Anionic Synthesis of Poly(9-methyl-9-trimethylsilyl-2-vinylfluorene) (PMSVF). Spontaneous Deprotection−Protonation of PMSVF with Potassium Methoxide/Methanol Gives Poly(9-methyl-2-vinylfluorene)

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Received February 24, 2003

ABSTRACT: The BuLi or potassium naphthalide initiated polymerization is described of 9-methyl-9-trimethylsilyl-2-vinylfluorene (MSVF) in tetrahydofuran at −78 °C. The purification is described of this monomer and of 9,9-dimethyl-2-vinylfluorene (DMVF) by polystyrene (PS) beads that are functionalized with 9-alkylfluorenyllithium groups that act as both scavengers and indicators. In both Li and K ion mediated polymerizations of MSVF, narrow molecular weight distribution PMSVFs are obtained. For the Li ion mediated termination of the living polymer by methanol, the PMSVF is readily isolated. However, in the presence of potassium ion a spontaneous and catalytic deprotection occurs of the trimethylsilyl group by potassium methoxide (MeOK). This reaction appears to be prevented in the case of the Li ion by strong ion pair or ionic aggregate interactions of MeOLi.

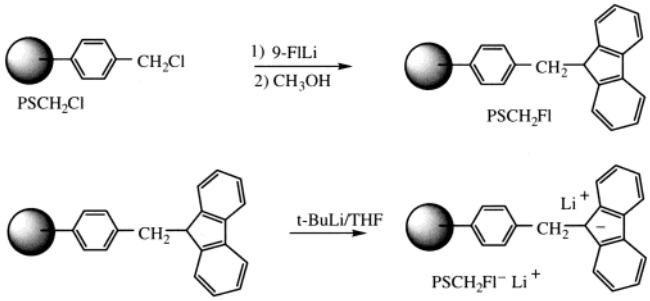
Introduction

Alkyl-substituted polyfluorenes have been extensively studied for optical devices due to their excellent optical and electroluminescent properties.[1,2] Thus, highly efficient polyfluorene-based organic light-emitting diodes (OLED) have been reported.[2a,b] Polyfluorenes also possess thermotropic liquid crystallinity, as reported by Grell et al.[2c] Recent OLEDs based on aligned liquid-crystalline polyfluorenes showed an electroluminescence with high, linear polarization ratios.[2d,e] On the other hand, due to fluorene's large molar adsorptivity (∼10^4) in the near UV and high fluorescence quantum yield (∼0.8),[3] vinylaromatic polymers containing fluorene pendent groups may be of interest as photon-harvesting materials.[4]

We recently reported the anionic polymerization of 9,9-dimethyl-2-vinylfluorene (DMVF) in THF at −78 °C, the molecular weight distributions of which indicated a living polymerization.[5] The presence of relatively acidic 9-fluorenyl protons is an attractive feature of polymeric fluorene derivatives, allowing relatively convenient alkylations and other pre- or postpolymerization functionalization.[6,7] These considerations also apply to monomer synthesis as the alkylation at the 9-position can be carried out in the presence of the 2-vinyl substituent.[8] Thus, the polymerization of 9-alkyl-9-trimethylsilyl-2-vinylfluorene should be possible, and deprotection of the trimethylsilyl groups with fluoride or other anions followed by protonation or other reactions of the resulting fluorenyl anion would allow the synthesis of the corresponding poly(2-vinyl-9-alkylfluorenes) or functionalized poly(vinylfluorenes). Due to the acidity of the 9-fluorenyl protons, such polymers are currently unaccessible by anionic polymerization. Although the acidic protons in the 9-position of conjugated polyfluorenes dramatically decrease the photochemical and chemical stability of such polymers leading to the formation of on-chain keto defects,[1a] this may not be true to the same degree in the case of unconjugated poly(vinylfluorene).

Here we report the synthesis and anionic polymerization of 9-methyl-9-trimethylsilyl-2-vinylfluorene (MSVF) and the subsequent deprotection/protonation of PMSVF to give poly(9-methyl-2-vinylfluorene) (PMVF).

Scheme 1. Synthesis of Polystyrene−Fluorenyllithium Beads ("Red Beads")



Experimental Section

Materials. Tetrahydrofuran (THF) was purified by distillation on the vacuum line from Na/K benzophenone, followed by bulb-to-bulb distillation from 1,1,4,4-tetraphenylbutane lithium. Anhydrous methanol was degassed and stored in ampules equipped with break seals. Chlorotrimethylsilane (Aldrich, 98%) was stirred over CaH_2 and distilled on the vacuum line. Naphthalene (Aldrich, 99+%) and fluorene (Aldrich, 98%) were recrystallized from methanol prior to use. Potassium naphthalide (K-Naph) was prepared by stirring naphthalene in THF over a potassium mirror for 20 min at 0 °C and used immediately. 2-Acetylfluorene (Aldrich, 98%) and lithium diisopropylamide (LDA, Aldrich, as a 2.0 M solution in heptane/THF/ethylbenzene) were used without further purification. Deuterated methanol (methanol-d_4) was purchased from Cambridge Isotope Laboratories, Inc.

Synthesis of Polystyrene−Fluorenyllithium (PS−FlLi) Beads. Chloromethylated cross-linked polystyrene beads with a chloride content of 1.0 ± 0.05 mequiv/g (Acros Organics) (1.40 g, 1.40 × 10^{-3} mol of Cl equiv) were evacuated under high vacuum followed by addition of 30 mL of purified THF. The mixture was stirred for 1/2 h, allowing swelling of the beads. A slight excess of fluorenyllithium (1.45 × 10^{-3} mol), prepared by the reaction of *n*-BuLi with fluorene in THF, was then added (Scheme 1). The mixture was stirred for 1 h followed by addition of methanol in order to protonate the excess fluorenyllithium. The fluorene-functionalized beads were then

10.1021/ma030133f CCC: $25.00
Published on Web 09/18/2003

Table 1. Block Copolymerization of PDMVF−Li with Styrene Monomer[a]

		PDMVF						
			M_n			PDMVF−PS[b]		
no.	initiator (mmol)	DMVF (mmol)	calcd	obsd[c] (SEC)	obsd[d] (NMR)	PDI[c]	M_n	PDI[c]
1	0.0264	0.909	7600	8670[e]	8070	1.07	24 100[f]	1.80
2	0.0384[b]	0.981	5620	6580[e]	6400	1.10	19 100[f]	1.03

[a] Polymerization in THF at −78 °C for 10 min. PDMVF precursor obtained by sampling (see Experimental Section). Addition of styrene/THF (2 mmol). [b] PS content of sample 2 obtained from proton NMR integration is 78 mol %. [c] SEC, polystyrene standards. [d] M_n determined by proton NMR intergration of the *tert*-butyl end goup. [e] Corrected for the MW of the DMVF units. [f] Based on PS standards only.

washed with THF, chloroform, and methanol and dried under high vacuum at 40 °C for 24 h.

Subsequently, polystyrene−fluorene (PS−Fl) beads (0.40 g, 4.0×10^{-4} mol of fluorenes) were placed in a flamed flask. After evacuation and addition of 10 mL of purified THF and cooling to −78 °C, a solution of *t*-BuLi in hexane (3.8×10^{-4} mol) was added. The characteristic red color of the 9-alkylfluorenyl anion appeared immediately on the bead surfaces (PS−FlLi) (Scheme 1). After stirring for 1 h at −78 °C, the mixture was warmed to room temperature.

Monomer Synthesis. DMVF was prepared as reported.[5] MSVF was prepared from 9-methyl-2-vinylfluorene. Thus, 2-vinylfluorene (967 mg, 5 mmol) was dissolved in 28 mL of dry THF under an argon atmosphere. The solution was cooled to −78 °C, and 0.0056 mol of lithium diisopropylamide (LDA) was added by syringe through a rubber septum. A deep orange red color appeared immediately. The solution was stirred at −78 °C for 1 h, after which 0.0064 mol of iodomethane was added. The color disappeared instantly, and the solution was warmed to room temperature. After removal of THF 30 mL of chloroform was added. The solution was washed successively with dilute solution of hydrochloric acid, dilute solution of sodium carbonate, and water. After drying over magnesium sulfate, chloroform was removed under high vacuum and 30 mL of dry THF was added. After the solution was cooled to −78 °C, another aliquot of LDA (0.0056 mol) was added. This time a deep purple color characteristic of the 2-vinyl-9-alkylfluorenyl anion appeared immediately. After stirring for 3 h at −78 °C, 0.0059 mol of chlorotrimethylsilane was added. As the solution was warmed to room temperature, the purple color slowly disappeared. After removal of THF, 30 mL of chloroform was added. The solution was washed with dilute hydrochloric acid, sodium carbonate solution, and water, dried over magnesium sulfate, filtered, and concentrated. The residue was purified by column chromatography (hexane as eluent) and by recrystallization (twice) from methanol (mp 85−86 °C). ^{1}H NMR (250 MHz, $CDCl_3$): −0.2 ppm (singlet, $Si(CH_3)_3$), 1.7 ppm (singlet, CH_3), 5.2−5.3 and 5.75−5.9 ppm (doublets, CH_2), 6.7−6.9 ppm (quadruplet, CH), 7.2−7.8 ppm (aromatic protons).

Purification of the monomer was carried out using two methods. In the first method MSVF (4.1 g, 18.6 mmol) was dissolved in 80 mL of purified THF under high vacuum and the solution was stirred over CaH_2. After filtration this was repeated with fresh CaH_2 and the solution was filtered into ampules that were sealed. DMVF could also be purified by dissolution (4.1 g, 18.6 mmol) in 70 mL of purified THF. After this solution was stirred once over CaH_2, the solution was added to the above $PSCH_2FlLi$ beads (0.5 mmol). The mixture was stirred for several hours at room temperature. The red color of the beads typically remained, and the monomer solution was then transferred to an ampule by filtration and used directly. In some cases the color of the beads disappeared, and this required the use of additional red beads. MSVF was generally purified according to the second method.

Polymerizations. All polymerizations were run under high vacuum in purified THF at −78 °C in flamed glassware using Teflon stopcocks and break-seal techniques as reported elsewhere.[9,10] Thus, a *t*-BuLi solution in 5 mL of hexane (0.0264 mmol of *t*-BuLi, Table 1, no. 1) was added to a polymerization flask. After evaporation of hexane, about 10 mL of THF was distilled into the flask that was kept at −78 °C and 3.7 mL of dry ice chilled DMVF/THF solution (0.909 mmol of DMVF) was added. The color changed immediately from light yellow to deep burgundy red. After 10 min, about 5−7 mL of the PDMVF−Li solution was transferred to a side flask for sampling and styrene monomer solution (2.0 mmol of styrene in 10 mL of THF) was added to the polymerization flask. Initiation of styrene was rapid, as indicated by an instantaneous color change from burgundy to orange red. The solution was stirred for 10 min and terminated with methanol (80 mg, 2.50 mmol). The polymerizations of MSVF were carried out in a manner identical with that for DMVF.[5] All polymers were precipitated by addition into methanol (10 times excess with respect to reaction volume) and dried overnight under high vacuum at 50 °C.

Characterization. Size exclusion chromatography (SEC) was carried out at room temperature with THF as eluent at a flow rate of 1 mL/min using a Waters Model 510 pump, a Perkin-Elmer LC-30 RI detector, and two "Ultrastyragel" 500 and 10^4 Å columns (10 μm) calibrated with polystyrene standards (Polysciences). Proton NMR data were acquired on a Bruker AC-250 FT instrument operating at 250 MHz with $CDCl_3$ as solvent.

Results and Discussion

The synthesis of 9-methyl-9-trimethylsilyl-2-vinylfluorene (MSVF) was carried out by the LDA mediated deprotonation of 9-methyl-2-vinylfluorene in THF at −78 °C followed by reaction of trimethylsilyl chloride (TMSCl) (Experimental Section). However, this monomer like the analogous DMVF cannot be purified by distillation for instance from CaH_2, metal mirrors, or triethylaluminum (Et_3Al).

We have reported the synthesis of narrow molecular weight (MW) distribution PDMVF initiated with either *t*-BuLi or naphthalene radical anions.[5] However, SEC analysis of a *t*-BuLi initiated PDMVF−polystyrene block copolymer, by addition of purified styrene monomer to the resulting PDMVF anion, showed a residual small peak corresponding to the PDMVF precursor (Table 1, Figure 1a). This peak indicated some deactivation before styrene addition, but there was no indication of termination prior to or during the DMVF polymerization as no shoulders were visible in the SEC chromatograms of the corresponding PDMVF precursor and the experimental MWs were in good agreement with the calculated values. Thus, a slowly terminating impurity appeared to be present. As we had purified the DMVF by stirring DMVF/THF solutions twice over CaH_2 (Experimental Section), this indicated the absence of reactive acidic impurities such as water and alcohols that are known to react rapidly with CaH_2 and with living polystyryl (PS) anion. Instead, less reactive impurities may be present such as 2-acetylfluorene, which is the precursor for the DMVF synthesis and which is sufficiently acidic to slowly deactivate the chain-end carbanions.[5] Trace amounts of this compound, which is not readily reduced with CaH_2, may have persisted in the vinylfluorene monomers.

2-Acetylnaphthalene has been shown to interfere in this manner in the anionic polymerization of 2-vinyl-

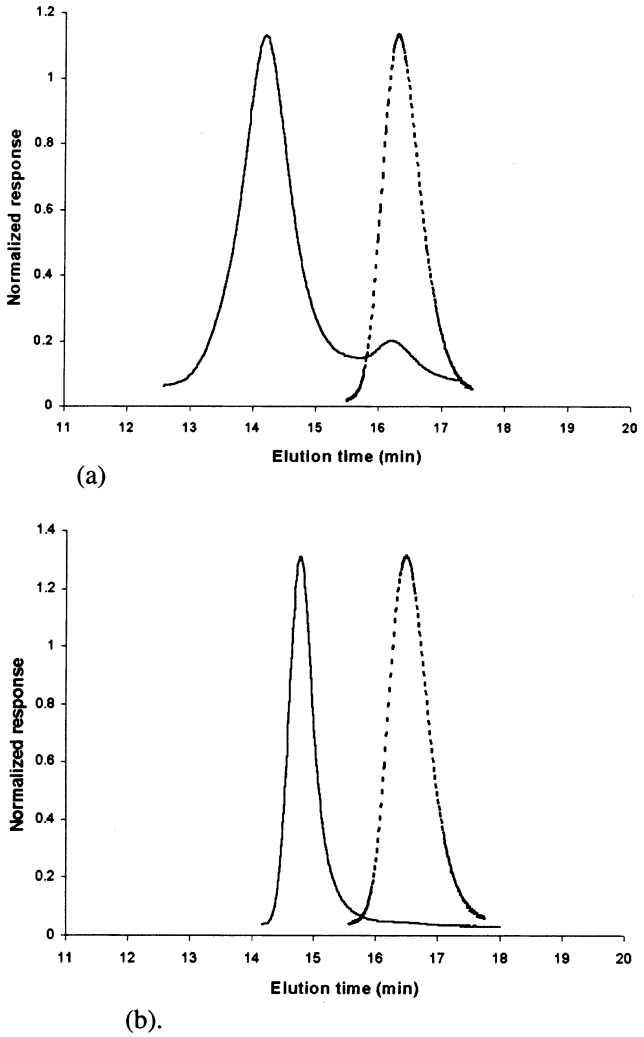


Figure 1. (a) Normalized SEC curves of PDMVF precursor (dashed line) and PDMVF−PS block copolymer (solid line) (Table 1, no. 1). (b) Normalized SEC curves of PDMVF precursor (dashed line) and block copolymer PDMVF−PS (solid line) (Table 1, no. 2).

naphthalene.[11] In that case the purification was carried out by successive treatments with calcium hydride and lithium aluminum hydride (LAH) followed by sublimation. As this last step is not possible for DMVF or MSVF, we designed a new method to purify these vinyl monomers (Scheme 1).

This method is based on cross-linked polystyrene beads functionalized with pendent fluorenyl anions. Thus, cross-linked chloromethylated polystyrene beads were derivatized with fluorene by reaction with fluorenyllithium in THF (Scheme 1). Upon reaction with *n*-BuLi or *t*-BuLi, the beads immediately acquire the characteristic orange red color of the 9-alkylfluorenyl anion. After evaporation of THF on the vacuum line, the beads are easily distributed by pouring the dried beads into ampules equipped with break seals. As the fluorenyl anion is highly nucleophilic as well as basic, it is useful in scavenging electrophilic impurities and acts as a sensitive indicator because it has a relatively high extinction coefficient (extinction coefficient of about 1200) in the visible spectrum.

Persistence of the color of the beads after prolonged exposure to monomers such as styrene and DMVF indicates the absence of even the less reactive impurities. Of course, complete decoloration indicates the need for additional amounts of red beads. The beads may be used to purify many vinyl monomers that are not subject to initiation by fluorenyl anions such as styrene, α-methylstyrene, and 4-vinylbiphenyl. However, it is not suitable for highly electrophilic vinyl monomers such as MMA and acrylates or for epoxides that react with the fluorenyl anions.

The absence of terminating impurities is indicated by block copolymerization studies using DMVF, purified with the beads, as the first block. Thus, upon addition of styrene to the PDMVF anion, SEC analysis reveals the absence of a residual SEC peak of the PDMVF precursor that was observed for the case of DMVF purified using only CaH_2 (Table 1, no. 2, Figure 1b). Compared to other methods, the above purification method is highly advantageous for styrene and similar monomers because it acts as both scavenger and colorimetric indicator. It is also rapid for the cases of the above monomers and does not require distillation and/or other steps. Contacting a monomer solution with the red beads and color persistence appears to be sufficient.

Polymerization of MSVF. The *t*-BuLi initiated anionic polymerization of MSVF purified by the "red bead" method is very similar to that of DMVF (Table 2).[5] Upon addition of MSVF to a solution of *t*-BuLi in THF, the deep burgundy color observed in the anionic polymerization of DMVF appeared immediately and disappeared after addition of methanol or water. As shown in Figure 2, the ^{1}H NMR spectrum of PMSVF shows resonances between −0.2 and −0.8 ppm corresponding to the TMS groups that were not affected by inadvertent deprotection during termination (see below) as shown by quantitative integration of the TMS and aromatic resonances and the protons in the 0.75−2.5 ppm region (Figure 2). The fine structure of the TMS resonance appears to reflect the relative stereochemistry of the nearby asymmetric center at the 9-position and that of the methine backbone carbon. The resonances between 0.75 and 2.5 ppm are due to partially overlapping 9-methyl, methylene, and methine protons. The small resonance at 0.35 ppm due to the *tert*-butyl group from the initiator was used to calculate the degree of polymerization of the low MW PMSVF (Table 2).

The SEC MWs of the PMSVF were obtained by correcting the SEC values based upon polystyrene standards for the mass of the MSVF units. The resulting PMSVF MW values are significantly higher than the

Table 2. Anionic Polymerization of MSVF and Formation of PMVF

				M_n			
no.	MSVF (mmol)		initiator (mmol)	calcd	obsd[a] (SEC)	obsd[b] (NMR)	PDI[a]
1	0.755	*t*-BuLi	0.0264	8 000	12 400[c]	9 640	1.09
2	1.169	*t*-BuLi	0.0240	13 500	24 200[c]		1.09
3[e]	0.836	K-Naph	0.0303	11 400[d]	11 700[c]		1.14
4[e]	1.754	K-Naph	0.110	6 570[d]	5 700[c]		1.12

[a] SEC, polystyrene standards. [b] M_n determined by proton NMR integration of the *tert*-butyl end group. [c] Corrected for the MW of MSVF or MVF units. [d] Calculated MW of poly(9-methyl-2-vinylfluorene). [e] PMVF.

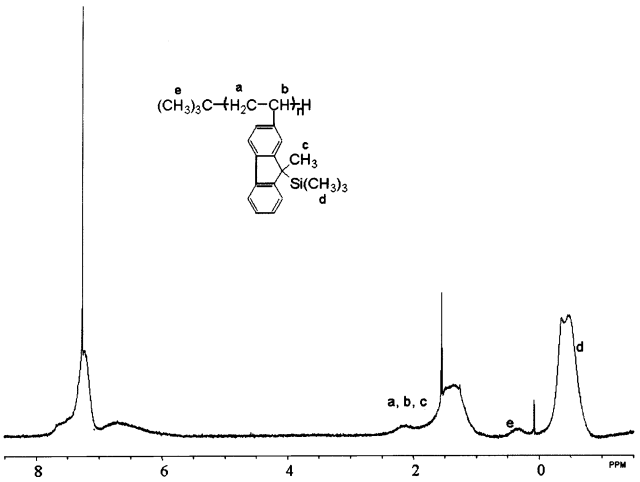


Figure 2. ^{1}H NMR spectrum of PMSVF (250 MHz, $CDCl_3$) (Table 2, no. 1).

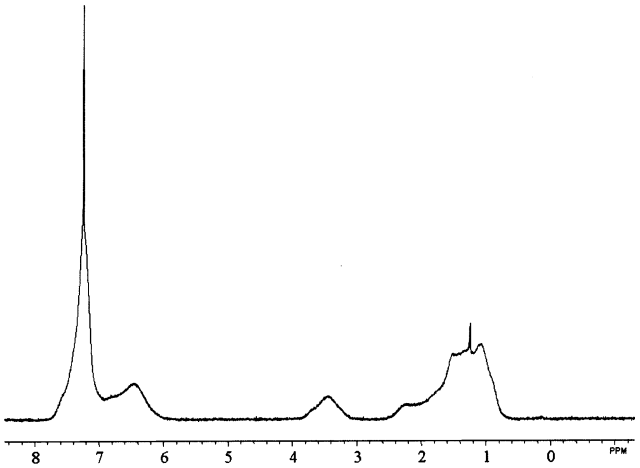


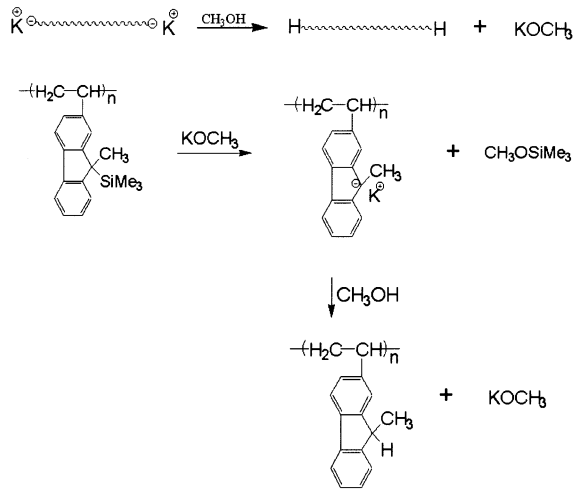
Figure 3. ^{1}H NMR spectrum of poly(9-methyl-9*H*-2-vinylfluorene) (250 MHz, $CDCl_3$) (Table 2, no. 3).

calculated values. This appears to be due to an expansion of the chain due to the large volume of the very large pendent 9-trimethylsilyl 2-alkylfluorenyl groups.

The polymerizations initiated by K-Naph show the same characteristic deep burgundy color of the living polymer anion, indicating that the intermediate anion was of the same type as that of the PDMVF anion.[5] Also, the same narrow distributions and good agreement of experimental and calculated MWs were obtained as the BuLi initiated polymerizations of DMVF[5] and that of the Li ion mediated MSVF polymerization as shown in Table 2. However, following the polymerizations upon addition of methanol, the burgundy color of the polymerization solutions instantly changed to a less intense orange red that disappeared after a few seconds.

After workup, the ^{1}H NMR spectrum of the polymer (Figure 3), surprisingly, shows the complete absence of the TMS groups and the quantitative formation of poly(2-vinyl-9-methylfluorene) (PMVF; Table 2, no. 3 and no. 4). Thus there is a new resonance between 3.2 and 3.8 ppm, due to the 9-fluorenyl proton that intergrates quantitatively with respect to the other protons. When deuterated methanol (CD_3OD) was used to terminate the polymerization, the resonance between 3 and 4 ppm is virtually completely absent (spectrum not shown). This indicates a potassium methoxide/methanol mediated deprotection of the TMS group as shown in Scheme 2.

Scheme 2. Proposed Mechanism of the Cleavage of the Potassium Methoxide Catalyzed Deprotection of the Trimethylsilyl Group in Methanol/THF



Thus, upon termination of the PDMVF−K_2 dianion with methanol, the resulting potassium methoxide reacts with the 9-fluorenyl−Si bond, thus generating the potassium fluorenyl anion (typical orange red color[12]). This anion now reacts with methanol to give the 9-methylfluorene group and regenerates potassium methoxide that, acting like a catalyst, continues cleaving the TMS groups leading to the efficient deprotection−protonation of the PMSVF to give poly(9-methyl-2-vinylfluorene) (PMVF). The relatively slow disappearance of the fluorenylpotassium indicates a relatively slow protonation by methanol consistent with the acidity of the 9-fluorenyl proton.

Interestingly, for the case of the Li ion mediated polymerization of MSVF, the termination with methanol and subsequent workup leaves the TMS groups intact. Thus either the MeOLi mediated deprotection of the TMS group generating fluorenyllithium or its subsequent protonation by methanol is greatly reduced or absent altogether. As fluorenyllithium is readily protonated by methanol, the above is consistent with effective inhibition of the TMS deprotection by MeOLi, presumably by the strong ion pair Li−oxygen anion in the MeOLi ion pair or its aggregate(s).[13]

Acknowledgment. This work was supported in part by NSF-DMR 9810283 and by NSF-STC 594-608.

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