The "Living" Free Radical Synthesis of Poly(4-hydroxystyrene): Physical Properties and Dissolution Behavior

G. G. Barclay,*,† C. J. Hawker,‡ H. Ito,*,‡ A. Orellana,†,§ P. R. L. Malenfant,†,‖ and R. F. Sinta†

Shipley Company, 455 Forest Street, Marlboro, Massachusetts 01752, and
IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120

Received July 29, 1996

ABSTRACT: The synthesis of a range of narrow polydispersity, well-defined poly(4-hydroxystyrene)s via a "living" radical polymerization technique is reported. The synthetic route chosen involves the 2,2,6,6-tetramethyl-1-piperidinyloxy mediated free radical polymerization of acetoxystyrene, followed by deacetylation with base. The efficiency and molecular weight control of the "living" free radical polymerization of 4-acetoxystyrene is compared to styrene. Further, the effect of initiating system, "unimolecular" or "bimolecular", on the "living" radical polymerization of 4-acetoxystyrene is also discussed. The physical and structural properties of these well-defined polymers were used to compare poly(4-hydroxystyrene) prepared via "conventional" free radical polymerization. A fundamental study of the dissolution of poly-(4-hydroxystyrene) in aqueous base was undertaken to elucidate the effect of polydispersity, molecular weight, and structure on the dissolution behavior of these polymers.

Introduction

The major component of a photoresist formulation is the matrix polymer, which therefore has the greatest effect on resist performance. At deep-UV wavelengths (220−260 nm) the polymers of choice are linear phenolic polymers, such as poly(4-hydroxystyrene) (PHOST), which have excellent absorption characteristics within the deep-UV region. Narrow polydispersity PHOST and poly(4-hydroxy-α-methylstyrene) have been previously prepared by living anionic polymerization of the silyl-protected hydroxystyrenes, followed by deprotection.[1,2] Recently, great interest has been generated by the possibility of carrying out "living" free radical polymerizations,[3−5] which afford accurate control over molecular weight distribution,[6] chain ends,[7] and polymer architecture.[8] This "living" radical polymerization proceeds via the reversible capping of growing chain ends with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), reducing free radical concentration and inhibiting premature chain termination. The initiating systems used for "living" radical polymerizations can be divided into two classes; unimolecular initiators in which the O-alkylated TEMPO derivative functions as both the initiating group and capping agent and bimolecular systems using a free radical initiator, such as benzoyl peroxide (BPO), in conjunction with TEMPO.[9] The main focus of research into the area of "living" free radical polymerizations has been directed toward the synthesis of polystyrene, with preliminary reports on the polymerization of functionalized styrenes.[10,11]

The present study investigates the TEMPO-mediated free radical polymerization of the moderately deactivated 4-acetoxystyrene (**1**) monomer relative to styrene. The efficiency of the "living" free radical polymerization of (**1**) and styrene, using a bimolecular initiating system consisting of TEMPO and BPO (**4**), was evaluated in terms of conversion, molecular weight control, and polydispersity (PD). Further, the TEMPO-mediated polymerization of 4-acetoxystyrene (**1**) was investigated using both the unimolecular initiator, 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (**5**), and the bimolecular system (**4**). The resulting well-defined poly(4-acetoxystyrene) (**2**) was then quantitatively converted to PHOST (**3**) by deacetylation with base. With this novel polymerization technique, a number of well-defined PHOSTs have been synthesized (PD = 1.1 to 1.4), with a variety of molecular weights, ranging from $M_n = 2000$ to 30 000.

Modern lithographic technology is exclusively based on the aqueous base development of phenolic resists. Thus, the aqueous base dissolution behavior of phenolic resins, such as novolac and PHOST, plays a critical role in resist performance. Further, as the minimum feature size required from photoresist compositions decreases below 0.25 μm, control of the macromolecular architecture of the matrix resin will play an increasingly important role. For example, in the case of I-line (365 nm) photoresists it has been observed that the molecular weight distribution of novolac resin profoundly affects the dissolution rate, softening point, and lithographic performance of the resist.[12,13] Although such optimization is mostly accomplished by empirical procedures, availability of resist polymers with well-defined structures could potentially make basic studies on material parameters and properties easier. Supercritical CO_2 extraction of a derivatized cresol novolac resin has produced nearly monodisperse fractions, allowing fundamental investigation of the novolac resin dissolution and thermal behavior, and a logical design of a high-performance I-line resist.[12,13]

To date, little research has been carried out on the effect of the molecular weight and polydispersity of linear phenolic polymers, such as PHOST. In contrast to novolac resins, PHOST can be prepared in a narrow PD form, without any fractionation, through "living"

[†] Shipley Company.

[‡] IBM Almaden Research Center.

[§] Present address: Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5.

[‖] Present address: Department of Chemistry, Baker Lab., Cornell University, Ithaca, NY 14853-1301.

S0024-9297(96)01129-1 CCC: $15.00

polymerization. The structural properties, thermal characteristics, and dissolution behavior of these well-defined polymers have been investigated as a function of molecular weight and PD. The behavior of these narrow PD polymers is also compared to polymers prepared via conventional radical polymerizations, with PD in the range 2.0−2.5. Furthermore, blending experiments using these narrow dispersity materials have been undertaken to study the dissolution behavior of polydisperse PHOST.

Experimental Section

Materials. 4-Acetoxystyrene (**1**) (Hoechst Celanese) and styrene (Aldrich) were distilled under reduced pressure prior to use. Benzoyl peroxide (BPO) (Aldrich) was recrystallized from diethyl ether. 2,2,6,6-Tetramethyl-1-piperidinyloxy (**6**) (Aldrich) was used as obtained. 1-Phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (**5**) and 1-benzyloxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (**7**) were prepared as previously reported.[9] PHOST prepared by anionic polymerization (BuLi/THF at −78 °C) was prepared as reported.[1] For comparison PHOST polymers were obtained from Hoechst Celanese (M_n = 5000−25000; PD = 1.8−2.4).

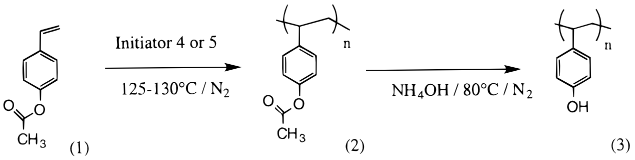
Bulk Polymerization of 4-Acetoxystyrene (1). 4-Acetoxystyrene (**1**) (75.0 g, 0.463 mol) was placed in a 250 mL round bottom flask and purged with N_2. The appropriate molar quantity of initiating system (**4** or **5**) was then added to obtain the desired molecular weight. For example, to obtain a molecular weight of approximately 16 200 amu, a molar ratio of 1:100, unimolecular initiator (**5**) to 4-acetoxystyrene, would be used. After addition of the initiator, the polymerization mixture was heated to 125−130 °C, under N_2, and stirred for 48 h. During the polymerization the polymer solidified in the reaction vessel. The reaction was then cooled to room temperature and the polymer dissolved in acetone (225 mL), and isolated by precipitation into hexanes (2250 mL). The polymer was then filtered, washed with hexanes, and dried in a vacuum oven overnight at 50 °C. Typical isolated yields are 80−95% of theory.

Solution Polymerization of 4-Acetoxystyrene (1). 4-Acetoxystyrene (**1**) (25 g, 0.154 mol) was dissolved in mixed xylenes (bp 138 °C) or chlorobenzene (bp 132 °C) as a 30% solution. To this monomer solution, 0.25 g (1.03 mmol) of benzoyl peroxide and 0.241 g (1.545 mmol) of TEMPO were added to the reaction vessel. The polymerizations were placed under nitrogen and held at reflux for 72−96 h. The reaction mixtures were then allowed to cool to room temperature and precipitated into methanol (500 mL). The filtered precipitate was dried under vacuum overnight at 50 °C. These solution polymerizations gave isolated yields of 40%−80% of theory depending upon reaction time.

Deacetylation of Poly(4-acetoxystyrene) (2). To a slurry of poly(4-acetoxystyrene) (**2**) (50.0 g, 0.308 mol) in isopropyl alcohol or methanol at reflux (200 mL), under N_2, ammonium hydroxide (24.25 g, 0.692 mol) dissolved in water (36 mL) was added dropwise over 15 min. After addition, the reaction mixture was heated at reflux for 18 h, during which time the polymer went into solution. The reaction is then cooled to room temperature, and the polymer isolated by precipitation into water (1500 mL), filtered, washed well with water, and dried in a vacuum oven overnight at 50 °C. Typical isolated yields of poly(4-hydroxystyrene) (**3**) are 80−90% of theory.

Preparation of Polymer Blends and Dissolution Rate Measurements. Polymer blends of PHOST were prepared by dissolving the appropriate polymer combinations (wt/wt) in ethyl lactate at ∼16 wt %. A monomodal blend was prepared by mixing polymers **3c** and **3d** (1:1, wt/wt) in ethyl lactate. Various tandem blends were prepared by combining the lowest M_w (**3a**) and highest M_w (**3e**) PHOST polymers, Table 5. A trimodal distribution was obtained by mixing polymers **3a**, **3b**, **3c**, and **3d** in the ratio 21.4:21.1:33.0:24.3. The molecular weight, polydispersity and modality of these PHOST blends were determined by gel permeation chromatography. Films of these PHOST polymers and blends cast on 1 in. Si wafers were baked at 150 °C for 1 min to remove the casting solvent. The film thickness (approximately 1.0 μm) was measured on a Tencor Alphastep. The dissolution rates of these films were then measured by immersion in 0.21 N aqueous tetramethylammonium hydroxide solution (MF321) using a Perkin-Elmer 5900 Development Rate Monitor.

Scheme 1. Synthesis of Well-Defined Poly(4-hydroxystyrene)



Characterization. Compositions were determined using a GE QE300 NMR spectrometer, ^{1}H (300 MHz) and ^{13}C (75.4 MHz) NMR, in acetone-d_6, with tetramethylsilane as an internal standard. For conversion studies, the samples were transferred directly from the polymerization reaction to an NMR tube and dissolved in acetone. The relative percenatges of poly(4-acetoxystyrene) and 4-acetoxystyrene monomer were determined by integration of the relevant peaks. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a Waters Model 150C equipped with four Ultrastyragel columns in tetrahydrofuran at 40 °C. The molecular weight values reported are relative to polystyrene standards. IR spectra were collected on a Mattson Polaris FTIR spectrometer. Absorbance spectra were taken on a Cary 3 UV−vis spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetery (DSC) were performed using a Perkin-Elmer TGA-7 and a Perkin-Elmer DSC-7 under N_2 (10 °C/min).

Results and Discussion

The ‘Living” free Radical Polymerization of 4-Acetoxystyrene. A convenient synthetic route to the preparation of well-defined poly(4-hydroxystyrene) (**3**) is necessary to explore the effects of PD, structure, and molecular weight on lithographic properties. The synthetic route chosen was the TEMPO-mediated “living” free radical polymerization of 4-acetoxystyrene (**1**) and subsequent deacetylation to form PHOST (Scheme 1).

In a recent report by Kazmaier et al.[10] it was observed that electron-withdrawing substituents, such as CF_3-functionalized styrene, increase the rate of nitroxide-mediated “living” free radical polymerization. To further elucidate the effect of substituents on “living” free radical polymerization, two monomers were investigated: 4-acetoxystyrene (**1**) and styrene. The TEMPO mediated bulk polymerization of (**1**) and styrene was carried out at 130 °C using the bimolecular initiator (TEMPO/BPO = 1.3/1) (**4**). As can be seen from Figure 1, the inclusion of the acetoxy group on the benzene ring increases the rate of polymerization compared to styrene. Further, the increase in reaction rate is more pronounced during the early stages of the polymerization. A similar increase in polymerization rate compared to styrene was also observed when the unimolecular initiating system (**5**) was used to control the radical polymerization of **1**.

Narrow PD was maintained below the theoretical limit for radical polymerization (M_w/M_n = 1.50) throughout the polymerization of the acetoxy and styrene monomers. In general, as can be seen from Figure 1, the acetoxy monomers exhibit slightly higher dispersities throughout the “living” polymerization than styrene. The molecular weights of the acetoxystyrene polymers

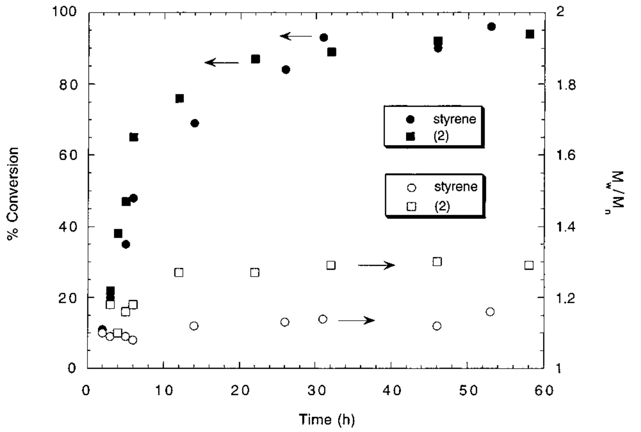


Figure 1. Evolution of monomer conversion and polydispersity with time.

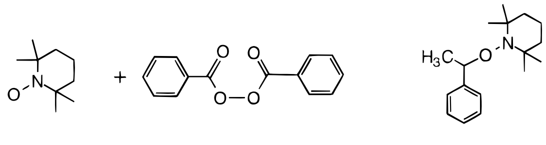
Table 1. Bulk vs Solution "Living" Free Radical Polymerization

solvent	TEMPO/BPO	M_n	M_w/M_n
neat	1.3:1	13620	1.31
chlorobenzene	1.3:1	12457	1.63
xylenes	1.3:1	11328	1.53
xylenes	1.5:1	11732	1.54
xylenes	2:1	11285	1.59
xylenes	3:1	10097	1.63

increase in an approximately linear fashion with conversion, indicative of a living polymerization. Furthermore, the control of PD and the incremental increase in molecular weight with time indicates that the "living" nature of the TEMPO-mediated radical polymerization is unaffected by the presence of the electron-withdrawing acetoxy moiety in the *para* position of styrene.

Due to the high glass transition temperature of poly(4-acetoxystyrene) (ca. 100−120 °C), and possible advantages in the ease of isolation, the solution "living" free radical polymerization of **1** was investigated. The two solvents used in this study were chlorobenzene (bp 132 °C) and mixed xylenes (bp 138 °C), at a concentration of 30% monomer (w/w). For this study the bimolecular initiating system **4** was used. Initially a TEMPO/BPO ratio of 1.3:1 was employed, since it has been reported that this ratio yields the best control over molecular weight and PD for styrene.[3] The bulk "living" free radical polymerization of **1** at 130 °C was compared to solution polymerization of **1** in either chlorobenzene or mixed xylenes, at reflux, using this bimolecular initiator ratio. As can be seen from Table 1, the neat polymerization of **1** resulted in good control of polydispersity (PD = 1.31), while the two solution polymerizations resulted in higher polydispersities (PD = 1.5−1.6). Further, it is interesting to note that there is little difference in the molecular weight and polydispersitiy between the TEMPO-mediated polymerizations in chlorobenzene or xylenes, despite the different chain transfer constants (C_s) of these two solvents (for a styrene polymerization at 60 °C: in chlorobenzene, $C_s = 0.133 \times 10^4$; in *p*-xylene, $C_s = 0.84 \times 10^4$).[14] A control polymerization of **1** in xylenes using BPO gave a polymer with a polydispersity of 2.6, indicating that TEMPO was affecting control over the radical polymerization of **1** in solution. However, it was also observed that the TEMPO-mediated solution polymerizations required a longer reaction time (72 h) to achieve high conversion (>70%) than the bulk polymerization (48 h). This reduction in the rate of the TEMPO-mediated solution polymerizations compared to bulk polymerizations can be attributed to the reduction in free radical concentration caused by the dilution effect of the solvent. In an attempt to further control the polydispersity of the solution polymerizations of **1**, the ratio of TEMPO to BPO was increased from 1.3:1 to 1.5:1 to 2:1 to 3:1. As shown in Table 1, no reduction in polydispersity was observed in the solution polymerizations of **1** with increasing ratio of TEMPO, the molecular weight distribution remaining constant at 1.5−1.6 (at equivalent conversion 70−75%), for all ratios. This is in contrast to the bulk "living" free radical polymerization of styrene in which higher TEMPO/BPO ratios yield lower polydispersity polymers.[3] Further as the ratio of TEMPO was increased, the reaction time required to obtained high conversion (>70%) was dramatically extended. For example, the 2:1 and 3:1 TEMPO/BPO ratios required polymerization time of greater than 96 h to obtain a conversion of >70%. The increase in polydispersity observed in the case of the solution polymerizations may be attributed to the longer polymerization time required to achieve high conversion. These extended reaction times permit the formation of new initiating species by autopolymerization, resulting in a broadening of the distribution. The reduced polymerization rate and broadening of the molecular weight distribution for the solution "living" free radical polymerization compared to the bulk are in agreement with a recent report on the effect of solvent on the "living" free radical polymerization of styrene.[9] As a result of the narrower polydispersities and faster reaction times obtained using bulk polymerization, all subsequent investigations on the "living" free radical polymerization of **1** were carried out neat.

Chart 1. Bimolecular and Unimolecular Initiating Systems



(4) TEMPO/BPO

(5) Unimolecular

Two initiating systems were investigated for the polymerization of 4-acetoxystyrene (**1**), a bimolecular system (**4**) (TEMPO/BPO = 1.3), and a unimolecular system (**5**), Chart 1. For both systems, **4** and **5**, it was observed that molecular weight is a linear function of the percent conversion and that narrow PD was maintained throughout the polymerization. However, as can be seen from Figure 2, for the TEMPO/BPO system there is a slight broadening of molecular weight distribution with increasing conversion, indicating a loss of control of the polymerization at higher conversion. In contrast, the unimolecular initiator results in low polydispersities even at high conversion. This loss of control in the TEMPO/BPO system may be due to the complex series of initiating steps of this bimolecular initiator, which have been shown to result in a variety of side reactions, leading to the loss of initiator efficiency.[15] The tighter control of molecular weight distribution obtained using the unimolecular initiator compared to the TEMPO/BPO system is in agreement with a recent study by Hawker et al. on the effect of initiating system on the "living" polymerization of styrene.[9] Due to the slightly narrower PD obtained using the unimolecular system, **5** was used to prepare a series of low PD poly(4-acetoxystyrene)s.

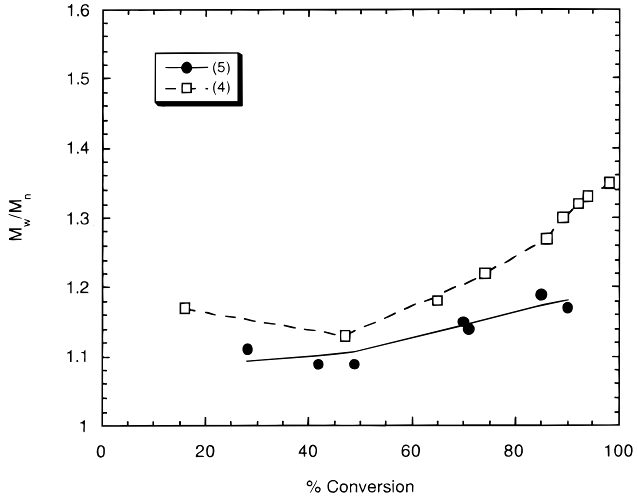


Figure 2. Effect of initiating system on PD Control.

Table 2. Narrow PD Poly(4-acetoxystyrene)

polymer	M_n calcd	M_n exptl	M_w/M_n
2a	2 525	2 857	1.20
2b	5 102	5 030	1.18
2c	8 100	8 997	1.10
2d	16 200	16 348	1.17
2e	32 330	29 961	1.29

Table 3. Narrow PD Poly(4-hydroxystyrene)

PHOST	M_n	M_w/M_n	T_g (°C)
3a	2 304	1.19	149
3b	3 874	1.18	172
3c	6 528	1.42	177
3d	12 726	1.38	185
3e	24 298	1.43	186

To determine the effect of PD and molecular weight on the thermal properties and dissolution behavior, a series of narrow PD PHOST polymers were prepared. One of the major advantages of "living" radical polymerizations is that the molecular weight of the polymer can be accurately controlled. As can be seen from Table 2, there is excellent agreement between the theoretical molecular weights calculated from the feed ratio of **1** relative to **5** and the experimentally determined molecular weights. Furthermore, the low molecular weight range (M_n < 20 000) of interest in microlithography is easily attainable. Excellent control of PD was observed; over the range of molecular weights prepared the molecular weight distribution was maintained below 1.3

Deacetylation of Poly(4-acetoxystyrene). The acetoxy groups of **2** were cleaved to generate poly(4-hydroxystyrene), under basic conditions, according to the literature procedure.[16] In some cases, a slight increase in polydispersity was observed upon deprotection of the acetoxy moiety (Tables 2 and 3). For example, the poly(4-acetoxystyrene) polymer **2d** with a PD of 1.17 showed an increase in PD to 1.38 upon deblocking (**3d**). The GPC traces of these polymers indicated that the deprotected PHOST exhibited high and low molecular weight shoulders, accounting for this increase in PD. It was postulated that this increase in PD may be due to chain-end recombination or other side reactions, under these deblocking conditions (NH_4OH, isopropyl alcohol, 82 °C). To address this problem, a lower boiling solvent (methanol, 65 °C) was used, and as can be seen from the two lowest molecular weight polymers (**2a** and **2b**), Tables 2 and 3, no increase in polydispersity was observed upon deblocking (**3a** and **3b**).

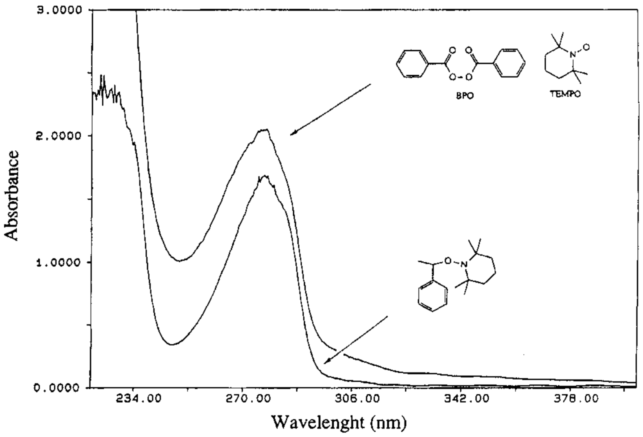
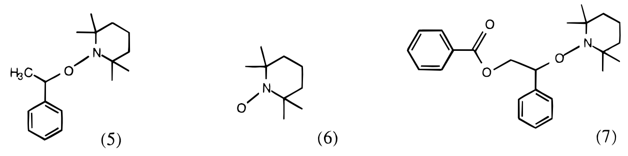


Figure 3. Effect of initiating system on deep-UV absorbance of PHOST (M_n ~ 4000).

Chart 2. Molecular Extinction Coefficients at 248 nm of Model Compounds 5, 6, and 7.



$\varepsilon_{248} = 301$ $\varepsilon_{248} = 1868$ $\varepsilon_{248} = 1581$

Effect of Initiating System on Deep-UV Absorbance. As has been previously reported, the initiating systems used and the resulting polymer end groups play an important role in the UV absorbance and the sensitivity of chemically amplified resist systems.[17] For example, it was shown that at high concentrations (low molecular weight polymers), nitrile end groups decrease the efficiency of the chemical amplification process and benzyloxy end groups increase deep-UV absorbance. To investigate the effect of the initiating systems **4** and **5** on deep-UV absorbance, the optical densities (OD/μm) at 248 nm of two low molecular weight PHOST polymers (M_n ~ 3500–4000), prepared using either **4** or **5**, were obtained. As can seen in Figure 3, for these low molecular weight polymers the absorbance within the deep-UV region (220–260 nm) of the PHOST prepared using the bimolecular system (**4**) is considerably higher ($OD_{248} = 1.1/\mu m$) than that for the PHOST prepared using the unimolecular initiator (**5**) ($OD_{248} = 0.32/\mu m$). The higher deep-UV absorbance resulting from the bimolecular TEMPO/BPO system precludes the use of this system from the preparation of polymers for deep-UV resist applications. To investigate the contributing factors to the deep-UV absorbance of these two polymers, the UV absorptions of three model compounds at 248 nm were determined: TEMPO (**6**); initiator **5**; and 1-benzyloxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (**7**). Compound **7** represents a unimer containing benzyloxy and TEMPO end groups, while **5** resembles a unimer with no benzyloxy moiety, Chart 2.

From comparison of the molecular extinction coefficients of **5**, **6**, and **7** at 248 nm (Chart 2), the absorption of the PHOST prepared using the TEMPO/BPO initiating system is high at 248 nm, due to the presence of excess TEMPO and benzyloxy end groups resulting from initiation by BPO. Further, it should be noted that the

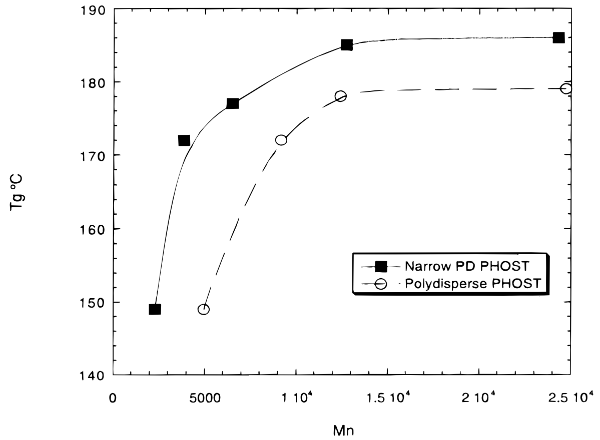


Figure 4. T_g comparison: "narrow" vs "broad" PD PHOST.

Table 4. "Broad" PD Poly(4-hydroxystyrene)

M_n	M_w/M_n	T_g (°C)
4 956	2.10	149
9 164	1.81	172
12 423	2.00	178
24 730	2.40	179

TEMPO free radical has a λ_{max} at 242 nm (ϵ = 1896); however, when the TEMPO radical is capped as in initiator **5**, the absorbance at 248 nm is reduced considerably. As a result of this reduction in absorbance the PHOST prepared using **5** has a considerably lower absorbance at 248 nm.

Physical Properties. It has been well documented that, for a constant PD, as the molecular weight of a polymer is increased there is a subsequent increase in glass transition temperature (T_g).[18] However, once a sufficiently high molar mass is obtained, the T_g remains essentially constant. This phenomenon can be rationalized by the reduction in free volume as the number of chain ends decreases with increasing molar mass. As expected a similar trend is observed in these narrow PD PHOST polymers, and polydisperse PHOST polymers of comparable molecular weight (Figure 4, Tables 3 and 4). From Figure 4, it can be seen that the T_g reaches a plateau value, for both "narrow" and "broad" PHOST polymers, above a molecular weight of 15 000 amu. Further, the "narrow" PD PHOST polymers exhibit higher glass transition temperatures than the "broad" PD PHOST over the entire range of molecular weights investigated. The difference in T_g between the "narrow" and "broad" PD polymers is more pronounced at lower molecular weights, e.g., ~20 °C at M_n = 5000, than at high molecular weights, e.g., ~5 °C at M_n = 25 000. The higher glass transition temperatures of the "narrow" PD PHOST compared to "broad" PD PHOST can be accounted for by a decrease in free volume. The thermal decomposition temperatures, as determined by TGA, for all of these PHOST polymers are similar, the onset of decomposition occurring at approximately 400 °C.

From ^{13}C NMR analysis, using the C1 aromatic carbon resonance (δ 139−135 ppm) attached to the polymer backbone, it was observed that the "living" radical PHOST exhibited only minor differences in tacticity from "conventional" radical PHOST, Figure 5. That is, the "living" radical polymer contains a slightly higher concentration of syndiotactic sequences and a slightly lower concentration of isotactic sequences relative to the conventional radically prepared polymer. In contrast, anionically prepared PHOST, using BuLi at −78 °C in THF, shows considerably more isotactic sequences than both the "living" free radical and "conventional" free radical polymers.

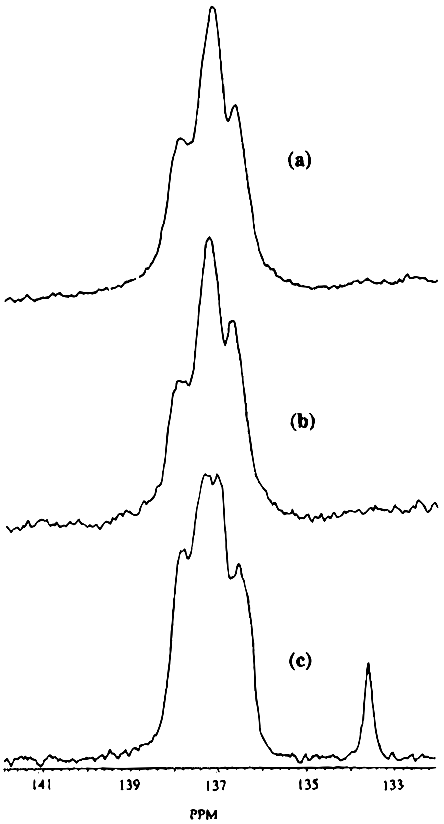


Figure 5. ^{13}C NMR of *ipso* carbon for (a) PHOST prepared by radical polymerization, (b) PHOST prepared by "living" free radical polymerization, and (c) PHOST prepared by anionic polymerization (BuLi/THF at −78 °C).

Effects of Molecular Weight and Polydispersity on Dissolution Rate. PHOST and its derivatives are the major component of chemically amplified positive and negative resists.[19] It has been reported that a chemically amplified resist employing PHOST with a narrow PD provided a higher resolution, relative to comparable resists prepared using a broad PD PHOST.[20] In the present study, we employed a number of narrow and broad PD PHOST polymers to investigate the effect of M_n, M_w, and PD on the dissolution behavior of this class of phenolic polymers, Tables 3 and 4. The molecular weight range covered by this study is quite wide (1000−50000).

The PHOST films were baked at 150 °C, to minimize any residual casting solvent. When phenolic polymer films are baked at a typical postapply bake temperature of ~100 °C, the concentration of residual solvents can amount to ~20%,[21] which can result in faster dissolution rates. The 150 °C bake provides reproducible and adequate dissolution rates in 0.21 N tetramethylammonium hydroxide (TMAH) (25 nm/s at 150 °C vs 49 nm/s at 110 °C for polymer **3e**).

The dissolution rates of the PHOST films as a function of the M_n and M_w are shown in Figures 6 and 7, for polymers with narrow and broad PD. The dissolution rate exponentially and rapidly decreases with increasing molecular weight when M_n is below ~10000 (M_w ~15000). Above these values, the effect of molecular weight on the dissolution rate is negligible.

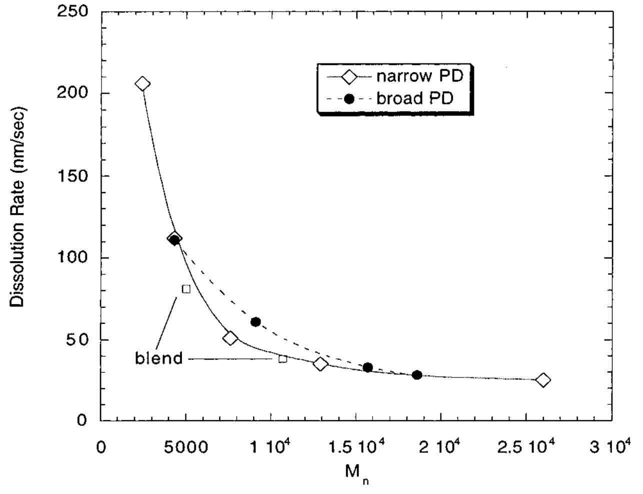


Figure 6. Effect of M_n on dissolution rate.

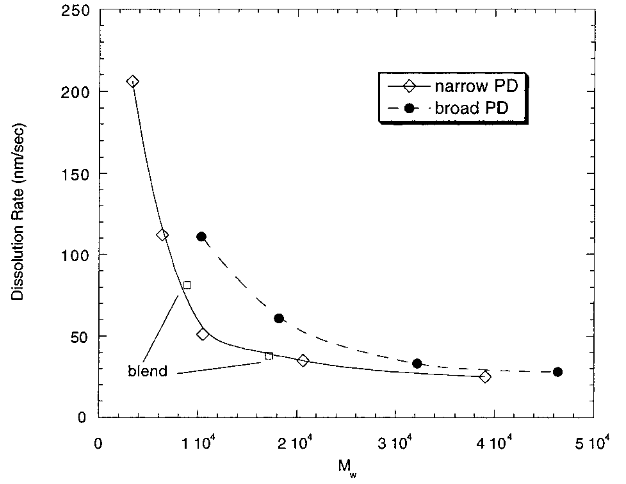


Figure 7. Effect of M_w on dissolution rate.

Rodriguez et al. reported a steady decrease in the dissolution rate of PHOST with increasing M_w in a sodium hydroxide aqueous solution, an abrupt increase in the rate at M_w ~20 000, and a constant rate above $M_w \sim 20\,000$.[22] As Figures 6 and 7 indicate, we only observe a monotonous molecular weight effect on the dissolution rate. The threshold-like molecular weight dependence of the dissolution rate is more pronounced in the case of narrow PD polymers. The broad PD polymers exhibit a more gradual change of the dissolution rate when the molecular weight is changed. Furthermore, the narrow PD polymers tend to dissolve more slowly than the broad PD polymers, especially in the molecular weight range of $M_n = 3000-15000$. Interestingly, PHOST commonly employed in resist formulations falls into this range. A closer examination of Figures 6 and 7 reveals that the effect of PD is much more significant in the M_w plot. In the M_n plot the difference between the narrow and broad PD polymers is very small, which suggests that the dissolution rate of PHOST can be directly correlated with the M_n, rather than with M_w. This observation in turn suggests that the dissolution of PHOST in aqueous base is controlled by lower molecular weight fractions, which represents a sharp contrast to the novolac systems reported by Willson et al.[13]

Blending Studies. As was the case with supercritical CO_2 extraction of novolac resins,[12,13] the ability to produce narrow PD provides a unique opportunity to gain further understanding of polymer properties. Blending of narrow PD polymers is an attractive, interesting, and useful technique in such studies. Two binary blends of narrow PD PHOST polymers are shown in Figures 6 and 7. These blends consisted of a 1:1 blend of polymers **3b** and **3c** and a 60:40 mixture of **3c** and **3d**, which gave $M_n = 5000$, $M_w = 8900$, PD 1.76 and $M_n = 10\,700$, $M_w = 17\,200$, PD = 1.6, respectively. Their dissolution rates in 0.21 N TMAH were 81 and 38 nm/s, respectively. Thus, the blends show dissolution rates that are an average of the rates of the individual components.

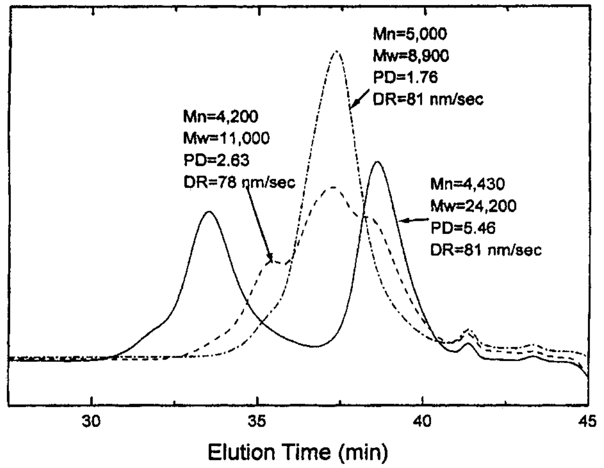


Figure 8. Monomodal, binary, and tandem blends.

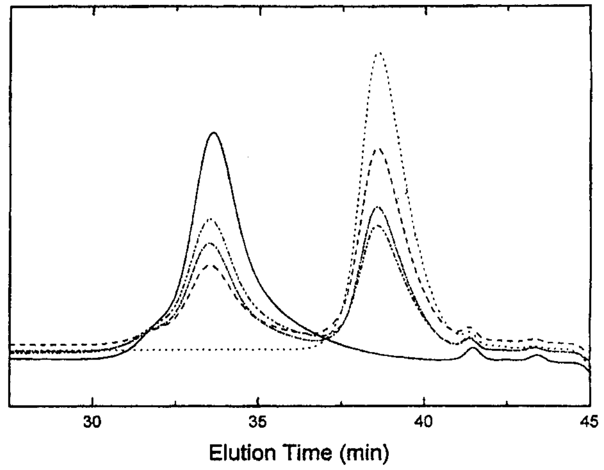


Figure 9. Binary blend compositions.

GPC curves, molecular weight data, and dissolution rates of three blends are presented in Figure 8. One binary blend consisting of a 1:1 mixture of polymer **3c** and **3d** gave a monomodal molecular weight distribution. The tandem blend was made by mixing equal amounts of polymers **3a** and **3e**, and the polymer with a trimodal distribution was prepared by mixing polymers **3a**, **3b**, **3c**, and **3d** (21.4:21.1:33.0:24.3). All these blends have an apparent GPC M_n of ~4500, while M_w and PD vary widely, and similar dissolution rates of ~80 nm/s. This study suggests that the dissolution rate of PHOST can be predicted from M_n irrespective of M_w or PD; the dissolution rate of PHOST in aqueous base is primarily governed by the lower molecular weight fractions.

Figure 9 and Table 5 show GPC curves, molecular weights, dissolution rates of the lowest (**3a**) and highest (**3e**) molecular weight, narrow PD polymers, and their

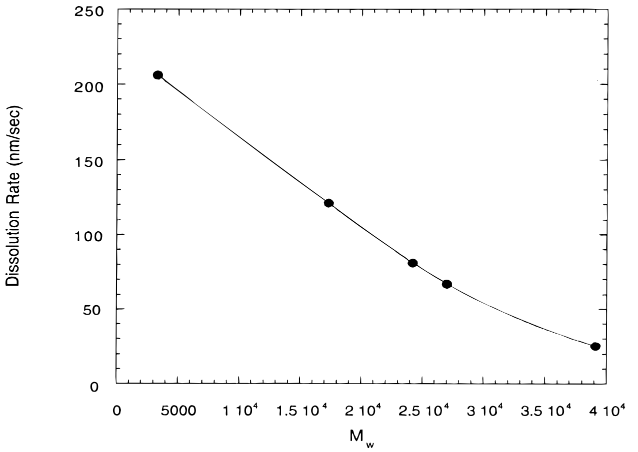


Figure 10. Dissolution rate vs M_w (binary blends).

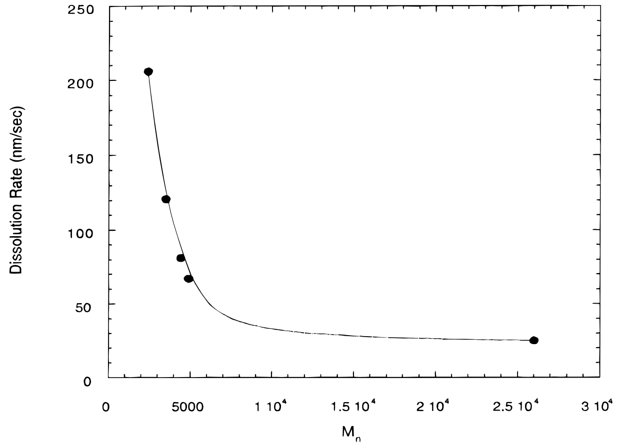


Figure 11. Dissolution rate vs M_n (binary blends).

Table 5. Dissolution Rates of Binary Blends

binary blend **3a/3e**	M_n	M_w	M_w/M_n	dissolution rate (nm/sec)
100/0	2 304	2 742	1.19	206
68/32	3 500	17 300	4.94	121
50/50	4 400	24 200	5.46	81
40/60	4 900	27 000	5.49	67
0/100	24 298	34 746	1.43	25

binary blends. The D.R. of the binary blends with tandem molecular weight distributions decreases as the concentration of the higher molecular weight component increases. Since the apparent M_w of the tandem blends is a linear function of the blend composition, the dissolution rate of such blends linearly decreases with increasing M_w (Figure 10). Further, because the apparent M_n of the tandem blends is an exponential function of the composition, the dissolution rates exhibit a sharp exponential decay with increasing M_n (Figure 11). The resemblance of Figure 11 to Figure 6 is quite astonishing and interesting.

The dissolution rates of all the PHOST systems (narrow and broad PD polymers and blends) with PD ranging from 1.2 to 5.5 are plotted against M_w in a log−log scale in Figure 12, which indicates that there is no straightforward relationship between the dissolution rate and M_w if the PD difference is not taken into consideration. In contrast, the similar plot of the dissolution rates of PHOST vs M_n can be nicely expressed by an exponential decay (linear log−log plot) even in a wide range of molecular weight distributions (Figure 13). Thus M_n is a more meaningful parameter for predicting the dissolution rates of PHOST. The dissolution rate of PHOST can be estimated if M_n is known. Although the molecular weights reported in this paper are not absolute but relative to polystyrene, our discussion is valid, as it deals with only mutual comparison of PHOST.

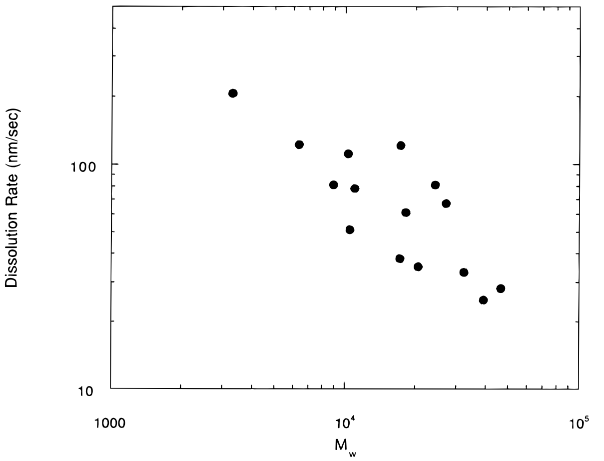


Figure 12. Dependence of dissolution rate on M_w.

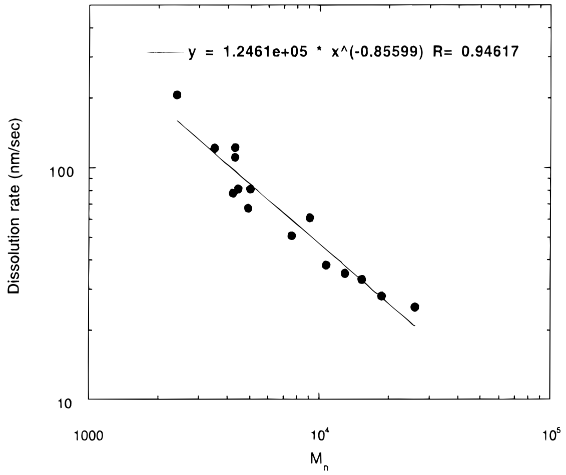


Figure 13. Dependence of dissolution rate on M_n.

Conclusions

The synthesis of a range of narrow PD PHOST via a “living” radical polymerization procedure has been demonstrated. The rate of the TEMPO-mediated radical polymerization of 4-acetoxystyrene is faster relative to styrene. Narrow molecular weight distribution was maintained throughout the polymerization of the 4-acetoxystyrene. It was observed that the solution “living” free radical polymerization of the acetoxy monomer resulted in reduced reaction rates and greater polydispersities, compared to bulk polymerization. Furthermore, at the low molecular weight range of interest in microlithography (M_n < 20000), the bimolecular initiating system (**4**) resulted in considerably higher absorbance within the deep-UV region (220−260 nm) relative to the unimolecular system (**5**). Model studies indicated that this increase in absorbance was due to the excess TEMPO used in the bimolecular system and the benzyloxy end groups.

The well-defined PHOST exhibit higher glass transition temperatures than broad PD PHOST. The higher T_g of the narrow PHOST is more evident at lower molecular weights. For example at $M_n = 5000$ the T_g is approximately 20 °C higher for the narrow PD polymer. A sharp increase in DR is observed as the M_n decreases below 10 000 for the narrow polymers, compared to a more gradual increase in DR for the broad polymers. That is, the threshold-like molecular weight dependence of DR in aqueous base is more pronounced in the case of narrow PD PHOST. Blending studies of the dissolution behavior of PHOST indicate that DR can be correlated with M_n. This study suggests that the dissolution behavior of PHOST in aqueous base is primarily governed by the lower molecular weight fractions. The DR of PHOST vs M_n can be expressed as an exponential decay, and as a result the DR can be estimated if M_n is known. In contrast, there is no straightforward relationship between DR and M_w.

Acknowledgment. We would like to thank M. Denison (Shipley) for GPC measurements.

References and Notes

(1) Ito, H.; Knebelkamp, A.; Lundmark, S. B. *Polym. Mater. Sci. Eng.* **1993**, *68*, 34.
(2) Ito, H.; England, W. P.; Ueda, M. *Makromol. Chem., Macromol. Symp.* **1992**, *53*, 139.
(3) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(4) Rizzardo, E. *Chem. Aust.* **1987**, *54*, 32.
(5) Matyjaszewski, K.; Gaynor, S.; Wang, J. S. *Macromolecules* **1995**, *28*, 2093.
(6) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11314.
(7) Hawker, C. J.; Hedrick, J. L. *Macromolecules* **1995**, *28*, 2993.
(8) Hawker, C. J. *Angew Chem., Int. Ed. Engl.* **1995**, *34*, 1456.
(9) Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J. *Macromolecules* **1996,** *29*, 5245.
(10) Kazmaier, P. M.; Daimon, K.; Georges M. K.; Gordon, K. H. *Polym. Prepr.* **1996**, *37*, 485.
(11) Keoshkerian, B.; Georges M. K.; Boils-Boissier, D. *Macromolecules* **1995**, *28*, 6381.
(12) Allen, R. D.; Rex Chen, K. J.; Gallagher-Wetmore, P. M. *Proc. SPIE* **1995**, *2438*, 250.
(13) Tsiartas, P. C.; Simpson, L. L.; Qin, A.; Willson, C. G.; Allen, R. D.; Krukonis, V. J.; Gallagher-Wetmore, P. M. *Proc. SPIE* **1995**, *2438*, 261.
(14) Young, L. J. In *Polymer Handbook, 2nd Edition*; Brandrup, J., Immergut. E. H., Eds.; John Wiley & Son: New York, 1975.
(15) Moad, G.; Rizzardo, E.; Solomon, D. H. *Macromolecules* **1982**, *15*, 909.
(16) Sheehan, M. T.; Shen L. US Patent, 5,136,011, 1992.
(17) Ito, H.; England, W. P.; Lundmark, S. B. *Proc. SPIE* **1992**, *1676*, 2.
(18) Fox, A.; Loshaek, S. *J. Polym. Sci.* **1955**, *15*, 371.
(19) Ito, H. Deep UV Resist Systems. In *Radiation Curing in Polymer Science and Technology*; Fouassier, J. P., Rabck, F., Eds.; Elsevier: London, 1993; Vol. 4, Chapter 11, p 237.
(20) Kawai, Y.; Tanaka, A.; Matsuda, T. *Jpn. J. Appl. Phys.* **1992**, *31*, 4316.
(21) Hinsberg, W. D.; MacDonald, S. A.; Snyder, C. D.; Ito, H.; Allen, R. D. In *Polymers for Microelectronics: Resist and Dielectrics;* Thompson, L. F., Willson, C. G., Tagawa, S., Eds.; ACS Symposium Series 537; American Chemical Society: Washington, DC, 1993; pp 101.
(22) Long, T.; Rodriguez, F. *Proc. SPIE* **1991**, *1466*, 188.

MA961129P