

Lithographic Performance of Isomeric Hydroxystyrene Polymers

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Abstract

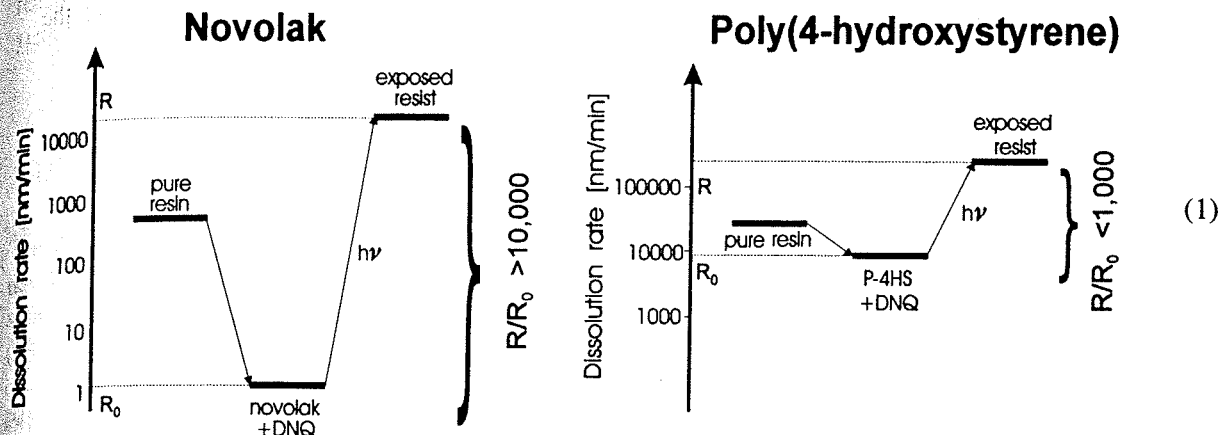
The synthesis and lithographic characterization of the three positional isomers of polyhydroxystyrene is described. Large differences in dissolution rates are found as a function of the position of the hydroxy group, which are explained in terms of intra- vs. intermolecular hydrogen bonding and steric shielding of the hydroxy group by the polymer backbone. In plots of $\log(\text{dissolution rate})$ vs. developer strength, linear plots are observed for the 2- and 4-isomers, whereas for poly(3-hydroxystyrene), a break occurs in the plot, leading to two linear regions. While the 2-hydroxy isomer is too slow and the 4-hydroxy isomer too fast for use in conventional dissolution inhibition systems, the copolymerization of both allows one to choose any dissolution rate between these extremes ("dial a dissolution rate"-copolymers). Determination of the copolymerization parameters of the corresponding 4- and 2-acetoxystyrene precursors by the method of Kelen and Tüdös shows the polymerization to be nearly ideal and azeotropic ($r_1 = 0.76$, $r_2 = 0.94$). Analysis of the dissolution rates as a function of developer strength according to the Huang-Reiser-Kwei equation shows that the critical concentrations c^ are a linear function of copolymer composition, whereas the penetration exponents n show a minimum near unity in the region of the 1:1 copolymer, down from the values of 3.2-3.3 observed for all three homopolymers. The 1:1 copolymer shows a dissolution rate comparable to novolak resins, and when formulated into a photoresist together with a diazonaphthoquinone sensitizer resolved 0.4 μm features at a dose of 340 mJ/cm^2 . The thermal flow resistance of the resist was found to be improved over that of novolak resists although not to the degree expected from the increased T_g of the 1:1 copolymer.*

1. Introduction

The photoresist materials used for device manufacture in the electronics industry today predominantly use cresol/formaldehyde polycondensates (novolaks) as matrix resins [1]. While novolaks are in many ways very well suited to the demands of the photolithography process (e.g., they exhibit good imaging properties and high resistance to dry etch plasmas), they also have a number of drawbacks, such as high polydispersity, low glass transition temperature and prohibitive opacity at shorter wavelengths. Even for the most successful type of novolak resist, the diazonaphthoquinone/novolak systems, this property leads to a low thermal stability (100-130 °C) of finished photoresist structures. Additionally, the comparatively high absorbance in the region around 250 nm has lithography [2]. These drawbacks have led researchers worldwide to look for alternative resins [3]. The currently most advanced materials are based on poly(4-hydroxystyrene) (P4HS) and its derivatives, which, however, have unfavorable dissolution and inhibition properties compared to novolaks.

The dissolution rate of poly(4-hydroxystyrene) in industry standard developers, such as 0.265N tetramethylammonium hydroxide (TMAH), is of the order of 15-20 $\mu\text{m}/\text{min}$, or about 3-4 times as high as that of novolaks which would be considered "fast". Moreover, the dissolution of P4HS is not inhibited efficiently by compounds such as diazonaphthoquinones or acetals, which have been used for novol

based systems. Indeed, diazonaphthoquinones (DNQs), even fully esterified types, sometimes lead to a dissolution rate increase at low sensitizer loadings (ca. 5%); only at higher levels of addition is a weak dissolution inhibition observed. The dissolution rate diagram for a P4HS-based dissolution inhibition system is therefore quite different from that of a novolak-based resist:



The high dissolution rate of P4HS is explained by the secondary structure model [4], which relates the ratio of intramolecular to intermolecular hydrogen bonds to the dissolution rate of a phenolic resin. In this model, intramolecular hydrogen bonds are supposed to be less accessible to the developer, resulting in a slower dissolution rate for resins possessing them in a large proportion; at the same time, there are fewer intermolecular hydrogen bonds available in such resins to strongly couple the movements of adjacent polymer chains, a phenomenon which leads to a lower glass transition temperature (T_g). Conversely, resins with predominantly intermolecular hydrogen bonds are predicted to have high dissolution rates and high glass transition temperatures. Due to its molecular structure, P4HS is assumed to be unable to form intramolecular hydrogen bonds between adjacent hydroxy groups; it is therefore predicted, and found, to have both a high dissolution rate and glass transition temperature ($T_g = 182^\circ\text{C}$).

Intramolecular hydrogen bonds between adjacent hydroxy groups have also been related to a phenomenon known as "novolak hyperacidity" [5]. Molecules capable of forming intramolecular hydrogen bonds are found to have first $\text{p}K_a$ values which are 2-4 units lower than observed for analogous compounds with an arrangement of hydroxy groups that precludes such hydrogen bonds. The phenomenon is most pronounced for structures involving extended or cyclic chains of hydrogen bonds, as observed in calixarenes [6] or open-chain all-ortho novolaks [7] (cf. Fig. 2). It has been suggested that such hyperacidic centers play an important role in the interaction of diazonaphthoquinones and novolaks [8]. Since P4HS cannot form intramolecular hydrogen bonds, it interacts only weakly with dissolution inhibitors, resulting in resists with imaging properties which are inferior to similar novolak-based formulations. This behavior is, of course, not a problem in systems relying on functional group deprotection schemes, in which the percolation parameter [9] is changed by deprotection of the previously capped hydroxy functionality, and in which P4HS may be used to good advantage.

2. Synthesis of Isomeric Hydroxystyrene Polymers

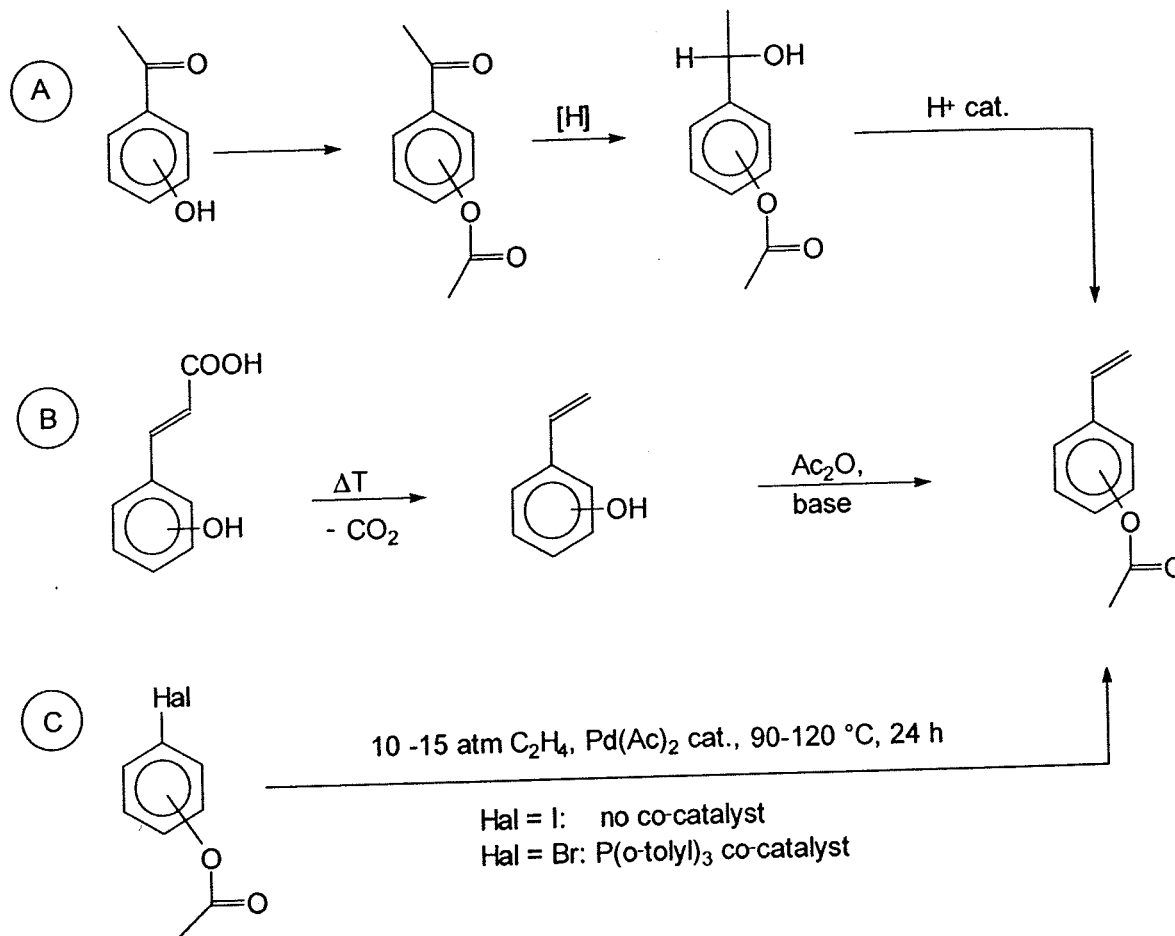
The acetoxystyrene precursors were synthesized by three different routes (A-C, Scheme I). Route A, the conventional synthesis for acetoxystyrenes, was employed for both 4- and 3-acetoxystyrene. In the case of 2-acetoxystyrene, the classical cinnamate route B proved to be more advantageous. Route 3, the Heck

Polystyrene is the hydroxylic shielding layer strength, which occurs in the ortho isomer (allows one to copolymerize). Polystyrene is azeotropic according to the 1:1 copolymerization of the 1:1 copolymer. The though not

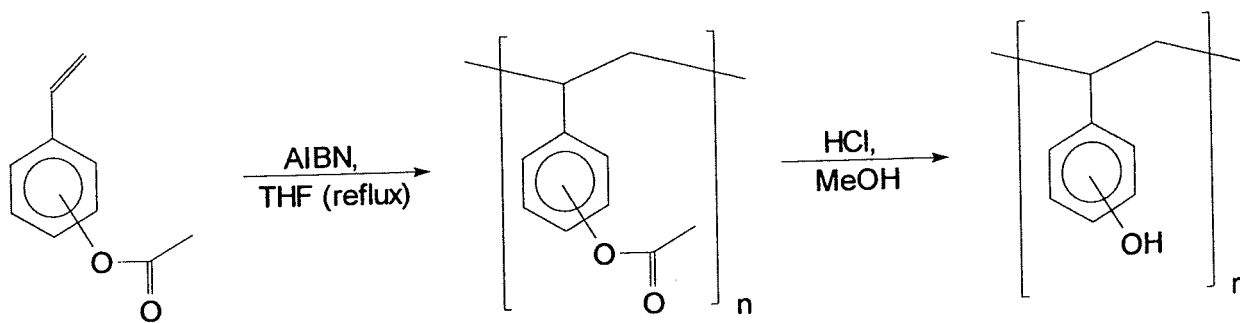
dominantly in many imaging processes as high resolution. Even for low resolution, it leads to a relatively high resolution. Researchers in poly(4-hydroxystyrene) inhibition

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reaction, was employed for 2-acetoxystyrene and 2-acetoxy-4-methylstyrene, starting from the corresponding bromo compounds, and employing a tris-*o*-tolylphosphine co-catalyst. Although selectivity was good, yields were lower (ca. 60% conversion) than reported for similar Heck reactions of substituted 4-hydroxystyrenes [3], probably because of increased steric hindrance in the 2-substituted derivatives. Possibly a sterically less hindered co-catalyst might improve conversion and thus yield [10]. Separation of 2-acetoxybromobenzene and 2-acetoxystyrene proved difficult by distillation, and the distilled mixture was used without further workup to make the 2-acetoxystyrene homopolymer.



Scheme I: Synthesis of acetoxystyrene precursors



Scheme II: Synthesis of Polyhydroxystyrenes

Polymerizations were carried out under nitrogen in refluxing THF using 1%(w/w) AIBN as an initiator. Molecular weights were consistently between 15,000 and 18,000 at a polydispersity of 1.3 to 1.4. Monomer purity was assayed by GC area-%, and the monomer ratios for the copolymerizations and the determination of the copolymerization parameters were adjusted according to the results. The deprotected polymers were obtained by refluxing in excess methanol/HCl for 12 h, then drowning the reaction solution into water. The polymers were collected by filtration and dried in vacuo at 40 °C to yield white to light tan powders.

3. Dissolution Rates of 2-, 3-, and 4-Hydroxystyrene Homopolymers

The 2-, 3-, and 4-hydroxystyrenes are found to have extremely different solubilities in aqueous base developers, depending on the position of the hydroxy group. Whereas P4HS already shows a detectable solubility in 0.04N tetramethylammonium hydroxide (TMAH) developer, poly(3-hydroxystyrene) (P3HS) requires a developer strength of almost 0.07N, and 2-hydroxystyrene only dissolves in very concentrated developers of >0.33N (Fig. 1). At this concentration, the (extrapolated) dissolution rate for P4HS is over 100 $\mu\text{m}/\text{min}$, or over 100,000 times higher than that of P2HS. The dissolution rates of P2HS and P4HS as a function of developer concentration follow a linear log-log plot fairly well, with a larger slope being observed for P2HS. For P3HS, however, there is a break in the log-log plot, which is seen to consist of two linear sections with a transition zone at a developer concentration of 0.20-0.25 N (Fig. 1).

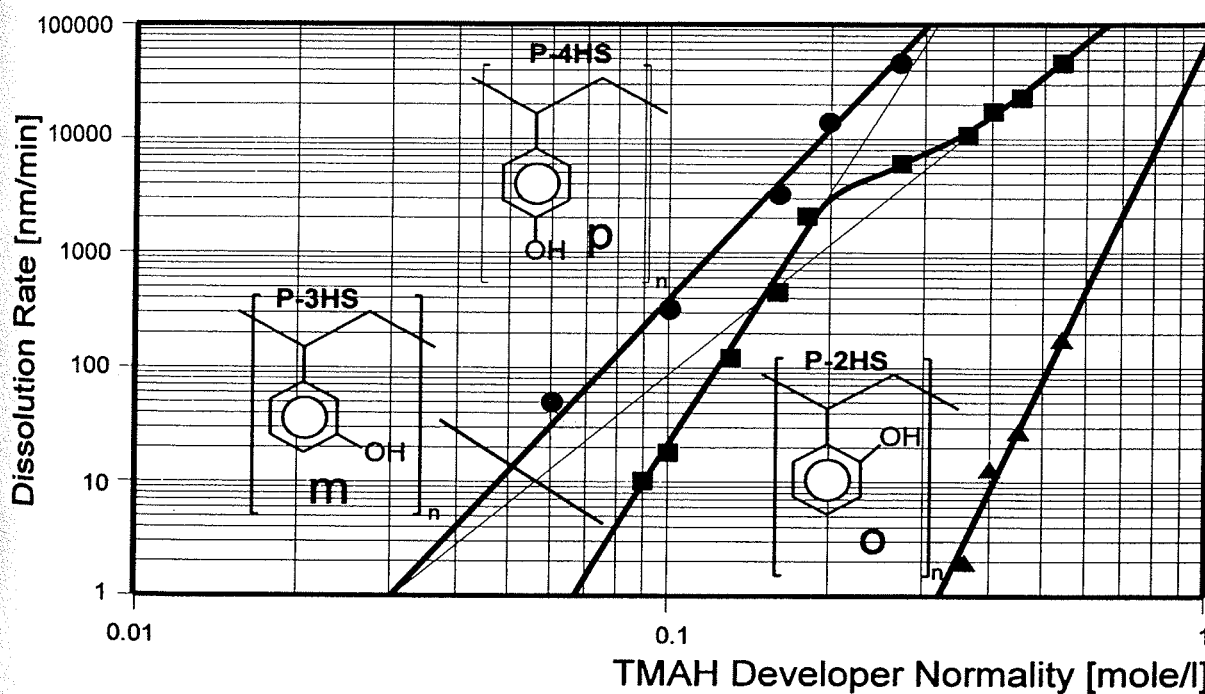


Figure 1: Log-log plot of the dissolution rates of the isomeric hydroxystyrene homopolymers as a function of developer concentration (TMAH, 23 °C).

- Two effects are usually invoked to account for differences in developer solubilities of phenolic polymers:
- the secondary structure effect [4], which relates the dissolution rate to the ratio of intramolecular to intermolecular hydrogen bonds;
 - the effect of steric shielding, in which large hydrophobic groups in the vicinity of the hydroxy groups impede the access of the developer [3a].

Poly-4-hydroxystyrene is usually considered the prototype of a molecule with no hydrogen bonding between the hydroxy groups [4] (Fig. 2a). In contrast, in P2HS, the closer proximity of the hydroxy groups to the backbone allows of easier formation of hydrogen bonds between nearest neighbors (Fig. 2c). According to the secondary structure model, this should result in a higher glass transition temperature for P4HS than for P2HS. This is indeed observed; however, the difference in T_g 's is not as large as might have been anticipated: P4HS: 182 °C > P2HS: 172°C [11]. A clue to the reason for this behavior is found in the T_g of P3HS, which would be expected to be intermediate between P4HS and P2HS. Instead, its T_g is determined as 167°C, noticeably lower than P2HS. It has been suggested [11] that the high T_g of P2HS is caused by an interaction of the hydroxy groups with the polymer backbone, leading to a stiffening of the chains and a concomitant increase in T_g . This interpretation is corroborated by the evolution of T_g in the three homologous series of partially acetylated resins (Fig. 3) [11]. In contrast, the T_g of the 1:1 copolymer between 2- and 4-hydroxystyrene was determined to be 143 °C, or 34 °C lower than would be expected from a simple linear law of mixtures [12].

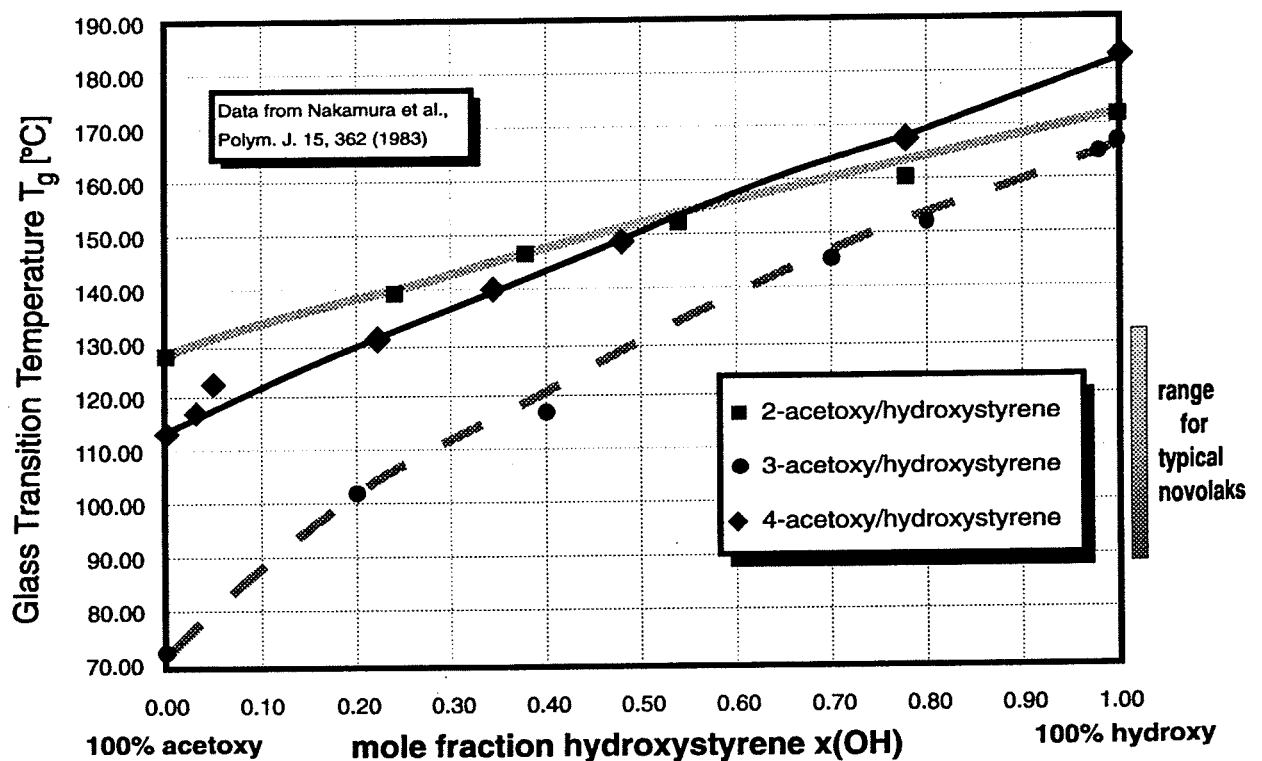


Figure 3: Glass transition temperatures in partially acetylated isomeric hydroxystyrene homopolymers (data taken from [11]). The unexpectedly high T_g 's and low slope determined for the 2-hydroxystyrene case have been attributed to an interaction between the hydroxyl/acetoxy groups and the polymer backbone, leading to a stiffening of the polymer chains and a concomitant T_g increase.

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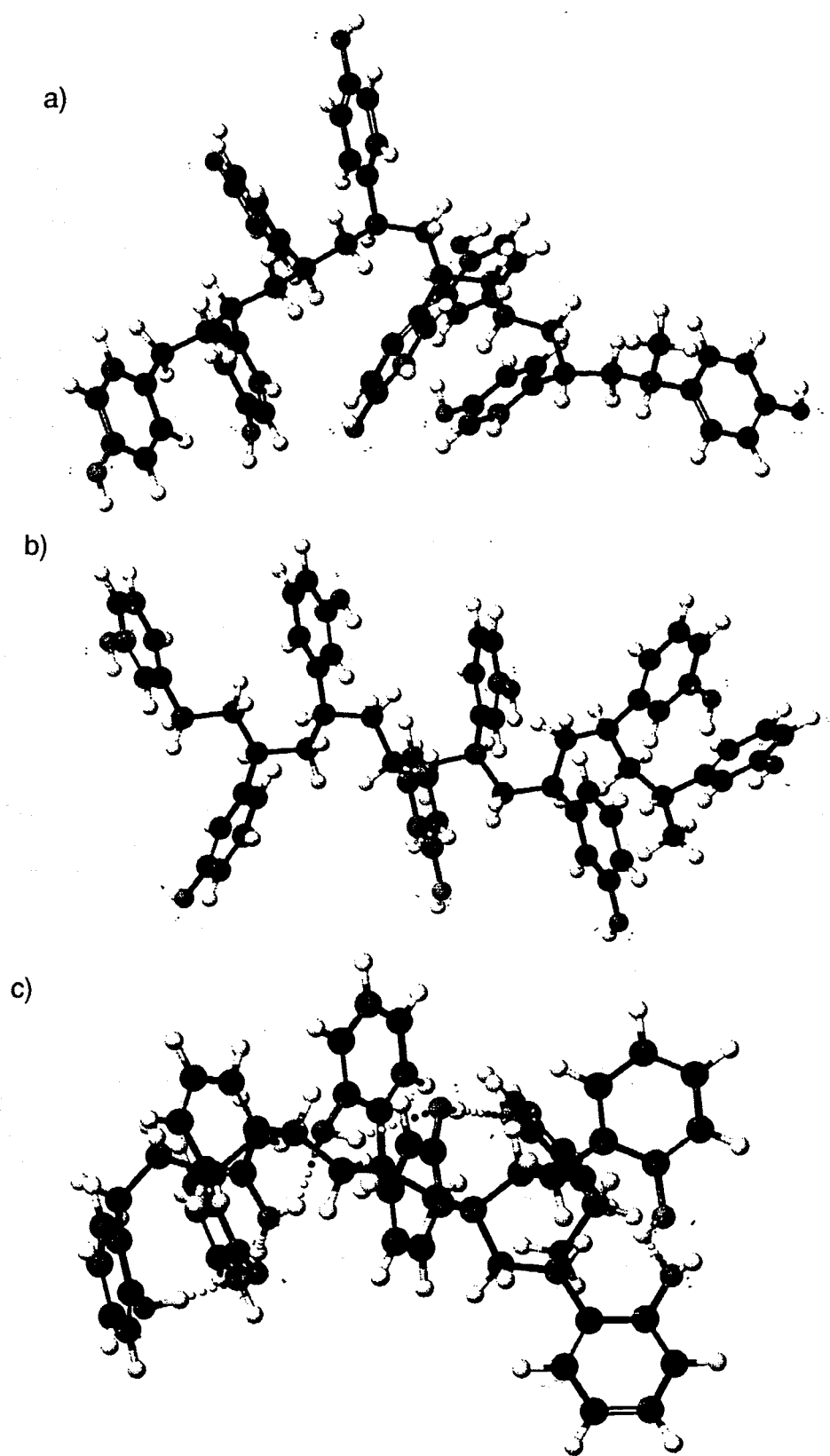


Figure 2: Molecular mechanics structures of atactic octamers of the isomeric hydroxystyrenes (augmented MM2 force field). a) 4-hydroxystyrene octamer, b) 3-hydroxystyrene octamer, and c) 2-hydroxystyrene octamer. Note the nearest neighbor hydrogen bonds evident in c).

The effect of steric shielding has been demonstrated in substituted 4-hydroxystyrene homopolymers [3], where it was found that the dissolution rates in 0.265N TMAH developers dropped precipitously with the size of an *o*-alkyl substituent: P4HS: 18 $\mu\text{m}/\text{min}$, poly(3-methyl-4-hydroxystyrene) 0.3 $\mu\text{m}/\text{min}$, poly(3-ethyl-4-hydroxystyrene) 0.05 $\mu\text{m}/\text{min}$, poly(3-isopropyl-4-hydroxystyrene) and poly(3-*t*-butyl-4-hydroxystyrene): 0 $\mu\text{m}/\text{min}$. As is evident by inspection of the structure calculated for 2-hydroxystyrene homopolymer (Fig. 4), the steric shielding of the hydroxy groups by the polymer backbone is very strong, presumably at least comparable to that of a *t*-butyl group. P3HS shows much reduced shielding, although somewhat more than P4HS.

With the present data, the relative importance of the hydrogen bonding characteristics and the steric shielding for the dissolution rate is not easily assigned. The observed solubility sequence (min. developer concentrations: P4HS 0.04, P3HS 0.07, P2HS 0.33) is roughly consistent with the amount of steric shielding in the series P2HS \gg P3HS $>$ P4HS. However, additional contributions due to nearest neighbor-hydrogen bonding cannot be excluded for P2HS.

4. Dissolution Characteristics of the Isomeric Hydroxystyrenes

In the plot of $\log R$ vs. $\log c$ (Fig. 1), P3HS was unique in showing two linear regions connected by a transition region. Apparently, a change in the dissolution mechanism occurs above a developer concentration of 0.2 - 0.25 N. This behavior was first reported in 1989 [3a], but at the time no explanation could be provided as to its origin.

Recent work by Reiser [13] has provided the tools for a more detailed description of the dissolution process. After immersion in the developer, a thin gel layer, the penetration zone, forms on the surface of the polymer film [14]. During development, this 50-100 \AA thick layer moves into the polymer bulk in a steady state, moving membrane-type situation. The speed of dissolution can be shown to depend on the rate of counter cation diffusion through the penetration zone as the rate-determining step [13]. The dissolution rate R of a polymer is then described by the Huang-Reiser-Kwei (HRK) equation [13b],

$$R = \frac{D}{\delta} = \frac{\alpha a^n}{\delta} \frac{n+2}{(n+1)^2} \frac{(c-c^*)^{n+1}}{(c+c^*)} \quad (2)$$

where c is the developer concentration, c^* is the critical developer concentration, below which no dissolution occurs, and n is the exponent with which the diffusion coefficient, $D = D_0 (1-x)^n$, decays with the distance x into the penetration zone. In the following, n will be called the penetration exponent. According to Eq. 2, a plot of $\log(R \cdot (c+c^*))$ vs. $\log(c-c^*)$ will result in a linear relationship, which unlike the conventional $\log R$ vs. $\log c$ plots will remain valid for low developer concentrations. Since

$$\begin{aligned} \frac{\log(R(c+c^*))}{\log(c-c^*)} &= \left[\frac{1}{c-c^*} \right]^{-1} \frac{\partial \log(R(c-c^*))}{\partial c} \\ &= (n+1)(c-c^*) \frac{\partial}{\partial c} (\log(c-c^*)) \\ &= n+1, \end{aligned} \quad (3)$$

the penetration exponent n may be determined from a plot of $\log(R \cdot (c+c^*))$ vs. $\log(c-c^*)$ (HRK plot), provided c^* is known.

For P2HS homopolymer, c^* is found as 0.35 by extrapolation of a linear R vs. c plot to zero; the slopes of the HRK plot then yield a TMAH penetration exponent of $n = 3.2$ for P2HS. For the first linear section of the P3HS dissolution curve (at lower concentrations; cf. Fig. 1), the critical concentration is determined as $c^* = 0.086$ mole/l, leading to a value of $n=3.28$. For the second linear branch (at higher concentrations), the critical concentration cannot be determined exactly; if it is estimated from an extrapolation to low dissolution rates, one obtains a value of $c^* = 0.02 \pm 0.01$ mole/l, which in turn gives $n=3.33 \pm 0.12$, where the limits given for n are only from propagation of the errors in c^* . As can be seen, n is rather stable towards small changes in the critical concentration in this range. For P4HS, the critical concentration is found as $c^* = 0.044$, corresponding to a penetration exponent of $n=3.19$.

Since nearly identical penetration exponents are found for all three PHS isomers, the large differences in dissolution rates result only from changes in critical concentrations c^* . This quite surprisingly also holds for both branches of the P3HS dissolution rate plot; apparently whatever change in mechanism is causing the break in the plot only affects c^* but not n .

Since P2HS has too slow, and P4HS too high a dissolution rate, it should be possible to obtain polymers with intermediate dissolution rates in a lithographically desirable range through co-polymerization of the corresponding acetoxystyrene precursors, followed by deprotection. Since we first advanced this idea [3a], two Japanese patents have been laid open describing the use of 2-/4-hydroxystyrene and 3-/4-hydroxystyrene copolymers for lithographic applications [15a], as well as a third one [15b], which claims the use of homopolymer mixtures.

5. Co-Polymerization of 2- and 4-Acetoxystyrene

In order to understand and control the polymer properties, it was necessary to analyze the polymer composition as a function of the monomer feed ratios, i.e., determine the co-polymerization parameters.

(2) The co-polymerization of various substituted acetoxystyrenes has been described previously in the literature [3]. 3-Methyl or 3,5-dimethyl substitution had little impact on the polymerization kinetics, leading to nearly ideal and azeotropic co-polymerizations. In contrast, 2-methyl substitution noticeably changed the polymer composition, with the 2-methylacetoxystyrene being incorporated at a lower rate. No polymer could be obtained from 2,4-dimethyl-substituted acetoxystyrene [3], presumably due to excessive steric hindrance. It was therefore expected that the 2-acetoxystyrene would prove to be less reactive than 4-acetoxystyrene. However, the contrary proved to be the case.

(3) A series of 2- and 4-acetoxystyrene samples of different monomer ratios were dissolved in freshly distilled THF, 1% w/w AIBN was added, and the samples polymerized in fully filled GC sample bottles at 70 C for 1 h. The polymerization mixtures were analyzed by GC for residual monomers, and the monomer conversion was calculated. Total conversions were of the order of 10 to 20 %. These results were analyzed by the method of Kelen and Tüdös [16] to give the copolymerization parameters $r_1 = 0.76$ and $r_2 = 0.92$ (monomer 1: 4-acetoxystyrene, monomer 2: 2-acetoxystyrene). Quite surprisingly, 2-acetoxystyrene is found to be slightly more reactive than 4-acetoxystyrene, resulting in a small enrichment of 2-acetoxystyrene units in the polymer relative to the monomer feed (Fig. 4). Since the deviation from the diagonal in Fig. 4 is always less than 5%, the polymerization may, however, still be considered approximately ideal and azeotropic.

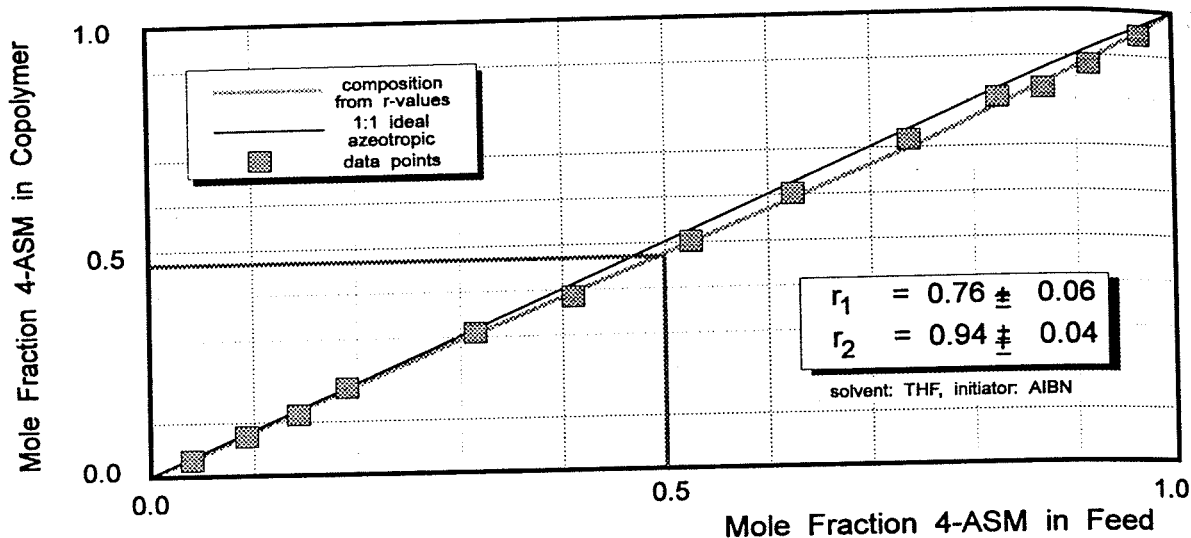


Figure 4: Copolymerization diagram (Kelen-Tüdös method) for 2- and 4-hydroxystyrene.

6. Characterization of the 2- and 4-Acetoxy styrene Copolymers

Copolymers of 2- and 4-acetoxy styrene were obtained and deprotected as described in Scheme 2. The dissolution rates of the deprotected polymers were determined as a function of TMAH developer normality by the film loss from 2-4 μm thick spin cast films (casting solvent propyleneglycol monomethyl ether (PGMEA), prebake: 2 min 110 $^{\circ}\text{C}$ on a hotplate). A regular progression of dissolution rate curves is obtained for the various co-polymers (Fig. 5).

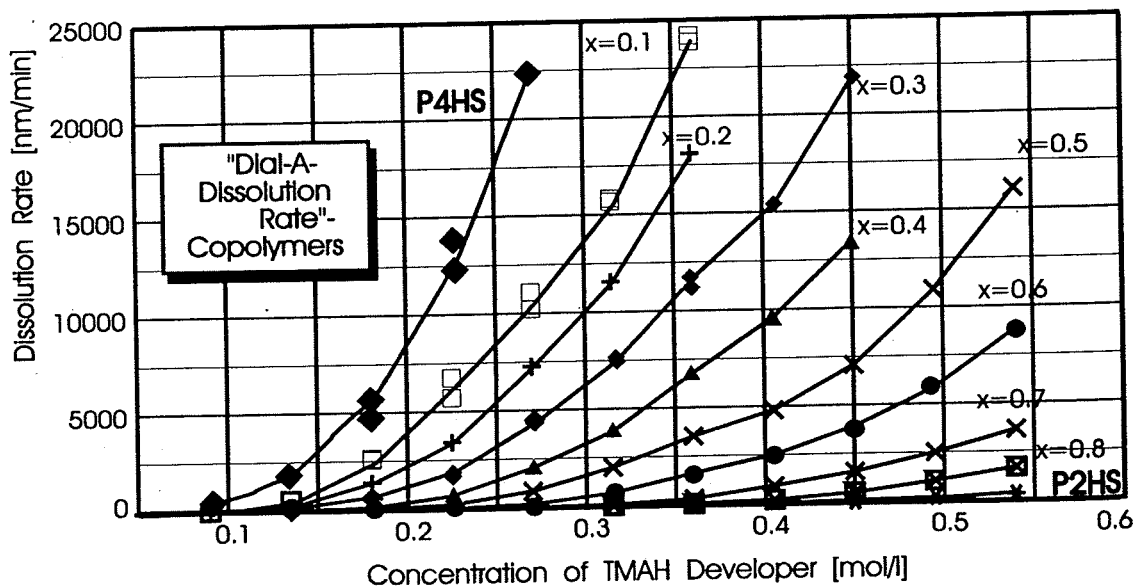


Figure 5: Dissolution rates for copolymers of 2- and 4-hydroxystyrene as a function of TMAH developer concentration. Co-polymerization allows one to choose any dissolution rate between that of 2- and 4-hydroxystyrene.

Further information on the dissolution process can be extracted from the data in Fig. 5 if they are analyzed according to the HRK equation (Eq. 2). Fig. 6 shows a plot of the critical concentrations c^* obtained from an extrapolation of the lower parts of the curves in Fig. 5 to zero. The critical concentrations are found to be a linear function of the mole fraction of 2-hydroxystyrene. Since this is the first study of this kind reported, it is unclear whether this is a generally observed behavior for copolymers.

With the critical concentrations c_i^* known, the penetration exponents n_i may be obtained from the HRK plots of the copolymers (Fig. 7). The corresponding linear regressions for $\log(R \cdot (c+c^*))$ vs. $\log(c-c^*)$ show high correlation coefficients and low residuals if the points with the lowest dissolution rates are excluded. This indicates that there seems to be a deviation from the HRK equation for very low dissolution rates.

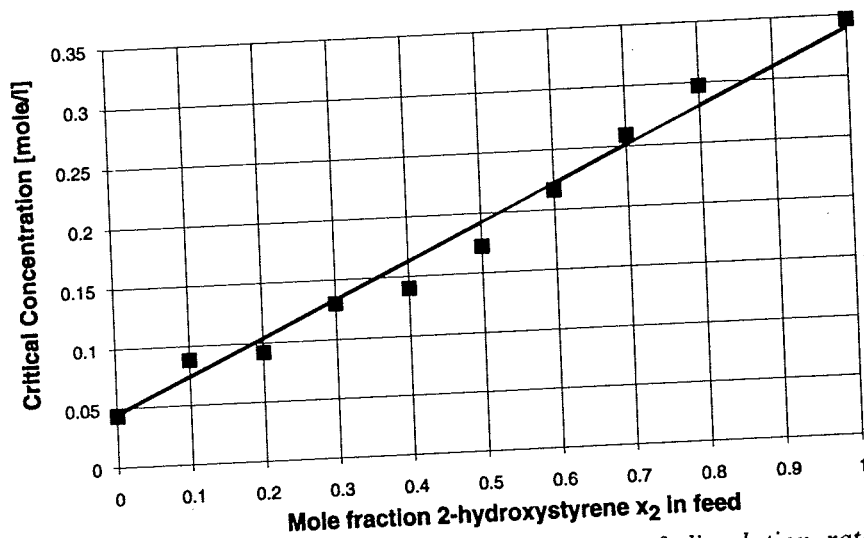


Figure 6: Critical concentrations c^* as determined from plots of dissolution rate R vs. developer concentration c : c^* is found to be a linear function of co-polymer composition.

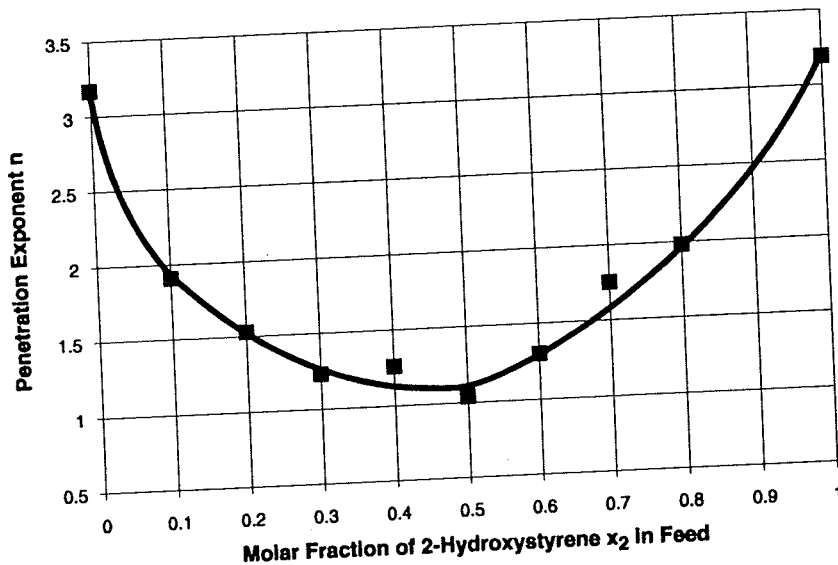


Figure 8: Evolution of the penetration exponent as a function of co-polymer composition.

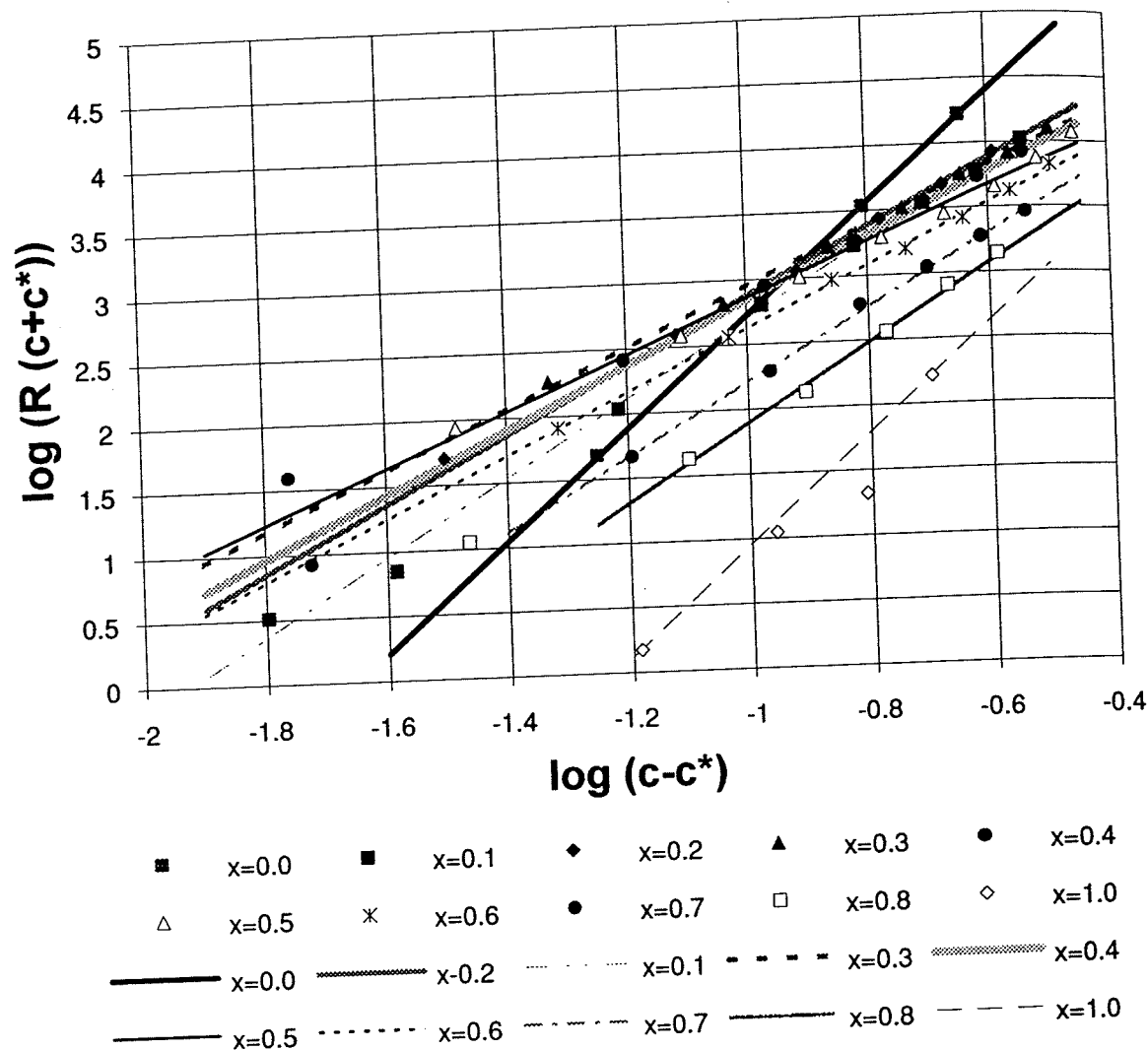


Figure 7: Huang-Reiser-Kwei (HRK) plots of $\log(R(c+c^*))$ vs. $\log(c-c^*)$ for the co-polymers of Fig. 5. The slope s of the plots is connected to the penetration exponent by $s = n + 1$. Since n is not monotonous over the range studied (cf. Fig. 8), the slope of the lines changes as a function of co-polymer composition, leading to the tangled appearance of the regression lines.

The penetration exponents $n_i = n_i(x_2)$ as determined from the slopes of the HRK plots in Fig. X decrease from the initial value for P4HS ($x_2 = 0$) to a minimum of about 1 at $x_2 = 0.45$ to 0.5, and then increase again until they reach the P2HS value of 3.3 at $x_2 = 1$ (Fig. 8).

Reiser's most recent work [17,18] on the temperature dependence of the dissolution rate has provided a possible clue to the underlying mechanism of the change in the penetration exponent. The diffusion mechanism can be described as a percolation process of the cations on a lattice formed by the hydrophilic sites in the resin, which are identified as the phenolate ion sites by an inspection of the energy barrier to the percolational jump [17]. Below the glass transition temperature of the penetration zone, the sites are immobile, the percolational jump is the rate-determining process. Above the glass transition temperature, the polymer chains have increased mobility, so that rotational or diffusional

formerly distant percolation sites into closer proximity. The rate constants are then determined by the activation parameters of polymer movement. For the 3-methylhydroxystyrene/hydroxystyrene copolymers, glass transition temperatures of the penetration zone are found to be between 30 and 50 °C, depending on the co-polymer composition [18].

Since the T_g of the 1:1 2-/4-hydroxystyrene copolymer is severely depressed compared to that of the homopolymers (143 °C vs. 182 °C for P4HS and 172 °C for P2HS), it is conceivable that the effects on the penetration exponent are related to a lowering of the glass transition temperature of the penetration zone. With increasing molar fraction of 2-hydroxystyrene, the polymer matrix progressively softens, and the diffusion of cations into the penetration zone becomes increasingly more facile, until at higher 2-HS contents the T_g rises again beyond the low point, and with it the penetration exponent.

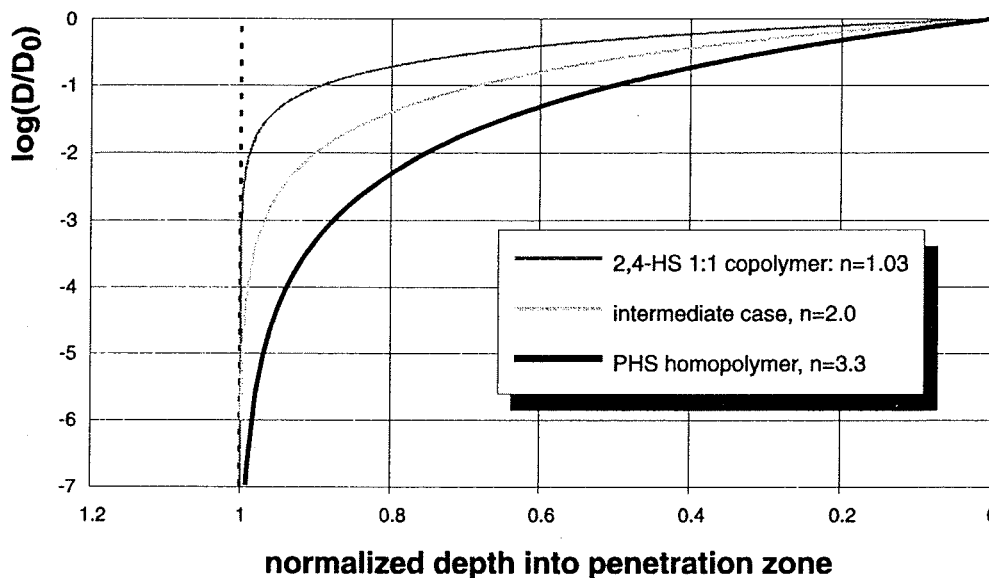


Fig. 9: Evolution of the normalized diffusion coefficient D/D_0 in the penetration zone for different values of the penetration exponent.

In a more recent paper, Reiser et al. [19] have investigated the dissolution of P4HS and phenolic polymers in KOH. They analyzed their data in terms of a dimensionless form of Eq. (1) which is valid for developers of much higher normality than the critical concentrations. If $c \gg c^*$, it is possible to write Eq. (1) as

$$R = P_r \cdot \frac{c - c^*}{c} \cdot \frac{(c - c^*)^n}{c^*}, \text{ or, using } y = (c/c^* - 1): \quad (4)$$

$$\frac{R}{P_r} = \frac{y^{n+1}}{1 + y}, \quad (5)$$

where P_r is the permeability of the penetration zone in the reference state $c_r = 2c^*$ (in this reference state, the dimensionless dissolution rates of all resins are equal, and their actual dissolution rates can differ only by virtue of differences in their reference permeabilities P_r [19]).

Table I: Values for c^* , P_r , and n obtained for selected phenolic polymers in TMAH (this work) and KOH (ref. [19]). Critical concentrations c^* are in mole/l, P_r is in nm/min.

Polymer	TMAH			KOH		
	P_r	c^*	n	P_r	c^*	n
P4HS (0:10)	260	0.0440	3.32	15,700	0.0564	0.23
2,4-HS 1:9 copolymer	2,072	0.0881	1.95			
2,4-HS 2:8 copolymer	5,553	0.0920	1.57			
2,4-HS 3:7 copolymer	8,551	0.1300	1.39			
2,4-HS 4:6 copolymer	9,190	0.1400	1.42			
2,4-HS 1:1 copolymer	9,508	0.1721	1.18			
2,4-HS 6:4 copolymer	7,954	0.2161	1.44			
2,4-HS 7:3 copolymer	5,550	0.2590	1.89			
2,4-HS 8:2 copolymer	4,027	0.2971	2.17			
P2HS (10:0)	1,552	0.3450	2.98			
o-methyl-P4HS				11,300	0.2466	1.31
o-isopropyl-P4HS				7,500	1.1010	1.66
m-cresol novolak				3,970	0.0211	1.22

Table I compares the c^* , P_r , and n values obtained for dissolution in TMAH developer in this work with a selection of corresponding numbers for dissolution in KOH from ref. [19]. For the one case of P4HS, both KOH and TMAH data are available. As can be seen from Table I, the critical concentration c^* is very similar for both developers, which may indicate that at the critical concentration, the ionization state of the polymer is independent of the counter cation. With respect to P_r , it is known from the literature [13] that the dissolution speeds of a resin in different developers of the same normality depend inversely on the area of the unhydrated diffusing counter cation, i.e. $R = \text{const.}/(\pi r^2)$. Since the unhydrated tetramethylammonium cation is much larger than the naked potassium cation, the dissolution rate in KOH will therefore be higher than the one in TMAH for any given developer concentration (provided it is greater than the critical concentrations). Since in this case $c^*(K^+) \approx c^*(TMA^+)$, $P_r(K^+)$ (i.e. the dissolution rate in KOH at $c_r=2c^*$) is thus expected to be higher than $P_r(TMA^+)$, as is indeed found. The n value for P4HS in TMAH is much higher than the one in KOH, an observation which possibly may also be explained by a cation size effect: the more difficult migration of the larger TMA^+ cation leads to a steeper decrease of the diffusion coefficient as a function of the depth into the penetration zone.

For the 2,4-HS copolymers, the P_r values show a large (about 30fold) increase up to an about 1:1 copolymer composition (Fig. 10). For higher molar fractions of 2-HS, the P_r values decrease again, until for P2HS they reach about the fivefold value of P4HS [20]. We note that the penetration exponents n reach a minimum and the permeabilities P_r a maximum at a copolymer composition of approx. 1:1, i.e., at the condition of maximum disorder.

7. Lithographic Evaluation of 2- and 4-Hydroxystyrene 1:1 Co-Polymer

The dissolution inhibition and promotion properties of the isomeric polyhydroxystyrenes have recently been investigated by workers from Hitachi [21]. Their results indicate that P2HS shows dissolution inhibition similar, although not quite as pronounced as, a meta-para-cresol novolak. All PHS isomers, as well as the novolak, showed comparable dissolution promotion in the fully exposed film, which lead the

his work) and KOH

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6	1.31
7	1.66
8	1.22

this work with case of P4HS, entration c^* is onization state the literature be inversely re anhydrated lution rate in n (provided it K^+) (i.e. the d found. The bly may also on leads to a ne. n about 1:1 again, until exponents n ox. 1:1, i.e.,

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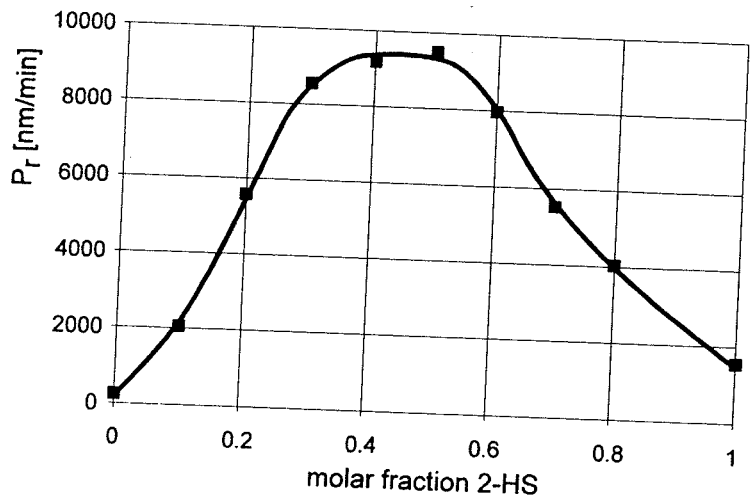


Figure 10: Evolution of the reference permeabilities P_r for 2,4-hydroxystyrene copolymers as a function of the copolymer composition.

authors to the conclusion that dissolution contrast is mainly determined by the dissolution inhibition effect [21]. In order to have acceptable dissolution rates, the Hitachi authors had to reduce the molecular weight of the P2HS homopolymer to 2,200 [21], a molecular weight which in a lithographic application may be expected to lead to substantially impaired thermal resist properties.

For 2,4-HS copolymers of constant molecular weight, it is possible to choose any dissolution rate between that of P4HS and P2HS by properly adjusting the monomer feeds in the copolymerization, as can be seen by inspection of Figure 5. The 1:1 co-polymer shows a dissolution rate which is comparable to that of novolak resins used in commercial resists, and was chosen for further lithographic evaluation.

A photoresist was formulated consisting of 80% w/w of solids of the 1:1 copolymer, and 20% w/w of a proprietary trifunctional sensitizer which is known to show strong dissolution inhibition. The resist solvent was propyleneglycolmonomethylether acetate (PGMEA). The resist was coated onto silicon wafers and prebaked for 60 sec at 110 °C to give a 0.978 μm film thickness. The wafers were exposed on a Nikon i-line stepper (NA=0.54), and a post exposure bake was carried out at 110 °C for 60 sec, followed by puddle development (52 sec) in AZ 300 MIF (0.265N). SEM analysis of the structures obtained showed resolution down to 0.4 μm lines and spaces, although with somewhat sloped sidewalls (Fig. 11). Standing waves are still in evidence on the resist structures, presumably due to the higher T_g of the copolymer relative to novolaks.

The thermal flow resistance of the resist structures was tested on large resist pads (500x500 μm). Fig. 12 shows the changes in wall angle in the pads as a function of temperature after heating on a hotplate for 2 minutes. A beginning degradation of the wall angle with concomitant "cushioning" is seen above 135 °C, and becomes more pronounced at 140 °C. While this temperature is higher by 15-20 °C than that observed for most novolak resists, it is much lower than expected from the T_g data for polyhydroxystyrenes (T_g of the 1:1 copolymer: 143 °C). It appears that the T_g increase of 30-40 °C over typical novolaks does not fully translate into increased thermal flow stability. One possible reason might be a decreased reactivity of PHS hydroxy groups with the ketene decomposition products of polyfunctional DNQ-photosensitizers, a reaction which is known to enhance thermal flow resistance in novolaks through partial crosslinking of the matrix.

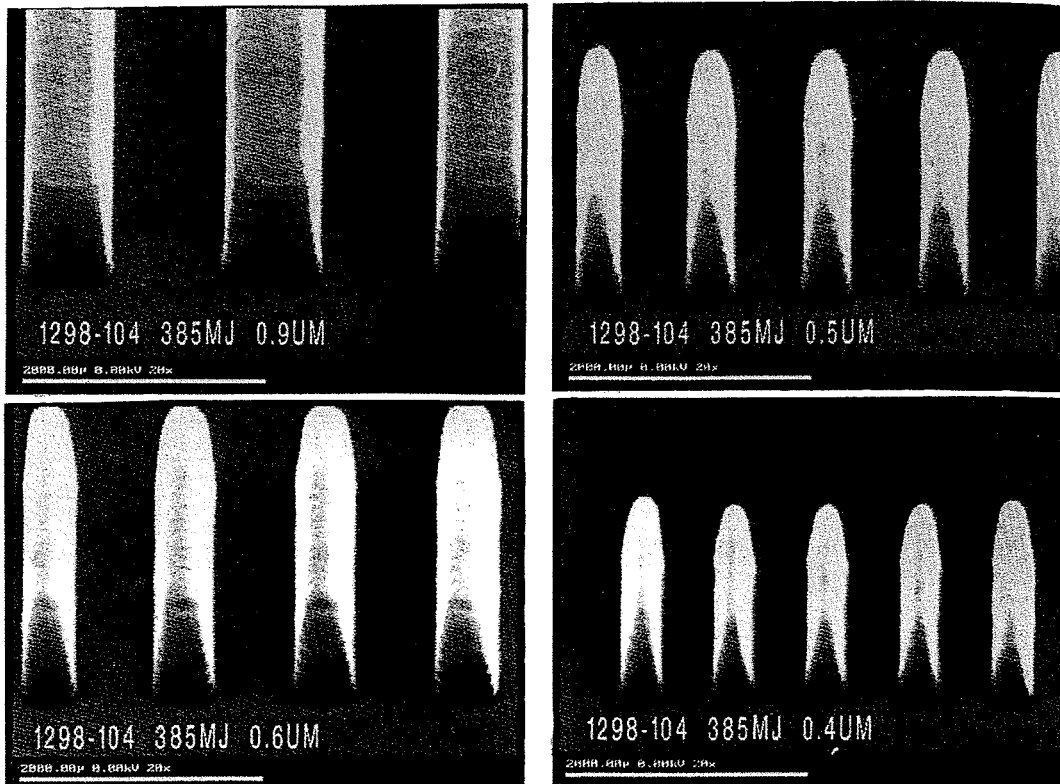


Figure 11: Structures imaged in a diazonaphthoquinone photoresist based on the 2-14-hydroxystyrene 1:1 copolymer as matrix resin (Nikon i-line stepper, NA = 0.54).

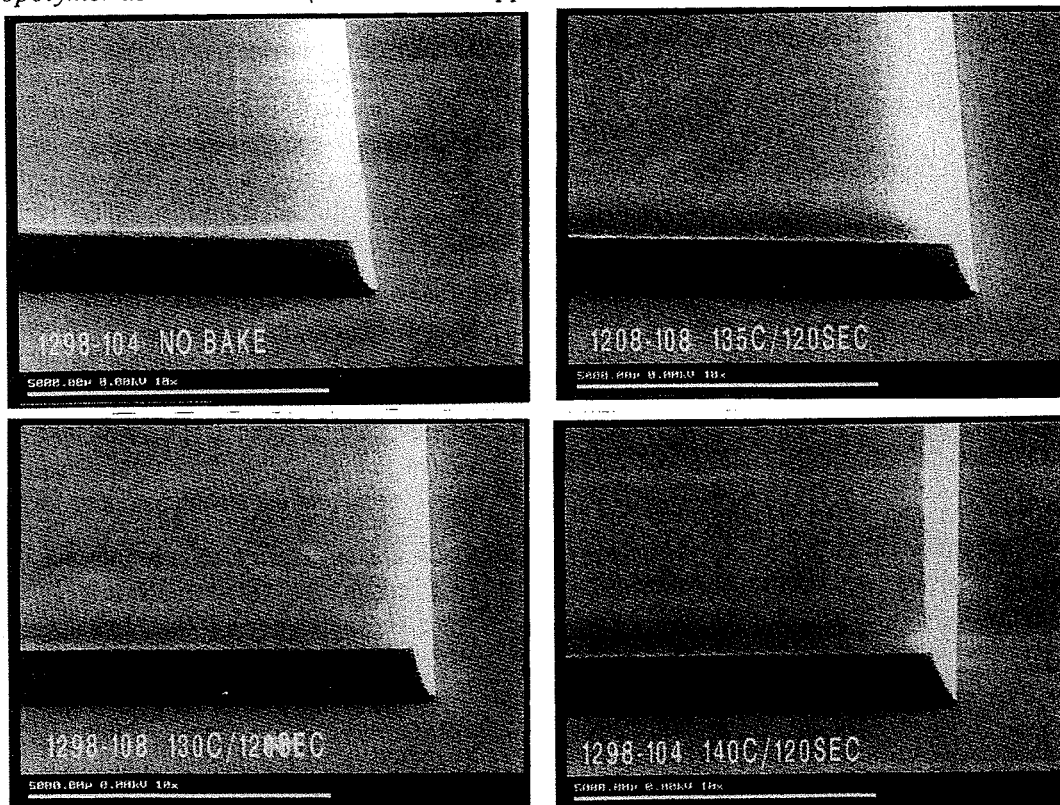


Figure 12: Thermal flow test on large resist pads ($500 \times 500 \mu\text{m}$) for the resist based on the 1:1 copolymer (see text).

8. Conclusion

The composition of 2- and 4-hydroxystyrene copolymers may be adjusted by the corresponding monomer feeds in such a way as to obtain, with good control, polymers showing any intermediate dissolution rate. The characterization of their dissolution by the HRK equation yields a linear correlation between the copolymer composition and the critical concentration c^* . Further work is needed to decide whether this behavior is a general characteristic of copolymer systems. In contrast, n is seen to sharply decrease to a minimum of close to unity for polymers of approximately 1:1 composition, down from the value of $n=3.2-3.3$ which is found for the homopolymers. This effect has tentatively been related to changes in the glass transition temperature of the penetration zone. The lower n values lead to dramatically different cation concentration profiles in the penetration zone.

The 1:1 copolymer was selected for lithographic evaluation on the basis of its dissolution rate. In a non-optimized formulation with a DNQ sensitizer, 0.4 μm lines and spaces could be resolved, although with somewhat sloped wall profiles. It is unfortunate that the range of target dissolution rates for the matrix resins coincides with the lowest penetration parameters, which may possibly negatively affect the imaging properties of the resist. The thermal stability of the finished resist structures (135 $^{\circ}\text{C}$), although quite acceptable compared to novolak resists, was seen to be inferior to the T_g of the matrix resin (143 $^{\circ}\text{C}$). In contrast, novolak-based diazonaphthoquinone resists typically show a thermal stability which is 20-30 $^{\circ}\text{C}$ higher than the T_g of the resin. One may speculate about differences in reaction efficiency between novolak and PHS hydroxy groups in the addition to polyfunctional ketenes which is generally thought to contribute to the thermal stability enhancement in novolak resists. However, it may simply mean that we do not understand very well what is going on when a resist flows, and that other properties not correlated to T_g also play an important role.

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