# Dissolution Rates for Thin Films of Miscible Polymer Blends

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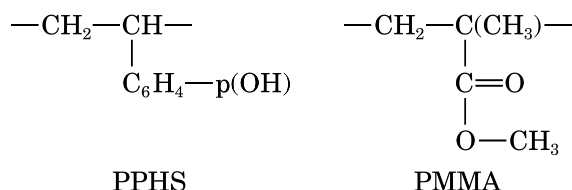
**ABSTRACT:** The dissolution rates of thin polymer films were measured and compared. Mixtures of various ratios of poly(methyl methacrylate), PMMA, and poly(*p*-hydroxystyrene), PPHS, were dissolved in methyl isobutyl ketone, MIBK. The polymer solutions were then spun into thin films on silicon wafers and dried. The coated wafers were immersed in an MIBK bath and the rate of dissolution was observed using laser interferometry. The results show that pure PPHS films have dissolution rates 1000 times greater than films of pure PMMA at comparable molecular weights. However, for films containing both PPHS and PMMA, a minimum dissolution rate occurs for a mixture with about 20% (by weight) PPHS. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 2015–2020, 1997

**Key words:** polymer blends; dissolution rate; poly(methyl methacrylate); poly(*p*-hydroxystyrene)

## INTRODUCTION

Poly(*p*-hydroxystyrene), PPHS, has been the subject of much investigation for several reasons. One is that the field of photolithography has made use of the polymer as part of various photosensitive resist systems. Another reason is the amazing number of polymers with which PPHS appears to form miscible blends. For example, workers at Kodak have found PPHS to be miscible with some cellulose esters, many polyesters, and polyamides.[1] In their work, they used a well-characterized PPHS with a $M_w$ of $68 \times 10^3$ and a $T_g$ of 188°C. They also cite other workers who have established the miscibility of PPHS with most polyacrylates, poly(ethylene oxide), poly(vinyl alkyl ethers), and so on. Other names used for PPHS are poly(4-hydroxystyrene) and poly(vinyl phenol).

In the present work the blending polymer of interest is poly(methyl methacrylate), PMMA.




Hikichi and co-workers[2] compared blends of PPHS with PMMA to blends of PPHS with poly(methyl acrylate), PMA. Unfortunately, the sample of PPHS they used had a rather low $M_w$ of 1.5 to $7.0 \times 10^3$ and a $T_g$ of 120°C. Both the molecular weight and the $T_g$ are considerably lower than those in the present study. Thus, their conclusions must be viewed with some caution because molecular size does have an important bearing on miscibility. Moreover, their samples were prepared by mixing solutions in tetrahydrofuran (THF). Landry and Teegarden[3] reported about the same time that PMMA and PPHS showed phase separation when cast from THF. The lower molecular weight of Hikichi's PPHS may have obscured the separation. However, on the basis of NMR measurements, Hikichi concluded that the alpha methyl group on PMMA interferes with hydrogen

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bonding, making it almost incompatible with PPHS. As a direct comparison, PMA was found to be quite miscible with PPHS in agreement with other work, also conducted with low molecular weight PPHS.[4,5] Hikichi's group made measurements that yielded "domain sizes" of 2 to 3 nm for PMA and 20 to 30 nm for PMMA. This evidence led them to the conclusion that miscibility of PMMA with PPHS is "poor." Once again, the condition under which the samples were prepared must be taken into account.

More recent work by Li and Brisson[6] confirms through dynamic mechanical analysis that two glass transition temperatures are indeed discernible for melt-mixed blends of PMMA and PPHS. However, FTIR analysis clearly shows that the free OH band in pure PPHS is not visible in a 3 : 7 blend of PPHS : PMMA. Also, the hydrogen bonding peak is shifted from 3370 $cm^{-1}$ to 3460 $cm^{-1}$ indicating that the hydrogen bonding in the blend is stronger than in neat PPHS. The PPHS used by Li and Brisson had a $M_w$ of 30,000 and a $T_g$ (DSC) of 156°C. Landry and Teegarden in their aforementioned work[3] reported that PMMA and PPHS showed no phase separation when cast from methyl ethyl ketone (MEK) or mixed in the melt. They also observed a shift in the hydrogen bonding peak in a 1 : 1 mixture of the polymers. The PPHS used by them had a $M_w$ of 35,000 and a $T_g$ of about 190°.

In the present work, dissolution behavior has been used as a tool to establish the possible interaction of PMMA with PPHS, using polymers with reasonably high molecular weights. As previously shown,[7,8] laser interferometry is a simple, noninvasive technique for measuring thickness changes in transparent polymer films. By making a continuous series of film thickness measurements, the rate of dissolution of the film can be calculated. Silicon wafers are used as a substrate on which to deposit the polymer film because silicon provides adequate reflection of visible light. They are also a convenient size for handling and they represent current systems in the semiconductor fabrication industry.

The purpose of the present study was to determine the effect on dissolution rate of the composition of a miscible binary polymer mixture. Poly(methyl methacrylate), PMMA, and poly($p$-hydroxystyrene), PPHS have very different dissolution rates, with the rate of PPHS being several orders of magnitude faster. Several different molecular weights of each polymer were also used to determine what effect the relative weights have on dissolution rates of binary mixtures. Methyl isobutyl ketone (MIBK, 4-methyl-2-pentanone) was used as the solvent both for preparing the films and for the dissolution measurements.

**Table I Polymers Used in Current Study**

| | $M_w$ ($\times 10^{-3}$) | $M_w/M_n$ | $T_g$ |
|---|---|---|---|
| PPHS | 25 | 2.3 | 185°C |
| | 99 | 2.3 | 185°C |
| PMMA | 34 | 1.5 | 110°C |
| | 287 | 2.5 | 110°C |

PPHS samples furnished by Hoechst Celanese; PMMA samples furnished by DuPont.

This work should be of interest to the fields of polymer science, and also semiconductor processing. First, if the relationship between the composition of the film and its dissolution rate is anything but linear, then some significant interaction must be taking place between the polymers on a molecular level. Also, the semiconductor industry uses polymer film technology on silicon wafers as part of their photoresist processes. They have an interest in controlling the dissolution rate of resist films.

## Apparatus and Procedure

The four polymers used are listed in Table I. The dissolution rate experiment involves three steps: preparing polymer solutions, spinning and drying the polymer into a film on a silicon wafer, and measuring the dissolution rate.

Polymer solutions in MIBK were made using various weight ratios of dry, powdered polymer samples. The mixtures were dissolved in MIBK. The concentration of the polymer solution is not a critical variable, because the MIBK is only used as a medium to deposit the polymer onto the wafer, and will be evaporated. It is more important that the solution have a viscosity that is convenient to work with and that allows the solution to be stirred and spun onto a wafer. All of the solutions were between 5 and 15% polymer. The solutions took between 2 and 10 days to dissolve completely.

Once the polymer sample was completely dissolved, it was deposited on a silicon wafer. A few milliliters of the polymer solution were poured onto the wafer, which then was spun at 1000 to 2000 RPM for 60 s on a vacuum-chucked spinning

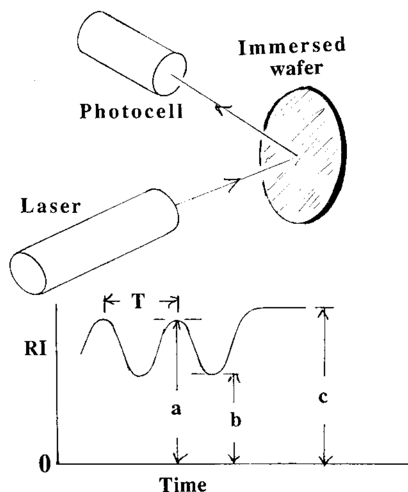


**Figure 1** To measure dissolution rates, the reflected light intensity from the incident laser beam is monitored. The resulting pattern is characterized by period T and by the maximum "a" and minimum "b" values of the reflected beam as well as the value "c" from the bare wafer.

apparatus. The film appeared thin enough to show light diffraction colors. The wafer was subsequently baked at 160°C for 30–45 min to drive out any remaining solvent.

To measure a dissolution rate, the wafer was immersed in a controlled-temperature MIBK bath (essentially a 500-mL transparent glass beaker). A schematic diagram of the laser interferometer is shown in Figure 1. A helium/neon laser beam at 632.8 nm wavelength impinges on the wafer at an incident angle of 10° and is reflected back through the wall of the beaker into a photocell. The signal is amplified and sent to a chart recorder where the changing reflection intensity of the polymer film appears as a sinusoidal wave (Fig. 1). Representative recorder printouts of the reflected light intensity from PMMA-rich films and from a pure PPHS film (Fig. 2) show little change in dissolution rate as a function of time or film thickness.

The method used to calculate the dissolution rate has been described in some detail.[8] The time, $T$, between peaks in the reflected light intensity is inversely proportional to the dissolution rate (Fig. 1). The corresponding change in film thickness, $D$, between peaks can be calculated from optics and is on the order of 0.2 $\mu$m.

$$D = (\lambda/2)(n_2^2 - n_1^2 \sin^2\theta)^{-1/2} \tag{1}$$

where $\lambda$ is the wave length of the light, 632.8 nm, $n_1$ is the index of refraction of the solvent, and $\theta$ is the incident angle, 10°. The index of refraction of the film, $n_2$, can be estimated from characteristics of the chart recorder readout (distances $a$, $b$, and $c$, Fig. 1).

$$(n_2)^2 = n_1 n_3 (y - z)/(y + z) \tag{2}$$

$$y = (n_1 + n_3)/(n_1 - n_3) \tag{3}$$

$$1 + z^2 = (b + a)/c \tag{4}$$

where $n_1$ and $n_3$ are the refractive indices of solvent and silicon, respectively. The same distances can be used to estimate an approximate thickness, $d_t$, of a surface "transition layer" during dissolution.

$$d_t = 0.0714\phi \tag{5}$$

$$(\sin \phi)/\phi = (a - b)/(2c - a - b) \tag{6}$$

where $\phi$ is in radians and $d_t$ is in $\mu$m. The latter equation assumes a linear concentration profile in the transition layer.[9]

## RESULTS AND DISCUSSION

As previously established,[10,11] the dissolution rate of PPHS does not change much with molecular weight for molecular weights above about 10,000. The films ranged in thickness from 0.5 $\mu$m to over 2 $\mu$m. The PPHS-rich films usually dissolved in a few minutes, while the films richer in PMMA often took as much as hours to dissolve. It can be seen (Fig. 3) that the higher molecular weight PPHS dissolved only slightly more slowly than the low molecular weight sample.

All three binary systems tested show a minimum dissolution rate at about 80 wt % PMMA, regardless of the absolute or relative molecular weights of the PMMA and PPHS (Fig. 3). If there were no interaction between the two species in the film then the dissolution rate for mixtures might be expected to lie between the dissolution rates of the two species as we have seen in the past for PMMA mixed with low molecular weight molecules such as ordinary phthalate plasticizers. Another possible behavior of a system with no interactions between the two species would have the faster dissolving PPHS dissolve out quickly and leave behind the PMMA, which would show up on the chart recorder as a pure PMMA film. However, as mentioned above, the dissolution for

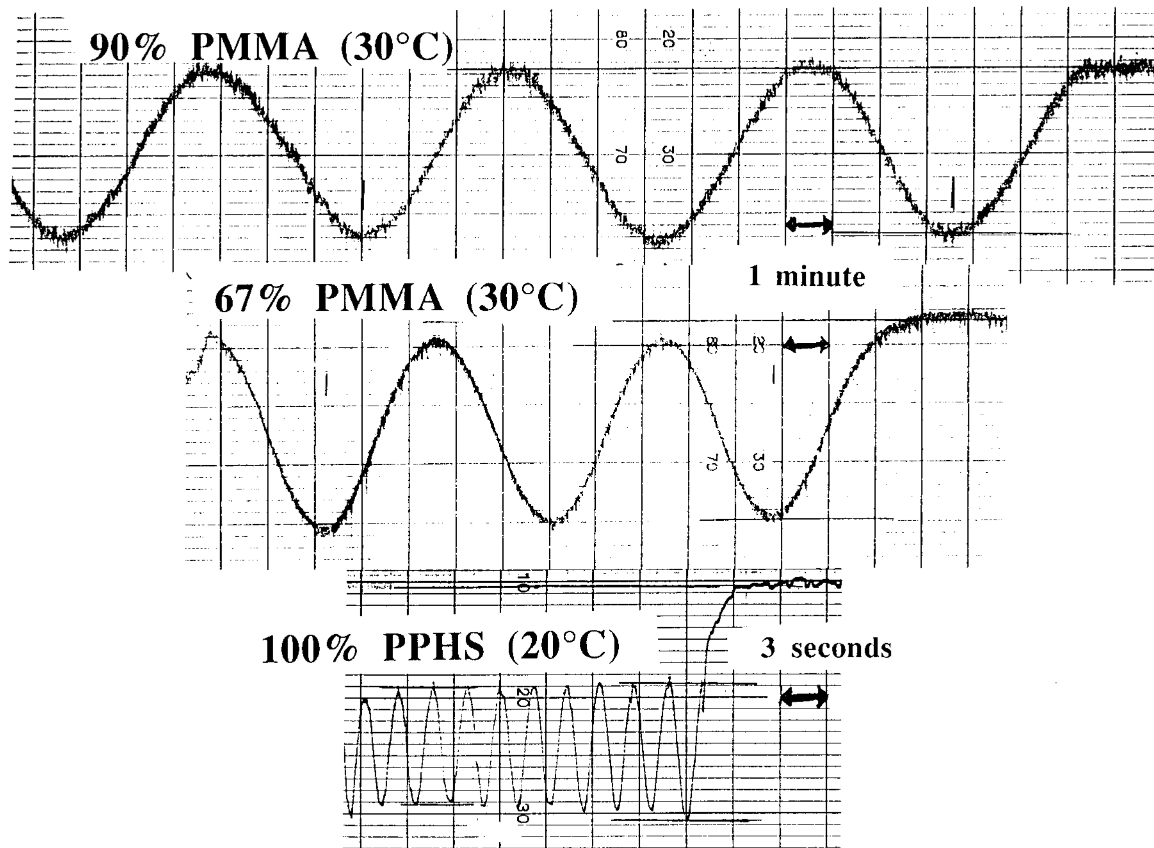


**Figure 2** Actual reflected light intensity patterns for the high molecular weight PMMA and the low molecular weight PPHS. The time scale is indicated.

all mixtures proceeded at an even rate with no evidence of extraction. Because neither of these expectations occurred, there must be significant interaction between the two species.

The addition of about 20 wt % of PPHS to a sample of pure PMMA actually decreases the dissolution rate by as much as 50%. The effects of molecular weight are along the lines one might expect. The higher molecular weight PMMA dissolves more slowly than the lower molecular weight PMMA. Also, the higher molecular weight PPHS causes a slightly greater decrease in rate than the lower one.

Temperature was varied for the series of blends with high molecular weight PMMA (Fig. 4). The behavior is consistent with what has been seen before for PMMA. When the rates are plotted logarithmically vs. arithmetic temperature, a reasonably linear relationship is seen (Fig. 5). Because the temperature range is narrow, a plot versus $1/T$ would also be almost linear, yielding a value for the energy of activation, $E_a$, which is about 25 kcal/mol (104 kJ/mol) for all compositions. The same $E_a$ was seen for a variety of solvents for PMMA.[12] However, when polymers with glass transition temperatures close to the dissolution temperature were examined, lower values of $E_a$ were observed.[13] Once again, the absence of any change in $E_a$ with the ratio of PMMA to PPHS is also consistent with compatibility.

As an independent measure of consistency, the index of refraction of each dissolving film (at a wave length of 632.8 nm) was calculated from the reflected light intensity patterns. The results (Fig. 6) are, for the most part, gratifyingly linear.

There is another feature worth noting. The difference between the maximum in the peaks compared to the reflected light intensity from the bare wafer when dissolution is complete (distances "a" and "c" in Fig. 1) has been interpreted as indicating the existence of a "transition layer."[9] This layer is formed early in the dissolution process

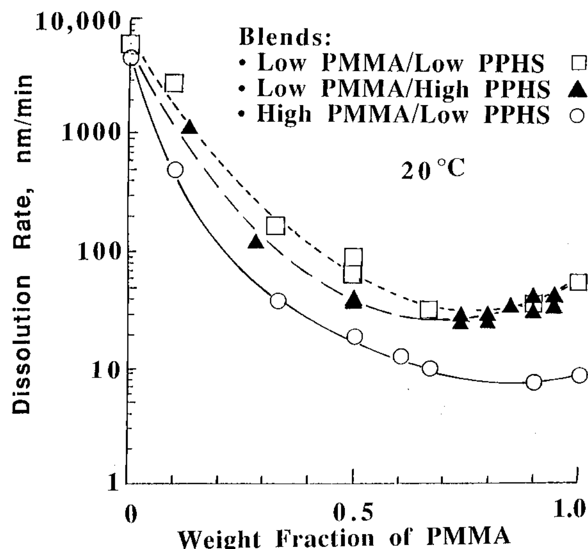


**Figure 3** The minimum in the dissolution rate is most pronounced in the blends of low molecular weight PMMA with high molecular weight PPHS.

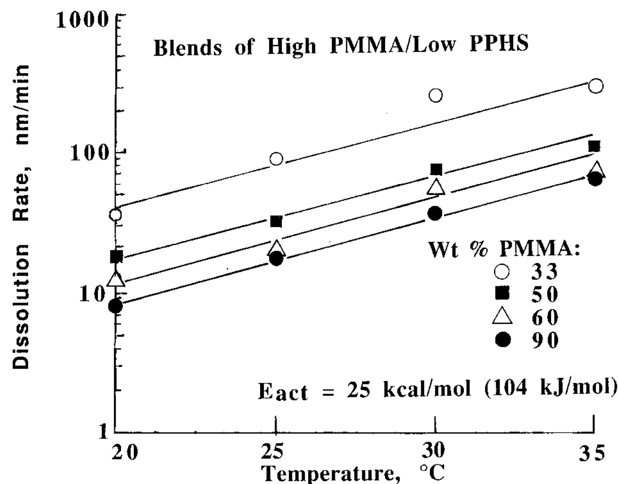


**Figure 5** The linear dependence of log rate on temperature can be used to estimate an energy of activation. A plot versus $1/T$ also appears linear due to the narrow range of temperatures involved.

and usually disappears only at the very end of the dissolution process. We have observed that the offset for thick films (greater than 0.5 $\mu$m) of PPHS is substantial, whereas the offset for mixtures with at least 50% PMMA is comparable to that for PMMA itself (Fig. 2). Transition layers for pure PMMA in our molecular weight range are about 0.05 $\mu$m thick[9] although there is a dependence on the mathematical model chosen for the layer. The transition layer thicknesses for neat PPHS correspond to about 0.15 to 0.20 $\mu$m. The transition layers for the blends appears to scale about linearly with composition (Fig. 7), but the accuracy and reproducibility of the measurements leaves an uncertainty of about ±0.04 $\mu$m. There is no discernible effect of temperature.

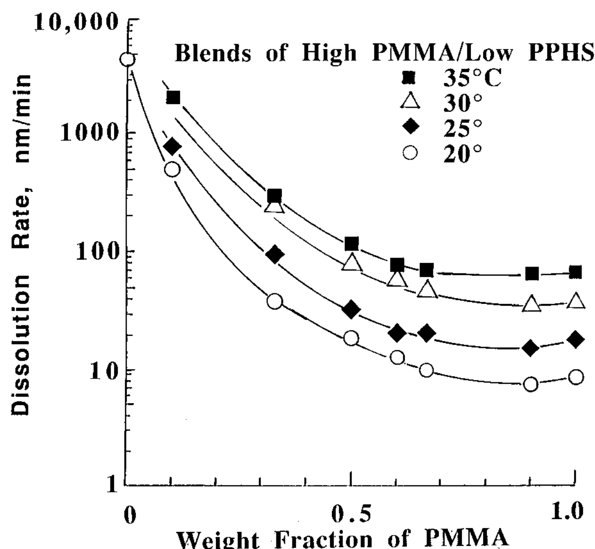


**Figure 4** The nonlinear dependence of dissolution rate on composition remains as the temperature is increased, but the minimum in the curve at the high PMMA end becomes less pronounced.

## CONCLUSIONS

The regular dissolution behavior of PPHS : PMMA blends coupled with the lowering of disso-

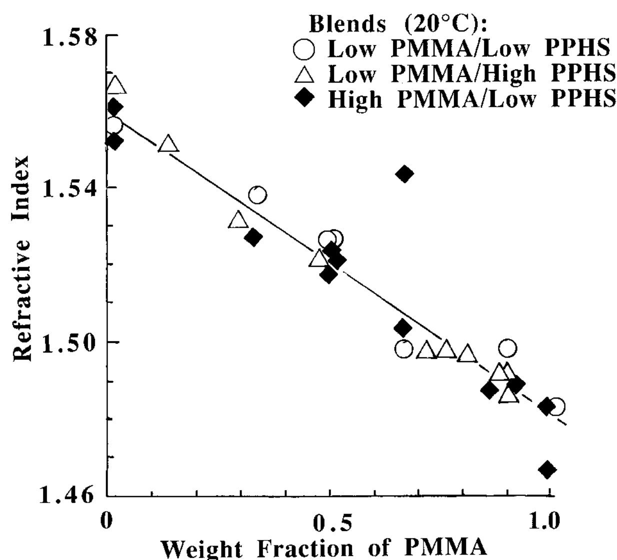


**Figure 6** The refractive indices of the films are calculated from the dissolution patterns.

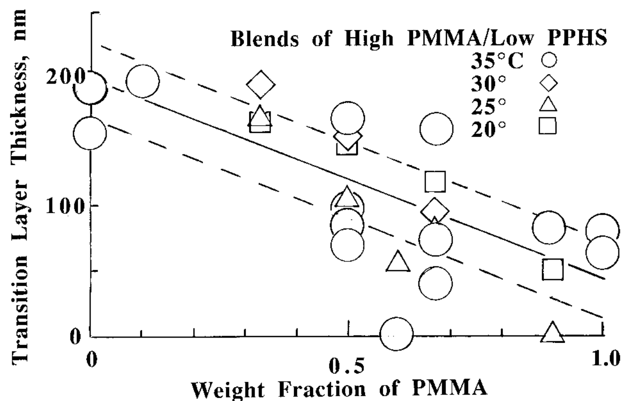


**Figure 7** The transition layer thickness at the polymer/solvent interface is greater for PPHS than for PMMA. The dependence on composition and temperature for the blends is not discernible within the accuracy of the measurements employed.

lution rate by a small amount of PPHS in PMMA is a reasonable indication that a specific interaction occurs. The FTIR measurements by Li and Brisson[6] and by Landry and Teegarden[3] lend support to the idea of hydrogen bonding between the polymers in contrast to the previous evidence from NMR by Hikichi.[2] In any case, some sort of interaction must be invoked to explain the dynamic behavior of the PMMA : PPHS blends. Hydrogen bonding seems the most likely explanation. The existence of separate submicroscopic phases, or microdomains, within the blends is neither supported nor contradicted by the dissolution behavior.

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