On Ferroelectric Phenomenon in Free-standing Poly (Dibenzo-crown Ether) Films

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Abstract: Conjugated polymers generally do not possess the ferroelectricity due to charge delocalization in various degree. We discover the distinct ferroelectric phenomenon (from 0.1 to 2.16 μC cm^{-2}) in freestanding films of three kinds of poly (dibenzo-crown ether) (PDBC, dibenzo-14-crown-4, dibenzo-15-crown-5 and dibenzo-18-crown-6) which are prepared by electrochemical polymerization in BFEE. Ferroelectricity in PDBC freestanding films appears on account of spontaneous polarization resulted from hydrogen bonds, generated due to the intermolecular association between carbons on the benzene rings and ether bonds. This paper find, as the number of ether bonds increases, the ferroelectric phenomenon of PDBC is more remarkable, which is coincident with the enhancing hydrogen bonding effect. Meanwhile, such effect is inexistent in polyphenyl.
***Keywords*:** ferroelectricity, dibenzo-crown ether, hydrogen bond

1. Introduction

There are broad applications for polymers of dibenzo-crown ethers based on ion exchange characteristic, including membrane utilization, solid supported reactants in phase transfer catalysis, analogues of biological membranes and ion-selective electrodes [1-6] due to their specific structure which contains benzene ring as rigid group and ether as flexible chain. However, ferroelectricity as one potential property explored in rising types of polymers [7-11] has not been studied in polymers of dibenzo-crown ether. The observation of ferroelectric phenomenon in polymers of dibenzo-crown ether must be beneficial for expanding their usage in electronic field. Ferroelectricity [12-14] is generally considered as the special property of some dielectric crystal with specific structure where spontaneous polarization exists caused by permanent dipole moment due to positive and negative centers of the cell do not coincide. Most of ferroelectrics [15-16] are group of inorganic salts, such as potassium dihydrogen phosphate (KH2PO4) and barium titanate (BaTiO3). Nevertheless, an increasing number of organics including PVDF [17-18], liquid crystalline and PANI [19] nanotubes have been reported to possess ferroelectricity in recent years though many of them are not characteristic of specific crystal form, even not crystals. Many studies [20-23] reveal that directional arrangement of structural elements in polymers on account of polar bond like C-F cause dipole moment, leading to spontaneous polarization, namely, ferroelectric phenomenon. Although conjugated polymers are difficult to possess ferroelectricity due to charge delocalization in various degree and conductivity to some extent, studies indicate that PANI [10] nanotube show remarkable ferroelectricity under the function of hydrogen bond. We discover the distinct ferroelectric phenomenon (from 0.1 to 2.16 μC cm-2) in freestanding films of three kinds of poly (dibenzo-crown ether) and the ferroelectric response enhances with the increase of hydrogen-bond interaction.

2. Experiments

Constant voltage deposition method was applied to prepare polymers of dibenzo-crown ethers. The electrochemical polymerization of DBC was carried out in a one-compartment cell with the use of potentiostat-galvanostat (Princeton Applied Research – VersaSTAT3) under computer control. In the three-electrode system, the working electrode and counter electrode are indium-tin-oxide (ITO) with Ag/AgCI as reference electrode. The polymers are deposited on working electrode and immersed in ammonium hydroxide for 24h after being removed for dedoping. Then, the films were dried in vacuum at 60℃ for 24h. The size of prepared films was 1×2cm with the thickness about 10μm. The samples were then used for FTIR measurements (Thermo IN10) and P-E loop tests (Ferroelectric analyzer, Precision Premier Ⅱ) The specific reaction conditions are shown in table 1.

Table 1. The polymerization conditions of DBC in BFEE

DBC	Concentration/M	Voltage/V	Duration/h
D14 (dibenzo-14-crown-4)	0.01	0.7	2
D15 (dibenzo-15-crown-5)	0.01	0.85	2
D18 (dibenzo-18-crown-6)	0.01	1.05	4

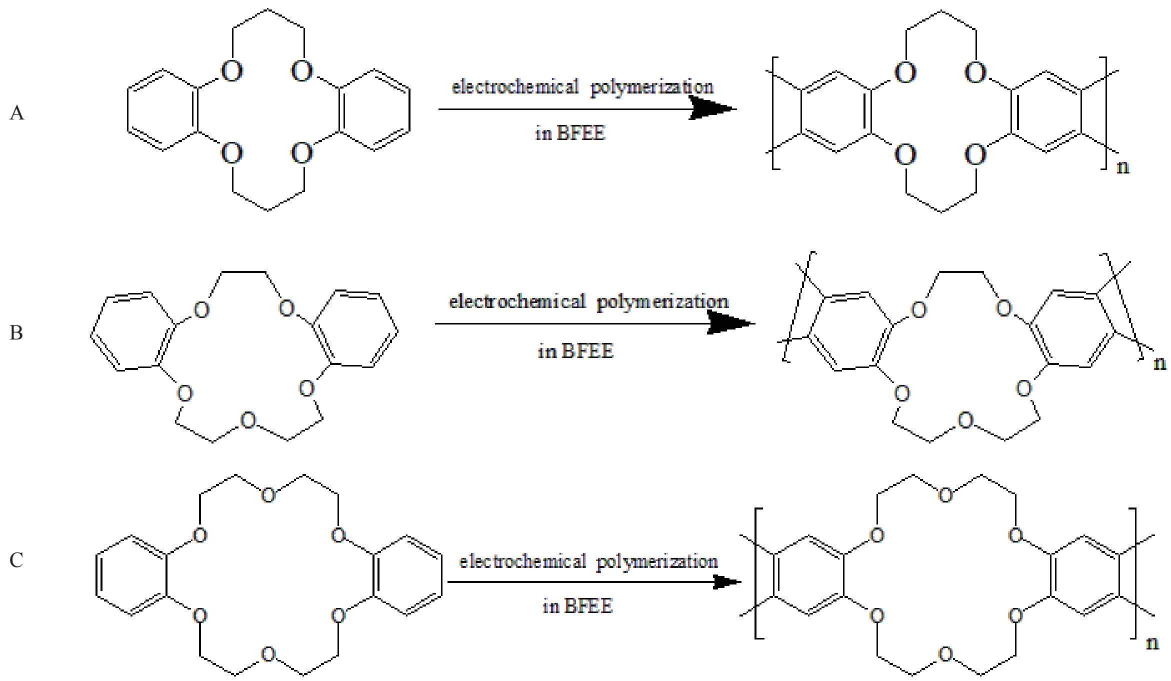

Figure 1. The electrochemical polymerization of (A) dibenzo-14-crown-4, (B) dibenzo-15-crown-5 and (C) dibenzo-18-crown-6.

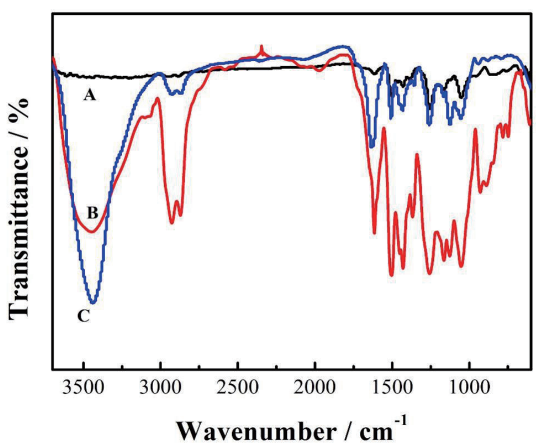

Figure 2. FTIR spectra of the (A) PDBC-14, (B) PDBC-15 and (C) PDBC-18 obtained potentiostatically at 0.7V, 0.85V and 1.05V, respectively from BFEE + 0.01 mol L-1DBC.

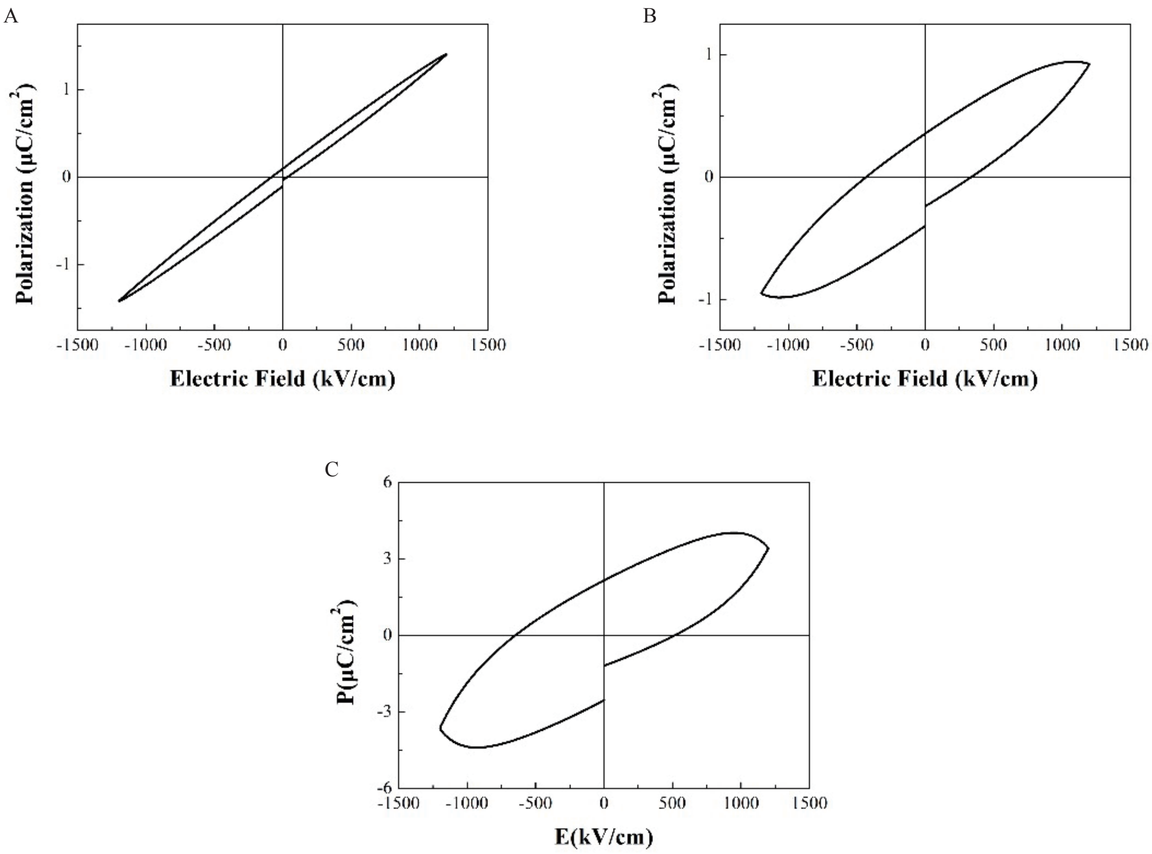

Figure 3. P-E loop at room temperature for (A) PDBC-14, (B) PDBC-15 and (C) PDBC-18. The values of remnant polarization are about 0.1, 0.36 and 2.16 μC cm-2, respectively.

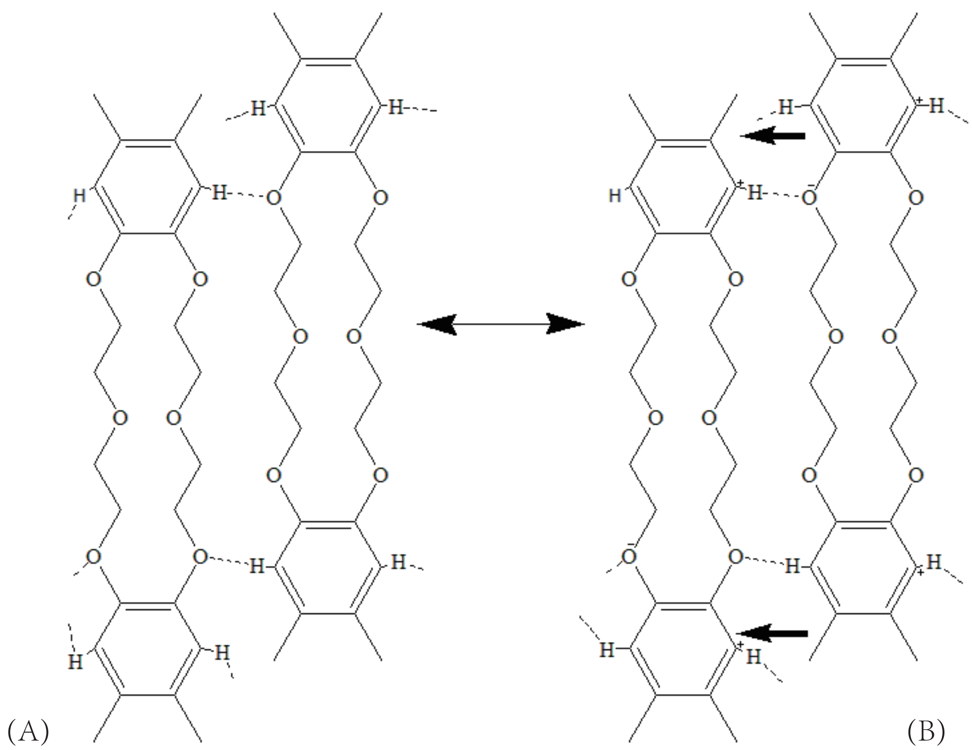

Figure 4. Schematic diagram of PDBC-18 chains which exhibit (A) interconnection through H bonds and (B) charge transfer process to create dipole in a specific direction.

3. Characterizations

Xu et al.[24-28] has been exploring electrochemical polymerization of numerous aromatic monomers in BFEE and gaining great achievements, which included the chemical polymerization of dibenzo-18-crown-6[28] in BFEE. Figure 1 shows the binding conditions of different DBC in BFEE. The electrochemical polymerization of DBC-14 and DBC-15 were attempted successfully in accordance with above principle. Figure 2 reveals the typical transmission infrared spectra of (A) PDBC-14, (B) PDBC-15 and (C) PDBC-18, the characteristic peaks between 600 and 1500 cm-1 indicates the existence of the polymers and the benzene rings were not destroyed during polymerization [28]. PDBC-18 has strong characteristic peak near 3500 cm-1 and the intensity of peak here is moderate while that of PDBC-14 is completely smooth. The characteristic peak of hydrogen bond is around 3500, which implies that PDBC-18 has the highest degree of hydrogen bonding among three polymers, followed by PDBC-15, and PDBC-14 has almost none. The ferroelectric response for polymers is shown in Figure 3. The ferroelectric phenomenon becomes more remarkable with PDBC-14, PDBC-15 and PDBC-18. Their remnant polarization correspondingly increases, changing from 0.1, 0.36 to 2.16 μC cm-2. Figure 4 reveals the process how hydrogen bond influences the ferroelectric phenomenon of PDBC. The carbon on the aromatic ring has a relatively strong ability to attract electrons, and can form weak interchain hydrogen bonds with the oxygen atoms on the ether chain. When an electric field is applied, hydrogen bonds form dipoles in its direction and remnant polarization remains with the disappearance of electric field, resulting in ferroelectric phenomenon. In the polymers of DBC, the quantity of hydrogen bond depends on the content of ether bond to a great extent. For the monomer of DBC-14, DBC-15 and DBC-18, their number of ether bond is 4, 5 and 6. The accumulation of varying degrees of hydrogen bond interaction leads to variable-strength ferroelectricity phenomenon, which is well proved by the ascending of corresponding remnant polarization. Additionally, similar experiment was applied to polyphenyl where ferroelectricity is not displayed, which corroborates that the hydrogen bond is the key to ferroelectric phenomenon.

4. Conclusion

In conclusion, we have prepared freestanding films of polymers of three kinds of DBC exhibiting increasing ferroelectric phenomenon due to their enhancing hydrogen bonding effect, which broadens the electronic applications of PDBC and provides improving direction of ferroelectricity of homologous polymers.

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