The Effect of Random and Block Copolymerization with Pendent **Carbozole Donors and Naphthalimide Acceptors on Multilevel** Memory Performance

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Abstract: Polymeric materials have been widely used in the fabrication of data-storage devices, owing to their unique advantages and defined conduction mechanisms. To date, the most-functional polymers that have been reported for memory devices were synthesized through random copolymerization, whilst there have been no reports regarding the memory effect of block polymers. Herein, we synthesized a random copolymer (PMCz₈-co-PMBNa₂) and its corresponding block copolymer (PMCz₈-b-PMBNa₂) to study the effect of the method of polymerization on the memory properties of the corresponding devices. Interestingly, both devices

Introduction

Owing to several advantages, such as excellent solution processability, low power consumption, structural tunability, and 3D stacking capabilities, polymeric materials have been widely applied in electronic devices, such as organic solar cells (OSCs),^[1-6] organic field-effect transistors (OFETs),^[7-10] organic light-emitting diode (OLEDs),^[11-15] and organic memory devices (OMDs).^[16-22] However, to date, most polymer-based OMDs have only exhibited the traditional binary memory behavior, which cannot meet the ever-increasing global demands for data storage. To solve this emergent problem, two main approaches have been put forward. The first approach involves the application of new technologies to downscale memory cells, thereby increasing their data-storage densities, which is largely limited by their physical form factor and process technologies. The second approach involves the development of multilevel OMDs (e.g., ternary devices), which would allow the

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units in their side chains, were also synthesized. Through tuning different connection sites on the 1,8-naphthalimide framework, different steric effects and ternary memory performance were achieved for PMNB and PMNN.^[42] However, the flexible chains were found to be different in the connection sites of the naphthalimide moieties in polymers PMNB and

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(ITO/PMCz₈-co-PMBNa₂/AI and ITO/PMCz₈-b-PMBNa₂/AI) exhibited ternary memory performance, with threshold voltages of -1.7 V/-3.3 V and -2.7 V/-3.8 V, respectively. However, based on comprehensive measurements, the memory properties of PMCz₈-co-PMBNa₂ and PMCz₈-b-PMBNa₂ were found to be owing to the operation of different conduction mechanisms, which resulted from different molecular stacking in the film state. Therefore, we expect that this work will be helpful for improving our understanding of the conduction mechanisms in polymer-based data-storage devices.

corresponding storage density to be increased to 3ⁿ, hundreds of millions of times greater than that of a binary system, which offers a density of 2ⁿ.^[23-27] In previous reports regarding OMDs, several conduction mechanisms, such as redox,^[28] filament formation,^[29,30] conformational change,^[31–33] charge trapping,^[34–36] and charge transfer,^[37-40] have been successfully introduced to interpret the properties of memory devices. Therefore, we wondered whether ternary memory performance could be realized through combining two individual conduction mechanisms into a single polymer.

In our previous work, we designed a ternary OMD that was based on polymer P4VPCz (poly(4-vinylpyridine) derivatives), which contained pyridine and carbazole (Cz) groups in the side chain. The conduction mechanism for the device based on this polymer was found to involve a combination of conformational-change and charge-trapping mechanisms.^[41] Furthermore, two pendent copolymers, poly(2-(naphthalen-1-yloxy)ethyl 5-(2-(7-bromo-1,3-dioxo-4,5-dihydro-1H-benzo[de]isoquinolin-2(3H)-yl)ethoxy)-2,2,4-trimethylhex-5-enoate) (PMNB) and (poly(2-(naphthalen-1-yloxy)ethyl 5-(2-((2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)amino)ethoxy)-2,2,4-trimethylhex-5-enoate) (PMNN), which contained electron-donor (naphthalene) and electron-acceptor (1,8-naphthalimide; Na) PMNN, which had a significant influence on the memory behavior of the corresponding devices. Thus, we wanted to design an "ideal" polymer that could improve upon the individual performances of PMNB and PMNN. In addition, our previously designed polymers were all obtained through random copolymerization; thus, we also wanted to consider the effect of other polymerization methods, such as block polymerization, on memory performance.

Carbazole and 1,8-naphthalimide groups both possess a high degree of π -conjugated planarity,^[43-45] which can induce a conformational change between the Cz and Na planes under an external electrical field. Furthermore, the Cz group, which contains a O=C-O-C-C spacer group in its side chain, has been shown to exhibit binary "write once read many" (WORM) memory behavior through a conformational-change mechanism.^[33] In addition, Cz groups are also attractive electron donors and Na chromophores are well-known electron acceptors,^[24] thereby readily allowing charge-transfer or charge-trapping mechanisms in the side chains. Finally, the same flexible O=C-O-C-C chains are connected to nitrogen atoms with sp³ hybridization at pendant Na moieties, which is theoretically favorable for the arrangement of Cz and Na moieties under an external stimulus.

Herein, we report the synthesis of two polymers, $PMCz_8$ -co- $PMBNa_2$ and $PMCz_8$ -b- $PMBNa_2$, through random copolymerization and block polymerization, respectively. *I*–*V* measurements showed that both polymers exhibited ternary memory performance, and the corresponding threshold voltages were -1.7 V/-3.3 V and -2.7 V/-3.8 V, respectively. However, ITO/ $PMCz_8$ -b- $PMBNa_2$ /LiF/AI (ITO=indium tin oxide) only exhibited binary memory performance, whereas ITO/ $PMCz_8$ -co- $PMBNa_2$ /LiF/AI still exhibited the typical ternary memory performance. Based on AFM, XRD, UV/Vis, and photoluminescence (PL) spectroscopy experiments, we attributed the ternary memory properties of $PMCz_8$ -co- $PMBNa_2$ and $PMCz_8$ -b- $PMBNa_2$ to the operation of different conduction mechanisms. We expect that this work will guide the design of new polymers with improved memory performance.

Results and Discussion

Synthesis and Characterization of $PMCz_8$ -co- $PMBNa_2$ and $PMCz_8$ -b- $PMBNa_2$

Scheme 1 shows our synthetic route to polymers PMCz₈-*co*-PMBNa₂ and PMCz₈-*b*-PMBNa₂; for detailed procedures, see the Supporting Information. The chemical structures of these polymers were confirmed by using ¹H NMR spectroscopy (Figure 1). Both polymers could be spin-cast into uniform thin films from solutions in cyclohexanone (12 mg mL⁻¹). The relative molecular weight (M_n) of random copolymer PMCz₈-*co*-PMBNa₂ was 20205 g mol⁻¹, with a polydispersity index (PDI) of 1.52, and the ratio of MCz/MBNa segments was measured by using the UV/Vis absorption of a solution of MBNa in DMF (see ref [41]). Subsequently, the M_n of polymer R-PMCz [R = Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT)] was 9447, with a PDI of 1.26, whilst that of the final block polymer,

PMCz₈-*b*-PMBNa₂, was 12551 g mol⁻¹, with a PDI of 1.33. Thus, the relative ratio of MCz/MBNa in block polymer PMCz₈-*b*-PMBNa₂ was 8:2. Both polymers exhibited good thermal stability, with a 5% decomposition temperature (T_{d}) of about 280 °C and a glass-transition temperature (T_{g}) of about 100 °C, thus implying good heat endurance for both polymers PMCz₈-*co*-PMBNa₂ and PMCz₈-*b*-PMBNa₂ in their corresponding memory devices.

Current-Voltage (*I-V*) Characteristics of PMCz₈-co-PMBNa₂ and PMCz₈-b-PMBNa₂

Figure 2a shows the structure of the memory devices, in which a thin film (thickness: ca. 80 nm) was sandwiched between an aluminum (Al) electrode and an ITO electrode (for a cross-sectional SEM image, see Figure 2b). Typical I-V characteristics of the memory devices were determined at a scan rate 0.1 $V\,s^{-1}\!.$ Figure 2 c shows the I-V characteristics of an ITO/PMCz₈-co-PMBNa₂/Al memory device, which was initially in its low-conductivity state (OFF or "0" state). When a negative voltage from 0 to -6 V was applied to the cell, two abrupt increases in current were observed at threshold voltages of -1.7 and -3.3 V, thus indicating the occurrence of two successive electrical transitions from the OFF state to an intermediate conductance state (ON1 or "1" state) and from the ON1 state to a high-conductivity state (ON2 or "2" state). The corresponding OFF-ON1 and ON1-ON2 transitions could both serve as the "writing" process in the memory device. The memory device remained in the ON2 state under a subsequent voltage sweep from 0 to -6.0 V. The long-term stability and performance of the device was also evaluated from the retention time and a stimulus effect test under the same conditions. As shown in the Supporting Information, Figure S1, the PMCz₈-co-PMBNa₂based device endured over 1×10⁸ continuous read pluses of -1.0 V, and no significant degradation in the current for any state was observed after 100 min.

Subsequently, to exclude the possibility of aluminum particles penetrating the active layer during the electrical measurements, a LiF layer (thickness: ca. 5 nm) was vacuum-deposited onto the PMCz₈-co-PMBNa₂ film as a buffer layer to prevent direct contact with the Al electrode. Then, the electrical behavior of the ITO/PMCz₈-co-PMBNa₂/LiF/Al device was measured under the same conditions as before. As shown in Figure 3 a, this device also exhibited ternary memory behavior, thus indicating that this behavior originated from the intrinsic properties of the active layer itself. Thus, a PMCz₈-co-PMBNa₂-based memory device exhibited nonvolatile ternary WORM-type memory behavior.

Similarly, the ITO/PMCz₈-*b*-PMBNa₂/Al device also showed typical ternary WORM-type data-storage performance, as shown in Figure 2 d, and the threshold voltage for the OFF–ON1 and ON1–ON2 transitions were -2.7 and -3.8 V, respectively, much larger than the corresponding values for the PMCz₈-*co*-PMBNa₂-based memory device. Then, the LiF layer was also applied to consider the possibility of metal-filament formation in the electrical measurements. Unexpectedly, the ITO/PMCz₈-*b*-PMBNa₂/LiF/Al device only showed binary

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Scheme 1. Synthesis of PMCz₈-co-PMBNa₂ and PMCz₈-b-PMBNa₂. AIBN = azobisisobutyronitrile, RAFT = reversible addition-fragmentation chain transfer.



Figure 1. ¹H NMR spectra of a) $PMCz_8$ -*b*- $PMBNa_2$ and b) $PMCz_8$ -*co*- $PMBNa_2$ in $CDCI_3$.

memory behavior, and the threshold voltage was about -3.0 V, as shown in Figure 3 b, thus illustrating that the second

transition from the ON1 state to the ON2 state was dominated by the penetration of the Al filament.

Macrostructures of $PMCz_8$ -*co*- $PMBNa_2$ and $PMCz_8$ -*b*- $PMBNa_2$ in the Solid State

To understand the Al-filament-penetration phenomenon in the PMCz₈-*b*-PMBNa₂-based device, AFM analysis was performed to investigate the surface morphologies of the PMCz₈-*b*-PMBNa₂ and PMCz₈-*b*-PMBNa₂ films. As shown in Figure 4a, non-continuous aggregation of PMCz₈-*b*-PMBNa₂ in the solid state were observed from the tapping-mode AFM profile images, whilst 3D AFM topography images also confirmed the high rootmean-square (RMS) surface roughness of the PMCz₈-*b*-PMBNa₂ film to be 8.6 nm, which offered the chance to form a conducting channel for the Al particles. In contrast, the AFM image of the PMCz₈-*co*-PMBNa₂ film showed a smooth surface (Figure 4b) with a RMS surface roughness of less than 1 nm (Figure 4d), which was beneficial for preventing the Al particles from penetrating into the active layers. Clearly, the different surface morphologies of the PMCz₈-*b*-PMBNa₂ and PMCz₈-*b*-PMBNa₂ and PMCz₈-*b*-PMBNa₂ and PMCz₈-*b*-PMBNa₂ and PMCz₈-*b*-PMBNa₂ film showed a smooth surface form penetrating into the active layers. Clearly, the different surface morphologies of the PMCz₈-*b*-PMBNa₂ and PMCz₈-*b*-PMBNa_3 an

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Figure 2. a) Schematic representation of the ITO/polymer/Al device; b) SEM image of a cross-section of an ITO/polymer/Al device; c) *I–V* characteristics of a PMCz₈-co-PMBNa₂-based memory device; d) *I–V* characteristics of a PMCz₈-co-PMBNa₂-based memory device.



Figure 3. a) /-V characteristics of the ITO/PMCz₈-co-PMBNa₂/LiF/AI device; b) /-V characteristics of the ITO/PMCz₈-b-PMBNa₂/LiF/AI device.



Figure 4. Tapping-mode AFM profile images (a, b) and 3D AFM topography images (c, d) of thin films of $PMCz_{s}$ -b-PMBNa₂ and $PMCz_{s}$ -co-PMBNa₂ that were spin-coated onto ITO substrates, respectively (scan size: 5 μ m × 5 μ m).

PMBNa₂ films was caused by their different polymerization methods. For the block polymer, the naphthalimide fragment possessed a relatively uniform arrangement and, thus, PMCz₈-*b*-PMBNa₂ had a tendency to aggregate in the film state. In contrast, the naphthalimide groups in PMCz₈-*co*-PMBNa₂ were randomly dispersed, which would increase its solubility and, thus, decrease the aggregation of PMCz₈-*co*-PMBNa₂ in the film state.

Photophysical and Electrochemical Properties of $PMCz_8$ -co- $PMBNa_2$ and $PMCz_8$ -b- $PMBNa_2$

To understand the memory properties of the PMCz₈-*co*-PMBNa₂- and PMCz₈-*b*-PMBNa₂-based devices in detail, UV/Vis and CV measurements were performed (Figure 5). PMCz₈-*co*-PMBNa₂ and PMCz₈-*b*-PMBNa₂ both exhibited a maximum absorption peak at $\lambda = 298$ nm and a shoulder absorption peak within the range $\lambda = 328$ -345 nm, which could be assigned to π - π * transitions of the Cz pendant groups (Figure 5 a). Further-

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Figure 5. a) UV/Vis absorption spectra of thin films of PMCz₈-co-PMBNa₂ and PMCz₈-b-PMBNa₂; b) cyclic voltammetry (CV) curves of PMCz₈-co-PMBNa₂ and PMCz₈-b-PMBNa₂ on ITO substrates in MeCN (scan rate: 100 mV s⁻¹).

more, the moderately intense broad absorption peak at $\lambda =$ 362 nm was attributed to the $n-\pi^*$ and $\pi-\pi^*$ transitions of the Na moieties (see the Supporting Information, Figure S2).^[24] However, the UV/Vis spectrum of the PMCz₈-co-PMBNa₂ film was slightly broader than that of the PMCz₈-b-PMBNa₂ film, which was mainly induced by the poor PDI, caused by the random polymerization method. The absorption onsets for the $PMCz_8$ -co- $PMBNa_2$ and $PMCz_8$ -b- $PMBNa_2$ films were both $\lambda =$ 390 nm, with a corresponding optical band-gap of 3.18 eV.

Next, CV measurements were performed to understand the electrochemical properties of the PMCz₈-co-PMBNa₂ and PMCz₈-b-PMBNa₂ films. Tetrabutylammonium perchlorate (TBAP; 0.1 M) was used as the electrolyte, whilst ferrocene was used as a reference. As shown in Figure 5b, the PMCz₈-co-PMBNa₂ and PMCz₈-b-PMBNa₂ films both exhibited an irreversible oxidation peak, with onsets at 1.46 and 1.22 eV, respectively. Thus, the HOMO and LUMO energy levels could be calculated according to Equations (1) and (2).

$$E_{\rm HOMO} = -[E_{\rm ox} + 4.80 - E_{\rm ferrocene}] \tag{1}$$

$$E_{\rm LUMO} = E_{\rm HOMO} + E_{\rm a} \tag{2}$$

The detailed HOMO and LUMO energy levels of the PMCz₈co-PMBNa₂ and PMCz₈-b-PMBNa₂ films are shown in the Supporting Information, Table S1. The energy barrier between the HOMO level of PMCz₈-co-PMBNa₂ and the work function of the ITO electrode (0.94 eV) was smaller than that between the work function of the Al electrode and the LUMO energy level (1.72 eV), thus indicating that PMCz₈-co-PMBNa₂ was a p-type semiconductor, and that the memory performance was holedominated. Similarly, PMCz₈-b-PMBNa₂ was also found to be a p-type active material and, thus, the PMCz₈-b-PMBNa₂-based data-storage device was also governed by hole-transport.

Proposed Conduction Mechanism for PMCz₈-b-PMBNa₂-**Based Devices**

Over the past decade, Kang and co-workers have demonstrated the generation of binary memory properties through an

electric-field-induced conformational-change mechanism by using the same O=C-O-C-C spacer group as a bridge between the framework backbone and the functional carbazole groups.^[33] Thus, we wonder whether this conformationalchange phenomenon could also be the case in the PMCz₈-co-PMBNa₂- and PMCz₈-b-PMBNa₂-based devices. First, we performed XRD measurements to understand the degree of regioregularity in the PMCz₈-co-PMBNa₂ and PMCz₈-b-PMBNa₂ films in their ground state. As shown in the Supporting Information, Figure S3, a clear diffraction peak at $2\theta = 9.23^{\circ}$ was observed for the PMCz₈-b-PMBNa₂ film, with a corresponding d spacing of 9.56 Å, which was consistent with long-range order. Furthermore, based on the optimized structure that was obtained from our theoretical calculations, the length of the Cz plane was confirmed to be 9.01 Å (see the Supporting Information, Figure S4), which matched the long-range order very well. Subsequently, a relatively weak diffraction peak at 21.24° was also detected, with a d space of 4.17 Å, which could be attributed to intermolecular π - π stacking of neighboring Cz units. In conclusion, the Cz moieties formed a close face-toface conformation and ordered long-range channels in the PMCz₈-b-PMBNa₂ film, which could facilitate the movement of charge carriers through the channels. Thus, we could rule out the conformational-change phenomenon in the PMCz₈-b-PMBNa₂-based device, owing to the highly ordered stacking in the film state.

We proposed a charge-transfer mechanism to explain the conduction mechanism for the OFF-ON1 transition in the PMCz₈-b-PMBNa₂ device, because Cz groups are well-known electron donors, whilst Na groups have been widely applied as electron acceptors. Owing to the highly ordered intermolecular stacking in the PMCz₈-b-PMBNa₂ polymer, the charge carriers could be readily transferred from the Cz donors to the Na electron-deficient acceptors under an external voltage sweep. Thus, a conduction channel could be formed for the movement of charge carriers. To confirm the operation of this charge-transfer mechanism, photoluminescence measurements were performed (see the Supporting Information, Figure S5). After a voltage sweep from 0 to -3.2 V, the intensity of the photoluminescence was significantly quenched in the ON1

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state; thus, the switch from the OFF state to the ON1 state was attributed to a charge-transfer process. Therefore, the ternary memory behavior of the PMCz₈-*b*-PMBNa₂ polymer was induced by charge-transfer and filament-formation mechanisms.

Proposed Conduction Mechanism for PMCz₈-co-PMBNa₂-Based Devices

In contrast, the degree of regioregularity was quite low for the $PMCz_8$ -*co*- $PMBNa_2$ copolymer in the ground state, as shown in Figure 6a, which would hinder the mobility of charge carriers through the active layer and, thus, the device would be in the OFF state. Because the content of carbazole units was much higher than that of 1,8-naphthalimide units, and because the oxidation potential of carbazole was lower than that of 1,8-naphthalimide (see the Supporting Information, Figures S6 and S7), the holes would first inject from the ITO electrode into the carbazole groups near the interface to form charged species with an increase in the negative bias. Subsequently, the active carbazole species would attract neighboring neutral carbazole groups to form a partial or full face-to-face conformation.

To confirm the operation of a conformational-change mechanism, XRD measurements were performed on the PMCz₈-co-PMBNa₂ film after the voltage sweep. Instead of depositing an Al electrode on the active-layer, a liquid droplet of Hg was placed on the PMCz₈-co-PMBNa₂ film to serve as the top electrode. The Hg droplet was removed immediately after an electrical sweep from 0 to -2.5 V on the Hg/PMCz₈-co-PMBNa₂/ITO device. As shown in Figure 6a, after the voltage sweep, a new diffraction peak at $2\theta = 21.27^{\circ}$ appeared, with a *d* spacing of 4.17 Å, which was also attributed to intermolecular π - π stacking of the Cz groups. Thus, an ordered face-to-face conformation of Cz units could be induced under an electric-field in the PMCz₈-co-PMBNa₂ film, and the charge carriers would migrate through the Cz conformational channel to induce a switch in conductivity from the OFF state to the ON1 state. AFM measurements were also performed on the PMCz₈-co-PMBNa₂ film before and after the voltage sweep to confirm the operation of a conformational-change mechanism, as shown in the Supporting Information, Figure S8.

Subsequently, an intermolecular charge transfer (ICT) process was also proposed for the subsequent transition from the ON1 state to the ON2 state. Because the pendent functional groups adopted a partial or full face-to-face conformation at the threshold voltage of about -1.7 V, a further increase in the sweeping voltage would cause the charge carriers to transfer from the Cz donors to the electron-deficient Na moieties to form another conduction channel. To confirm the charge-transfer mechanism, UV/Vis absorption spectroscopy was performed on the PMCz₈-co-PMBNa₂ film before and after the voltage sweep (Figure 6b). Compared with the corresponding film in the OFF state, the UV/Vis absorption spectrum of the PMCz₈co-PMBNa₂ film was significantly broadened in the normalized absorption spectrum after the voltage sweep, thus indicating an increased polarity and dipole moment of PMCz₈-co-PMBNa₂, owing to charge-transfer interactions between the Cz electron donor and the Na electron acceptor. Furthermore, photoluminescence measurements were also performed to confirm the charge-transfer process, as shown in the Supporting Information, Figure S9. After the voltage sweep from 0 to -6 V, the intensity was significantly quenched in the ON2 state, thus confirming the operation of a charge-transfer process under an external voltage. Therefore, the ternary memory property of the PMCz₈-co-PMBNa₂-based device was attributed to conformational-change and charge-transfer mechanisms, as shown in Figure 7 b.

Conclusion

In summary, we synthesized two copolymers, PMCz₈-*co*-PMBNa₂ and PMCz₈-*b*-PMBNa₂, that contained the same electron-donor (carbazole) and electron-acceptor (1,8-naphthalimide) units through random copolymerization and block polymerization, respectively. The corresponding sandwich-structured devices, ITO/PMCz₈-*co*-PMBNa₂/AI and ITO/PMCz₈-*b*-PMBNa₂/AI, for both copolymers exhibited ternary memory behavior. However, copolymer PMCz₈-*co*-PMBNa₂ and block polymer PMCz₈-*b*-PMBNa₂ possessed completely different molecular stacking properties and surface morphologies in the film state. Furthermore, the switching mechanisms for the polymerbased memory devices were also different. For block polymer



Figure 6. a) X-ray diffraction patterns of PMCz₈-co-PMBNa₂ in different states (OFF and ON1); b) comparison of the ex situ UV/Vis spectra of thin films of PMCz₈-co-PMBNa₂ in the low-conductivity (OFF) and intermediate-conductivity (ON1) states.

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Figure 7. Schematic representation of the conductive switching processes in memory devices based on PMCz₈-b-PMBNa₂ (a) and PMCz₈-co-PMBNa₂ (b).

PMCz₈-*b*-PMBNa₂, the switching phenomenon was attributed to charge-transfer and filament-formation mechanisms, whereas the ternary behavior for copolymer PMCz₈-*co*-PMBNa₂ was attributed to a combination of conformational-change and charge-transfer mechanisms. This is the first report that compares the performance of memory devices that were fabricated from polymers that were synthesized by using different polymerization methods, and we expect that this work will facilitate better understanding of memory switching for ternary polymeric materials.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: conducting materials • memory devices • molecular stacking • nitrogen heterocycles • polymers

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FULL PAPER

Thanks for the memories: Two copolymers, PMCz₈-co-PMBNa₂ and PMCz₈-b-PMBNa₂, were synthesized through random and block copolymerization, respectively. Their corresponding datastorage devices exhibited different memory properties, which was attributed to the operation of different conduction mechanisms.



Polymers

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The Effect of Random and Block Copolymerization with Pendent **Carbozole Donors and Naphthalimide Acceptors on Multilevel Memory** Performance

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