acetate) in acetone or carbon tetrachloride<sup>5</sup> vapors could be increased several-fold when water vapor was introduced. Uebberreiter<sup>6</sup> also states that some thermodynamically poor solvents may penetrate a polymer matrix at a much faster rate than thermodynamically good solvents. As a result of this "plasticization," the effective diffusion coefficient of the good solvent is increased leading to an increased dissolution rate of the film. This enhancement of the dissolution rates resulting from the addition of these molecules must, therefore, be a kinetic effect. As the present results demonstrate, the smallest nonsolvent molecules, or those with the greatest mobility, show the greatest kinetic effects. Important kinetic factors, such as diffusivity and viscosity, are rate-controlling in this enhancement regime and become less important as the nonsolvent molecules increase in size. Thermodynamics then becomes important and negative polymer-solvent interactions result in the decreased dissolution rates and/or swelling of the polymer film. The transition between domination by kinetic effects and domination by thermodynamic effects occurs between ethanol and the propanols. Sfirakis and Rogers<sup>7</sup> reported similar results for the sorption of alcohol vapors by PMMA. They observed that the amount of penetrant sorbed decreased linearly with increasing molecular size for methanol, ethanol, and propanol, followed by a drastic decrease in solubility for 2-propanol and 1-butanol. The PMMA samples used for their studies were compression-molded films.

Thermodynamics also becomes important in the higher concentrations of nonsolvents. That is, for methanol and ethanol, a maximum occurs in the plot of dissolution rate versus percent solvent in MEK. Again, residual films were noticed in the higher concentrations. In the water-MEK system the solubility limit of water prevents the observation of a maximum. These results also demonstrate the importance of solvent polarity. The addition of ethylene glycol to MEK decreases the dissolution rate more than the propanols having the same molecular weight. The ethylene glycol mixture also gives us important information about the dissolution mechanics. Figure 5 shows the resultant waveform of reflected intensity v. time for the dissolution of PMMA in a 25% by weight ethylene glycol-MEK mixture. This pattern is the superposition of two sinusoidal curves, which indicates that during the dissolution process a gel layer formed that is bounded by two interfaces moving at different rates. The gel layer thickness increases with time. In the case where no appreciable gel layer is formed, only a single sinusoid is observed (Fig. 5) The latter case is noted in the lower concen-

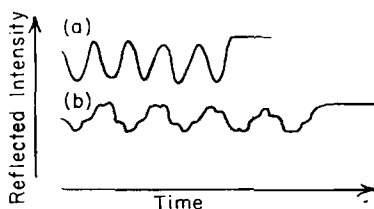


Fig. 5. Sinusoidal reflection patterns for PMMA dissolving in (a) MEK and (b) a mixture of 75 wt % MEK, 25 wt % ethylene glycol.

trations of water, methanol, and ethanol in MEK. Residual films and double sinusoidal curves were always observed in the regions where the rates of dissolution were decreased significantly.

### Effect of Temperature

The increase in rate with temperature is much greater than is predicted from the usual viscosity or diffusivity temperature dependance<sup>6</sup> (Fig. 6). Activation energies were calculated from an Arrhenius plot of dissolution rate *v.* inverse temperature. No significant differences in the energy of activation (about 25 kcal/mol were noticed when three types of behavior were compared (Fig. 6). These are dissolution without swelling (MEK), accelerated dissolution without swelling (MEK with methanol), and dissolution with swelling (MEK with ethylene glycol). The activation energy corresponds well to Greeneich's<sup>8</sup> results for PMMA dissolution in methylisobutylketone. The similarity of these energies suggest a similar mechanism for these processes, or a very similar rate determining step. An essential feature of dissolution without swelling is control by a relaxation mechanism. Also, a sharp penetration front between the glassy polymer and swollen gel which advances with a constant velocity must exist. In the case where no appreciable gel layer exists, a sharp boundary between the glassy core and solvent must be maintained. Other transport processes may be limited by diffusion or by a coupled diffusion and relaxation mechanism. The type of transport encountered here is a relaxation controlled process occurring at the gel-polymer interface. This is substantiated by the independence of activation energy with diffusivity. Activation energies for diffusion-controlled processes typically vary significantly with solvent size or diffusion coefficient.<sup>9</sup> The values for such activation energies are usually about 10 kcal/mol.<sup>6</sup>

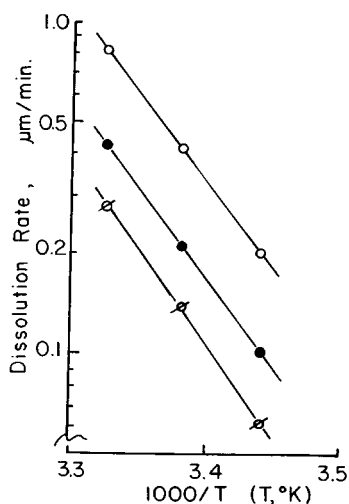


Fig. 6. Arrhenius plots for PMMA in MEK (●), 18 % methanol in MEK (○), and 20% ethylene glycol (⊙). Slope corresponds to an activation energy of 25 kcal/mol.

## Effect of PMMA Molecular Weight

The enhancement effect was compared for two molecular weights of PMMA. The lower molecular weight was synthesized using free radical polymerization. The enhancement effect (Fig. 1) is less pronounced in the lower molecular weight as compared to the higher molecular weight of PMMA. In the solvent mixture containing 8% by weight water, the lower molecular weight shows a 1.9-fold increase in the dissolution rate of the case where pure MEK is the solvent. The higher molecular weight, however, shows a 2.1-fold increase in dissolution rate. Similar results were found for the methanol-MEK system (Fig. 7). The polydispersities ( $M_w/M_n$ ) of the two polymers are shown in Table I. Molecular weight distribution can have an effect on a polymer's viscosity, or resistance to flow. For example, polymers with broad distributions of molecular weights are generally easier to extrude than those with narrow distributions.<sup>10</sup> The variation in polydispersities used in these experiments probably is not large enough to affect the rate measurements. It is also known that the importance of chain entanglements increases with molecular weight. Once chains are long enough to become entangled, flow becomes more difficult. Studies on polystyrene have shown that high molecular weight samples relax more slowly than lower molecular weight samples.<sup>11</sup> It is reasoned that this is caused by a greater resistance to chain uncoiling and viscous flow in the higher molecular weight samples. The Rouse theory defines the relaxation time  $\tau$  in terms of molecular parameters such that  $\tau$  increases with molecular weight.<sup>12</sup> If the movement of polymer chains is accelerated by the penetration of small solvent molecules, this effect would be more pronounced in the longer chains.

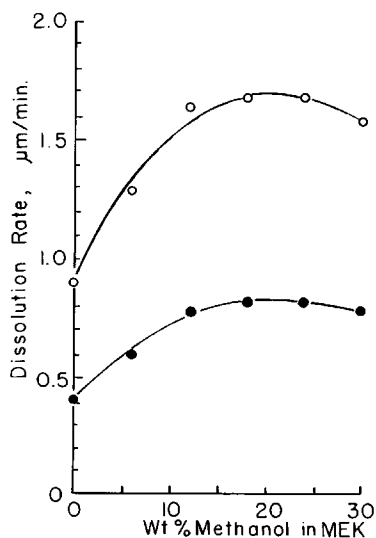


Fig. 7. Dissolution rates of PMMA in methanol-MEK mixtures at 27.5°C.  $M_n$ : (●)  $320 \times 10^3$ ; (○)  $29 \times 10^3$ .



## CONCLUSIONS

It was found that the addition of small nonsolvent molecules to a good solvent, MEK, resulted in a significant increase in the dissolution rate of PMMA films. This enhancement of the rate is thought to be a result of "plasticization" of the polymer films by the small, rapidly diffusing nonsolvent molecules. Those molecules found to exhibit this enhancement effect at lower concentrations are: water, methanol, and ethanol. Higher alcohols only decreased the dissolution rate of the films. It was also noted that at high concentrations the nonsolvent molecules caused the films to swell appreciably.

An Arrhenius plot of the activation energy yielded an activation energy of 25 kcal/mol. This compares favorably with the values quoted in the literature for relaxation in controlled diffusion processes.

The enhancement effect was found to be less significant in lower molecular weight PMMA when compared with higher molecular weights. This is thought to be a result of a higher concentration of end groups in the low molecular weights and a slower relaxation rate in the high molecular weights.

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## References

1. O. S. Heavens, *Optical Properties of Thin Films*, Butterworths, London 1955.
2. P. D. Krasicky and F. Rodriguez, paper read at Mid-Atlantic Regional meeting of the American Chemical Society, Newark, N.J., May, 1984.
3. A. F. M. Barton, *Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, 1983, pp. 59, 153-161.
4. C. R. Wilke and Pin Chang, *AIChE J.*, **1**, 264 (1955).
5. F. A. Long and L. J. Thompson, *J. Polym. Sci.*, **14**, 321 (1954).
6. K. Ueberreiter, in *Diffusion in Polymers*, J. Crank and G. S. Park, Eds., Academic, New York, 1968.
7. A. Sfirakis and C. E. Rogers, *Polym. Eng. Sci.*, **21**, (9), 542 (1981).
8. J. S. Greeneich, *J. Electrochem. Soc.*, **122**, (7), 970 (1975).
9. J. S. Vrentas and J. L. Duda, *Macromolecules*, **9**, (5), 785 (1976).
10. L. E. Nielsen, *Polymer Rheology*, Marcel Dekker, New York, 1977.
11. J. E. Rudd, *J. Polym. Sci.*, **1**, 1 (1963).
12. G. H. Pearson and L. J. Garfield, *Polym. Eng. Sci.*, **18**, (7), 583 (1978).

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