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# Dissolution Rates of Copolymers Based on 4-Hydroxystyrene and Styrene

by

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# Dissolution Rates of Copolymers Based on 4-Hydroxystyrene and Styrene

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## ABSTRACT

Copolymers were synthesized by free-radical polymerization using 4-acetoxystyrene and styrene in various ratios. These polymers then were hydrolyzed to the corresponding 4-hydroxystyrene (phenol) copolymers. . The dissolution rates of the copolymers (using laser interferometry) decreased with a decrease in hydroxyl group content in aqueous developers (sodium hydroxide, potassium hydroxide, and a tetramethylammonium hydroxide based commercial developer). While an increase in pH value enhances the dissolution, an increase in cation size of these hydroxides at constant pH decreases the dissolution rate. The polymers become essentially insoluble in aqueous developers whe the content of the monomer containing the hydroxyl group is less than 70 mole%. The dissolution rate of P(4HS/S) in organic solvents , methyl isobutyl ketone (MIBK), isopropyl alcohol (IPA), and their mixtures, increases as the styrene content increases. However, in IPA, dissolution rate goes through a maximum and then drops down with styrene content greater than 50 mole%. In mixtures of these two solvents, the polymer dissolves faster than it does in either pure solvent.

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# INTRODUCTION

For many years, novolak polymers have been widely used in commercial photoresists because they have the properties of dissolution inhibition on alkali development and possess reasonable etch resistance [1]. In alkali developers, they exhibit minimal swelling, a major problem which is often encountered with organic developers. However, novolaks have other inherent problems, such as low molecular weights, broad molecular weight dispersities, and difficulties in the control of structure during synthesis. Especially, novolak has high absorptivities in the wavelength of 240 - 300 nm. That means it will strongly absorb the 248 nm wavelength light generated by KrF excimer lasers and result in poor profiles [2,3].

Poly(4-hydroxystyrene) [P4HS] has been suggested as a replacement candidate due to its similar phenolic functionalities to novolak polymers (Figure 1). P4HS provides better structure control and possible higher molecular weight in the synthesis process. In addition, it offers adequate thermal stability and etch resistance as well as high transparency in DUV range. However, in a comparison of P4HS with novolak in aqueous developers, Hanrahan and Hollis [4] concluded that the dissolution speed of this polymer in aqueous base is unacceptably high in comparison with commercial resist products.

In the present work, an effort has been made to improve the understanding of the P4HS dissolution and to approach the goal of finding a suitable replacement for the novolaks. Copolymers of 4-hydroxystyrene and styrene were synthesized in order to evaluate the influence of composition on polymer dissolution rates. The dissolution rates in both aqueous and organic developers were measured by laser interferometry. The influence of the reduction in phenolic hydroxyl groups of P4HS on dissolution behavior is also discussed.

## EXPERIMENTAL

Polymer Synthesis. The two monomers used in the polymer synthesis were 4-acetoxystyrene (4AOS), (courtesy of M. T. Sheehan of Hoechst Celanese Company), and styrene, obtained from Eastman Kodak Company. Benzoyl peroxide, purchased from Aldrich Chemical Company, was used as the initiator. In order to obtain various polymer compositions, the copolymers of 4AOS with 0 to 60 mole% styrene were synthesized by free radical polymerization. Each copolymer of P(4AOS/S) was hydrolyzed with more than five times potassium hydroxide (KOH) to hydroxyl mole ratio to obtain P(4HS/S), the copolymer of 4HS with styrene. A series of P(4HS/S) were thus formed with a styrene content from 0 to 60 mole%. Complete hydrolysis of the P(4AOS/S) copolymers was confirmed using infrared analysis by the loss of the carbonyl peak at 1760 cm -1 concurrent with the appearance of a strong hydroxyl band at 3200-3600 cm-1.

Gel Permeation Chromatography. All (polystyrene equivalent) molecular weights were determined using the method of size exclusion chromatography by gel permeation chromatography (GPC). The instrument used was a GPC system produced by Waters associates with Du Pont's Zorbax columns. THF was used as the eluting solvent. Polystyrene standards, obtained from Polymer Laboratories Limited, were used for calibration. The number-average molecular weights of both the P(4AOS/S) and the P(4HS/S) were in the range of 18,000 - 22,000 and their polydispersities were around 4 (Table 1). After hydrolysis, the molecular weights of P(4HS/S) would be expected to decrease due to the cleavage of the acetoxyl groups. Larger GPC molecular weights forn the P(4HS/S) copolymers than expected may result from a difference in the interaction of the hydroxyl groups with column packing.

Laser Interferometry. In preparing the samples, each polymer of P(4HS/S) was first dissolved in methyl isobutyl ketone (MIBK) at 10 % by weight. The solution was spin-coated onto a clean, 3-inch diameter, oxide-coated silicon wafer. The spinning speed and time were set at 1,500 rpm for 60 seconds to obtain about 0.6~1 μm thick films. After spin coating on wafers, these polymer films were baked in an oven at the temperature of 160°C for one hour and then cooled down gradually in the oven for about 30 minutes. All the measurements of P(4HS/S) dissolution rates were carried out at room temperature (23±1°C) using a laser interferometer apparatus (Spectra Physic Model 102-4, wavelength 632.8 nm). Details of the procedure have been described previously [5,6,7]. The wafer coated with a thin film of polymer was placed in a transparent beaker filled with a developing solvent which was stirred by a magnetic stirrer. The laser beam was directed horizontally towards a vertically placed wafer with an incident angle of 10 degrees. The reflected beam was collected by a silicon photocell and the signals were recorded as a function of time by a chart recorder with adjustable chart speed. The periodicity of the reflected light intensity was used to calculate the rate of dissolution [5,6].

## RESULTS AND DISCUSSION

Glass Transition Temperatures. All glass transition temperatures of P(4AOS/S) and P(4HS/S) were determined by differential scanning calorimetry (DSC). Except for slightly higher than expected values, the Tg of the P(4AOS/S) copolymers tend to decrease regularly from 120°C to 101°C as the styrene content increases (Figure 2). However, after hydrolysis, the Tg of P(4HS/S) decreases regularly only up to a styrene content of 30 mole%. Above 30 mole%, there is a steep drop in the Tg (Figure 2). One possible explanation for this phenomenon would be hydrogen bonding. The hydrogen bonding between OH groups is strong and leads to an increase of Tg when 4HS content is more than 70% by mole. On the other hand, when styrene content is more than a certain amount (30 mole%), it separates the OH groups and breaks the hydrogen bonding, resulting in the drop in Tg. Further evidence to corroborate this result is found in the dissolution behavior. It will be shown that 30 mole% styrene seems to be the critical composition for the solubility of P(4HS/S) in aqueous base.

Dissolution of P(4HS/S) in Aqueous Base. P(4HS/S) copolymers were developed in aqueous solutions of sodium hydroxide (NaOH) and potassium hydroxide (KOH). In either base, a uniform sinusoidal pattern was obtained during film dissolution, indicating that the polymer dissolution rate did not change with time. Some results of dissolution rates are shown in Figure 3. It is known that P4HS is soluble in strong aqueous base but polystyrene does not dissolve in aqueous solution. So the decrease in dissolution rate of P(4HS/S) copolymer with the increase of the styrene content was predictable.

The NaOH solution with pH=13 yields a much higher dissolution rate for P(4HS/S) than that with pH=12.8. A difference of pH of 0.2 makes a significant difference in dissolution rates. This observation matches the dissolution behavior of P4HS previously reported by Long and Rodriguez [8]. However, there seems to be a critical point for the solubility of P(4HS/S) in aqueous base. The dissolution rate of P(4HS/S) with styrene content more than 30 mole% is close to zero even though the pH value is as high as 13.

In addition, it is obvious that at a similar pH value, P(4HS/S) dissolves faster in NaOH solution than it does in KOH solution. The decrease in dissolution rate with the increase in the cation size of aqueous base developers is not an unexpected phenomena. It has been demonstrated by other authors in the dissolution study of novolak polymers with metal hydroxides as developers [9,10].

Microposit Developer MF-319 is a tetramethylammonium hydroxide (TMAH) based developer. The initial dissolution rates for P(4HS/S) in MF-319 are shown in Figure 4. The decrease in dissolution rate of P(4HS/S) with the increase of styrene content is found to be similar to the dissolution behavior in NaOH. It is also observed that the styrene content of the polymer must be less than 30% in order for the polymer to be soluble in MF-319. In addition, the dissolution rate of P(4HS/S) in MF-319 consistently decreased with time from the initial rate. Special thicker polymer films (around 1.5 μm) were made to examine the change in dissolution rate during developing. The results are presented in Figure 5. The polymer dissolves faster in the beginning and then slows down as the wafer surface is approached. For each polymer, the dissolution near the starting point is 2 to 2.5 times faster than it is at the end point. Although the swelling of positive photoresists in alkali developing has been observed before [9], the exact mechanism and the reason for the change in dissolution remains unknown.

Dissolution of P(4HS/S) in Organic Solvents. MIBK, IPA, and their mixtures were also used as developers for P(4HS/S). While P4HS is soluble in both MIBK and IPA, polystyrene dissolves rapidly in MIBK but not at all in IPA. The solubilities of P(4HS/S) copolymers in these organic solvents were therefore of interest for study.

The dissolution behavior of P(4HS/S) in both MIBK and IPA are shown in Figure 6. As expected, the dissolution rate in MIBK increases with the increase in styrene content. In IPA, the dissolution rate also increases as the styrene content increases until it reaches a maximum and then drops off with styrene content greater than 50 mole%. This presents additional evidence for the effects of hydroxyl groups on the dissolution of P(4HS/S) copolymers. When the copolymer contains enough hydroxyl groups to dominate the dissolution, a higher hydroxyl content gives a higher dissolution rate. On the other hand, when hydroxyl groups are no longer in majority, the polymer tends to be insoluble in IPA like polystyrene.

It is usually difficult to predict the dissolution behavior in solvent mixtures. In some cases, a small amount of nonsolvent added to the solvent increases the dissolution rate significantly [5,6]. In this study, two solvents, MIBK and IPA, were mixed with different weight ratios to carry out the dissolution behavior. The results are presented in Figure 7. It is obvious that dissolution rate of P(4HS/S) in mixtures increases with the increase of styrene content. In each mixture, P(4HS/S) dissolves faster than it does in either pure MIBK or pure IPA. This is true for every P(4HS/S) copolymer. Moreover, in mixtures, the dissolution rate goes through a maximum as the IPA ratio increases (Figure 8).

## CONCLUSIONS

In alkaline developers (NaOH, KOH solutions, and Microposit Developer MF-319), the dissolution rate of P(4HS/S) decreases as the styrene content increases. In any one developer, higher pH values yield higher dissolution rates. At similar pH values, dissolution rates decrease with an increase in cation size. These observations are consistent with literature results. However, when the hydroxyl (phenol) group content is less than 70 mole%, P(4HS/S) becomes nearly insoluble even at a developer pH value as high as 13. In the TMAH based commercial developer, a change in dissolution rates was found during development. That is, the dissolution rate decreases with development time.

In organic developers (MIBK, IPA, as well as their mixtures), the dissolution rate of P(4HS/S) increases as the styrene content increases. However, in IPA, dissolution rate of P(4HS/S) goes through a maximum and then drops down with styrene content greater than 50%. In mixtures of MIBK and IPA, P(4HS/S) dissolves faster than it does in pure MIBK or pure IPA. In addition, the more IPA in the mixture, the faster the dissolution rate.

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## REFERENCES

1. McKean, D.R., Hinsberg, W.D., Sauer, T.P., Willson G., Vicari, R., and Gordon, D.J., J. Vac. Sci. Technol. B 8 (6), 1466 (1990).
2. Pawlowski, G., Sauer, T., Dammel, R., Gordon, D.J., Hinsberg, W., McKean, D., Lindley, C.R., Merrem, H.-J., Roschert, H., Vicari, R., and

Willson, C.G., Advances in Resist Technology and Processing VII, SPIE, 1262, 391 (1990).

3. Przybilla, K., Roschert, H., Spie, W., Eckes, Ch., Chatterjee, S., Pawlowski, G., and Dammel, R., Advances in Resist Technology and Processing VIII, SPIE, 1466, 174 (1991).
4. Hanrahan, M.J., and Hollis, K.S., Advances in Resist Technology and Processing IV, SPIE, 771, 128 (1987).
5. Groele, R.J., Ph.D Thesis, Cornell University, Ithaca, New York (1988).
6. Krasicky, P.D., Groele, R.J., and Rodriguez, F., Chem. Eng. Comm., 54, 279 (1987).
7. Rodriguez, F., Krasicky, P.D., and Groele, R.J., Solid State Tech., 28 (5), 125(1985).
8. Long, T., and Rodriguez, F., Advances in Resist Technology and Processing VIII, SPIE, 1466, 188 (1991).
9. Arcus, R.A., Advances in ResistTechnology and Processing III, SPIE, 631, 124 (1986).
10. Hinsberg, W.D., and Gutierrez, M.L., Processing Kodak Microelectronics Seminar, Interface 1983, San Diego (1983).

Table 1 Molecular weights (polystyrene equivalent) and polydispersities (Mn/Mw) for P(4AOS/S) and P(4HS/S).

| Styrene | Content | | | | |
|---|---|---|---|---|---|
| (wt.%) | (mole%) | Polymer | Mn | Mw | Mw/Mn |
| 0 | 0 | P(4AOS/S) | 22,100 | 77,400 | 3.50 |
| | | P(4HS/S) | 17,700 | 92,800 | 5.12 |
| 5 | 7.62 | P(4AOS/S) | 22,300 | 92,300 | 4.14 |
| | | P(4HS/S) | 20,000 | 98,800 | 4.89 |
| 10 | 14.8 | P(4AOS/S) | 22,600 | 92,600 | 4.10 |
| | | P(4HS/S) | 17,600 | 97,800 | 5.30 |
| 12.5 | 18.3 | P(4AOS/S) | 20,600 | 75,000 | 3.65 |
| | | P(4HS/S) | 19,600 | 99,300 | 5.06 |
| 15 | 21.7 | P(4AOS/S) | 21,100 | 81,400 | 3.87 |
| | | P(4HS/S) | 18,900 | 94,300 | 4.73 |
| 20 | 28.2 | P(4AOS/S) | 20,500 | 75,000 | 3.66 |
| | | P(4HS/S) | 19,700 | 74,700 | 3.80 |
| 25 | 34.3 | P(4AOS/S) | 22,100 | 80,900 | 3.66 |
| | | P(4HS/S) | 19,000 | 94,200 | 4.97 |
| 30 | 40.2 | P(4AOS/S) | 19,500 | 73,300 | 3.82 |
| | | P(4HS/S) | 17,900 | 76,100 | 4.26 |
| 40 | 51.1 | P(4AOS/S) | 18,200 | 73,400 | 4.04 |
| | | P(4HS/S) | 17,300 | 75,000 | 4.33 |
| 50 | 61.1 | P(4AOS/S) | 19,000 | 76,800 | 4.03 |
| | | P(4HS/S) | 18,300 | 83,200 | 4.54 |

Table 2 Refractive index list of developers (measured by Abbe Refractometer)

| Developers | Refractive Indices |
|---|---|
| Sodium Hydroxide (NaOH) | 1.333 |
| Potassium Hydroxide KOH) | 1.333 |
| Methyl Isobutyl Ketone (MIBK) | 1.396 |
| Isopropyl Alcohol (IPA) | 1.377 |
| 25% MIBK and 75% IPA | 1.392 |
| 50% MIBK and 50% IPA | 1.386 |
| 75% MIBK and 25% IPA | 1.381 |
| Microposit Developer MF-319 | 1.333 |

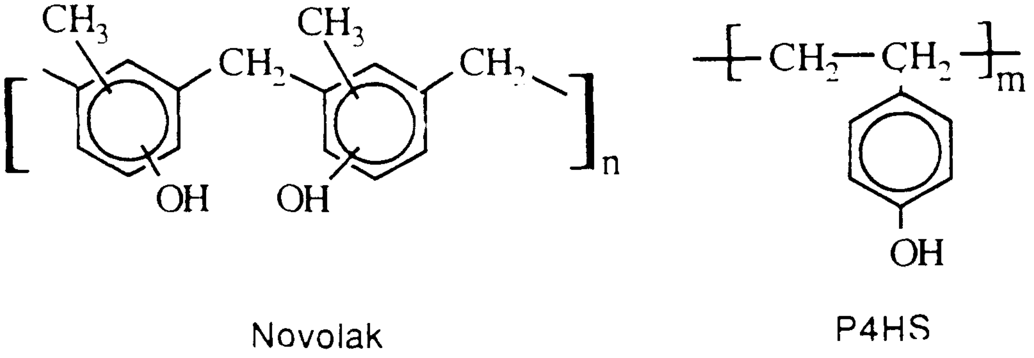

Figure 1 Structures of novolak and poly(4-hydroxystyrene) (P4HS)

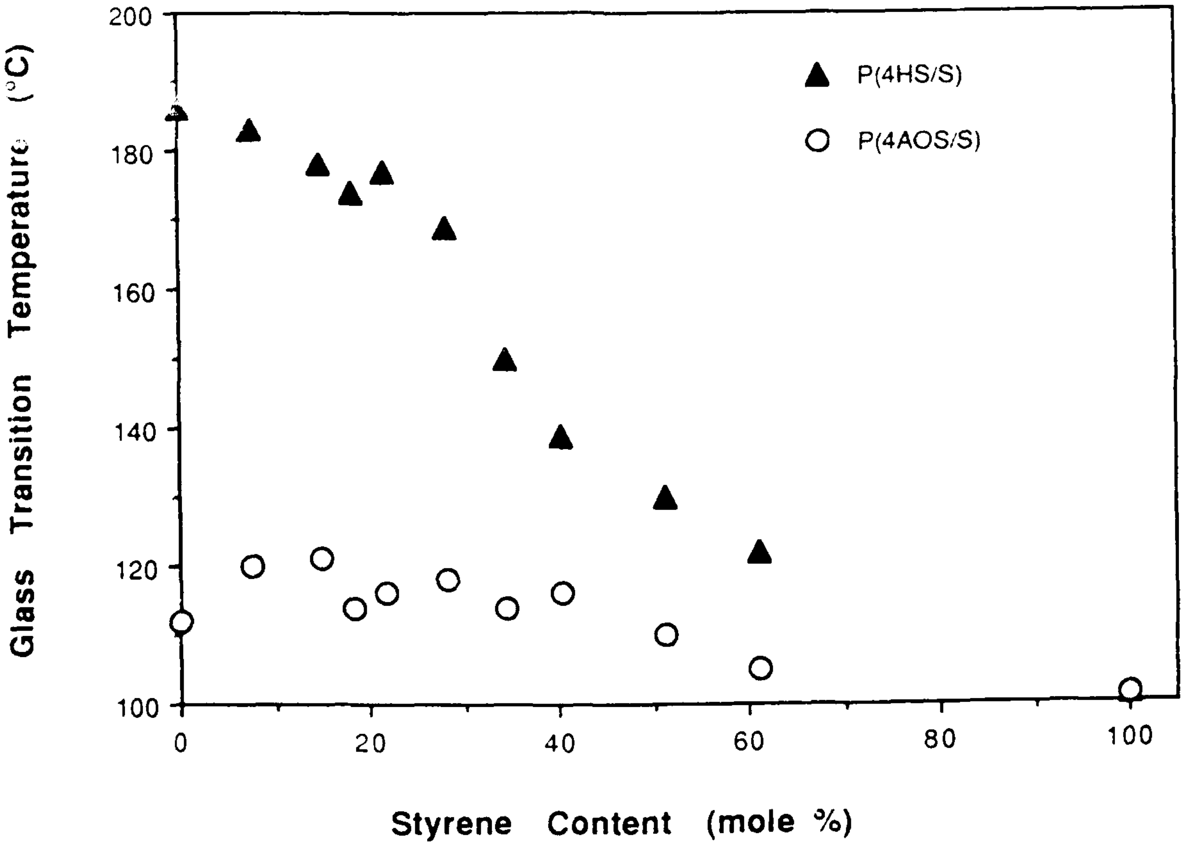

Figure 2 Glass transition temperature of P(4HS/S) and P(4AOS/S)

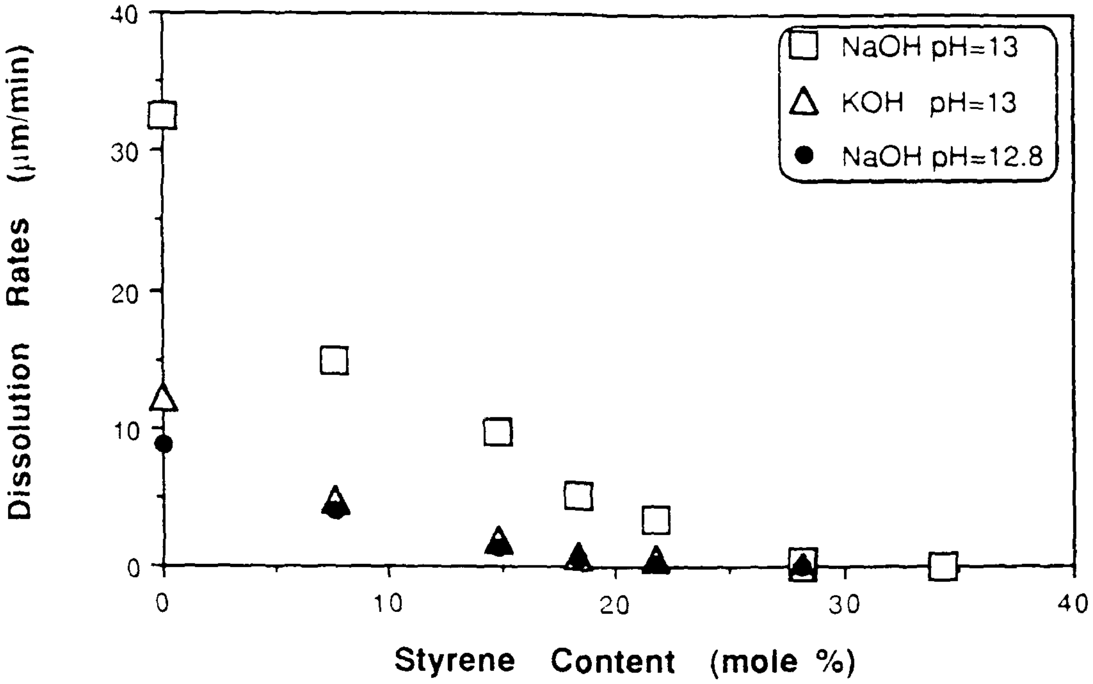

Figure 3 Dissolution behavior of P(4HS/S) in aqueous developers, NaOH and KOH solutions.

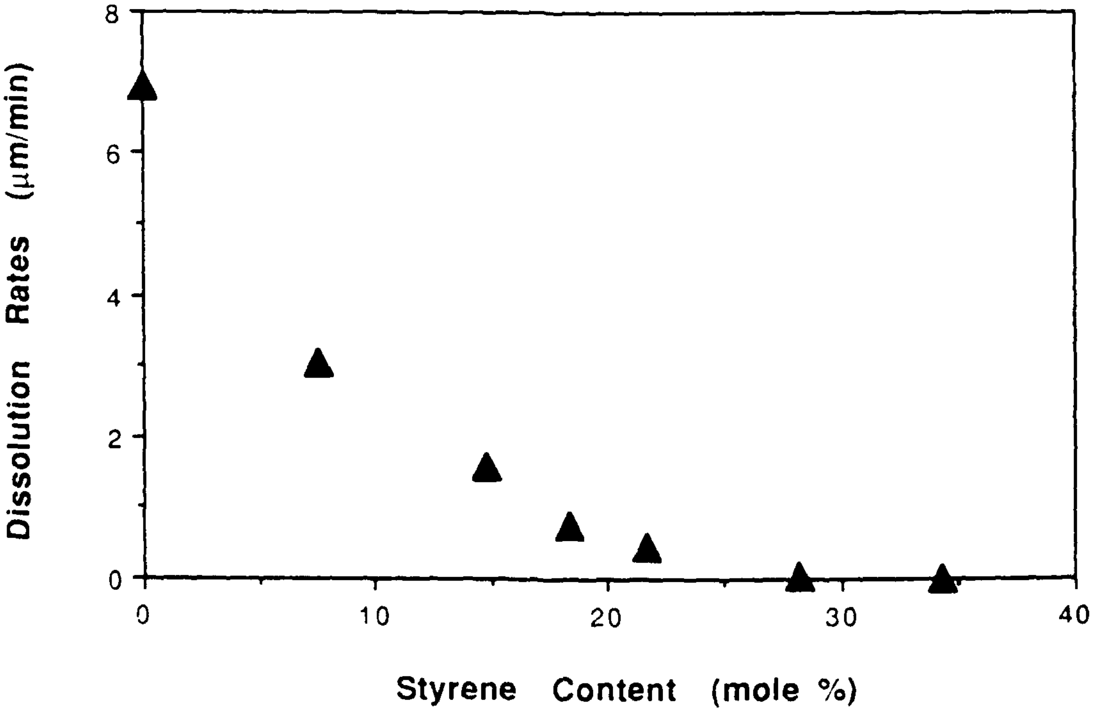

Figure 4 Dissolution behavior of P(4HS/S) in Microposit Developer MF-319, a TMAH based commercial developer.

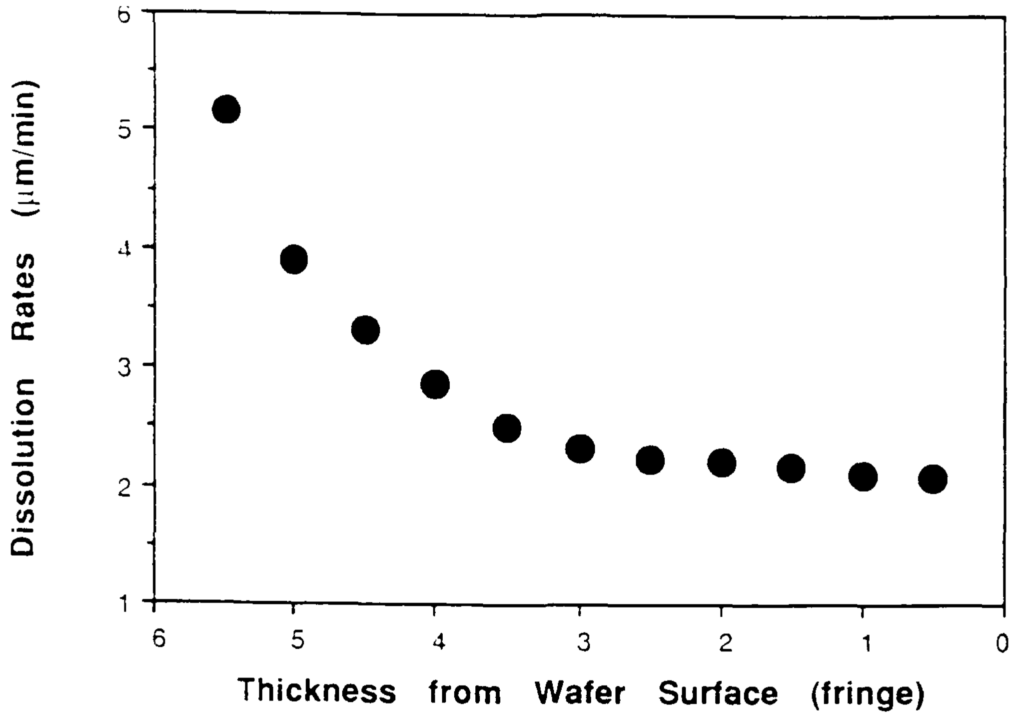

Figure 5 Dissolution rate of P(4HS/S) changes during dissolving in Microposit Developer MF-319.

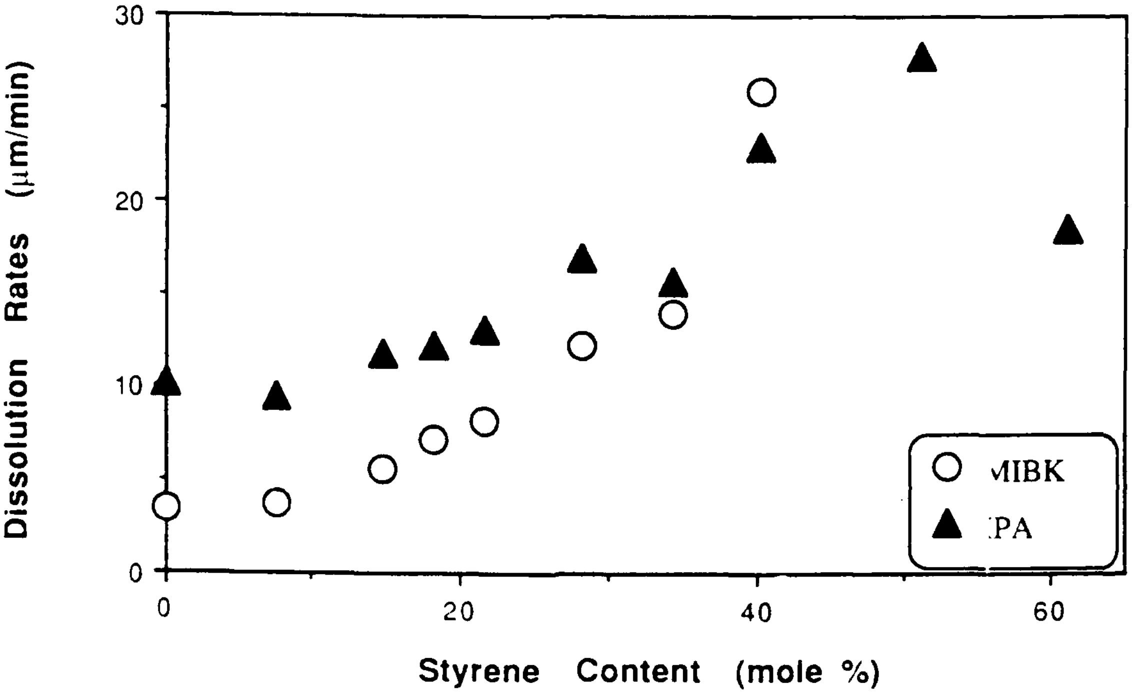

Figure 6 Dissolution behavior of P(4HS/S) in organic solvents, methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA)

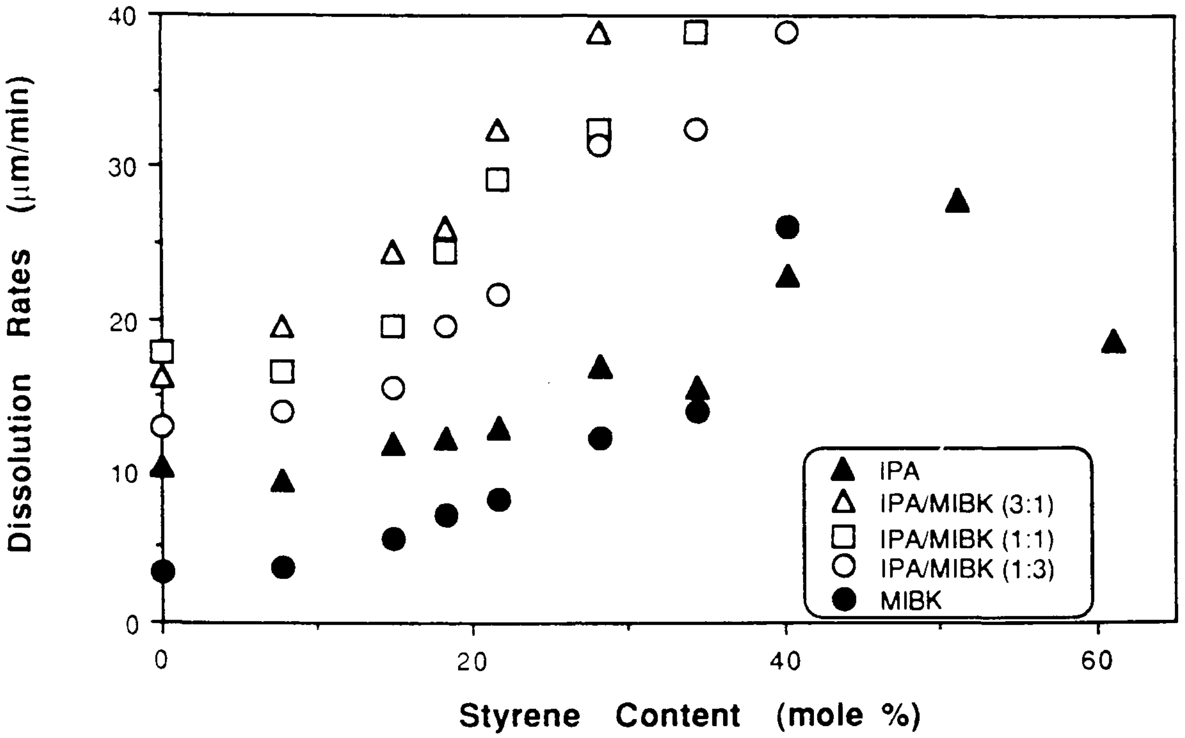

Figure 7 Dissolution behavior of P(4HS/S) in mixtures of MIBK) and IPA.

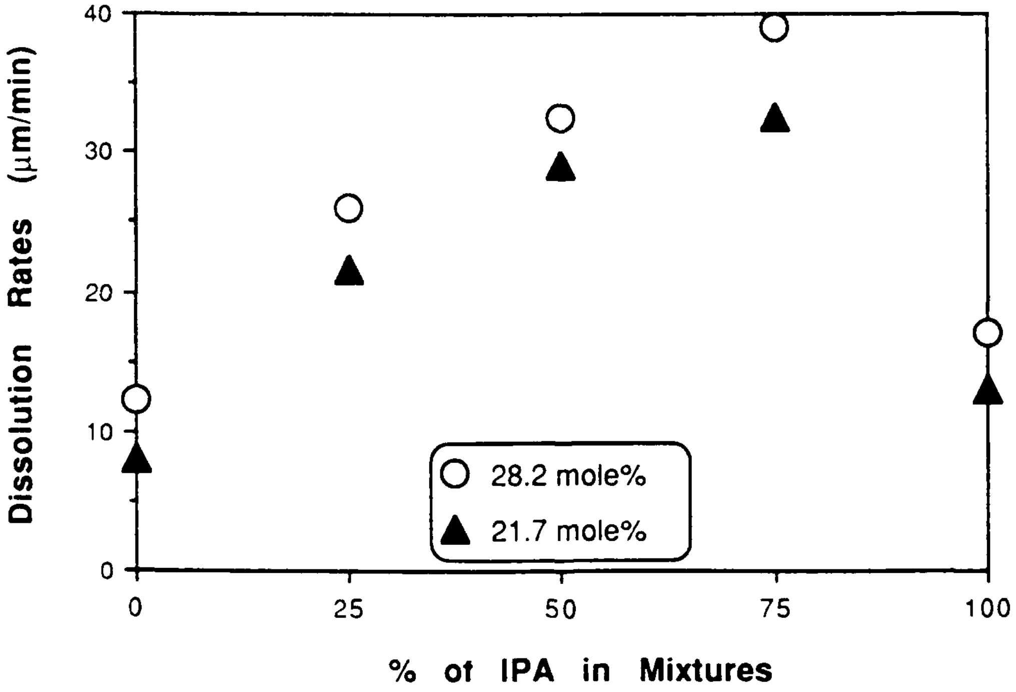

Figure 8 In mixtures of organic solvents, dissolution rate of P(4HS/S) increases as IPA content increases.

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