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研究課題名(和文) Manipulating Crystallization of Ferroelectric Polymers in Two-Dimensional Spatial Confinement and Its Mechanistic Understanding
研究課題名(英文) Manipulating Crystallization of Ferroelectric Polymers in Two-Dimensional Spatial Confinement and Its Mechanistic Understanding
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研究成果の概要(和文)：本研究では、気水や液液界面において、強誘電性高分子のナノ構造化と結晶化を同時に制御することを成功した。界面の閉じ込め効果より、作製した強誘電性高分子の超薄膜やナノ粒子は約97%以上に強誘電相を含んで、バルク材料より小さい結晶ドメイン(3-6ナノメートル)であることを示す。したがって、外部電場下で強誘電体ドメインが容易に整列しており、外部電場を切るとすぐに元の状態に戻る。また、コンデンサデバイスを作製し、エネルギー貯蔵挙動も明らかに調べた。

研究成果の学術的意義や社会的意義
環境に優しく高効率のエネルギー貯蔵が注目されている。圧力、熱、電気に応答する強誘電性高分子は、さまざまな場面でエネルギーを蓄えることができる。デバイスのパフォーマンスを向上させるため、結晶特性を適切に制御し、デバイスのパフォーマンスとの相関関係を深く理解する必要がある。本研究では、界面での強誘電性高分子の結晶化とナノ構造化の制御を同時にでき、デバイス特性との関係を調べた。

研究成果の概要(英文)：In this study, we succeeded in simultaneously controlling nanostructuring and crystallization of ferroelectric polymers at the air-water and liquid-liquid interfaces. From the confinement effect of the interface, it is shown that the prepared ferroelectric polymer ultrathin film and nanoparticles contain about 98% or more of the ferroelectric phase, and the crystal domain is in the range of 3-6 nanometers, which are much smaller than that of polymer bulks. Therefore, the polar ferroelectric domains are easily aligned under the external electric field and return to the original state as soon as the external electric field is turned off. In addition, capacitor devices were prepared and the energy storage behavior was clearly investigated.

研究分野：強誘電性高分子材料

キーワード：Ferroelectric polymers Langmuir-Blodgett films Nanoparticles Crystallization control Crystal size Energy storage

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1. 研究開始当初の背景

Poly(vinylidene fluoride) (PVDF)-based dielectrics having higher dielectric constant ($k \sim 10-12$) than most of polymers and high temperature capability are attractive for a broad range of applications such as film capacitors, gate dielectrics, artificial muscles and electrocaloric cooling. Unfortunately, large dielectric loss in high- k PVDF ($\tan \delta \sim 0.02$) hampers their applications, which is even 1000 times larger than some commercial polymer dielectric films. To suppress dielectric hysteresis loss ($\tan \delta$) and increase energy density (U_e) and charge-discharge efficiency (η), manipulating PVDF crystallization, i.e. increasing content of electroactive β crystal (**Figure 1a**) for higher spontaneous polarization value (P_s , **Figure 1b**) but decreasing β crystal domain size to nanometer scale for smaller remanent polarization value (P_r) was effective (Eqns. in **Figure 1b**), namely a “slimming” hysteresis loop. It can be realized through nanoconfinement-effect (a) chemical methods: inducing structural defects into traditional PVDF polymers through electron irradiation or chemical molecular design and (b) physical methods: designing multilayered dielectric films consisting of PVDF and high breakdown/low loss/high thermostable polymers to reduce migrational loss from impurity ions and confine the growth of crystal size and having specific crystal orientation. However, these approaches always produce an enhancement in one of the properties (e.g., high energy density) but a reduction in another (e.g., high dielectric and hysteresis losses) because of the difficulties on simultaneous control of PVDF crystallization and film configurations.

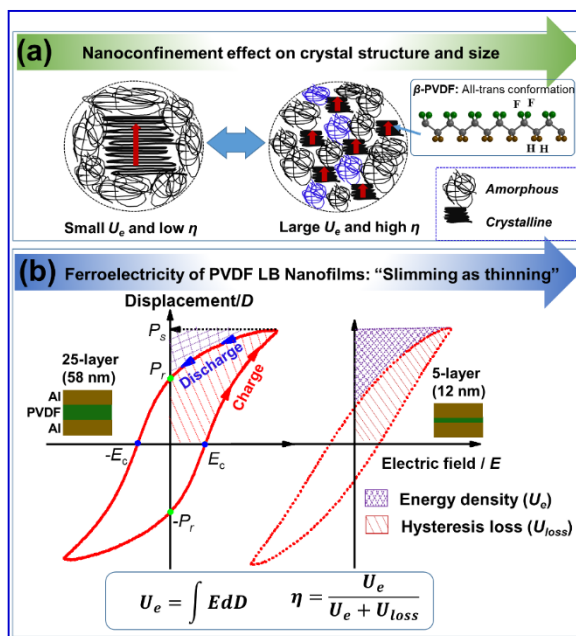


Figure 1. Schematic illustration of PVDF crystal miniaturization under nanoconfinement effect (a) and film thickness dependent ferroelectric hysteresis loops (b).

2. 研究の目的

In this study, crystallization control of ferroelectric polymers toward selective polar crystal with small domain size through interfacial methods is targeted to effectively suppress dielectric loss in ferroelectric dielectrics through depicting the following research aspects.

- (1) manipulating crystallization of ferroelectric polymer at interface towards simultaneously control of nanostructure size, crystal phase and domain size;
- (2) develop blend monolayers and their multilayered nanosheet films consisting of traditional ferroelectric polymers (PVDF and Nylon);
- (3) high-performance energy storage devices based on ferroelectric polymer nanosheets.

3. 研究の方法

Interfacial nanostructuring methods were used to prepare ferroelectric polymer monolayers and nanoparticles. The nanostructures including monomer layer nanosheets and nanoparticles were investigated.

- (1). Optimizing monolayer formation of PVDF polymers (homo-, co- and ter-polymers) and insulating linear dielectric polymers at the air-water interface: Surface pressure-area isotherms of different ferroelectric polymers at air-water interface; In-situ investigation of monolayer morphologies using Brewster angle microscopy (BAM).
- (2). Confirmation of monolayer transfer and multilayered film structure:
 - ① Monolayer transfer: quartz crystal microbalance (QCM) analysis and UV-Vis spectra will be used for monitoring monolayer transfer;
 - ② Multilayered structure and crystallization confirmation: X-ray diffraction (XRD) measurement.
- (3). Effect of layering structures on output energy density and hysteresis loss as a function of layer thickness and/or layer sequences:
 - ① Device preparation: capacitor type;
 - ② Dielectric spectroscopy in time and frequency domain;
 - ③ Systematical investigation of ferroelectric behaviors under different external electric field and energy storage behaviors.

4. 研究成果

(1) Interfacial nanostructuring of ferroelectric polymers

① Langmuir-Blodgett films of PVDF based polymers and their crystallization properties

Figure 1 shows the chemical structure of amphiphilic polymer pDDA and PVDF based ferroelectric polymers used in this study. Amphiphilic polymer, poly(*N*-dodecylacrylamide) (pDDA) was used to enhance the monolayer stability at the air-water interface. Monolayer formation of PVDF polymers (homo-, co- and ter-polymers) was confirmed through surface pressure (π)-area (A) isotherm measurements. As shown in **Figure 2**, a tiny amount of pDDA could greatly improve the monolayer elasticity of PVDF based terpolymers. The monolayers were successfully transferred onto substrates through vertical deposition to form multilayer polymer nanosheets. Confinement effect on crystalline properties of PVDF based polymers in the LB films were confirmed using FT-IR and XRD spectra. For instance, in the case of PVDF homopolymer, only ferroelectric phase (β crystal) was found in the thin films with a crystal size of 3-4 nm.

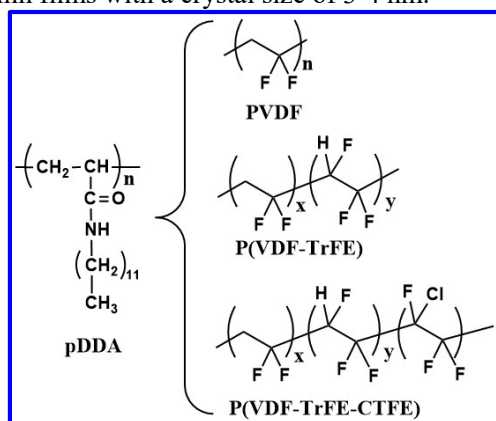


Figure 1. Chemical structures of pDDA and PVDF based polymers for preparation of blend LB films.

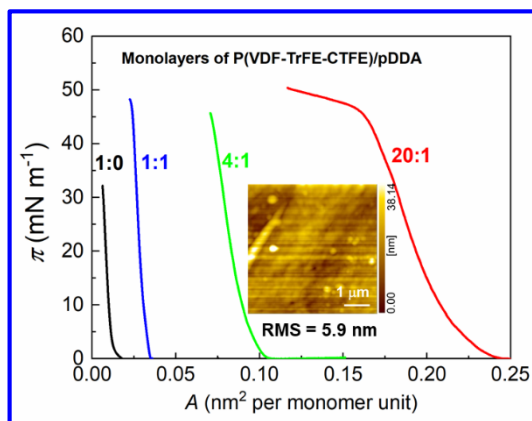


Figure 2. Surface pressure (π)-area (A) isotherms of pure and blend monolayers of P(VDF-TrFE-CTFE) and pDDA. The inset image is an AFM image of a 6-layer film transferred on silicon substrate.

② Langmuir-Blodgett films of Nylon 11 and their crystallization properties

Monolayer formation of Nylon 11/pDDA was also confirmed. The layer structure of the Nylon 11/pDDA was investigated using small-angle X-ray reflection (XRR) patterns at different mixing ratio (**Figure 3**). With the increase of Nylon 11 content, the Kiessing fringes and the Bragg's peak at $2\theta =$ about 2.5° became weak, which indicates the layer structure of the amphiphilic pDDA was interrupted by the blending with Nylon 11. The crystallization of the Nylon 11/pDDA LB films was confirmed by FT-IR and XRD measurements. Results indicate that the Nylon 11/pDDA LB films contain ferroelectric δ' phase in comparison with the hot-press and solution-cast samples which contain paraelectric γ phase. The unique crystallization was generally achieved through quenching treatment in melting samples because it induced the hydrogen bonding disordering. It is a new achievement that the LB films were favorable to disturb the ordered hydrogen bonding in crystalline Nylon 11, thereby contributing to the formation of the ferroelectric δ' phase.

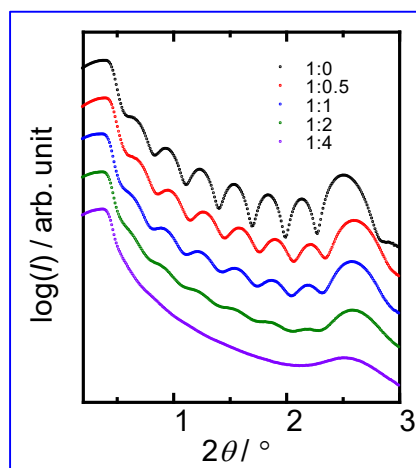


Figure 3. XRR patterns of LB films at different molar ratios of pDDA/Nylon 11.

③ Liquid-liquid interfacial nanoparticle formation of PVDF based polymers and their crystallization properties

Nanostructuring and preferential crystallization of PVDF homopolymers were realized simultaneously in a nonsolvent (water)-solvent (DMF)-polymer (PVDF) ternary system (**Figure 4**). Results show that a clear liquid-liquid interface (**Figure 4a**) generated between DMF and water provided PVDF NPs (approximately 250 nm) with a narrow size distribution (**Figure 4b**). Nonsolvent was found to be crucially important not only for nanostructure morphologies but also for selective crystallization into the ferroelectric phase. When water was used as a nonsolvent, the content of the ferroelectric

electroactive (EA) phase (sum of β and γ phases) was found to be greater than 97 % among the crystalline portion (**Figure 4c**). The crystal size was calculated using the Debye–Scherrer equation based on XRD results. Results indicate that the crystalline size for the spherical nanostructures (6 nm) is smaller than that of pristine PVDF (12 nm).

(2) Device performance and energy storage behaviors

PVDF LB nanofilms have a unique layer structure consisting of PVDF β crystals surrounded by amphiphilic pDDA, which is suitable for high energy density and low loss dielectrics investigation. The discharge curve in nonlinear dielectrics (ferroelectrics) does not follow the charge curve because the remanent polarization generated unreleased energy, which is the energy loss (**Figure 5a**). The energy stored (U_{nl}) and energy loss (U_{loss}) were marked clearly. Based on ferroelectric hysteresis loops obtained for devices in different electric fields, details of the energy storage behaviors were investigated for these ferroelectric capacitors. We show the stored energy as a function of electric field for each sample (**Figure 5b**). All the devices exhibited similar trends: the energy density stored increased as the electric field increased. The highest energy stored was 6.0 J/cm³ (5-layer PVDF LB film: termed as 5LB) at 500 MV/m, which is comparable to those of most polymer-based dielectrics. The highest energy stored was obtained as 6.0 J/cm³ for the film with a charge–discharge efficiency of 34.8%. The energy loss invariably increased as the electric field and the film thickness increased because of the increased remanent polarization (**Figure 5c**). The small β -crystal size (3–4 nm based on XRD data) is beneficial for the suppression of hysteresis-induced dielectric loss because the ferroelectric domain coupling can be “nanoconfined” at discontinuous boundaries, in which the polarized domain readily switches back to its original state once removed from the external electric field. The charge–discharge efficiency (η) of the devices is presented in **Figure 5d**. It is noteworthy that the 5LB devices proved to have the highest efficiency over the thicker devices because of their slim hysteresis. The efficiency value for 25LB decreases from 90% to 20% as the electric field increases, which might be ascribed to the greater energy loss induced by the ferroelectric hysteresis with higher remanent polarization and the current leakage from the breakdown of the pDDA component.

(3) Summary

Crystallization control of ferroelectric polymers toward selective polar crystal with small domain size was achieved through interfacial methods. The PVDF LB films were investigated for energy storage behaviors. The results proved that in the thinner films with small crystal size of the ferroelectric phase is helpful for approaching higher performance.

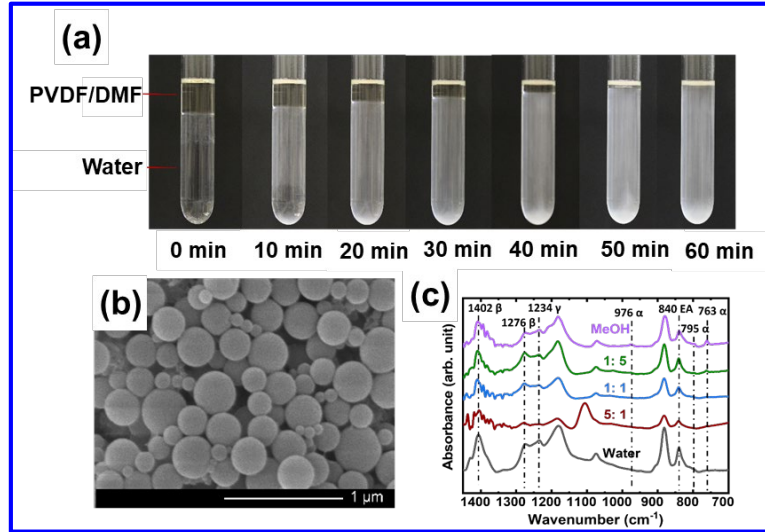


Figure 4. (a) Nanoparticle formation process at the DMF-Water interface, (b) SEM image of the PVDF nanoparticles and (c) FT-IR spectra of PVDF nanostructures prepared from different ternary systems with varying nonsolvent.

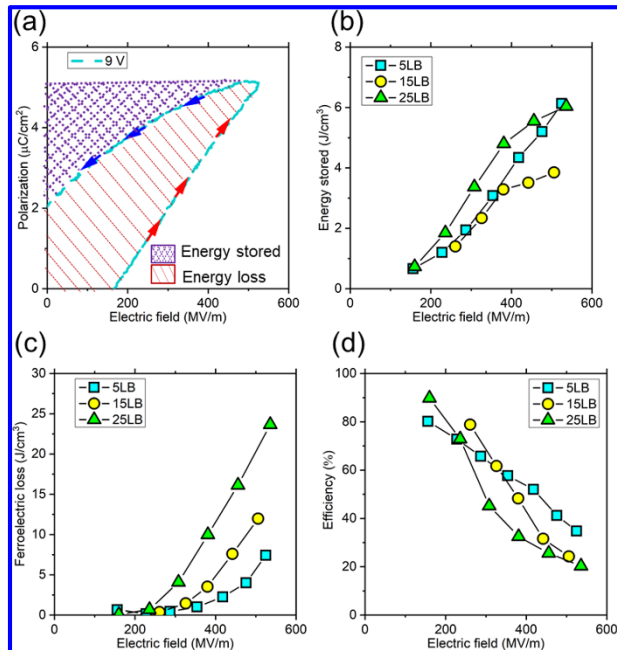


Figure 5. (a) Schematic description of the energy storage characteristics for the 5LB capacitor induced by a triangle-wave AC voltage with 9 V amplitude, (b) the calculated energy storage density, (c) the ferroelectric energy loss, and (d) the discharged energy efficiency for each sample.

5. 主な発表論文等

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掲載論文のDOI (デジタルオブジェクト識別子) 10.1038/s41428-019-0194-3	査読の有無 有
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3. 雑誌名 Polymer Journal	6. 最初と最後の頁 In press
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〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考

7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関