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Synthesis and Living Anionic Polymerization of 9,9-Dimethyl-2-vinylfluorene

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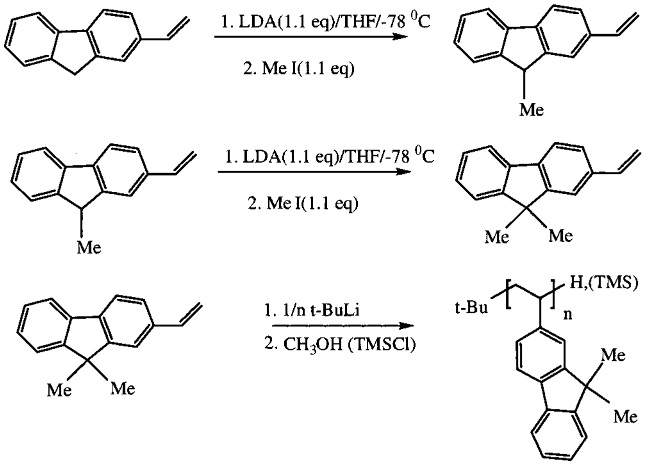
Introduction. Polyfluorenes have interesting luminescent properties and good chemical and thermal stability.[1−8] They have been studied in such applications as light-emitting diodes and hole- or electron-conducting materials.[2−8] The possibility for convenient remote functionalization at the 9-position(s) is an attractive feature of these polymers, allowing significant variation of structure with regard to solubility and other properties. This is the case also for vinylaromatic polymers containing fluorene pendent groups. Such polymers or copolymers may be of interest in studies of energy transfer[9−11] and as photon-harvesting materials.[12,13] Thus, the molar absorptivity of fluorene in the near-UV is on the order of 10^4, and its fluorescence quantum efficiency is relatively high (about 0.80).[9] The Forster radius for energy transfer is 23 Å, roughly double that of naphthalene and comparable to that of carbazole and methylanthracene.[9]

Here we report the synthesis and living polymerization of 9,9-dimethyl-2-vinylfluorene (DMVF), a new vinyl aromatic monomer. The corresponding polymer (PDMVF) had molecular weights (MW) in the 2500−250 000 range and may be an attractive candidate for photochemical studies of well-defined vinylaromatic polymers. For instance, a comparison of the properties and anionic polymerization of DMVF with that of 4-vinylbiphenyl[14] would be of interest.

In contrast to the radical[15] and cationic[16] polymerization of 2-vinylfluorene (2VF), the anionic polymerization of 2VF is prevented by the high acidity of the 9-fluorenyl protons ($pK_a = 23$).[17] However, these protons are absent in DMVF and, as shown below, the *t*-BuLi or lithium naphthalide anionic polymerizations of DMVF in THF at −78 °C appear to give a living polymerization system.

Experimental Section. a. Materials. THF was purified by distillation from benzophenone Na/K and then from the lithium salt of 1,1,4,4-tetraphenylbutane. Anhydrous methanol was degassed and stored into several ampules. Chlorotrimethylsilane (Aldrich, 98%) was stirred overnight over CaH_2, distilled twice on vacuum line, and then divided into several ampules equipped with break-seals. Iodomethane (Aldrich, 99%) was distilled two times from CaH_2 prior to use. 2-Acetylfluorene (98%), Red-Al (65+ wt % solution of sodium bis(2-methoxyethoxy)aluminum hydride in toluene), *p*-toluenesulfonic acid monohydrate (98.5%), and LDA (lithium diisopropylamide, 2.0 M solution in heptane/THF/ethylbenzene) were purchased from Aldrich and used without further purification. Reduction of 2-acetylfluorene (Red-Al in dry THF) gave the corresponding alcohol[18] that was dehydrated in toluene under reflux in the presence of *p*-toluenesulfonic acid to give 2-vinylfluorene.[19]

Scheme 1. Synthesis and Polymerization of 9,9-Dimethyl-2-vinylfluorene



b. Monomer Synthesis. 9-Methyl-2-vinylfluorene was obtained by the repeated deprotonation of 2-vinylfluorene with LDA[20] and methylation with iodomethane in dry THF at −78 °C (Scheme 1). DMVF was obtained by repeating the deprotonation/methylation procedure with MVF under the same conditions. Thus, 2-vinylfluorene (0.012 mol) was dissolved in about 60 mL of dry THF under an argon atmosphere, and the solution was cooled to −78 °C. LDA (0.0132 mol) was added by syringe through a rubber septum, and a deep red color appeared immediately. The solution was stirred at −78 °C for 2 h, after which 0.0132 mol of iodomethane was added. The deep red color disappeared, and a pale yellow solution was obtained that was allowed to slowly warm to room temperature. After cooling the solution to −78 °C another aliquot of LDA (0.0132 mol) was added. This time a purple color appeared instantly. After stirring for 2 h at −78 °C 0.0132 mol of iodomethane was added. The purple color disappeared, and the solution was warmed to room temperature, giving a pale yellow solution. After removal of THF 60 mL of chloroform was added, and the solution was washed with dilute hydrochloric acid and water. The organic phase was dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography (hexane as eluent) to afford a TLC (silica gel 60 F_{254} plates, Merck) pure DMVF with a melting point of 72−73 °C. The monomer was dissolved in purified THF, stirred over fresh CaH_2, and divided into ampules. Proton NMR (250 MHz, $CDCl_3$): methyl singlet (6H, 1.5 ppm) ($=C\boldsymbol{H}_2$, doublets, at 5.20−5.30 and 5.75−5.90 ppm) ($=C\boldsymbol{H}$, quadruplet, 6.70−6.90 ppm) aromatic resonances at 7.20−7.80 ppm (7H). GC-MS: m/z 220 (M^+), 205, 202, 189, 178.

c. Characterization. Size exclusion chromatography (SEC) was carried out at room temperature with THF as the carrier solvent at a flow rate of 1 mL/min using a Waters model 510 pump, a Perkin-Elmer LC-30 RI detector, and two Waters "Ultrastyragel" 500 and 10^4 Å columns calibrated with polystyrene (Polysciences) standards. Proton and carbon-13 NMR were carried out on a Bruker AC 250 at 250 and 62.5 MHz, respectively. Melting points (uncorrected) were determined with an electrothermal digital melting point apparatus. A 70−230 mesh silica gel (Aldrich) was used for the liquid

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Table 1. Anionic Polymerization of Monomer DMVF in THF at −78 °C[a]

run	DMVF (mmol)	initiator (mmol)		$10^{-3}M_n$ calcd	$10^{-3}M_n$ obsd[c] (SEC)	$10^{-3}M_n$ obsd[d] (NMR)	M_w/M_n[c]	T_g (°C)
1[b]	0.527	*t*-BuLi	0.0480	2.41	1.50	2.90	1.08	
2	0.760	*t*-BuLi	0.0360	4.64	2.40	4.70	1.10	147
3[e]	0.909	*t*-BuLi	0.0264	7.60	4.10	8.10	1.07	168
4	0.636	Li-naph	0.0106	26.40	13.0		1.09	176
5	0.941	Li-naph	0.00758	54.60	27.0		1.12	
6	2.810	Li-naph	0.00212	582	258		1.43	185

[a] Polymerization time was 30 min in 10−15 mL of THF and termination by methanol. [b] Polymerization at −78 °C for 1 h and at −40 °C for 0.5 h. [c] SEC, polystyrene standards. [d] M_n determined by NMR. [e] Polymerization was terminated by chlorotrimethylsilane.

chromatography separations. GC-MS was carried out with a Hewlett-Packard 5890 series II gas chromatograph and a 5971 mass selective detector in series. The glass transition temperature (T_g) was determined on a TA Instrument DSC 910S (scanning rate 15 °C/min). The value of T_g was defined as the midpoint of the heat capacity change. Thermogravimetric analysis was carried out with a Shimadzu TGA-50 thermogravimetric analyzer (heating rate: 5 °C/min, under argon atmosphere).

d. Polymerizations. The anionic polymerizations of DMVF were carried out in THF at −78 °C by high-vacuum techniques as reported elsewhere.[21] Both lithium naphthalide and *t*-BuLi were used as initiators. Thus, *t*-BuLi (0.048 mmol) was introduced to a flask cooled to −78 °C, and 10 mL of purified THF was distilled into the flask, giving a light yellow solution. To this solution was added dropwise DMVF (0.527 mmol) dissolved in 4 mL of THF with rapid stirring. The color of the solution changed instantly to a deep red. After a polymerization time 30 min terminatation by methanol or chlorotrimethylsilane resulted in the instant disappearance of the red color. The sample was analyzed by SEC before precipitation, thus ensuring that the possible formation of oligomers was not overlooked.

Results and Discussion. The title monomer was synthesized by repeated deprotonation of 2-vinylfluorene (2VF) by LDA at −78 °C in THF (Scheme 1). This reaction is favored by the high acidity of fluorene ($pK_a = 23$)[17] and the low nucleophilicity of LDA.[20] Thus, there was no evidence of LDA addition to the vinyl group. The polymerizability of DMVF was confirmed by the successful AIBN initiated radical polymerization, yielding a PDMVF with a number-average molecular weight (M_n) of 7700 and a polydispersity index of 1.90.

The anionic polymerization of DMVF was investigated under conditions similar to those used for styrene, i.e., in THF at −78 °C using *tert*-butyllithium or lithium naphthalide as initiator (Scheme 1). Upon addition of a DMVF solution to a rapidly stirred THF solution of *t*-BuLi at −78 °C, an immediate deep red color was observed, indicating rapid initiation. This color remained stable for hours even at −40 °C. Lithium naphthalide gave a similar rapid color change from green to red. The polymerizations were terminated with methanol or TMSCl.

The anionic polymerization of DMVF shows features consistent with "living" polymerizations. Thus, the number-average degrees of polymerizations determined by NMR correlate well with the monomer/initiator ratios (Table 1). Monomer conversions at polymerization times of 30 min or longer are quantitative and as also demonstrated by SEC and MW distributions are narrow, typically between 1.07 and 1.12. Only for very high MW polymers (M_n of 2.58×10^5) showed lower MW tailing and somewhat higher polydispersity ($D = 1.43$), presumably due to residual impurities.

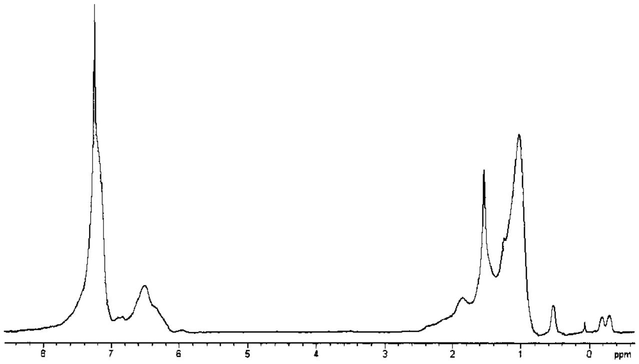

Figure 1. Proton 250 MHz NMR spectrum of PDMVF (Table 1, run 3) in $CDCl_3$ at 30 °C.

Figure 1 shows the ^1H NMR spectrum of PDMVF obtained with *tert*-butyllithium as initiator and chlorotrimethylsilane as terminating agent (Table 1, run 3). The resonances at δ 6.0−7.8 ppm (7H) are due to the aromatic ring protons, and those between 0.8 and 2.4 ppm (9H) correspond to partially overlapping 9-methyl, methylene, and methine protons. The *tert*-butyl and TMS resonances are observed at 0.5 ppm and between −0.15 and −0.35 ppm, respectively, and their relative magnitudes indicate the persistence of the benzylic chain end anion. As shown in Table 1, the ratios of the *tert*-butyl and the aromatic or aliphatic resonances appear to provide reliable M_n values for the low-MW polymers ($M_n < 10\,000$) as they correspond well with the calculated ones. However, the M_n values determined by SEC using polystyrene standards are only about half of the calculated MW's and the corresponding NMR values. This indicates that at the same molecular mass PDMVF may have a smaller hydrodynamic volume compared to that of polystyrene. As the molecular mass of DMVF is about twice that of styrene, it appears that the hydrodynamic volume may roughly correlate with the PDMVF contour length (DP) rather than the polymer mass. Thus, SEC molecular weights may be underestimated by a factor of almost 2. We have recently found similar results for poly(2-vinylnaphthalene).[22]

As illustrated in Figure 2, a typical ^{13}C NMR spectrum of PDMVF (Table 1, run 4) shows the methyl carbons at 27 ppm and the quaternary carbon-9 at 46 ppm. The peaks between 45 and 41 ppm are due to the methine and methylene chain carbons. The broad peak at 145 ppm is attributable to the stereochemically sensitive quaternary carbon-2[23] that is directly connected to the polymer backbone. This broad peak seems to indicate that the polymer is stereoirregular. This is not surprising as the polymerization of styrene under the same conditions gives atactic polystyrene.[24]

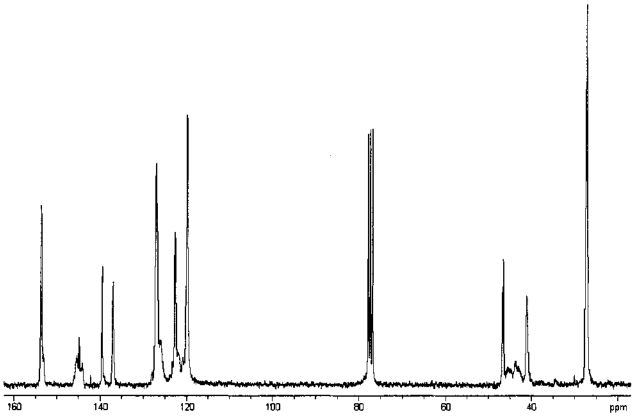

Figure 2. Carbon-13 NMR (62.5 MHz) spectrum of PDMVF (Table 1, run 4) in $CDCl_3$ at 30 °C.

PDMVF (run 4) obtained with lithium naphthalide as initiator (SEC M_n = 13 000) was characterized by DSC and TGA. The polymer shows a glass transition temperatures between 147 and 185 °C, which is comparable to that of poly(4-vinylbiphenyl) (161 °C),[25] poly(2-vinylnaphthalene) (151 °C),[25] and poly(2-vinylanthracene) (175 °C).[26] TGA shows that thermal degradation starts at 330 °C (5% weight loss at 365 °C), which is higher than that of polystyrene where thermal degradation starts at 275 °C (5% weight loss at 330 °C).[27]

In conclusion, the anionic polymerization of 9,9-dimethyl-2-vinylfluorene in THF at −78 °C in the presence of Li ion is well-controlled and appears to be consistent with a "living" polymerization.

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References and Notes

(1) Fukuda, M.; Sawada, K.; Yoshino, K. *J. Polym. Sci., Part A* **1993**, *31*, 2465.
(2) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.
(3) Grell, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Adv. Mater.* **1997**, *9*, 798.
(4) Klaerner, G.; Miller, R. D. *Macromolecules* **1998**, *31*, 2007.
(5) Marsitzky, D.; Klapper, M.; Müllen, K. *Macromolecules* **1999**, *32*, 8685.
(6) Millard, I. S. *Synth. Met.* **2000**, *111*, 119.
(7) Lee, J. I.; Hwang, D. H.; Park, H.; Do, L.-M.; Chu, H. Y.; Zyung, T.; Miller, R. D. *Synth. Met.* **2000**, *111*, 195.
(8) Chen, J. P.; Klaerner, G.; Lee, J.-I.; Markiewicz, D.; Lee, V. Y.; Miller, R. D.; Scott, J. C. *Synth. Met.*, in press.
(9) (a) Birks, J. B. *Photophysics of Aromatic Molecules;* John Wiley: London, 1970. (b) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules;* Academic Press: London, 1971. (c) Berlman, I. B. *Energy Transfer Parameters of Aromatic Compounds;* Academic Press: New York, 1973.
(10) Semarak, S. N.; Frank, C. W. *Adv. Polym. Sci.* **1983**, *54*, 33.
(11) Guillet, J. E. *Polymer Photophysics and Photochemistry;* Cambridge University Press: Cambridge, 1985.
(12) (a) Guillet, J. E. *Trends Polym. Sci.* **1996**, *4*, 41. (b) Nowakowska, M.; Strorsberg, J.; Zapotoczny, S.; Guillet, J. E. *New J. Chem.* **1999**, *23*, 617.
(13) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469.
(14) (a) Shima, M.; Bhattacharyya, D. N.; Smid, J. Szwarc, M. *J. Am. Chem. Soc.* **1962**, *85*, 1306. (b) Miertus, S.; Kysel, O.; Majek. P. *Macromolecules* **1979**, *12*, 421.
(15) (a) Goutiere, G.; Gole, J. *Bull. Soc. Chim. Fr.* **1965**, *1*, 153. (b) Goutiere, G.; Gole, J. *Compt. Rend.* **1963**, *257*, 674.
(16) Chernobai, A. V.; Tirakyants, Z. S.; Delyatitskaya, R. Y. *Vysokomol. Soedin.* **1966**, *8*, 997.
(17) (a) Streitwieser, A., Jr.; Ciuffarin, E.; Hammons, J. H. *J. Am. Chem. Soc.* **1967**, *89*, 63. (b) Ritchie, C. D.; Uschold, R. E. *J. Am. Chem. Soc.* **1967**, *89*, 2752.
(18) Guillet, J. E.; Rodpath, A. E. U.S. Patent 4,618,566.
(19) Wong, K.-H.; Ambroz, L.; Smid, J. *Polym. Bull.* **1982**, *8*, 411.
(20) Nagasaki, Y.; Tsuruta, T. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 437.
(21) Szwarc, M. *Carbanions Living Polymers and Electron-Transfer Processes;* John Wiley & Sons: New York, 1968.
(22) Nossarev, G. G.; Hogen-Esch, T. E. Manuscript in preparation.
(23) Tonelli, A. E. *Macromolecules* **1983**, *16*, 604 and references therein.
(24) Matsuzaki, K. Uryu, T.; Asakura, T. In *NMR Spectoscopy of Stereoregular Polymers*; Japan Scientific Societies Press: Tokyo, 1996; Chapter 12.
(25) Utracki, L. A.; Simha, R. *Makromol. Chem.* **1968**, *117*, 94.
(26) Stolka, M.; Yanus, J. F.; Pearson, J. M. *Macromolecules* **1976**, *9*, 710.
(27) Andrews, R. J.; Grulke, E. A. In *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley-Interscience: New York, 1999; Chapter V, p 93.

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