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Facile Anionic Synthesis of Well-Controlled Thermally Cross-Linkable Block Copolymer for Polymer-based Resistive Memory Device Applications

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The reactivities of 4-[(trimethylsilyl)ethynyl]styrene (**A**) and 4,4'-vinylphenyl-*N,N*-bis(4-*tert*-butylphenyl)benzenamine (**B**) were investigated by sequential anionic block copolymerization to synthesize the thermally cross-linkable block copolymer for memory device applications. From the investigation on the reactivities of the monomers, the well-defined poly(**B-*b*-A**) was simply synthesized by sequential addition of **B** as the first monomer and **A** as the second monomer using commercially available *s*-butyllithium (*s*-BuLi) initiator in THF at -78 °C. The sequential deprotection was then performed to prepare the deprotected polymer (d-poly(**B-*b*-A**)) containing triphenylamine group as the conducting moiety and ethynyl group as the thermal cross-linker, and the resulting thermally cross-linked polymer was used as an active layer of memory device. The device fabricated with cross-linked d-poly(**B-*b*-A**) exhibited the write-once-read-many times (WORM) nonvolatile memory behavior, which is governed by the space-charge-limited current (SCLC) conduction mechanism and filament formation.

Introduction

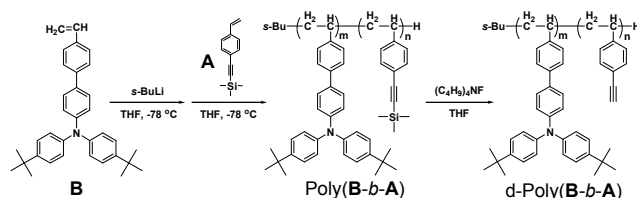
It has been well known that living anionic polymerization is the most established polymerization method to synthesize the polymers with controlled molecular weights (M_n) and narrow molecular weight distributions (M_w/M_n).¹⁻⁶ From the synthetic viewpoint, successful living anionic polymerization of certain monomers allows functional block copolymers with precise macromolecular structures to be prepared by sequential addition of monomers.⁷⁻⁹ Especially, the order of monomer addition should be carefully considered for the precise synthesis of block copolymers because reactivities of monomers might be different.¹⁰⁻¹³ In general, the block copolymerization has to be performed by sequential addition of less reactive monomer as the first monomer and more reactive monomer as the second monomer to obtain the well-defined block copolymers. For example, styrene is first needed to be polymerized in the block copolymerization of styrene (St) and methyl methacrylate (MMA) to afford the well-defined PSt-*b*-PMMA because the propagating chain-end carbanion derived from MMA cannot initiate the polymerization of St.

In our group, we have investigated the reactivity order of various monomers through sequential block copolymerization in order to successfully synthesize the well-defined functional block copolymers.¹¹⁻¹³ For instance, from the living nature of 4,4'-vinylphenyl-*N,N*-bis(4-*tert*-butylphenyl)benzenamine (**B**), the reactivity of **B** could be determined by block copolymerization with functional monomers such as St and 2-vinylpyridine (2VP).¹² As a result, the reactivity of **B** was found to be between that of St and 2VP, and thus the well-defined PSt-*b*-Poly(**B**) and Poly(**B**)-*b*-P2VP were quantitatively prepared by living anionic polymerization.

It has been reported in many literatures that the ethynyl group can be cross-linked by heat treatment.¹⁴⁻¹⁸ Such a functionality of the ethynyl group provides the thermally cross-linked polymers with chemical resistance for common solvents. Based on this, a variety of types of polymers containing the ethynyl group have been designed and synthesized for different applications such as optical waveguides, fuel cells and polymer light-emitting diodes (PLEDs).¹⁹⁻²¹ In addition, the triphenylamine-containing

polymers have significant attention in polymer-based electronic device applications such as PLEDs and resistive memory devices due to their good hole-transporting properties.²²⁻²⁴ It has been particularly reported that the block copolymer containing pendent triphenylamine can be used as suitable active layers of memory devices.²⁴ The devices fabricated with the polymer showed resistive switching characteristics with high performances.

From these unique functionalities of ethynyl and triphenylamine group mentioned above, thermally cross-linkable block copolymer (poly(4-ethynylstyrene)-*b*-poly(**B**)-*b*-poly(4-ethynylstyrene)) containing triphenylamine group as the hole-transporting moiety and ethynyl group as the thermal cross-linker was synthesized recently as an effective alternative hole-transporting layer to PEDOT:PSS for solution processed multilayer PLEDs by combination of block copolymerization of **B** with 4-[(trimethylsilyl)ethynyl]styrene (**A**) using potassium naphthalenide (K-Naph) initiator and the sequential deprotection.²¹ However, in an aspect of synthetic simplicity, the preparation of a bidirectional initiator (K-Naph) by the reaction of a small excess amount of naphthalene with potassium in dry THF at room temperature complicates the polymerization procedure. Accordingly, such a synthetic method to prepare thermally cross-linkable block copolymer containing triphenylamine and ethynyl group allowed us to further search for facile anionic block copolymerization conditions. In particular, we highly thought that it is worthwhile to simplify the synthetic procedure under the anionic reaction conditions because the anionic polymerization is very much sensitive to impurities present in the reagents such as initiators, monomers, and solvents.



Scheme 1. Synthesis of poly(**B-*b*-A**) and d-poly(**B-*b*-A**).

On the basis of previous reports that both **A** and **B** have been quantitatively polymerized by commercially available *s*-butyllithium (*s*-BuLi) that can be used without preparation process, in this paper, we report on the facile anionic synthesis of thermally cross-linkable block copolymer for polymer-based resistive memory device applications. The reactivities of the monomers were first investigated by changing the order of monomer addition to synthesize the well-controlled block copolymer (poly(**B**-*b*-**A**)). The sequential deprotection was then carried out to obtain thermally cross-linkable ethynyl group (d-poly(**B**-*b*-**A**)) and the resulting cross-linked film was used as an active layer of memory device. The memory device based on cross-linked d-poly(**B**-*b*-**A**) showed the write-once-read-many times (WORM) nonvolatile memory behavior with high performances. The switching characteristic of memory device was explained by filamentary conduction mechanism. For the further research, this study will be able to open up the possibility of multilayer stacked device fabrication by simple spin-coating process for practical memory applications with increased cell density.

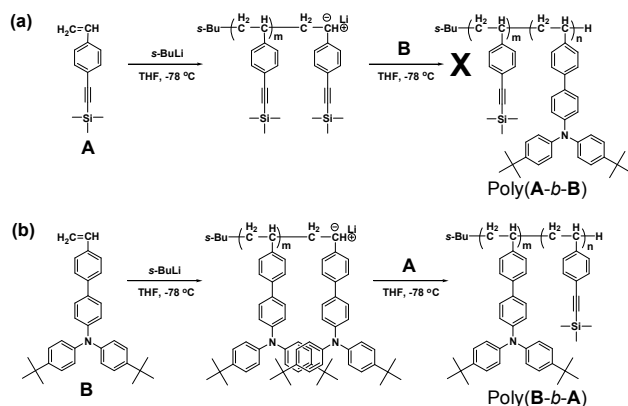


Figure 1. Block copolymerization of (a) **A** with **B** and (b) **B** with **A** using *s*-BuLi in THF at $-78\text{ }^{\circ}\text{C}$.

Experimental section

Materials

4-[(Trimethylsilyl)ethynyl]styrene (**A**) and 4,4'-vinylphenyl-*N,N*-bis(4-*tert*-butylphenyl)benzamine (**B**) were prepared according to papers previously reported.^{12,25} These monomers were diluted with THF and divided in ampoules with break-seals on a vacuum line. Commercially available *s*-butyllithium (*s*-BuLi, 1.0 M in cyclohexane, Kanto Chemical Co., Inc.) was used without purification and was diluted with dry *n*-heptane. The diluted monomers and *s*-BuLi were stored at $-30\text{ }^{\circ}\text{C}$ in ampoules equipped with break-seals prior to anionic polymerization.

Measurements

^1H NMR spectra were obtained using CDCl_3 as a solvent at $25\text{ }^{\circ}\text{C}$ (JEOL JNM-ECX400). Chemical shifts were referred to tetramethylsilane (TMS) at 0 ppm. FT-IR spectra were obtained by Perkins-Elmer Spectrum 2000 using KBr pellets. The polymers were characterized by size exclusion chromatography (SEC, Waters M77251, M510). The molecular weight distributions of polymers were determined using SEC calibration with polystyrene standards (American Polymer Standards Corp.) in a THF solution containing 2% triethylamine as the eluent at

$40\text{ }^{\circ}\text{C}$. Thermal properties were examined by thermogravimetric analysis (TGA, TA Instrument (TGA-Q50)) and differential scanning calorimetry (DSC, TA Instrument (DSC-Q20)) at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ under nitrogen. UV-Vis absorption spectra were obtained using an Agilent 8453 UV-Vis spectrophotometer.

Block copolymerization

The first-stage polymerization of **B** was performed with *s*-BuLi in THF at $-78\text{ }^{\circ}\text{C}$ for 0.5 h in an all-glass apparatus equipped with break-seals under high vacuum. After sampling poly(**B**), **A** was added into the living poly(**B**) solution and the reaction continued at $-78\text{ }^{\circ}\text{C}$ for 0.5 h (Scheme 1). After termination with methanol, the polymerization solutions were poured into a large amount of methanol to obtain poly(**B**) and poly(**B**-*b*-**A**). The resulting block polymer was characterized by SEC, ^1H NMR and FT-IR. Poly(**B**-*b*-**A**) ($M_n(\text{obsd}) = 6,000\text{ g/mol}$, $M_w/M_n = 1.08$ (Table 1, run 2)). ^1H NMR (400 MHz, CDCl_3): $\delta = 0.25$ (SiCH_3), 1.05–2.25 (backbone and *tert*-butyl group), 6.25–7.35 (triphenylamine and phenyl group). FT-IR (KBr, cm^{-1}): 1250 ($\text{Si}-\text{CH}_3$), 2158 ($\text{C}\equiv\text{CSi}(\text{CH}_3)_3$).

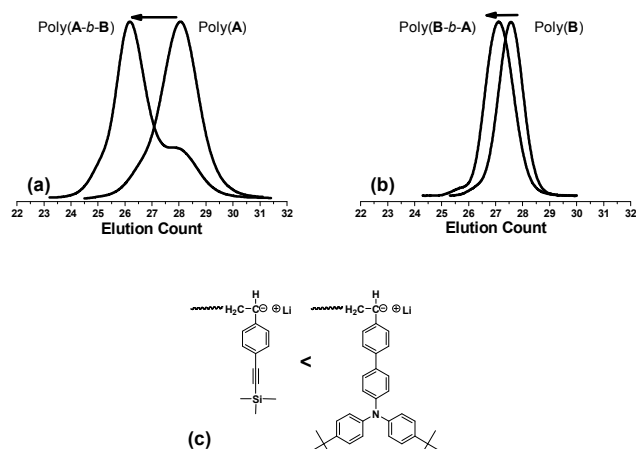


Figure 2. SEC curves of (a) poly(**A**) at the first-stage polymerization and copolymerization product at the second-stage polymerization with **B** (Table 1, run 1) and (b) poly(**B**) at the first-stage polymerization and copolymerization product at the second-stage polymerization with **A** (Table 1, run 2). (c) Nucleophilicity order of living poly(**A**) and poly(**B**).

Deprotection

Poly(**B**-*b*-**A**) (0.51 g) was dissolved in dry THF (10 mL). After $(\text{C}_4\text{H}_9)_4\text{NF}$ in THF (1 M, 10 mL) was added into the solution at $0\text{ }^{\circ}\text{C}$, the reaction mixture was stirred for 3 h (Scheme 1). The reaction solution was poured into methanol to precipitate the deprotected block copolymer (d-poly(**B**-*b*-**A**)). The resulting polymer was purified by reprecipitation in THF/methanol two times to obtain highly pure polymer, and then dissolved in benzene and freeze-dried under vacuum condition for characterization. The d-poly(**B**-*b*-**A**) was characterized by SEC, ^1H NMR and FT-IR. d-Poly(**B**-*b*-**A**) ($M_n(\text{obsd}) = 5,600\text{ g/mol}$, $M_w/M_n = 1.08$). ^1H NMR (400 MHz, CDCl_3): $\delta = 1.05$ –2.25 (backbone and *tert*-butyl group), 3.04 ($\text{C}\equiv\text{CH}$), 6.25–7.35 (triphenylamine and phenyl group). FT-IR (KBr, cm^{-1}): 2110 ($\text{C}\equiv\text{C}$ of $\text{C}\equiv\text{C}-\text{H}$), 3295 ($\text{C}-\text{H}$ of $\text{C}\equiv\text{C}-\text{H}$).

Fabrication and characterization of memory device

First, a bare glass substrate was cleaned by the typical ultrasonic cleaning process using acetone, 2-propyl alcohol and de-ionized water for 5 min, respectively, and dried with nitrogen gas. The bottom ITO electrodes (100 nm) were deposited and subsequently patterned with 8 lines by conventional photolithography and wet etching process. The d-poly(**B-b-A**) active material solution dissolved in toluene (1.0 wt%) was spin-coated onto the patterned ITO electrodes at 2000 rpm for 45 sec. The coated film was soft-baked on a hot plate at 60 °C for 5 min to dry solvent from active layer. The unnecessary film on the contact pads of bottom ITO electrodes was removed by using methanol for electrical probing, followed by thermal cross-linking on the hot plate at 240 °C for 50 min. Finally, the top Al electrodes (30 nm) were deposited by a thermal evaporator using a shadow mask with 8 lines. The current-voltage (I-V) measurements were performed with a Keithley 4200 SCS semiconductor analyzing system in a nitrogen-filled glove box system at room temperature in order to measure the electrical characteristics of the memory device.

Results and discussion

Anionic synthesis of block copolymer

First, the block copolymerization of **A** with **B** was carried out by sequential addition of **A** as the first monomer and **B** as the second monomer (Figure 1(a)). Although the polymer yield was quantitative, the well-defined block copolymer was not obtained. The SEC curve of the resulting polymer showed bimodal shape. As shown in Figure 2(a), the peak at the low M_n region well matched that of poly(**A**) and the peak at the high M_n region corresponded to the block copolymer possessing M_n value much higher than expected M_n due to slow initiation with rapid consumption of **B** by the newly formed polystyryl anion.^{11,12,26} These polymerization results indicate that living poly(**A**) is not nucleophilic enough to polymerize **B** completely, meaning low nucleophilicity of living poly(**A**) toward **B**.

Table 1. Block copolymerization with *s*-BuLi in THF at -78 °C.^a

run	<i>s</i> -BuLi mmol	monomer		block copolymer (homopolymer)		M_w/M_n^d
		1 st , mmol	2 nd , mmol	$M_n \times 10^{-3}$ calcd ^b	obsd ^c	
1	0.0759	A , 2.16	B , 0.570	12.9 (5.7)	- ^e (5.8)	- ^e (1.19)
2	0.165	B , 1.69	A , 1.04	6.3 (4.7)	6.0 (4.9)	1.08 (1.07)

^a Polymerization times were total 1 h, 0.5 h for **A** and 0.5 h for **B**. ^b M_n (calcd) = (molecular weight of monomer) \times [monomer] / [initiator]. ^c M_n of the block copolymer was determined by using M_n of the homopolymer and the molar ratio of each block estimated by ¹H NMR. ^d M_w/M_n was determined by using SEC calibration with polystyrene standards in a THF solution containing 2% triethylamine as the eluent at 40 °C. ^e The initiation efficiency was not quantitative, forming a mixture of homopolymer and block copolymer.

In contrast, the well-defined block copolymer, poly(**B-b-A**), with predictable M_n (6,000 g/mol) and narrow M_w/M_n (1.08) was quantitatively synthesized by the reverse addition of two monomers (Figure 1(b)). The SEC curve of poly(**B-b-A**) was unimodal, and completely shifted from the starting poly(**B**) toward the higher M_n region, as shown in Figure 2(b). These outcomes suggest that the propagating chain-end derived from **B** can polymerize **A**, indicating that living poly(**B**) is sufficiently

nucleophilic to polymerize **A** under the polymerization conditions employed here. From the results of the sequential block copolymerization, the nucleophilicity of living poly(**B**) was observed to be higher than that of living poly(**A**) (Figure 2(c)).

Deprotection of block copolymer

As illustrated in Scheme 1, the deprotection of the trimethylsilyl group from poly(**B-b-A**) was performed with $(C_4H_9)_4NF$ in THF to afford thermally cross-linkable block copolymer. ¹H NMR, FT-IR and SEC were used to verify the successful deprotection reaction. First, ¹H NMR spectra showed complete removal of trimethylsilyl group (Figure 3(a)). After deprotection process, the signal of the methyl proton of the trimethylsilyl group was not detected at 0.25 ppm and the new signal of the ethynyl proton appeared at 3.04 ppm. In FT-IR spectra shown in Figure 3(b), successful conversion of the (trimethylsilyl)ethynyl group to the ethynyl group was found. The characteristic bands of Si-CH₃ and C≡Si(CH₃)₃ at 1250 and 2158 cm⁻¹ disappeared, whereas the new bands were clearly observed at 2110 (C≡C of C≡C-H) and 3295 cm⁻¹ (C-H of C≡C-H), respectively. The SEC measurement also provided an additional evidence for deprotection. As shown in Figure 3(c), the SEC curve of d-poly(**B-b-A**) was still unimodal and narrow ($M_w/M_n = 1.08$), and shifted from elution volume of poly(**B-b-A**) toward lower M_n region. Such a SEC result also indicates no undesirable side reactions during the deprotection reaction. Therefore, these analyses demonstrate the successful deprotection proceeded to obtain d-poly(**B-b-A**) containing thermally cross-linkable ethynyl group.

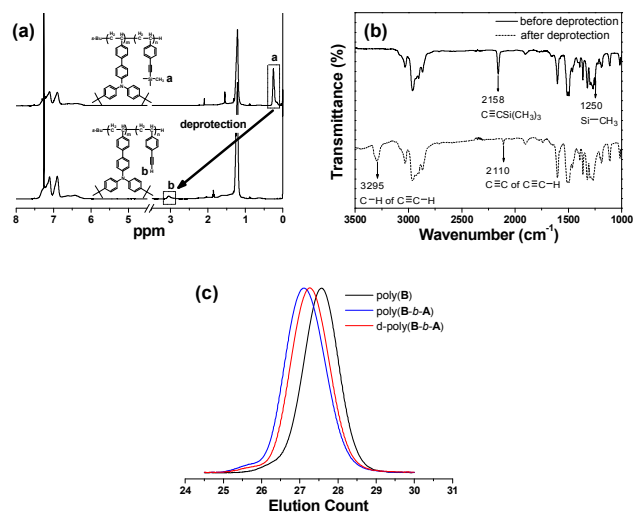


Figure 3. (a) ¹H NMR and (b) FT-IR spectra of poly(**B-b-A**) before and after deprotection. (c) SEC curves of poly(**B**), poly(**B-b-A**) and d-poly(**B-b-A**).

Thermal cross-linking of deprotected block copolymer

The thermal properties of d-poly(**B-b-A**) were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen in order to examine the thermal cross-linking of d-poly(**B-b-A**). First, the thermal stability of d-poly(**B-b-A**) was compared with that of poly(**B**) using TGA. Figure 4(a) shows that d-poly(**B-b-A**) is more thermally stable than poly(**B**). Although the M_n of d-poly(**B-b-A**) was much lower than that of poly(**B**), the value of the 5% weight loss temperature (T_5) of d-poly(**B-b-A**) ($T_5 = 405$ °C) was estimated to be higher than that of poly(**B**) ($T_5 = 387$ °C). In addition, DSC thermogram

showed that a large exothermic was observed at ~ 240 °C on the first scan and no intense exothermic peak appeared until 300 °C during the second scan (Figure 4(b)). Accordingly, it can be suggested from these TGA and DSC results that ethynyl groups of d-poly(**B-b-A**) were cross-linked by thermal treatment.¹⁹⁻²¹

The optimum conditions of thermal cross-linking of d-poly(**B-b-A**) were further determined by the solvent resistance test. The film was uniformly formed on quartz by spin-coating of d-poly(**B-b-A**) solution in toluene. This sample was then thermally treated at 240 °C for 50 min. As shown in Figure 4(c), absorption spectrum of thermally treated film remained unchanged even after rinsing with toluene. This unchanged absorption spectrum indicates that completely cross-linked d-poly(**B-b-A**) film can be formed by heating at 240 °C for 50 min.^{21,27,28}

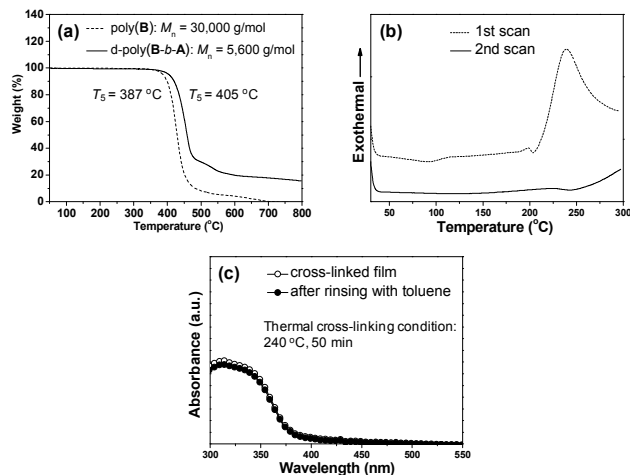


Figure 4. (a) TGA thermogram of poly(**B**) and d-poly(**B-b-A**). (b) DSC thermogram of d-poly(**B-b-A**). (c) UV-Vis absorption spectra of cross-linked d-poly(**B-b-A**) film before and after rinsing with toluene.

Memory device performances

Figure 5(a) shows the schematic illustration of ITO/cross-linked d-poly(**B-b-A**)/Al memory device with an 8×8 cross-bar array structure. The voltage was applied to Al top electrodes while ITO bottom electrodes were grounded. The representative semilogarithmic I-V curve of the device is shown in Figure 5(b). The electrical measurements were performed by first dual voltage sweep from 0 to 6 V (red line) and subsequent single voltage sweep from 0 to 11 V (blue line). In the first dual voltage sweep process, the current of the device was initially low (high resistance state, OFF state) in the low voltage region and slowly increased as the applied voltage further increased. Then, the current abruptly increased at a threshold voltage ($V_{th} \sim 3$ V), switching the device to low resistance state (ON state), and the ON state was retained even during the recovery from 6 to 0 V. In the second voltage sweep process from 0 to 11 V, the ON state still remained in the low voltage region, indicating the nonvolatile memory properties. The ON current was stably maintained without current transition until the applied voltage reached 11 V, suggesting the write-once-read-many times (WORM) memory behavior. The ON/OFF ratio of $\sim 10^5$ was obtained.

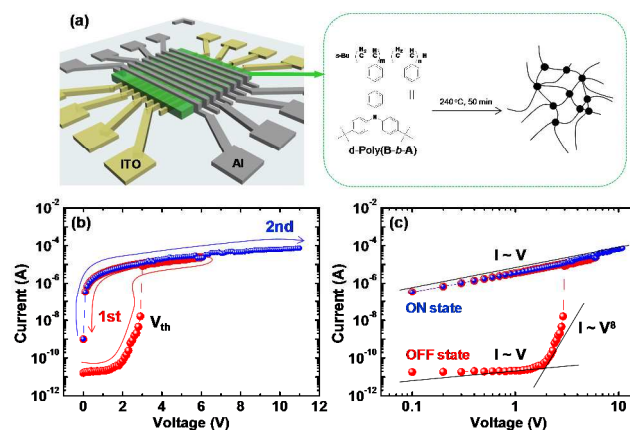


Figure 5. (a) The schematic illustration of ITO/cross-linked d-poly(**B-b-A**)/Al memory device with an 8×8 cross-bar array structure. (b) The representative current-voltage (I-V) switching characteristic and (c) double-log I-V plot analysis of the memory device.

In order to understand the conduction mechanism of cross-linked d-poly(**B-b-A**)-based memory device, I-V curve was analyzed by using a double-log I-V plot, as shown in Figure 5(c). It was found in the OFF state that a current transition happened. While the general ohmic conduction behavior ($I \sim V$), which the current is linearly proportional to the applied voltage, was observed in the low voltage region, the current drastically increased in the high voltage region ($I \sim V^8$). The value of I-V slope is correlated to trap-controlled space-charge-limited current (SCLC) switching mechanism. As the voltage was applied to cross-linked d-poly(**B-b-A**) active layer, a considerable number of injected charge carriers from Al electrodes were trapped in the **B** block, which might act as charge-trapping sites. Once all traps were filled, the current increased nonlinearly at V_{th} . Then, as shown in Figure 5(c), the I-V slope followed the ohmic conduction behavior ($I \sim V$) again after the current state switched to the ON state, indicating that the ON current is related to the filament conduction.²⁹⁻³⁴ For the possible mechanism for our memory devices, it is now believed that the resistive switching is based on the formation and rupture of conductive paths mainly consisting of triphenylamine moieties by an electrical field.^{33,35,36}

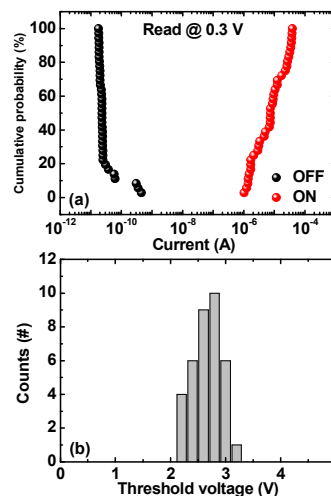


Figure 6. (a) Cumulative probability of ON and OFF states and (b) statistical distributions of the threshold voltages of the operative memory cells.

In array-type memory device, it is important to evaluate the statistical data of the switching characteristics of the operative memory cells for practical device applications. Figure 6 shows the cumulative probability of the switching current and statistical distribution of the threshold voltages of 36 cells selected from the device. As shown in Figure 6(a), the ON and OFF states of the operative cells were cumulatively plotted. The ON and OFF currents at a read voltage of 0.3 V were consistently separated by more than three orders of magnitude, which is enough value to demonstrate reliable bistability of resistive memory device. In addition, the statistical distributions of the threshold voltages of the operative cells show that the transition from the OFF state to the ON state occurred at voltages in the very narrow range of 2.2–3.2 V (Figure 6(b)), suggesting excellent cell-to-cell uniformity.

The retention test was finally examined to evaluate the performance of memory device. Figure 7 shows the retention characteristics of the ON and OFF states at a read voltage of 0.3 V. The memory device maintained the ON/OFF current ratios of over 10^4 and showed stable retention properties during a long retention period of 10^4 s without significant variation, exhibiting excellent nonvolatile memory performances.

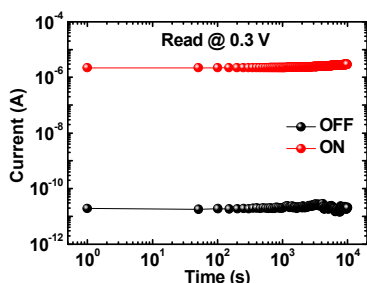


Figure 7. Retention time.

Conclusions

The investigation on the reactivities of **A** and **B** through sequential block copolymerization allowed us to simply synthesize the well-defined thermally cross-linkable block copolymer for polymer-based resistive memory applications. The well-defined poly(**B-b-A**) with controlled M_n and narrow M_w/M_n was successfully synthesized by sequential addition of **B** as the first monomer and **A** as the second monomer using *s*-BuLi. The sequential deprotection reaction of poly(**B-b-A**) was carried out to remove trimethylsilyl group of **A** block to obtain thermally cross-linkable ethynyl group. The memory device based on the cross-linked film at 240 °C for 50 min showed excellent write-once-read-many times (WORM) nonvolatile memory performances. The memory exhibited narrow distributions of threshold voltages (2.2–3.2 V) and good retention times ($\sim 10^4$) with high ON/OFF current ratios of $\sim 10^5$. The space-charge-limited current (SCLC) conduction mechanism and filament formation were proposed to explain the switching behavior of memory device. For the developed work, it is expected from solvent resistance of the cross-linked film that d-poly(**B-b-A**) will allow to fabricate polymer-based memory devices with stackable 3D architectures.³⁷

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