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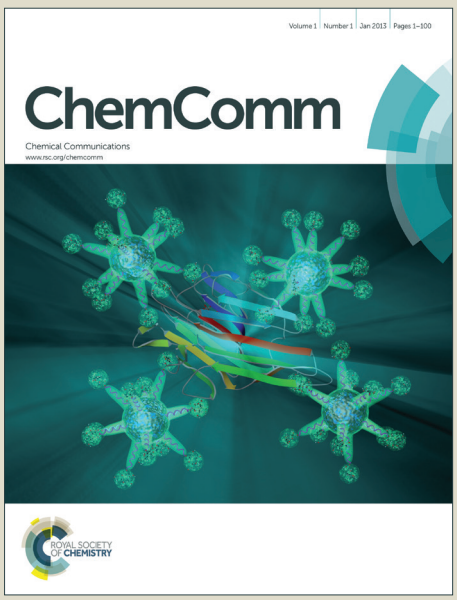

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The Opposite Gating Behaviors of Solid-State Nanochannels Modified with Long and Short Polymer Chains

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Juntao Zhang,[a,b] Nannan Liu,[a] Benmei Wei,[a] Xiaowen Ou,[a] Xuemei Xu,[a] Xiaoding Lou[a] and Fan Xia*[,a,b]

The influence of long and short polymer chains on the gating properties of nanochannel systems modified with NIPAAm-*co*-PBA copolymer are explored. We not only discover the negative temperature gating behavior in NIPAAm modified nanochannel systems for the first time, but also achieve these two fully opposite gating behaviors (negative/positive) in the same platform.

Inspired by the outstanding performance of the biological channels on gating functions, the artificial smart nanofluidic architectures were constructed by incorporating functional groups into the solid-state synthetic nanochannel systems (NCS), in which the high and low conducting states can be switched in response to the environmental stimulus. These smart nanochannel systems have promising applications in nanofluidic devices,[1] sensing,[2] filtration,[3,4] energy conversion,[5] and many other areas. Many phenomena that are not detectable on the microfluidic platforms had been discovered in the nanochannel systems, because of their dramatic increase in surface to volume ratio.[6] For example, the electrical double layers overlap is a very important phenomenon, and many unique properties which exist in nanochannel systems are directly related to it (Figure 1A). In the presence of electrical double layers overlap in nanochannels, only the counterions flow could be controlled by the modified surface charge (Left in Figure 1A), while, both counterion and coion flows could be controlled at the same time in the absence of this overlap (Right in Figure 1A).

One important thing, however, seems to be neglected in the macromolecular nanochannel systems. Similar to "electrical double layer overlap phenomena", the gating molecule layers overlap phenomena may also exists in nanochannel systems, along with changing of the gating molecule length in the same nanochannel (Figure 1B). To the best of our knowledge, the influence of gating molecule length on the gating performance of nanochannel systems has not been reported previously. The exploration of this phenomenon in nanochannel systems might help us to further understand the gating properties of macromolecular valves and can help the design of complex nanofluidic sensing devices.

Here, the solid-state nanochannel systems modified with multiresponsive copolymer chains are used as models to explore the influence of gating molecule length on their gating properties

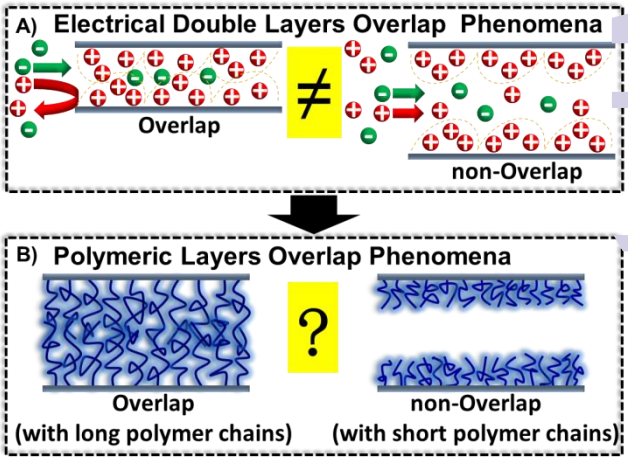

Figure 1. Schematic representation of the nanochannels with (r without electrical double layers overlap phenomena (A). We speculate that the nanochannels may also have similar phenom caused by the long and short polymer chains (B).

(Figure 2). The macromolecular nanochannel systems can be constructed by grafting poly(N-isopropylacrylamide-*c* acrylamidophenylboronic acid) (NIPAAm-*co*-PBA)[7] onto the inn surface of the solid-state nanochannels by a typical surface-initiate atom transfer radical polymerization (ATRP).[8] The detaile procedure is illustrated in the Experimental Section (Figure S Supporting Information). Additional X-ray photoelectro spectroscopy (XPS) analysis and contact angle (CA) measurement before and after modification confirmed the successful bonding the copolymers (Tables S1 and S2 and Figure S2, Supporting Information). The nanochannel system prepared by polymeriza on for 60 min is named **NCS-60** and polymerization for 10 min is nam **NCS-10**. As is known to all, ATRP method is an effective way t prepare the grafted polymer chains of controlled length b adjusting the polymerization time.[8,9] In our case, the P(NIPAAm-*co* PBA) with a lower critical solubility temperature (LCST) of 20-40 °C in water based on pH and glucose concentration,[7,10,11] is used regulate effective cross section area and the hydrophobic interaction in nanochannels.

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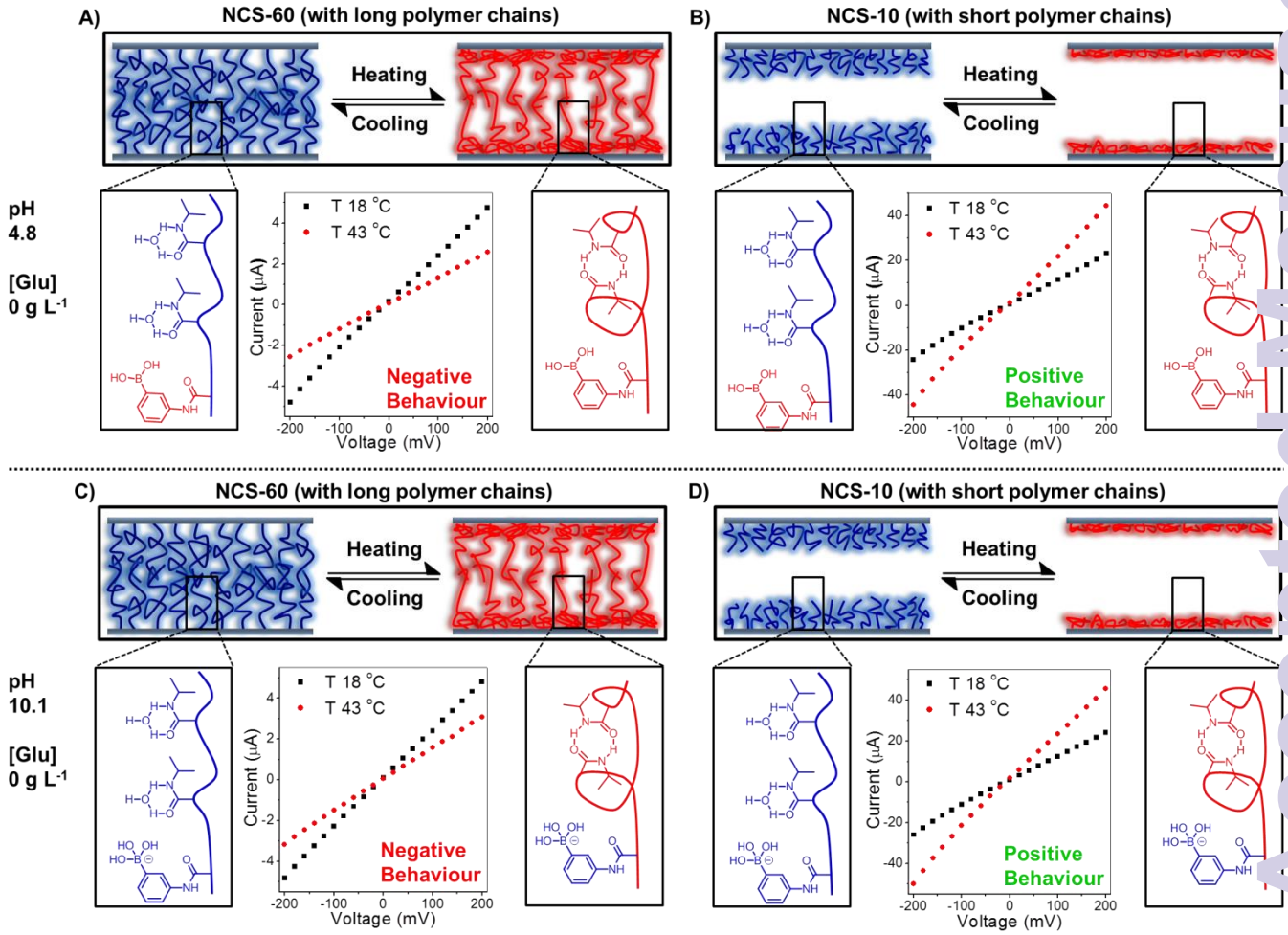

Figure 2. The influence of long and short polymer chains on the gating performances of nanochannel systems, when the pH is 4.8 and glucose concentration is 0 g L^{-1} (A,B) and the pH is 10.1 and glucose concentration is 0 g L^{-1} (C,D). Simplified illustration indicating the copolymer layer morphology and hydrophilic (indicated by the blue color)/hydrophobic (indicated by the red color) changes occurring in **NCS-60** and **NCS-10** upon variation of temperature. *I-V* curves of **NCS-60** (middle insets of A and C) and **NCS-10** (middle insets of B and D) at 18 and 43 °C, and the corresponding conformation changes of the copolymers on the inner surface of nanochannels (left and right insets).

The gating performances of **NCS-60** and **NCS-10** under the same conditions are compared to explore the influence of long and short polymer chains on the gating properties. When pH and glucose content are kept constant, the thermal gating capability of nanochannel systems is measured by the temperature gating ratio, which is defined as the ratio of the transmembrane current at 43 °C to that at 18 °C recorded at +2V. When the pH is 4.8 and the glucose concentration is 0 g L^{-1}, the ionic current of **NCS-60** decreases with a temperature gating ratio of 0.7 (Figure S3, Supporting Information) (negative gating behavior), along with the temperature increases from 18 °C to 43 °C (Figure 2A). As a comparison, the ionic current of **NCS-10** increases with a temperature gating ratio of 1.98 (Figure S3, Supporting Information) (positive gating behavior) in this process (Figure 2B). This is the first report about the opposite gating behaviors caused by the different length of the same gating molecule. The negative gating behavior showed by **NCS-60** never been reported in the solid-state nanochannel systems. While the positive gating behavior showed by **NCS-10** had been disclosed in current available nanofluidic devices modified with PNIPAAm.[12] Then the reason of the opposite gating behaviors is discussed in the following. The gating property of nanochannel systems is mainly governed by three mechanisms: 1) effective cross section area, based on proportionality of the total flux to the effective cross section area of the nanochannel,[13] 2) hydrophobic interaction, based on hydrophobicity switching,[14] and 3) electrostatic interaction, which should be considered if the pore walls have nonuniform charge distribution,[4,6,15] or the diameter of the channel is comparable to the thickness of the electrical double-

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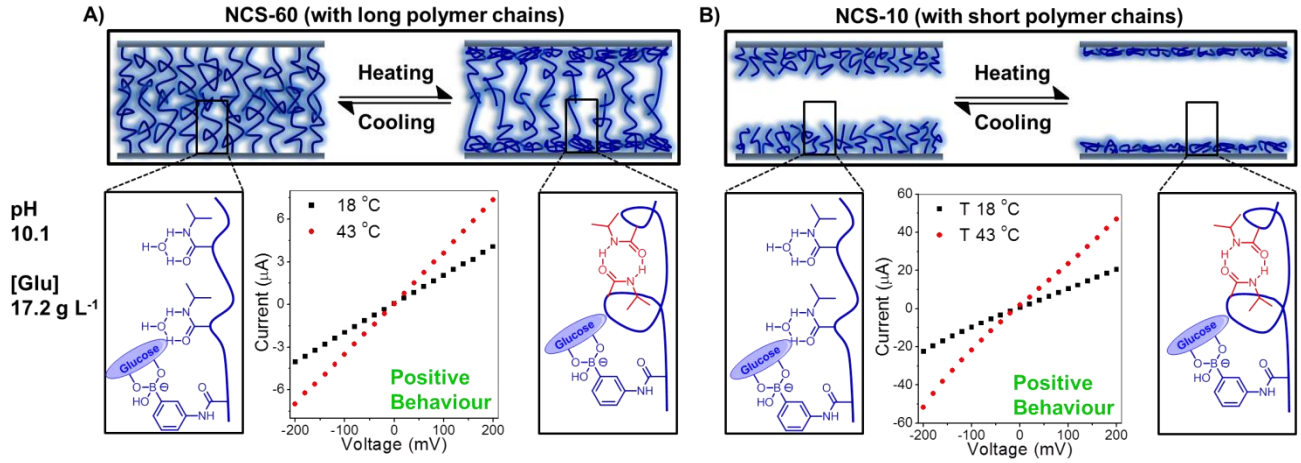

Figure 3. The influence of long and short polymer chains on the gating performances of nanochannel systems when the pH is 10.1 and glucose concentration is 17.2 g L^{-1}. Simplified illustration indicating the copolymer layer morphology and hydrophilic (indicated by the blue color) changes occurring in **NCS-60** (A) and **NCS-10** (B) upon variation of temperature, *I-V* curves of **NCS-60** (middle inset of A) and **NCS-10** (middle inset of B) at 18 and 43 °C, and the corresponding conformation changes of the copolymers on the inner surface of nanochannels (left and right insets).

layer.[16,17] Because the symmetric AAO channels are used to construct the nanofluidic system, and the molar ratio of PBA which could take the negatively charged under alkaline condition in the polymer is only 5%, the electrostatic interaction is ignored, and only effective cross section area and the hydrophobic interaction are considered in our case. In the temperature increasing process, the copolymers inside nanochannel collapse to make the polymer-free volume increasing, leading to the increasing of ionic current. At the same time, the copolymers dehydrate to form a hydrophobic conformation, leading to the decreasing of ionic current. Our result, therefore, shows that the ionic current of **NCS-60** is mainly controlled by the hydrophobic interaction (to show negative gating behavior), while the ionic current of **NCS-10** is mainly controlled by the effective cross section area (to show positive gating behavior). For **NCS-60**, a sufficiently long polymerization time makes the copolymer chains growing from the nanochannel walls long enough to interpenetrate with each other. Such a structure is highly porous and allows diffusion of water and ion molecules at 18 °C (below LCST). When the temperature is increased to 43 °C (above LCST), a portion of copolymer chains collapses onto the nanochannel surface to make the effective cross section area increasing. On the other hand, the overlapped portion of copolymer chains becomes dehydrated and impermeable to water. Our result shows that hydrophobic interaction is predominant for **NCS-60**. While, for **NCS-10**, the NIPAAm and PBA monomers are polymerized for a short period of time to form short brush which could not effective interpenetrate with each other. In the absence of the overlapped portion of copolymers, the copolymers dehydrate and collapse onto the nanochannel surface and cannot form impermeable porous networks in the effective cross section area. In this case, the ionic current of the nanochannel systems is mainly controlled by the changing of effective cross section area caused by the conformational change of copolymers. Similar results and mechanism have also been disclosed in colloidal films system assembled with silica spheres.[9] Therefore, the negative temperature gating behavior is discovered for the first time in the NIPAAm modified solid-states synthetic nanochannel systems, and we speculate that the observed opposite gating performances between **NCS-60** and **NCS-10** are directly related to the influence of long and short polymer chains.

Then, the temperature gating behaviors of **NCS-60** and **NCS-10** is further studied when the pH is changed to 10.1 without glucose (Figure 2C,D). Under this condition, **NCS-60** also shows a negative temperature gating behavior with a gating ratio of 0.5 (Figure S4, Supporting Information), along with the temperature increased from 18 °C to 43 °C (Figure 2C), while the **NCS-10** shows a positive temperature gating behavior with a gating ratio of 2.0 (Figure S5, Supporting Information) (Figure 2D). In this process, the PBA unites take negatively charge to result in a hydrophilic state. But our experiment result shows that their hydrophilic effect could be ignored, which is attributed to that the molar ratio of PBA is only 5% in the polymer. The copolymers inside nanochannels also dehydrate to form a compact and hydrophobic conformation as described above. Our result shows that the ionic current of **NCS-60** is still mainly controlled by the hydrophobic interaction, and which of **NCS-10** is controlled by the effective cross section area. In addition, when pH is 4.8 and glucose concentration is 17.2 g L^{-1} (Figure S6, Supporting Information), **NCS-60** also shows a negative temperature gating behavior along with the temperature increased from 18 °C to 43 °C, and the **NCS-10** shows a positive temperature

gating behavior. These results verify our speculation that the observed opposite gating performances between **NCS-60** and **NCS-10** are directly related to the influence of long and short polymer chains.

In the follow-up experiment, it is proved that these two systems can also show consistent temperature gating behaviors by changing the external stimuli. When the pH is 10.1, and the glucose concentration changes from 0 to 17.2 g L^{-1}, the temperature gating behaviors of **NCS-60** change from negative to positive with a temperature gating ratio of 1.8 (Figure S3, Supporting Information), along with the temperature increases from 18 ^{o}C to 43 ^{o}C (Figure 3A), and the **NCS-10** also shows positive gating behavior with a temperature gating ratio of 2.2 (Figure S3, Supporting Information) (Figure 3B). In this process, the copolymers inside nanochannels also dehydrate to form a compact conformation as described above. But the stable complex between the charged borate and the glucose is formed to keep copolymer chains at hydrophilic state at both low and high temperature states. Our result shows that the ionic current of both **NCS-60** and **NCS-10** is mainly controlled by the effective cross section area. These results further verify that gating performances of nanochannel systems are directly related to the influence of long and short polymer chains. In addition, when pH is 7.4, the experiments are performed again, and the results similar as that under basic conditions (Figure S5, Supporting Information). The temperature gating performances of **NCS-60** is also studied when glucose concentration is 8.6 g L^{-1} under different pH conditions, the results shows that **NCS-60** has similar gating performances with 8.6 and 17.2 g L^{-1} glucose in solution (Figure S6, Supporting Information).

In conclusion, we discover that the macromolecular nanochannels (**NCS-60** and **NCS-10**) could show opposite gating behaviors, which is caused by the different lengths of the same gating molecule. Therefore, this work illustrates the importance of the gating molecule length for the sensitive nanochannel systems, and might help us to further understand the reversible gating properties of macromolecular gates and may have implications for future nanofluidic sensing.

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Notes and references

[a]Key Laboratory for Large-Format Battery Materials and System, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, P. R. China. Email: xiafan@hust.edu.cn

[b]National Engineering Research Center for Nanomedicine, College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan, Hubei 430074, P. R. China.

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