

# Dissolution behavior of fluoroalcohol substituted polystyrenes

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## ABSTRACT

$\alpha$ -Fluoroalcohols have been proposed as transparent, base-soluble functional groups for use in the design of new 157 nm photoresist polymers. The two most common and easily prepared fluoroisopropanol groups are *bis*-trifluoromethyl carbinols (hexafluoroalcohol) and methyl-trifluoromethyl carbinols (trifluoroalcohol). This paper describes studies designed to assess the suitability of both of these functionalities as acidic groups. Dissolution rate studies were carried out on polystyrene films that incorporate these groups. The dissolution rates of the sample polymers were compared to that of poly(hydroxystyrene) (PHOST) to provide a reference for the measurements. It was found that the trifluoroalcohol polymers do not exhibit any solubility in basic media, while the hexafluoroalcohol polymers dissolve rapidly relative to PHOST in 0.13N TMAH. Further, it was found that the two fluoroalcohol polymers can be blended to adjust the inherent dissolution rate of the resin and that the hexafluoroalcohol polymer is sensitive to incorporation of classical dissolution inhibitors. The study concludes that hexafluoroalcohol is a promising candidate for incorporation into the design of 157 nm photoresists.

Keywords: 157 nm photolithography, hexafluoroalcohol, trifluoroalcohol, dissolution rates, *bis*-trifluoromethyl carbinol, methyl-trifluoromethyl carbinol, poly(hydroxystyrene)

## 1. INTRODUCTION

### 1.1 Base-soluble functional groups for 157 nm photolithography

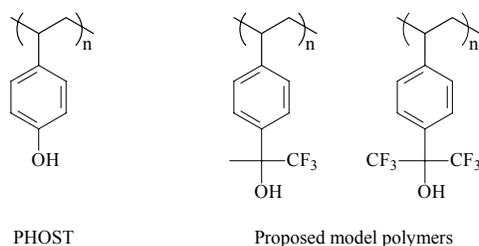
The push to design photoresists that provide high performance at 157 nm has led to much research on *bis*-trifluoromethyl carbinols, which currently appear to offer one of the best combinations of acidity and transparency of the proposed base-soluble functional groups for use at 157 nm.<sup>1</sup> Our research group has therefore focused a great deal of effort on the preparation of monomers and polymers that contain fluorinated isopropanol groups.<sup>2-4</sup>

One drawback to these compounds is that they must be prepared via Grignard synthesis with hexafluoroacetone, a compound that is expensive, toxic, and difficult to work with, as it is a gas at room temperature. A possible alternative is to use 1,1,1-trifluoroacetone in place of hexafluoroacetone, to produce an alcohol with one  $\alpha$ -methyl group and one  $\alpha$ -trifluoromethyl group. Trifluoroacetone is less expensive, less dangerous, and much easier to work with, as it can be stored as a liquid at refrigerated temperatures. Others have reported<sup>5</sup> that an alcohol with one  $\alpha$ -trifluoromethyl group has a  $pK_a$  of 14.1, compared to a  $pK_a$  of 11.2 for the hexafluoroalcohol. Though less acidic, it seemed reasonable that methyl-trifluoromethyl carbinols would still dissolve in base aqueous media. So we set out to determine whether this functional group is sufficiently acidic to render polymers like styrene soluble under standard resist development conditions.

### 1.2 Comparative dissolution rate study

Two model polymers were prepared that differ only in the presence of either one or two  $\alpha$ -trifluoromethyl groups. The dissolution rates of the compounds in base developer were used to evaluate the suitability of the two groups as base-soluble units for resists. All dissolution rate measurements were made relative to a standard polymer, poly(hydroxystyrene) (PHOST), to determine the suitability of these compounds for use in 157 nm photoresists. Another study<sup>6</sup> had shown that the hexafluoroalcohol-substituted analog of poly(styrene) functioned in a resist film. We chose to prepare this polymer and its trifluoromethyl analog (**Figure 1**). Both model polymers are structurally similar to PHOST, but derive their acidity from the trifluoromethyl carbinol rather than the phenolic functionality.

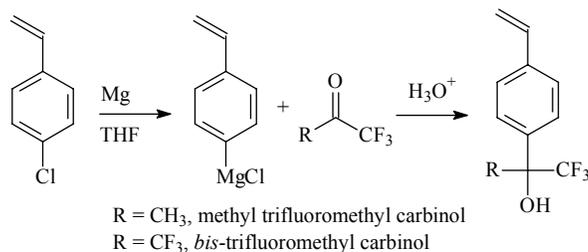
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**Figure 1:** PHOST and the suggested model polymers

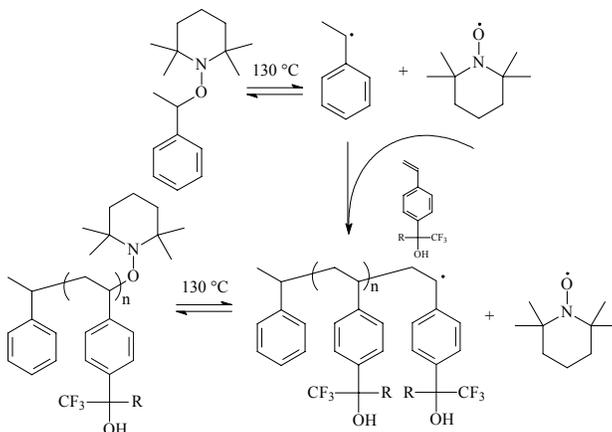
### 1.3 Overview of study

The easiest route to the target monomers was via Grignard synthesis with 4-chlorostyrene and either 1,1,1-trifluoroacetone or hexafluoroacetone (**Figure 2**).<sup>7</sup>



**Figure 2:** Grignard synthesis with trifluoroacetone

Recent studies have shown that the TEMPO unimer initiator, 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)-ethane, can be used to perform “living” free radical polymerizations of styrene monomers (**Figure 3**) to provide excellent molecular weight control and narrow polydispersities.<sup>8</sup> Nearly monodisperse samples of PHOST are available commercially, so it was decided to select three PHOST molecular weights, and then prepare samples of fluoroalcohol substituted analogs by the TEMPO system with nearly identical molecular weights. Having three different molecular weights for each polymer allowed for the examination of dissolution rate as a function of both chemical functionality and molecular weight. The effect of polydispersity (PD) on dissolution rate was neglected since all of the polymers would have similar and very narrow PDs.



**Figure 3:** TEMPO unimer initiator living polymerization process

The model polymers were synthesized and characterized, and spin coated on silicon wafers. The dissolution behavior of the films measured. Blends of the two experimental polymers were also coated and their dissolution properties measured. The effect of the dissolution inhibitor 4,8-bis[(2-diazo-1-oxo-naphthoquinone-5-sulfonyloxy)methyl] tricyclo[5.2.1.0]-decane, or TDQ, on the dissolution rate was quantified. Finally, the UV-Vis absorption spectra of films of all three polymers was measured.

## 2. EXPERIMENTAL

### 2.1 Synthesis of monomers

4-(2-(1,1,1-trifluoro-2-propanol))styrene Into a dry 500-mL flask was placed 3.51 g of magnesium (0.144 mol) and 10 mL of dry THF. To this was added 4 g of 4-chlorostyrene, and the mixture heated to reflux. Once the Grignard reaction initialized, 200 mL of dry THF was added, the solution was heated to reflux, and the remainder of the initial 20 g of 4-chlorostyrene (0.144 mol, 1 eq.) was added dropwise. After stirring at reflux for 30 minutes, the reaction vessel was cooled to 0 °C, and 16.17 g of 1,1,1-trifluoroacetone (0.144 mol, 1 eq) dissolved in 50 mL of dry THF was added slowly. The resulting mixture was stirred under nitrogen overnight at room temperature, cooled to 0 °C and 300 mL of 3M hydrochloric acid was added to obtain two clear phases. The volume of organics was increased with 300 mL of diethyl ether. The organic layer was separated and washed with 300mL of 4M HCl, and then with 300 mL of water. The organic phases were combined and dried over MgSO<sub>4</sub>. Following filtration, the solvent was removed under reduced pressure to give the crude product as a clear, yellowish liquid. A few crystals of hydroquinone were added to the crude product, which was then distilled under reduced pressure to give the desired product as a clear, colorless oil. Bp @ 4mmHg = 92-95 °C. Yield: 20.55 g (66%). FTIR (NaCl, cm<sup>-1</sup>): 3441 (O-H), 3088 (aromatic C-H), 3003 (C-H), 1630 (C=C), 1615, 1498 (benzene ring) 1165 (-CF<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 7.57-7.40 (q, 4H, aromatic), 6.78-6.66 (2d, 1H, vinyl), 5.85-5.75 (d, 1H, vinyl), 5.36-5.26 (d, 1H, vinyl), 2.49 (s, 1H, -OH), 1.78 (s, 3H, -CH<sub>3</sub>). Mass spectrum (mass = 216, m/e): 217 (M+H<sup>+</sup>).

4-(2-(1,1,1,3,3,3-hexafluoro-2-propanol))styrene Into a dry 500-mL flask was placed 3.51 g of magnesium (0.144 mol) and 10 mL of dry THF. To this was added 4 g of 4-chlorostyrene, and the mixture heated to reflux. Once the Grignard reaction initialized, 200 mL of dry THF was added, and the remainder of the initial 20 g of 4-chlorostyrene (0.144 mol, 1 eq) was added dropwise. After stirring at reflux for 1 hour, the reaction vessel was cooled to -78 °C, and 25 g of hexafluoroacetone (1.05 eq) was collected at -78 °C and added dropwise. The resulting mixture was stirred under nitrogen overnight at room temperature, cooled to 0 °C and then 2M hydrochloric acid added to produce two clear phases. The volume of organics was increased with 200 mL of diethyl ether. The organic layer was separated and washed twice with 300 mL of 1M HCl, and washed twice again with 300 mL of water. The organics were collected and dried over MgSO<sub>4</sub>. Following filtration, the solvent was removed under reduced pressure to give the crude product as a clear, yellowish liquid. A few crystals of hydroquinone were added to the crude product, which was then distilled under reduced pressure to give a clear, colorless oil, which was shown by <sup>1</sup>H NMR to be the desired product as a 4:1 complex with THF. Bp @ 10 mmHg = 78-83 °C. Yield: 17.09 g (41%). FTIR (NaCl, cm<sup>-1</sup>): 3603, 3544 (O-H), 3081 (aromatic C-H), 2983 (=C-H), 1633 (C=C), 1610, 1516 (benzene ring) 1266, 1212, 1165 (-CF<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 7.72-7.46 (q, 4H, aromatic), 6.80-6.68 (2d, 1H, vinyl), 5.93-5.82 (d, 1H, vinyl), 5.44-5.35 (d, 1H, vinyl), 4.05 (s, 1H, -OH). Mass spectrum (mass = 270, m/e): 271 (M+H<sup>+</sup>).

### 2.2 Polymerizations

The molecular weights M<sub>n</sub> selected for study were five thousand, eight thousand, and 15,000 g/mol. The polymerizations were carried out in bulk. The general procedure for the polymerizations was to combine the monomer with the TEMPO unimer in appropriate ratio to achieve the desired molecular weight, and to heat the resulting mixture to 130 °C for 100 hours under a nitrogen blanket. Several solvents were tested to obtain optimal precipitation conditions. The most successful options are precipitation from toluene into hexane or from dichloromethane into hexane. All polymers were precipitated twice, and yields for the entire synthesis were typically between 50 and 60%. It should be noted that due to the tendency of trifluoromethyl carbinols (especially *bis*-trifluoromethyl carbinol) to complex with THF, attempts to precipitate the crude polymers from THF into other solvents resulted in large losses in yield. The absence of any remaining monomer or initiator in the final products was confirmed by <sup>1</sup>H NMR.

### 2.3 Dissolution rate studies

For the dissolution rate study, the polymers were dissolved in propylene glycol monomethyl ether acetate (PGMEA) as a casting solvent, in solutions that were 20-30% wt/wt. Solutions were filtered and then spin coated on 4 inch silicon wafers, at 1500-2000 rpm, with a post application bake (PAB) of 130 °C for 90 s. The resulting films were between 700 and 2400 nm thick. Both of the model polymers were coated without prepping the wafer with HMDS. Treating the wafer with HMDS before spin coating typically improves adhesion and the quality of the film, but it was found that for these fluorinated polymers that thicker and more uniform films could be obtained without HMDS. After spin coating, film thicknesses were measured. All dissolution rate measurements were made with 0.13N TMAH. The procedure was identical for the blended films and the films with inhibitor added. The UV-Vis absorption data was obtained by spin coating the polymers onto a

quartz wafer under identical conditions, measuring the absorbance through the film, and then dividing by the film thickness to obtain absorbance per micron.

### 3. DATA

Table 1 is a summary of the GPC data for the prepared polymers, and Table 2 summarizes the spin coating conditions and the data obtained from the dissolution rate measurements.

	Trifluorinated polymers			Hexafluorinated polymers			
Intended $M_N$	5000	8000	15000	5000	8000	8000	15000
Molecular weight ( $M_W$ )	2800	4500	3900	5700	6900	9000	16800
Polydispersity	1.33	1.66	1.59	1.53	1.46	1.49	1.99

Table 1: GPC data

	PHOST				Hexafluorinated polymers				Trifluorinated polymers		
Molecular weight ( $M_W$ )	3000	5000	8000	15000	5700	6900	9000	16800	2800	4500	3900
Polydispersity	1.1	1.1	1.08	1.1	1.53	1.46	1.49	1.99	1.33	1.66	1.59
Polymer wt% in PGMEA	20	20	20	20	33.3	33.3	33.3	30	20	20	20
HMDS on spin coat	yes	yes	yes	yes	no	no	no	no	no	no	no
Spin speed (rpm)	1500	2000	2000	2000	1500	1500	1500	1500	1500	1500	1500
Film thickness (nm)	1420	1390	1440	1700	1800	1900	2400	2050	700	870	970
Dissolution rate (nm/s)	$34.7 \pm 0.4$	$16.2 \pm 0.2$	$4.2 \pm 0.3$	$0.94 \pm 0.06$	$120 \pm 10$	$91 \pm 1$	$78 \pm 9$	$62.9 \pm 0.7$	0	0	0

Table 2: DRM data

### 4. RESULTS

#### 4.1 Dissolution behaviors of fluorinated polymers

The most immediately striking result is that the polymer bearing the methyl-trifluoromethyl carbinol group is not soluble. This result was confirmed by unsuccessful attempts to dissolve films in stronger concentrations of TMAH (0.26N) and in both weak and strong solutions of potassium hydroxide (0.5N and 3.0N KOH). This behavior is very surprising given the reported  $pK_a$  of the methyl-trifluoromethyl carbinol. Also striking is the rapid (*ca.* one order of magnitude faster) dissolution of the *bis*-trifluoromethyl carbinol polymers relative to PHOST.

The relationship between dissolution rate and molecular weight is shown in **Figure 4**. The dependence has the expected exponential relationship,<sup>9</sup> but the slopes of the lines differ substantially.

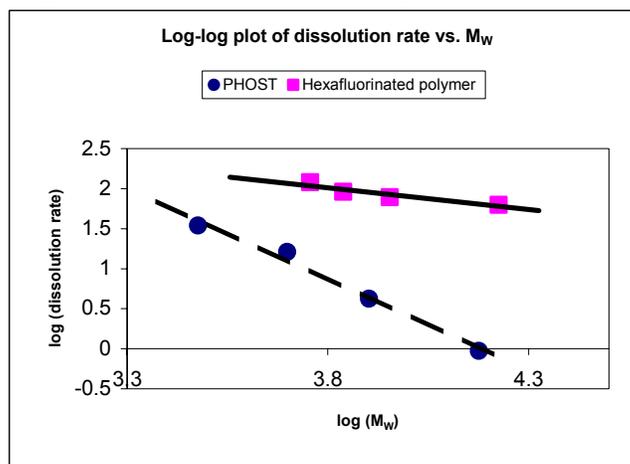
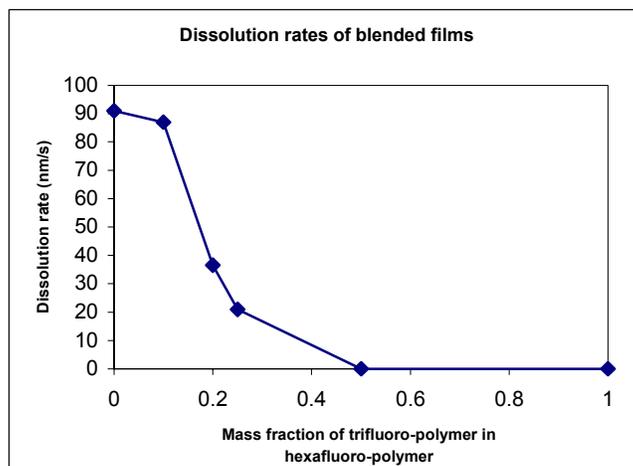


Figure 4: Exponential dependence of molecular weight on dissolution rate

## 4.2 Blending Studies

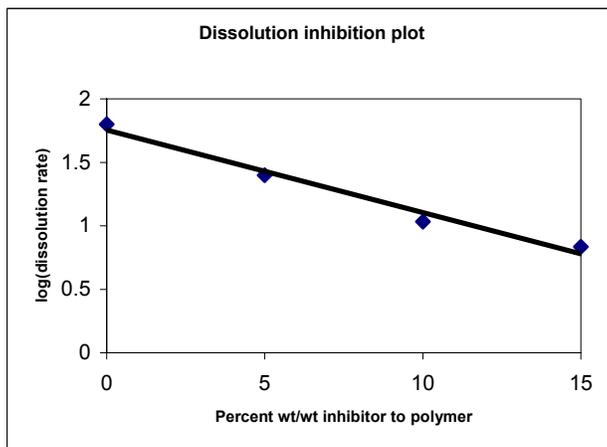
Blended formulations of the two polymers were prepared and spin coated, and the dissolution properties measured. The two polymers chosen for blending were the hexafluoroalcohol polymer of  $M_w$  6900 and the trifluoroalcohol polymer of  $M_w$  4500. We were pleased to find that these polymers are phase compatible over a wide range of compositions. This sort of behavior has been seen before.<sup>10</sup> **Figure 5** shows the dissolution rates of the blended films as a function of composition. The results show that the trifluoroalcohol polymer significantly inhibits the dissolution of the hexafluoroalcohol polymer in amounts as low as 20 weight % of the polymer film. This data suggests that blends of the two polymers could be used to fine tune the dissolution rate of the base resin.



**Figure 5:** The effect of blending the two fluoropolymers on dissolution rate

## 4.3 Dissolution Inhibitor

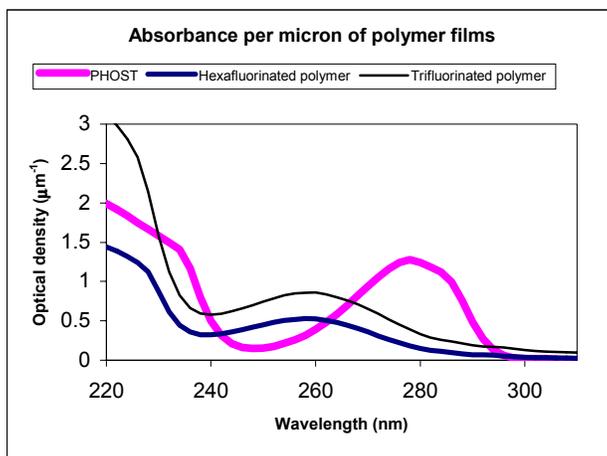
A previous study<sup>6</sup> had reported that the hexafluoroalcohol polymer was sensitive to dissolution inhibitors that were functionalized derivatives of bisphenol A. We were interested in whether an inhibitor similar to diazonaphthoquinone (DNQ) would inhibit this polymer. The dissolution inhibitor TDQ was added to formulations of the hexafluoro-polymer of  $M_w$  16800 as 5, 10 and 15 weight % of polymer weight in order to determine whether base solubility could be inhibited by a photoactive compound. Significant inhibition of the dissolution rate was observed, falling from 63 nm/s in uninhibited polymer all the way to 7 nm/s with 15 wt % TDQ. One uncertainty in this measurement is that the PAB conditions (130 °C for 90 s) may have led to small amounts of thermal decomposition of the inhibitor. Further research is being conducted to clarify this issue. **Figure 6** is similar to a Meyerhofer plot, showing the log of dissolution rate against wt % inhibitor.<sup>11</sup> The significant finding is that the hexafluoroalcohol group is sensitive to DNQ-type dissolution inhibitors.



**Figure 6:** Modified Meyerhofer plot of the dissolution inhibitor TDQ in the hexafluoroalcohol polymer of  $M_w$  16800

#### 4.4 UV-Vis absorbance measurements

Finally, UV-Vis absorbance measurements were made for the three polymers. **Figure 11** shows that the presence of the geminal trifluoromethyl groups significantly shifts the absorbance peak for the aromatic ring relative to hydroxystyrene but the polymers are not more transparent at 248 nm than PHOST. A previous study<sup>6</sup> reported the absorbance of PHOST and the hexafluoroalcohol-styrene polymer at 248 nm to be  $0.13$  and  $0.11 \mu\text{m}^{-1}$  respectively. Our PHOST showed an absorbance of  $0.15 \mu\text{m}^{-1}$ , but the hexafluorinated polymer was much higher,  $0.42 \mu\text{m}^{-1}$ . The source of this difference is not clear. It may be related to the initiator end groups on our polymer. Also, the absorbance peak of the commercial sample of PHOST centered near 280 nm is much larger in these measurements than in the previous study.



**Figure 11:** UV-Vis absorbance spectra for polymer films

## 5. CONCLUSIONS

A study of the dissolution behavior of polymer films containing the methyl-trifluoromethyl carbinol moiety (trifluoroalcohol) and the *bis*-trifluoromethyl carbinol moiety (hexafluoroalcohol) has demonstrated that the trifluoroalcohol group is not sufficiently acidic for use in photoresist applications that are to be developed with aqueous base. In fact, the trifluoroalcohol substituted polystyrene exhibits no apparent solubility in basic aqueous media. The hexafluoroalcohol, exhibits rapid dissolution rate relative to poly(hydroxystyrene). This fact alone would suggest that the *bis*-trifluoromethyl carbinol moiety is a promising candidate for further research towards use in 157 nm photoresists. However, this group shows additional promise by its ability to be inhibited by a photoactive compound in small concentrations. Also, the early indications of phase compatibility between these two fluorinated polymers opens up exciting lines of research into how the inherent dissolution properties of the resin can be adjusted by blending.

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## REFERENCES

1. Patterson, K.; Somervell, M.; Willson, C. G. *Solid State Technol.* **2000**, *43*(3), 41-48.
2. Patterson, K.; Yamachika, M.; Hung, R.; Brodsky, C.; Yamada, S.; Somervell, M.; Osborn, B.; Hall, D.; Dukovic, G.; Byers, J.; Conley, W.; Willson, C. G. *Proc. SPIE* **2000**, *3999*, 365-374.
3. Chiba, T.; Hung, R.; Yamada, S.; Trinquet, B.; Yamachika, M.; Brodsky, C.; Patterson, K.; Vander Heyden, A.; Jamison, A.; Lin, S. H.; Somervell, M.; Byers, J.; Conley, W.; Willson, C. G. *J. Photopolym. Sci. Technol.* **2000**, *13*, 657-664.

4. Hung, R.; Tran, H. V.; Trinqué, B.; Chiba, T.; Yamada, S.; Osborn, B.; Brodsky, C.; Yamachika, M.; Brodsky, C.; Vander Heyden, A.; Sanders, D.; Grubbs, R.; Klopp, J.; Frechet, J.; Thomas, B.; Shafer, G.; DesMarteau, D.; Conley, W.; Willson, C. G. *Proc. SPIE, this volume*, **2001**.
5. Gandler, J. R.; Jencks, W. P. *J. Amer. Chem. Soc.* **1982**, *104*, 1937-1951.
6. Przybilla, K. J.; Roschert, H.; Pawlowski, G.; *Proc. SPIE* **1992**, *1672*, 500-512.
7. Reynolds, D. W.; Cassidy, P. E.; Johnson, C. G.; Cameron, M. *Polym. Prepr.* **1990**, *31(1)*, 299-300.
8. Georges, M. K.; Veregrin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules*, **1993**, *26*, 2987-2988.
9. Tsiartas, P. C.; Flanagan, L. W.; Henderson, C. L.; Hinsberg, W. D.; Sanchez, I. C.; Bonnacaze, R. T.; Willson, C. G. *Macromolecules* **1998**, *30(16)*, 4656-4664.
10. Pearce, E. M.; Kwei, T. K.; Min, B. Y. *J. Macromol. Sci. Chem.* **1984**, *A21*, 1181-1216.
11. Meyerhofer, D. *IEEE Trans. Electron. Devices* **1980**, *ED-27*, 921-926.