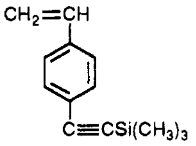
Communications to the Editor

Protection and Polymerization of Functional Monomers. 16. Anionic Living Polymerization of 4-[(Trimethylsilyl)ethynyl]styrene

Well-controlled polymers with respect to their chain lengths are essential materials for understanding the relations between polymeric structures and properties. Moreover, if useful functions can be added to these polymers, they would become more valuable materials with widespread applications from a viewpoint of molecular design.

For synthesis of such polymers, we have recently developed a new strategy, which involves the anionic living polymerization of a monomer with a protected function, followed by deprotection of the resulting polymer.[1] A variety of polystyrenes having hydroxy, amino, formyl, and carboxy groups were practically synthesized by means of this strategy. They have controllable molecular weights and very narrow molecular weight distributions as well as functional groups in all monomer units. It seems desirable to extend this strategy to monomers with other functional groups, which can be suitably protected during anionic living polymerization.

This paper describes the synthesis of a well-controlled poly(4-ethynylstyrene) by means of the above-mentioned strategy using 4-[(trimethylsilyl)ethynyl]styrene (1) as the protected functional monomer. The point of this study is whether or not a trimethylsilyl group protects efficiently the ethynyl function during the anionic living polymerization and whether the silyl protecting group can be completely and selectively removed from the resulting polymer.



1

A new monomer 1[2] was synthesized by a palladium-catalyzed coupling reaction of 4-bromostyrene with silylacetylene, according to a method previously reported.[3] The anionic polymerization of 1 was performed under high-vacuum conditions (10^{-6} mmHg) in an all-glass apparatus equipped with break-seals in the usual manner.

Polymerizations of 1 were carried out in THF at −78 °C for 0.5 h with either a monofunctional oligo(α-methylstyryl)lithium or a difunctional oligo(α-methylstyryl)dipotassium. The polymerization mixtures always exhibited a characteristic dark red color, which remained as long as the temperature was kept at −78 °C. The color immediately disappeared upon adding a few drops of methanol. The polymers were precipitated into methanol and purified by reprecipitation from THF solutions to methanol. Yields of polymers were quantitative in all cases. The structure of each polymer was identified to be poly[4-[(trimethylsilyl)ethynyl]styrene] by IR and ^{1}H and ^{13}C NMR spectra.[4] The signal characteristic of the methyl proton of the trimethylsilyl group appeared at 0.24 ppm with reasonable integral ratios to the other signals, indicating that no cleavage of the silicon–carbon bond had occurred. The molecular weights and their distribution parameters ($\bar{M}_w/\bar{M}_n$) are summarized in Table I.

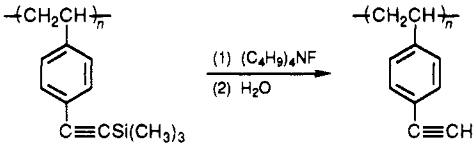
Table I
Anionic Polymerization of 1 in THF at -78 °C for 30 min[a]

mmol of 1	initiator type	initiator mmol	mmol of α-MeSt[b]	mol wt $10^{-3}\bar{M}_n$ (calcd)	mol wt $10^{-3}\bar{M}_n$ (obsd)[c]	$\bar{M}_w/\bar{M}_n$[d]
3.69	BuLi[e]	0.0456	0.304	17	15	1.04
3.08	K-Nap[f]	0.105	0.322	12	10	1.04
3.72	K-Nap	0.0633	0.319	25	25	1.04

[a] Yields of polymers isolated were 97–100%. [b] α-Methylstyrene. [c] $\bar{M}_n$(obsd) was obtained by vapor pressure osmometry. These values were very close to those by SEC based on the calibration of standard polystyrene. [d] $\bar{M}_w/\bar{M}_n$ was determined by the SEC curve. [e] Butyllithium. [f] Potassium naphthalenide.

As can be seen, the observed values of $\bar{M}_n$ are in good agreement with those calculated from the [M] to [I] ratios. The size-exclusion chromatograms (SEC) show that each polymer possesses a narrow molecular weight distribution, the values of $\bar{M}_w/\bar{M}_n$ being less than 1.05. The polymerization of 1 with polystyryldipotassium resulted in the formation of a well-defined triblock copolymer of poly(1-*b*-styrene-*b*-1), which was essentially free of homopolymers.[5] All these evidences clearly indicate the living character of the anionic polymerization of 1.

The deprotection of the trimethylsilyl group from poly(1) was performed with 2 equiv of tetrabutylammonium fluoride in THF at 0 °C for 2 h.[6]



The resulting polymer was isolated by the precipitation in methanol. The quantitative conversion of the (trimethylsilyl)ethynyl group to the ethynyl function was ascertained by the ^{1}H and ^{13}C NMR spectra, which showed the disappearance of the resonances at 0.24 ppm (^{1}H NMR) and 0.2 ppm (^{13}C NMR) characteristic of the methyl proton and of the carbon of the trimethylsilyl group. New signals for the ethynyl proton and carbon appeared at 3.04 ppm (^{1}H NMR) and 83.8 and 77.1 ppm (^{13}C NMR).[7] An additional evidence is provided by IR spectra of the polymers before and after deprotection. The two sharp bands at 2159 and 1260 cm^{-1} characteristic of $\nu_{C\equiv CSiMe_3}$ and ν_{Si-C} disappeared, while new bands at 3294 cm^{-1} ($\nu_{\equiv CH}$) and 2109 cm^{-1} ($\nu_{C\equiv C}$) appeared. The SEC profile of the deprotected polymer shows that the peak is unimodal and is located in the expected molecular weight region. The molecular weight distribution is almost identical with that of the parent polymer of 1, suggesting that neither main-chain degradation nor branching has occurred during the deprotection process. Accordingly, the poly(4-ethynylstyrene)s thus obtained have ethynyl groups in all monomer units. It also exhibits a narrow molecular weight distribution, and its molecular weight is controlled by the

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ratio of the monomer to initiator. Furthermore, the reactivity of the ethynyl moiety has attracted special interest, because a variety of functional groups may be introduced into the carbon–carbon triple bond by means of both electrophilic and nucleophilic addition reactions and by cycloaddition reactions induced thermally or photochemically.

The detailed anionic living polymerization of 1 and the above reactions using poly(1) will be published in the near future.

References and Notes

(1) For a review, see: Nakahama, S.; Hirao, A. *Prog. Polym. Sci.* **1990**, *15*, 299.

(2) A colorless liquid 1 was obtained in 70% yield by conventional column chromatography with hexane followed by distillation under reduced pressure [68–69 °C (0.33 mmHg)]: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.48–7.25 (m, 4 H, Ar), 6.69 (dd, 1 H, CH=), 5.75, 5.28 (2d, 2 H, J = 11 and 17 Hz, CH_2=), 0.25 (s, 9 H, $SiCH_3$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 137.8 (Ar, C1), 136.3 (=CH), 132.2 (Ar, C3), 126.1 (Ar, C2), 122.5 (Ar, C4), 114.8 (CH_2=), 105.2 (Ar*C*≡), 94.8 (≡CSi), 0.07 ($SiCH_3$).

(3) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1990**, 627.

(4) ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.35–7.00 (br s, 2 H, Ar), 6.60–6.10 (br s, 2 H, Ar), 2.10–0.90 (m, 3 H, CH_2CH), 0.24 (s, 9 H, CH_3Si); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 145.3 (Ar, C1), 132.1 (Ar, C3), 127.6 (Ar, C2), 120.8 (Ar, C4), 105.5 (Ar*C*≡), 93.7 (≡CSi), 43.6 (CH), 40.6 (CH_2), 0.2 (CH_3Si); IR (KBr) 2159 (C≡CSi), 1260 (SiC) cm^{-1}.

(5) The block copolymer was prepared by the anionic sequential polymerization of styrene and 1 with potassium naphthalenide in THF at −78 °C. The first polymerization was allowed to proceed for 10 min, and an aliquot was removed from the polymerization mixture for SEC analysis, which gave $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of 10 000 and 1.03, respectively. The second (block) polymerization was then allowed to proceed for 30 min at −78 °C. The polymers at first and second polymerizations were obtained quantitatively by precipitation into methanol. The observed value of $\bar{M}_n$ for block copolymer was 22 000, very close to the $\bar{M}_n$(calcd) of 21 000. The polymer was observed by SEC to possess a unimodal peak with a narrow distribution of molecular weight ($\bar{M}_w/\bar{M}_n$ = 1.06).

(6) Nakamura, E.; Kuwajima, I. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 498.

(7) ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.40–6.20 (m, 4 H, Ar), 3.04 (s, 1 H, CH≡C), 2.30–0.70 (m, 3 H, CH_2CH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 145.8 (Ar, C1), 132.1 (Ar, C3), 127.6 (Ar, C2), 119.9 (Ar, C4), 83.8 (Ar*C*≡), 77.1 (C≡*C*H), 43.0 (CH), 40.8 (CH_2); IR (KBr) 3294 (≡C), 2109 (C≡CH) cm^{-1}.

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Registry No. 1 (homopolymer), 135005-25-3; oligo(α-methylstyryl)lithium, 37372-03-5; oligo(α-methylstyryl)dipotassium, 52219-57-5.