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## Polymer-based dielectrics with high permittivity for electric energy storage: A review

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### Abstract:

Polymer-based dielectrics (PDs) with improved permittivity ( $k$ ) have considerable applications including capacitors, actuator devices and electrical power systems due to their flexibility, easy processability and low weight, etc. However, the permittivity values of commonly used polymers (usually  $k < 3$ ) fails to meet the requirements of the advanced electrical components. Enormous research, including numerical and experimental works has shown that developing polymer based multi-phase materials represents the most promising avenue. This review will clarify the concepts and relationships based on the polarization mechanisms and meanwhile some key factors of improving permittivity will also be discussed including polymer chains/segments, morphology, the

interface of nanofillers-matrix, processing, and multilayer structures. Combining with the recent specific advances in PDs, the latest developments in this field will be summarized which are the introduction of polar functional groups/copolymer segments, the application of core-shell nanofillers and the technology of multi-layers structures. We hope to help readers to comprehensively understand the fabrication of PDs from the selection of molecular units to the design of composites in order to provide guidance on achieving polymer based materials with high permittivity.

**Keywords:**

Dielectric polymers; Multi-structures; High permittivity; Processing.

## 1. INTRODUCTION

Polymer-based dielectrics (PDs) have considerable applications in dielectric-based capacitors, communication devices, field-effect transistors (FETs) and actuators, etc. which are important units in advanced intelligent equipment and electrical/electronic device. [1-7] Comparing with the other dielectric materials such as ceramics, PDs can provide a more possibility of being molded into various configurations and thus have more potential applications. For instance, they can be used as insulation layer or semiconducting layer in an electrical cable, as a dielectric film in a capacitor to store energy in the power systems. Furthermore, as functional materials in an actuator device, the flexibility of the PDs can result in the mechanical deformation under an applied electric field which achieves the conversation between electric and mechanical energies. However, due to their low permittivity, PDs have fallen behind current developments. Hence, developing polymer based

materials with high dielectric performances have obtained more attention in both industry and academia fields.

Commonly used polymers include polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), poly(dimethylsiloxane) (PDMS), epoxy and poly(vinylidene fluoride) (PVDF). The major drawback of these polymers is their relatively low permittivity values (usually  $k < 3.5$ , except PVDF), which consequently results in the limitation of the performance improvement in the practical devices. For instance, in a capacitor, the permittivity of the dielectric film is the key point which determines the energy storage of a capacitor. In an actuator device, the permittivity of the dielectric material is also of the great importance because it affects the stress generated by electrostatic force from charges [8-17]. Therefore, improving the permittivity of PDs has been an appealing topic which has attracted huge amounts of researchers in the recent years.

Based on the dielectric theory, the permittivity is the ability of a material to polarize in an alternating current (AC) electrical field and the polarizations have four types depending on the range of frequency from high to low: the electric, ionic, dipolar and interfacial polarizations. Most of the polymers are composed by C-H covalent bonds which can arouse little polarization and thus it is difficult to obviously increase the permittivity of a neat polymer. However, when a polymer based material is consisted by more than one phase, the permittivity will be significantly improved due to the dipolar polarization from some polar groups, certain crystal phases as well as the interfacial polarization in the interfacial regions.[4] Therefore, strengthening polarization in a polymer based material is a basic idea to improve material's dielectric performance.

In various composite systems where a polymer is matrix incorporated by fillers with different contents, such as ceramic, semiconducting oxides, giant dielectric oxide particles, metal or carbon, enhancing interfacial polarization responses is a main strategy to obtain high permittivity.[18-41] In order to arouse stronger polarization, more interfacial regions should be created and consequently, fillers of nano-scaled size are more popular than those of micro-scaled size because the smaller the size of the fillers, the larger surface areas can be obtained. A high fraction of inorganic nonmetal particles (ceramic, semiconducting oxides, giant dielectric oxide particles *etc.*) for high- $k$  composites certainly is the key issue in flexible dielectric materials, which usually causes severe damage to the processability and mechanical flexibility of polymer composites. Meanwhile the introduction of conductive fillers (metal, carbon *etc.*) with incremental contents will experience an abrupt increase about one or even several orders of magnitude due to the percolation phenomenon, which usually results in high leakage current. Thus how to eliminate the negative factors in high- $k$  composites discussed above is the priority issue that needs to be solved. Moreover fillers with different shapes, structures and geometries (e.g., spheroids (0D), fibers (1D), platelets (2D), *etc.*) are introduced in a polymer matrix for studying the morphology effect on the permittivity and the basic principle also focuses on the interfacial regions. Although the permittivity of composites can be enhanced, a significant drawback of these methods is the reduction of the dielectric breakdown strength and the sacrifice of the flexibility of a polymer based composites. Hence, developing approaches to increase the permittivity and maintain the breakdown strength and flexibility challenges the researchers working on the polymer based composites.[42-63] Recent experimental investigations have indicated that a composite with multilayered structures can resolve this

problem. Compared to conventional blending composites, in a multilayered composite, layers with high permittivity and layers with high breakdown strength are stacked layer-by-layer and this combination can provide synergistic advantages. The application of the multilayered composites can provide more possibility for exploiting intelligent combination of fillers and polymer by taking advantage of the hierarchical effect.

Increasing polarization responses is also used in developing and designing all-polymer dielectrics and the efficient methods include selecting polar segments, ameliorating crystalline and amorphous regions, and the co-extrusion processed films by polymer pairs. The simulation works by Sharma et al. [64] provided the function of the corresponding computed band gaps with molecular structures of hydrocarbon-based polymers and the permittivity from electronic and atomic (or ionic) parts by the density functional theory calculations. They have summarized the appropriate polymer repeat units that enhanced the ionic part of the permittivity and according to their results, synthesizing polymers by the rational selection of chemical functionalities has become popular which have also created many new polymers with modified structures and repeated units. Furthermore, crystalline properties have similarly exhibited a significant influence on the permittivity of semi-crystalline polymers as their aggregation structures (e.g., crystalline polymorph, average size of crystal grain, and crystallinity) [65-67]. PVDF is a typical example and surrounding the PVDF and its copolymer family, the applications of ferroelectric polymers in the high permittivity fields have also been widely studied. Tuning their crystalline structures by certain defect modifications by high-energy irradiation light has been proved as an effective method to improve the permittivity in PVDF copolymers. In addition, the co-extrusion processed multilayered polymer films are as similar as the

multilayered composites which consist of alternating layers of a polymer with high permittivity and a dielectric polymer with high dielectric strength [68]. Differently from the simply blending more than one polymer, co-extrusion processing can resolve the incompatibility of different polymers and the combination of the polymer pairs can even achieve higher dielectric strength than that of the individual polymer due to the block effect.

The rapid development of high technology applications generates more needs for multifunctional polymer materials with improved dielectric properties. Based on the dielectric polarization mechanism, this review will summarize the recent advances in the PDs with high permittivity by three major methods: the direct chemical synthesis based on the rational design, the polymer matrix composites with tailed interfaces and the application of multilayered structures. Our objective of preparing this review is to help readers to understand how to select the appropriate methods to prepare PDs based on the fundamental concepts and current processing conditions in order to achieve PDs with high dielectric performances.

## **2. DIELECTRIC FUNDAMENTAL AND ISSUES FOR ELECTRIC ENERGY STORAGE**

### **2.1 Dielectric fundamental**

Dielectrics are a kind of materials which can induce polarization when an electric field is applied.

For a parallel plate capacitor, neglecting edge effects, the capacitance  $C$  is given by

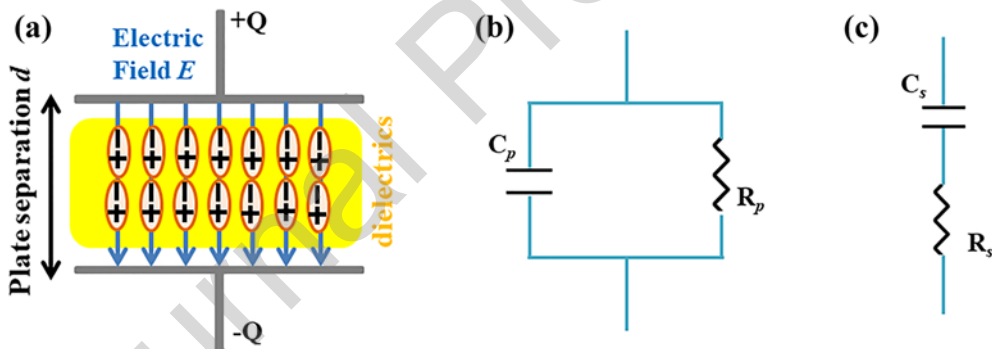
$$C = \frac{k_0 A}{d} \quad (1)$$



where  $A$  is the area of electrodes,  $d$  is the distance between two electrodes,  $k_0$  is the permittivity in vacuum. When a dielectric material is placed between the electrodes, the capacitance increases due to the polarization of the dielectric materials, and it is described by

$$C = \frac{k'k_0A}{d} \quad (2)$$

where  $k'$  is called as the relative permittivity of the dielectric material. In fact, dielectric materials are not really insulating, they can conduct electricity to some small extent when a direct current (DC) voltage is applied across it. In this case, a parallel combination of capacitance ( $C$ ) and resistance ( $R$ ) can be equivalent to the circuit as shown in Figure 1.



**Figure 1.** The dielectrics between the parallel plates (a) and the defined equivalent circuit of the dielectrics (b) parallel and (c) series.

The  $C_p$ ,  $R_p$  of the parallel circuit are given by

$$C_p = k'(\omega) C_0 \quad (3)$$

$$R_p = 1/\omega k''(\omega) C_0 \quad (4)$$

And the parameters of the series circuit can be converted by the parallel circuit as follows

$$(\omega C_S R_S)^{-1} = \omega C_P R_P \quad (5)$$

$$\omega C_S R_S + \omega C_P R_P = \omega C_S R_P \quad (6)$$

To be brief, the performance of a dielectric material is often characterized by its complex permittivity and loss tangent, which can be described as:

$$k^*(\omega) = k'(\omega) + jk''(\omega) \quad (7)$$

$$\tan \delta(\omega) = k''(\omega)/k'(\omega) \quad (8)$$

where  $\omega$  is angular frequency ( $\omega = 2\pi\nu$ ,  $\nu$  is frequency in Hz),  $k'(\omega)$  denotes the real part of permittivity which always different from zero and represents the contribution to the polarization responsible for the energy storage in the material. And  $k''(\omega)$ , the imaginary part, its physical meaning can be expressed by the equivalent circuits mentioned above. The parallel circuit describes the loss caused by the leakage current, in which the parallel resistance represents the tiny conductance in the dielectric. In addition, the series circuit describes the loss caused by dielectric polarization under AC voltage. It can be seen from the Eq. (3)-(8), the polarization loss represented by the series circuit is dominant at high frequency. On the contrary, the leakage conduction loss represented by the parallel circuit is dominant at the low frequency. The dielectric performance commonly includes permittivity ( $k$ ) and dielectric loss ( $\tan \delta$ ) for dielectric materials used in weak electric fields and its polarization-electric field ( $P$ - $E$ ) relationship and its breakdown field ( $E_b$ ) for the dielectric materials used in high electric fields.

In order to address its basic independence from electric field, it is often referred to as the relative permittivity ( $k_r$ ) of a material. The imaginary part  $k''$  (dielectric loss) is also critical for the performance of the high- $k$  dielectrics. Low dielectric loss should be paid more attention when the high- $k$  dielectrics are studied because usually higher dielectric loss at low field will be introduced by adding the high- $k$  or high conductivity fillers compared with the pure linear dielectrics. [15-19] The dielectric loss can be even more increased at a high electric field.

In order to advantageously exploit applications of a dielectric material, beside permittivity, the dielectric loss and breakdown field or breakdown strength ( $E_b$ ) of materials should be also considered. [69] The effective loss factor should be kept as low as possible. In fact, losses not only waste part of the input energy, but also worsen the insulation properties of the materials. For any dielectric material it is possible to identify a threshold electric field, which results in irreversible modifications in the medium accompanied by the onset of an intense and disruptive flow of charges. Such a sudden loss of insulation due to a very high electric field is called dielectric breakdown of the material. The minimum field responsible for such an effect is named as breakdown field or breakdown strength ( $E_b$ ). For most dielectric polymers,  $E_b$  is in the range  $10^6$ - $10^8$  V/m. [70-74] Until now, it is still difficult to make a reliable prediction of  $E_b$  using existing physical models because the  $E_b$  is not only dependent on the structure but also thickness and morphology of dielectric materials. [69] For the material with same composition, the  $E_b$  value of thin film is often higher than that of thick one because there is a very small quantity of defects in thin films.[73]

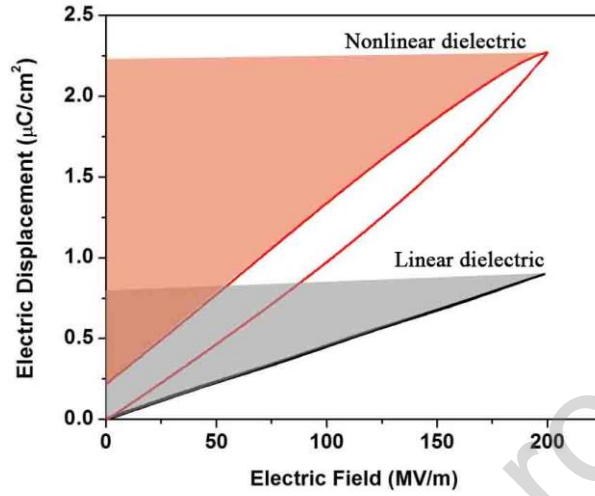
## 2.2 Present issues for electric energy storage

Dielectrics are widely used in a broad range of applications such as capacitors, transformers, cables and switched-mode power supplies. The most nature is used as an insulating layer to separate electrical conducting surfaces where electrical separation of charged elements is necessary. With the development of advanced electronics and electrical power engineering, dielectric capacitors with electrical energy storage have been attracted more attention due to their fast charge-discharge capability. However, the big issue impeding their potential applications in industry is their low energy storage density which is lower than those of electrochemical energy storage devices. The energy storage density is given as follows.

$$U = \int E dD \quad (9)$$

where  $U$  is the total stored energy density,  $E$  is the applied electric field and  $D$  is expressed in  $C m^{-2}$  and is known as the electric displacement. As shown in Figure 2, The charging curve of linear dielectric almost overlaps with the discharging curve, and the nonlinear dielectric shows utterly different phenomenon because of the strong coupling interaction between dipole in the process of charging and discharging materials. And there are still polarization exists (residual polarization, the intercept of D-E loop on the Y-axis in Figure 2) even after the revocation of the applied electric field. In practical application, the energy storage density we need is actually the integral of discharge curves of dielectric film materials on Y-axis, that can be represented by the shaded part in

Figure 2.



**Figure 2.** D-E loops of linear and nonlinear dielectrics at the same electric field.

Considering linear dielectrics, the energy storage density  $U$  also can be calculated as follows.

$$U = \frac{1}{2}DE = \frac{1}{2}k'k_0E^2 \quad (10)$$

where  $k'$  is the relative permittivity and  $k_0$  is the vacuum permittivity. Thus,  $U$  is strongly dependent on both  $k'$  and  $E^2$ . To improve the energy storage density, high permittivity of the dielectrics as well as high breakdown strength should be considered. Among the Polymer-based dielectrics, one method to improve the energy density is using polymer nanocomposites as an alternative.

Dielectric breakdown strength of the dielectric materials can be detected through Voltage Withstand Test Instrument, associating with electrodes to measure the breakdown voltage of dielectric films. And the data can be processed through the two-parameter Weibull equation, which is described as follows.

$$P(E) = 1 - \exp(-(E / E_b)^\beta) \quad (11)$$

where  $P(E)$  is the cumulative probability of electric failure,  $E$  is the experimental breakdown strength,  $E_b$  is a scale parameter which there is a 63.2% probability for the sample to breakdown (Weibull  $E_b$ ), and  $\beta$  is a Weibull modulus which evaluates the scatter of the data. In other words, a higher  $\beta$  means less scattering in the experimental data. Usually, at least 10 tests per sample are needed to calculate the more accurate Weibull  $E_b$ .

How to improve the breakdown strength of polymers turns out to be a huge problem. Ramprasad analyzed the mechanism of breakdown strength for polymers through mathematical method, and claimed that introducing dipoles into a polymer greatly promoted the dipole-induced scattering which was beneficial for diminishing and constraining the hot electrons. [75] In addition, electron scattering by dipoles and phonons was used to explain temperature dependence of breakdown field. Due to the dipoles units distributed randomly along molecular chains, the amorphous polymers showed great potential in the high voltage field. It was demonstrated that dipole scattering limited mobility could evaluate the influence of dipole scattering on intrinsic breakdown field of polymers. Compared with ceramic dielectrics, polymer-based dielectrics are more attractive for these applications because they have the advantage of cheap, high dielectric strength, high energy density and low dielectric loss, and easy processability. However, the continuous miniaturization and increased functionality in modern electronics and electrical power systems demand further increases in energy and power density of dielectric materials since these capacitors contribute significant (> 30%) volume and weight to these systems. One major challenge in developing Polymer-based

dielectrics is realizing high electric energy density while maintaining low dielectric loss, even at very high applied electric fields. [76-112]

### 3. PURE HIGH-k POLYMERS

With development of electrical and electronic technologies, some polymer materials with excellent dielectric properties such as relatively high permittivity, low dielectric loss and high breakdown field at the frequencies and voltages of operation would be useful. [24,113-120] Commonly, a high dielectric constant material is defined as a material with a dielectric constant higher than that of the silicon oxide ( $k \approx 4.0$ ). Unfortunately, polymer materials typically possess low dielectric constants as shown in Table 1, though they have a high breakdown strength. [121] Therefore, much effort has been devoted to enhance the intrinsic dielectric constants of polymer materials via modifying the polymeric chain architecture, blending polymers with different polymers, and dispersing ceramics and conducting nanoparticles into polymers. For example, the permittivity of polymethylmethacrylate (PMMA) is as low as 2.9, thus You et al. applied styrene butyl-acrylate copolymer loaded reduced graphene oxide (SBA@rGO) as the conducting fillers to promote the dielectric properties of PMMA, and the results showed that permittivity of SBA@rGO/PMMA composite with only 0.14 wt% rGO was up to 15.5 at 1 kHz. [122] Zhong and Gao found that PVDF could effectively improve the dielectric and energy storage performances of PMMA, because the structure with rigid amorphous layers can induce a spatial confinement effect of chain motion and structural change. [123] Herein, we would like to highlight some accomplishments which are representative of the results in recent decades.

**Table 1.** Dielectric permittivities of conventional polymers at room temperature

Polymer	Dielectric permittivity	Polymer	Dielectric permittivity
Polystyrene	2.6	Fluorinated polyimide	2.6~2.8
Poly(phenyl quinoxaline)	2.8	Poly(arylene ether oxazole)	2.6~2.8
Poly(arylene ether)	2.9	Polynaphthalene	2.2
Polyquinoline	2.8	Poly(tetrafluoroethylene)	1.9
Silsesquioxane	2.8~3.0	Fluorinated Poly(arylene ether)	2.7
Poly(norborene)	2.4	Nonfluorinated aromatic polyimide	3.2~3.6
Poly(ether ketone ketone)	3.5	Poly(vinylidene fluoride-co-hexafluoropropylene)	12

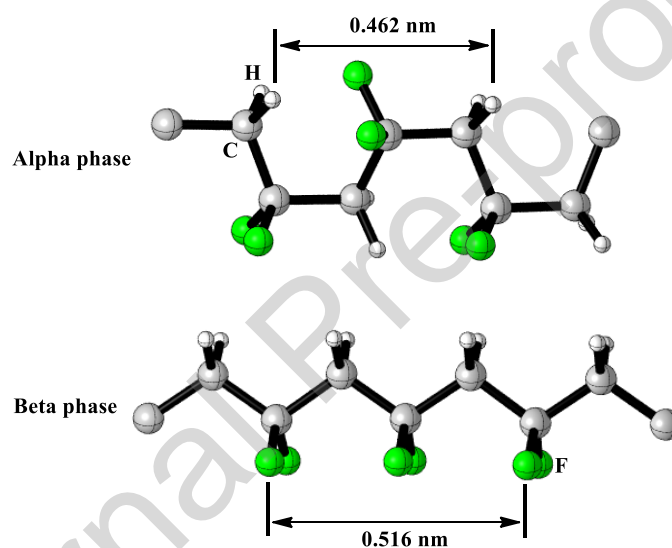
### 3.1 Poly(vinylidene fluoride) and Its Derivatives

Poly(vinylidene fluoride) (PVDF) and the random copolymer of poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] are the best known and most widely used as ferroelectric polymers.[124-126] This kind of crystal already possesses a finite polarization vector due to the separation of positive and negative charges in the crystal and it has a critical temperature called the Curie temperature ( $T_c$ ). Around the  $T_c$  there is a transformation in crystal phase which results in a change from ferroelectric to paraelectric. It is due to the ferroelectric phase that PVDF and its derivatives exhibit much higher electromechanical response and better dielectric properties than other polymers. [127] Therefore, in this section, we will focus on the excellent dielectric properties of PVDF and its various copolymers.

PVDF, as a well-known semi-crystalline polymer, exhibits at least five crystalline phases ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$ ) in an amorphous surrounding. It was reported that these possible crystalline phases exist singly or as mixed phases in the semi-crystalline PVDF. The most common crystalline phase in PVDF is  $\alpha$ -PVDF with a (tg+ tg-) conformation, while  $\beta$ -PVDF, which has an all-trans zig-zag



conformation as shown in Figure 3, is more polar. As discussed, the interesting electric properties of PVDF originate from the strong dipole in the  $\text{CF}_2$  units disposed along the polymer chain. Thus, methods that theoretically facilitate the polarization of dipoles can affect the dielectric properties of the PVDF substantially. By the means of proper preparation processing, the crystal phase can be adjusted in the crystalline region of PVDF from the melting state. It will increase the polarity increment of the material and is theoretically beneficial for storing charges and electric energy. [40]



**Figure 3.** Conformation of PVDF chains in two phases. Reprinted with permission from ref. 40. Copyright 2010 The Royal Society of Chemistry.

Recently, much work has focused on the adjustment of crystal phases in PVDF. Some were physical approaches such as controlling the annealing temperature [128, 129] and electric field [130] during PVDF crystallization from the melted state. Others utilized chemical approaches such as copolymerization facilitates formation of  $\beta$ -PVDF with zig-zag conformation. Furukawa in Japan has done important work on the dielectric spectrum of P(VDF-TrFE) copolymers in last 10 years. [131-135] Historically, poly(vinylidene fluoride-trifluoroethylene chlorotrifluoroethylene) [P(VDF-

TrFE-CTFE)] terpolymer was first reported in 2001 and poly(vinylidene fluoride-trifluoroethylene chlorofluoroethylene) [P(VDF-TrFE-CFE)] terpolymer in 2002. [136,137] Besides the discussed terpolymers, poly(vinylidene fluoride chlorotrifluoroethylene) [P(VDF-CTFE)] and poly(vinylidene fluoride- hexafluoropropylene) [P(VDF-HFP)] copolymers have also been developed as high- $k$  polymers.[137] Among these copolymers and terpolymers, perhaps the most typical example is the copolymer of P(VDF-TrFE) reported by Zhang.[125, 138] This kind of VDF/TrFE copolymer with some weight fraction of TrFE units converted to all-trans ( $t_m > 4$ ) chain conformation as a ferroelectric phase ( $\beta$  phase) at a low temperature. The extra fluorine atoms in TrFE comonomers prevented the polymer chain from adopting a trans-gauche conformation and resulted in an extended planar zig-zag all-trans conformation. Such an electron-irradiated P(VDF-TrFE) copolymer does not have a typical ferroelectric behaviour so that the irradiated P(VDF-TrFE) does not have large remnant polarization, also the dielectric constant at low field will be larger than the original P(VDF-TrFE). Finally the maximal permittivity of the irradiated P(VDF-TrFE) is near 30 at 100 Hz and ambient temperature. Furthermore, it should be noticed although both PVDF and P(VDF-TrFE) have the same zig-zag conformation, they are not identical in terms of unit cell dimensions and symmetry. Therefore, it is incorrect to call the low temperature ferroelectric phase in P(VDF-TrFE) as the beta phase.

It should also be mentioned that ferroelectricity in such copolymer was strongly evidenced by the existence of  $T_c$  and one major drawback is its relatively high  $T_c$ . Although it was partly dependent on the copolymer composition, the lowest  $T_c$  observed was  $>60$  °C in VDF/TrFE (55/45) copolymer, which was well above ambient temperature (the most convenient application temperature).[139]

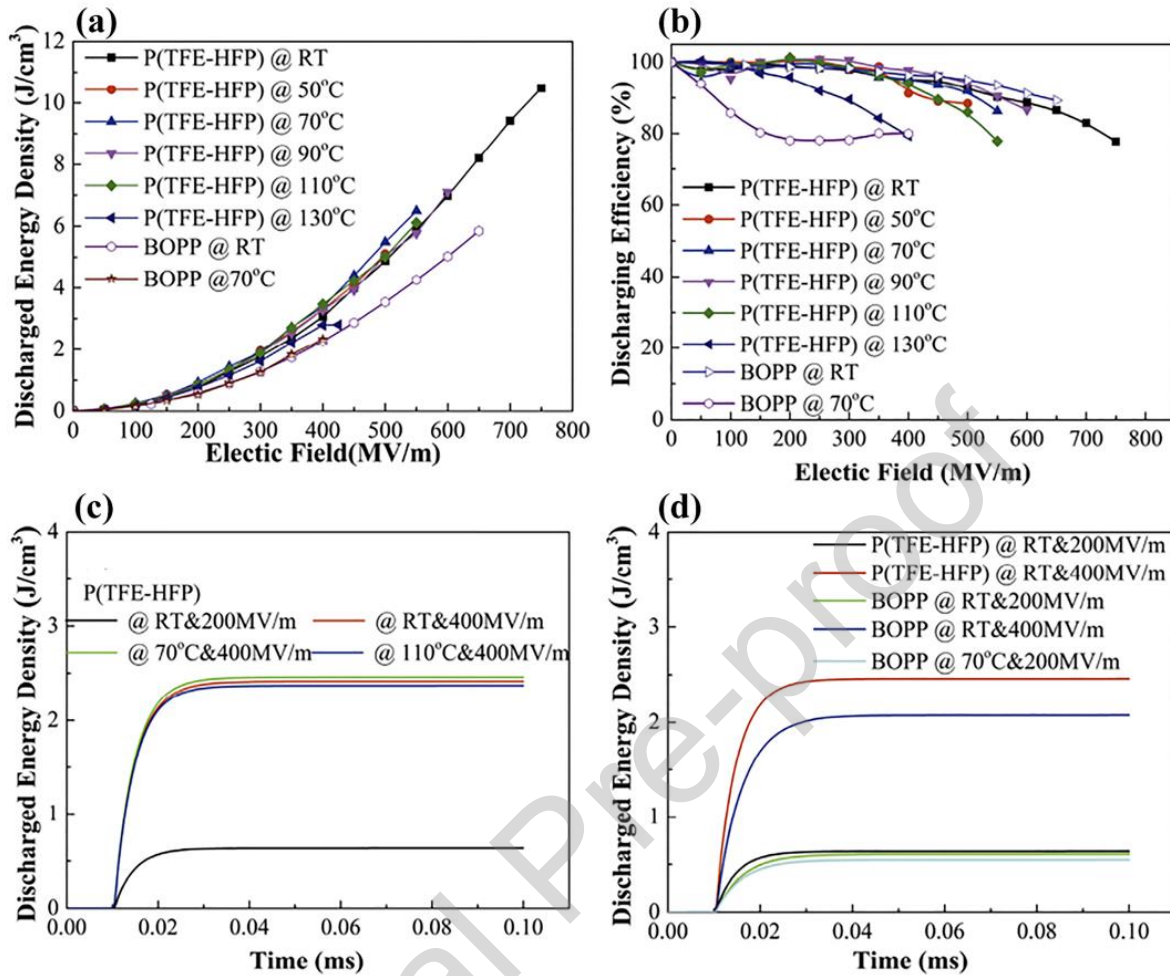
When the transition happens, the all-trans polymer chain conformation in the ferroelectric  $\beta$  phase changed to trans-gauche chain conformation in a paraelectric  $\alpha$  phase. This results in a small dielectric response of the dipoles to the electric field, which means a low dielectric constant and a large polarization hysteresis loop due to the high energy barrier of switching the dipole direction at ambient temperature.[140-141]

In past decades, many researchers have focused their efforts related to PVDF and VDF/TrFE copolymers on the general goal of reducing the  $T_c$  and generating a large electromechanical response at ambient temperature. Direct correlation between the reduced polar domain size and lower energy barrier as shown in ferroelectric ceramic materials could give analogical attempts to alter the  $T_c$  of copolymers.[142] Some efforts including mechanical deformation, electron irradiation, uniaxial stretch, crystallization under high pressure or under high electric field can be used to alter the  $T_c$  value.[143-145]

Recently, Chung reported a new family of ferroelectric and high dielectric fluoro-terpolymers comprised of vinylidene difluoride (VDF), trifluoroethylene (TrFE), and a chlorine-containing monomer, such as chlorodifluoroethylene (CDFE) or chlorotrifluoroethylene (CTFE). The small amount of chlorinated monomer incorporated causes a kink in the polymer chain, which altered the chain conformation and reduced the crystalline domain size. The terpolymers with uniform molecular structure and few impurities were prepared by bulk polymerization process using an oxygen-activated organoborane initiator at ambient temperature.[146,147]

Zhu also made a lot of efforts on the PVDF and its copolymers.[148-152] For example, due to the promising application in electrical energy density, narrow single hysteresis loop behaviour of

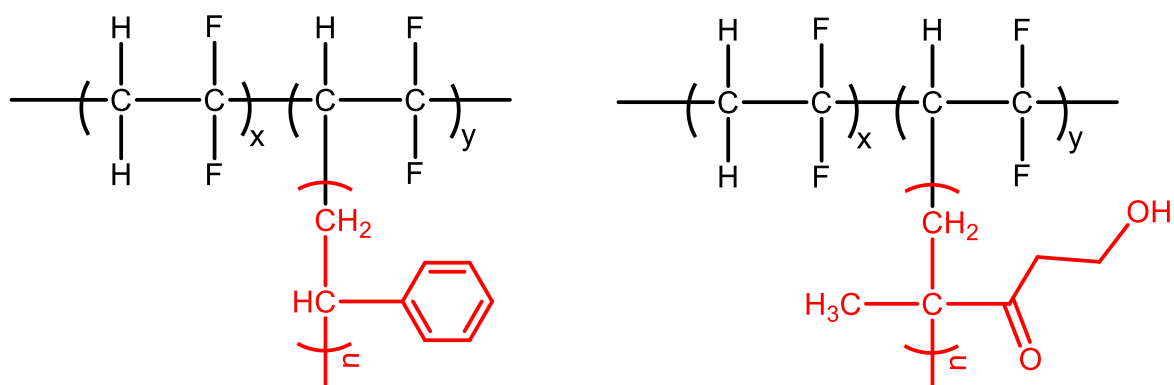
relaxor ferroelectric P(VDF-TrFE-CTFE) was achieved through the uniaxially stretching and 80°C annealing procedure.[150] The uniaxially stretched poly(VDF-CTFE) film was also investigated, and an antiferroelectric-like behaviour was found at an proper poling frequency (e.g., 10 Hz) and 100°C because of the competition between polarization fields and depolarization upon reverse poling.[151] They also demonstrated that biaxially oriented PVDF (BOPVDF) films showed a breakdown strength as high as commercial BOPP.[148] Electronic conduction, dipolar polarization, charge injection and ionic polarization of the BOPVDF film were investigated, and dipolar polarization (i.e., polarization of crystalline and amorphous dipoles) was proved to be partially responsible for the decrease of electronic conduction. Zhang also has paid much attention to the dielectric polymer field for energy storage application, and kinds of ferroelectric polymers such as PVDF, P(VDF-CTFE), P(VDF-TrFE) and P(VDF-TrFE-CTFE) were investigated, respectively.[153-156] In addition, they found that the dielectric properties of poly(tetrafluoroethylene-hexafluoropropylene) (P(TFE-HFP)) was remarkable.[157] HFP units in PTFE molecular chains could effectively reduce  $T_m$  of polymer, which made it easy for film processing. P(TFE-HFP) still maintained a high degree of crystallinity, which was beneficial for the excellent mechanical properties. Due to its high  $T_m$  and low polarity, The P(TFE-HFP) film showed excellent breakdown strength, energy density and charge-discharge efficiency. The maximum breakdown strength and energy density was over 750 MV/m and 10 J/cm<sup>3</sup> at room temperature. What's more, P(TFE-HFP) still maintained a high breakdown strength up to 500 MV/m at 110°C, which resulted a high energy density of 6 J/cm<sup>3</sup>, as shown in Figure 4. [158]



**Figure 4.** Discharged energy density (a) and discharging efficiency (b) of P(TFE-HFP) at elevated temperature. Energy discharging profiles of P(TFE-HFP) (a) and comparison with BOPP (b) at varied temperature and elevated charging electric field. Reprinted with permission from ref. 158. Copyright 2017 Elsevier Ltd.

Besides forming  $\beta$ -crystalline sites, other ways to enhance the dielectric properties of PVDF have also been reported. For example, grafting some polymer to PVDF has been very promising. It is well-known that graft copolymerization of polymers forms a large number of new materials with excellent dielectric properties that are influenced by the ability to tailor the surface of materials while retaining the bulk properties. These grafted copolymers are usually synthesized by special

methods including ionizing radiation, ultraviolet light and plasma treatment. And they frequently possess a combination of properties related both to the backbone and the grafted chains. [140, 159] For instance, fluoropolymers such as PVDF and PTFE can be grafted with conventional polymers that can display excellent dielectric properties and processability. [160, 161] For example, Thakur has studied the dielectric properties of the PVDF grafted with PS initiated by electron beam radiation, which can produce free radical graft copolymerization in solution. They found that the dielectric constant of polystyrene (PS) grafted PVDF copolymers reached about 90 at 100 Hz at room temperature, representing a more than seven folds increase compared with the pristine PVDF matrix, while maintaining a dielectric loss of 0.005 at 1 kHz.[161] In addition, they also have reported that the permittivity of PVDF-graft-poly(2-hydroxyethyl methacrylate) (PVDF-g-HEMA) was 48 at 100 Hz, about 4.5 times higher than that of pure PVDF at room temperature.[162] Though the high- $k$  values are in experiment realized in these grafted polymers initiated by electron beam radiation, these results cannot be believable theoretically because the injected electrons during radiation might make these 'false' high- $k$  results. Therefore, more effort should be paid to confirm these results further. The chemical structures of these grafted copolymers in Thakur are shown in Figure 5. Although these PVDF and its derivatives show excellent dielectric properties, they are difficult to use in practice due to poor processability and high cost.



**Figure 5.** Chemical structures of grafted copolymers based on PVDF. Reprinted with permission from ref. 162. Copyright 2011 The Royal Society of Chemistry.

To meet a need of next-generation dielectric capacitors in areas of high energy density/low loss and/or high temperature/low loss polymer dielectric, Zhu and Wang reported in recent work novel ferroelectric polymers for high energy density and low loss dielectrics by reducing the spontaneous polarization.[163] Novel ferroelectric crystalline polymers exhibiting relaxor ferroelectric and antiferroelectric-like behaviours have demonstrated great potential for high energy density/low loss dielectrics and many other practical applications including electrostriction and solid-state refrigeration. Reasonable success has been achieved for relaxor ferroelectric polymers such as P(VDF-TrFE)-based terpolymers. However, further optimization in terms of monomer composition and crystalline morphology is still needed to enhance their performance in a specific application. On the other hand, genuine antiferroelectric crystalline polymers have not yet been reported so far. In the future, more research needs to focus on new paraelectric and novel ferroelectric polymers for high energy density and low loss dielectrics.

### 3.2 Conjugated Polymeric Systems

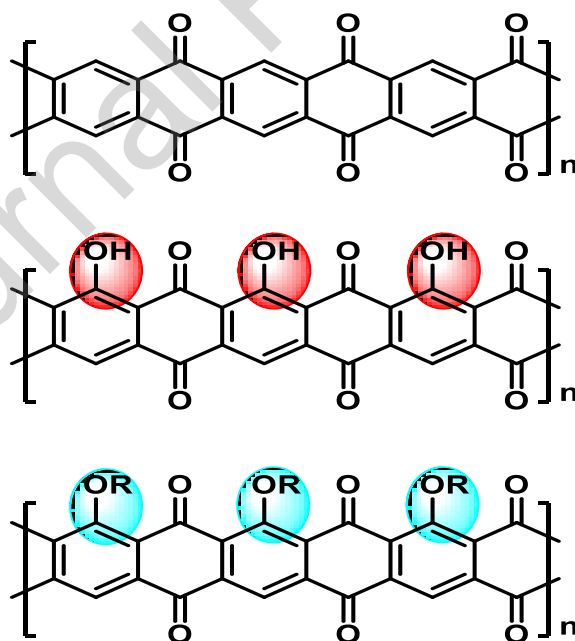
Conjugated polymeric systems are highly conjugated and have a large planar structure which is predominantly aromatic and  $\pi$ -electrons are completely delocalized over the entire molecule chain. Reynolds has done a lot of work in this field, such as biology and Solar Cell. [164-168] In addition, a number of conjugated polymers with sufficiently high permittivity have been studied. For example, polyacene quinone radical polymers (PAQRs) have a permittivity ranging from 10 to  $3 \times 10^5$  or even higher at elevated temperatures and pressures. [169,170] Another kinds of conjugated polymer systems exhibiting enhanced dielectric characteristics are metallo-organic polymers [e.g. poly-Cu(II)-N, N'-dimethyl rubeanate], poly(carbon-disulphide), quinazone polymers, and pyropolymers. This type of unusual dielectric behaviour of conjugated polymers appears to be due to a new type of polarization called "hyperelectronic nomadic polarization" as suggested by Rosen and Pohl. [170, 171]

#### A. PAQR polymers

Pohl found giant permittivities in conjugated PAQR polymers due to hyperelectronic polarization. [169,170] Polyphthalocyanines and various derivatives have been synthesized, and their dielectric properties are studied widely, including the formation composite materials with high permittivity and with actuator applications. In 2008, Zhang et al. synthesized PAQRs by solid-state polymerization and measured a dielectric constant of about 1,200,000 at 100 Hz. [172] However, the dielectric loss of the PAQRs was as high as 30 (dry-process) and 14 (wet-process) at 100 Hz so that this large loss cannot be ignored in practical applications. Such a high dielectric loss at low frequency is possible to be caused by the low frequency conduction, which could severely limit the



performance for the PAQR polymers. In addition, they synthesized hydroxyl- or alkoxy-modified derivatives (HO-PAQR and RO-PAQR) and measured their dielectric permittivities (HO-PAQR prepared by dry-processing has a permittivity of  $10^4$ ). From their results, it was suggested that the planar conjugation of the associated  $\pi$  orbitals plays an important role in achieving the high dielectric constants deserved. The delocalized charges arising from inherent ionization levels of the long-conjugated molecules would form a collection of highly polarizable monopoles or dipoles and thereby lead to high bulk polarizabilities in an external electrical field. This collection of highly field-sensitive structures exhibits what might be termed ‘hyperelectronics’ polarization, resulting in high-dielectric permittivities. The chemical structures of PAQR, HO-PAQR and RO-PAQR are shown in Figure 6.



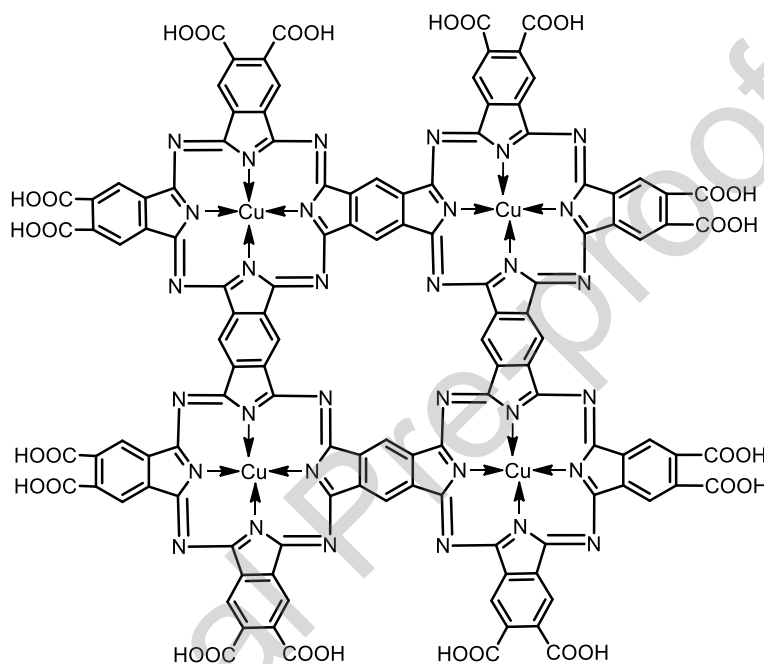
**Figure 6.** Chemical structures of conjugated polyacene quinone radical polymers with high permittivities. Reprinted with permission from ref. 172. Copyright 2008 Elsevier.

## B. Phthalocyanine (Pc) materials

Pc materials, another kind of conjugated polymers, have also been studied for applications in solar cells, fuel cells, optical-limiting materials, gas sensors and field-effect transistors. [173-181] Moreover, there have been increasing interest in applications of high permittivity materials in capacitors recently. [4, 182-187] The electronic properties of phthalocyanine can also be tuned by substituting the central metal atom, the axial and peripheral groups, as well as by adding dopants or varying the polymerization conditions. A series of reports have appeared regarding to the synthesis of phthalocyanine materials. [188-190]

Among the phthalocyanine based materials, copper phthalocyanine (CuPc) has attracted interest due to its excellent thermal and chemical stability, and unique electric properties. [191] It has been reported by Voet and Suriani that a CuPc monomer pellet could exhibit a permittivity of about 5 and the dielectric dispersion was relatively low over a wide frequency range compared to other monomeric phthalocyanines (e.g. CuPc, FePc). [192] However, compared to the monomeric CuPc, polymeric CuPcs show much higher permittivity due to the strong conjugation and large planar structural features. For instance, the permittivity of poly-CuPc samples measured at room temperature at 100 Hz could reach 1500, which was quite high compared with conventional polymers (see Table 2). This result indicated that there were remarkable changes in permittivity since conjugation of the  $\pi$ -electron system was enhanced by the polymerization of phthalocyanine macrocycles. [193] Furthermore, it has been found that poly-CuPc showed hyperelectronic polarization with high permittivity at room temperature. And, it has shown great potential in high permittivity applications. The chemical structure of a poly-CuPc is shown in Figure 7. The

permittivity of PVDF and its copolymers was able to be greatly improved by poly-CuPc. [194, 195] What's more, poly-CuPc could be chemically grafted onto the molecular chain of P(VDF-TrFE-CFE) to improve the compatibility between the poly-CuPc and the terpolymer, which was helpful for the uniform dispersion and the breakdown strength. [194]



**Figure 7.** Chemical structure of poly-CuPc. Reprinted with permission from ref. 193. Copyright 1985 Elsevier.

### C. Polymer materials with conjugated side chain

A new kind of nanodielectric energy storage materials based on conducting nanodomains and an insulating matrix was reported. Due to the huge electronic polarization of the conducting domains in the applied electric field leads, a high permittivity of polymer can be achieved. Reversible addition fragmentation transfer (RAFT) polymerization was the common strategy for preparing these supramolecular block copolymers. [196,197]

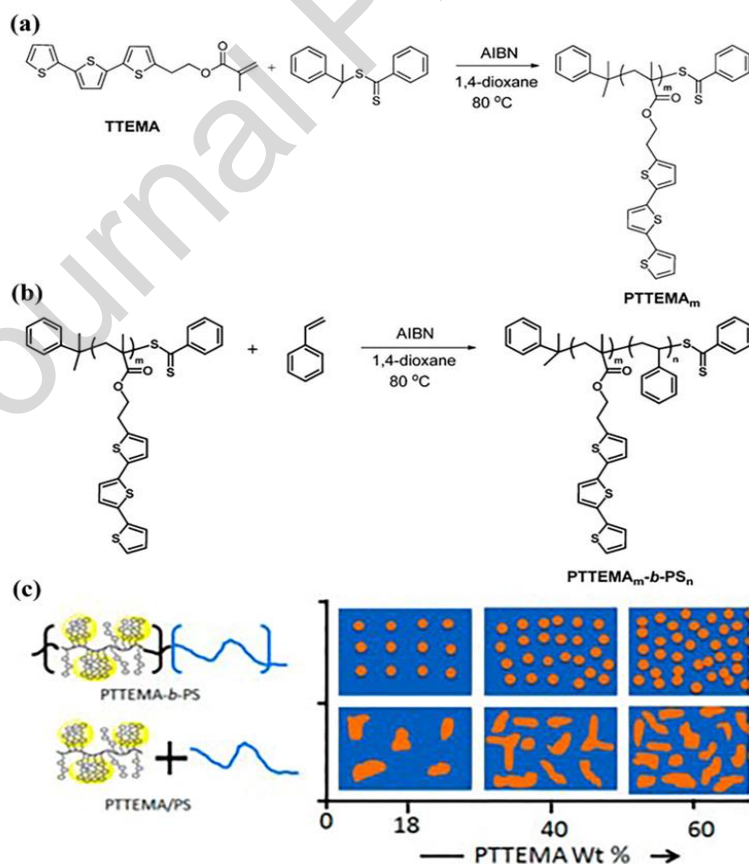
Tang applied poly-(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA), a strongly acidic

dopant moiety as the conducting segment, while poly(methyl acrylate) (PMA) as the insulating segment.[198] The PAMPSA block was complexed with an oxidated oligoaniline trimer. The results showed that the increased PMA block length turned the ionic conductor into an insulating polymer with excellent dielectric properties. The discovery of nanodipolar  $\pi$ -conjugated oligomer-containing polymers. Based on this, they fabricated the terthiophene-containing methacrylate homopolymers, which exhibited high permittivity and low dielectric loss over a wide range of frequency from 100 Hz to 4 MHz. [199] It was demonstrated that the side chains of terthiophene formed small crystalline domains in the amorphous matrix, and this is responsible for the highly polarizable and fast-responsive nanodipoles. As a result, a high energy density of 1.56 J/cm<sup>3</sup> was achieved at 200 MV/m. They further prepared oligothiophene-containing polymer brushes via a “grafting from” strategy by RAFT polymerization and ring-opening metathesis polymerization (ROMP). [200] The results suggested that polymer brushes formed small nanoscale crystalline domains with a size of 2 nm in the amorphous matrix, which was beneficial for the better processability as well as the improved dielectric properties.

Recently, Ploehn et al. explored a kind of high-performance dielectric materials, namely, block copolymers and homopolymer blends containing a terthiophene-rich, electronically polarized block (PTTEMA) and an insulating polystyrene block (PS). [201] PTTEMA-b-PS block copolymers were synthesized by reverse addition-fragmentation chain transfer (RAFT) polymerization as shown in Figure 8.

For comparison, the PTTEMA/PS homopolymer blends with the same PTTEMA weight percentages were prepared by solution blending. With the same PTTEMA loading, the dielectric

permittivities of PTTEMA-*b*-PS copolymers are much higher than that of the corresponding PTTEMA/PS blends, while all of the PTTEMA-*b*-PS copolymers and PTTEMA/PS blends exhibit lower loss tangent values. The enhanced dielectric properties were due to the electronically polarized terthiophene-rich crystalline domains and the insulating PS block which inhibits current leakage. Meanwhile, the polarization mechanisms were also investigated, showing that PTTEMA-*b*-PS copolymers and PTTEMA/PS blends have linear polarization behavior and low hysteresis at electric fields of 10 MV/m. The addition of PTTEMA increased energy losses caused by current leakage between nearby terthiophene-rich domains. However, the addition of PTTEMA recovered energy density values approaching  $0.5 \text{ J/cm}^3$  at the concentration of 18 wt% PTTEMA, which is 40% higher than that for pure PS at the same maximum applied electric field.



**Figure 8.** (a, b) Synthesis of PTTEMA<sub>m</sub> homopolymer and PTTEMA<sub>m</sub>-*b*-PS<sub>n</sub> copolymer by

RAFT polymerization; (c) The proposed nanoscale structure in PTTEMA-b-PS copolymers and PTTEMA/PS blends with the PTTEMA loading. Reprinted with permission from ref. 201.

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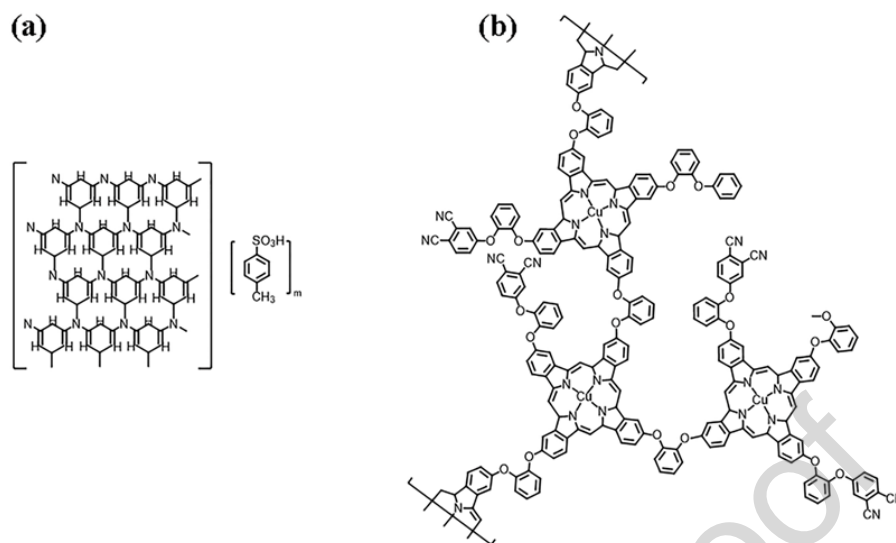
#### **D. Polymers with Hyper-Branched Structures**

Conjugated polymers are macromolecules with conjugated  $\pi$ -bonded structure and many repeating units. The delocalization of  $\pi$  electrons along the backbone of the conjugated system can result special electronic properties in comparison to saturated polymers. Since the first report of  $\pi$ -conjugated conductive polyaniline (PANI) nearly 150 years ago, much effort has devoted to understanding the electric properties of such  $\pi$ -conjugated polymers. In 1976, Heeger, MacDiarmid and Shirakawa discovered metallic conductivity in iodine-doped polyacetylene and which ultimately led to the Nobel Prize in 2000. [202] This breakthrough has stimulated more extensive research to the electric properties of many  $\pi$ -conjugated. Examples of widely investigated  $\pi$ -conjugated polymers include polythiophenes, [203-206] polyanilines [207-209] and polyfluorenes. [210-212] These conjugated polymers show low dielectric loss and high breakdown voltages, while maintaining good processibility and excellent thermal stability. Nevertheless, the major bottle neck with conjugated polymers for applications is their low permittivity. Hence, to overcome the difficulty, researchers have forced on special conjugated polymer structures since most agree that polymer structure can greatly influence its properties.

Recently it has been reported that an ultrafast delocalization process occurs in some of the conjugated polymers with dendritic structures, especially at high frequency. The polaron delocalization originating from intra-molecular charge transfer in dendrimers would substantially

enhance their electronic properties.[213] Hyper-branched polymers are a type of imperfect dendrimers that constitute a novel class of highly branched polymers with a large number of end groups. The driving forces behind the study hyper-branched structures of conjugated polymers for electronic application are as follows. First, such hyper-branched structures may provide a substantially longer polaron delocalization length in 3-dimensions. This longer delocalization length may increase the dielectric constant and where avoiding an anisotropy of dielectric response. Second, such materials may show ultrafast polaron delocalization due to intramolecular charge transfer, which produces a fast dielectric response at high frequencies. Third, the largely planar structures may facilitate molecular self-assembly restricting unfavorable movement along the chain due to increased rigidity and steric effects.

Consistently, significant improvement in the dielectric properties of hyper-branched polyaniline has been observed by Goodson group in comparison to that of linear polyaniline.[214] The permittivity of these hyper-branched polyanilines reached ca. 200 at 1MHz, twice that of linear PANI. The polaron hopping process in these hyper-branched PANI materials was dominated by the Marcus-Hush mechanism and the hopping energy was  $<0.1$  eV. The improvement in dielectric response originates from the strong polaron delocalization and hyperelectronic polarization in this hyper-branched system. [214,215] In addition, Goodson has also reported an impressive permittivity of  $\sim 46$  up to 1MHz in a hyper-branched copper phthalocyanine (HBCuPc) polymer compressed pellet (see Table 2). The dielectric loss of such a dendrimer film was as low as 0.002 at 1MHz with very small dielectric dispersion. [184] The chemical structures of PANI and CuPc with hyper-branched structures are shown in Figure 9, respectively.



**Figure 9.** Chemical structures of (a) hyperbranched PANI and (b) a hyperbranched copper phthalocyanine. Reprinted with permission from ref. 214 and 184. Copyright 2006 American Chemical Society.

Peng and Hou successfully prepared polyimide–copper complexes with bipyridine-containing diamine monomer through polymerization, complexation and imidization processes.[216] The dielectric properties of PICuCs were able to be easily tuned by changing the content of Cu in polyimides. A high permittivity of over 133 and low dielectric loss of less than 0.08 were obtained, which resulted in a high energy density of  $11.39 \text{ J/cm}^3$ . In addition, due to the unique molecular structure, good thermal properties as well as outstanding mechanical properties were observed, which were highly desirable for polymer film capacitors.

Based on these results it seems that the hyper-branched polymers have similarly impressive dielectric properties over a wide range of frequencies due to a long range polar hopping mechanism accompanied by strong intramolecular interactions in the highly branched system. In addition, dendrimers and hyper-branched polymers have very different properties compared with the corresponding linear polymers, including viscosity, low interchain entanglement and high solubility, owing to their highly branched three-dimensional and sphere-like molecular architectures.



[217,218] The improvement in permittivity for hyperbranched system is not remarkable with that for the polymer systems with large planar aromatic structures. In order to provide a meaningful comparison, the structure and dielectric properties of some representative polymers are summarized in Table 2.

**Table 2.** Structures and dielectric permittivities of some polymers

Type and structure characteristics	Polymer	Dielectric permittivity
PVDF and its derivatives [CF <sub>2</sub> units]	Electron-irradiated P(VDF-TrFE) copolymer	30 at 100 Hz
	PS grafted PVDF copolymers	90 at 100 Hz
	PVDF-graft-poly(2-hydroxyethyl methacrylate)	90 at 100 Hz
Conjugated Polymer	PAQRs; hydroxyl-PAQR	10 <sup>5</sup> at 100 Hz
[Large planar aromatic structure nature]	Polymeric CuPc	1500 at 100 Hz
[Conjugated polymer hyper-branched structure]	hyper-branched polyanilines	200 at 1 MHz
	hyper-branched CuPc	46 at 1 MHz

### 3.3 Polythiourea Dielectrics with Aromatic Structures

The contents mentioned above focus on an increase in permittivity of dielectric materials. Actually, the stored energy density is direct proportion to a square of applied electric field. To reach a maximal energy storage density, it is more effective approach to improve the breakdown field of dielectric materials. Zhang et al. have recently reported aromatic structure polythiourea dielectric material with ultrahigh breakdown field strength ( $> 1 \text{ GV m}^{-1}$ ), low dielectric loss and high electric energy density, which are attributed to the aromatic, amorphous, polar polymers containing high

dipolar moments with very low defect levels. [219] Specifically, the aromatic structure polythiourea films maintain a lower loss (much lower than that of BOPP) up to the highest field measured.

#### 4. HIGH-k POLYMER BLENDS

Blending different polymers is an important and efficient method to improve the permittivity and achieve the desired properties of polymer systems based on the structure and properties of each component. By blending some polymers with relative high permittivity into the other polymer matrices with low permittivity, researchers can achieve polymer blends with a high permittivity. The enhanced permittivity originates from significant interfacial polymer-polymer interactions and new structures formed in the blends. Generally, the permittivity of polymer blend system ( $k_{\text{blend}}$ ) is intermediate between the components, where  $k_{\text{polymer-A}} < k_{\text{blend}} < k_{\text{polymer-B}}$ . Here, the  $k_{\text{polymer-A}}$  and  $k_{\text{polymer-B}}$  represent the different polymers in the blend. Moreover, this blending method is a simple and effective route for organic materials, compared with other complicated synthetic approaches, producing good dielectric and mechanical properties, especially convenient for a capacitor industrial manufacture.

##### 4.1 Dielectric/Dielectric Polymer Blends

Dang has investigated the polypropylene/poly(vinylidene fluoride) (PP/PVDF) blended system.[220] In order to improve the permittivity of PP, PVDF is blended with the PP matrix. As a result, the permittivity reached 5.4 at 1000 Hz which was nearly 3 times than that of pure PP (~2.2). Furthermore, such blended system displays the advantage of combining the excellent dielectric properties of PVDF and the processability of conventional polymers. For these reasons, they could

provide a new generation of dielectric films for capacitors. Poly(methyl methacrylate) (PMMA) blended with PVDF provides another example where the permittivity of PMMA is improved.[221] Such polymer blend films were prepared via a solution mixing and casting process. The permittivity of this film can reach 12 at 100 Hz. This value is much higher than that of PMMA (~ 2.9) and approaches that of PVDF.

Nan blended aromatic polythiourea (ArPTU) to PVDF to fabricate composite films by the solution casting method.[222] The optimized permittivity and dielectric loss are 9.2 and 0.02 at 1 kHz, respectively. In addition, the blend films can also the early polarization saturation at low fields was inhibited, which resulted in the improved breakdown strength as well as energy density. The PVDF/ArPTU(90/10) film showed an energy density as high as  $10.8 \text{ J/cm}^3$  at 700 MV/m with a charge-discharge efficiency up to 83%. In addition, it has been reported that the permittivity of poly- $\omega$ -aminoundecanoyl (PA11)/PVDF blends at certain volume fractions could reach 60 which was twelve times higher than that of PA11 (~5) alone and about five times higher than that of PVDF (~12). It is interesting that the measured dielectric permittivities ( $k_{\text{blend}}$ ) exceeded those of the individual polymers, in contrast to conventional polymer blended system. [223] These results have suggested that polymer blended systems with high permittivity components represent a novel type of material that can be flexible, easy to process, with relatively high permittivity. As a result, they may be suitable for potential applications in flexible electronics.

Zhang et al. reported polar-fluoropolymer blends with tailed nanostructures for high energy density low loss capacitor applications.[71] The blends consist of a high energy density poly(vinylidene fluoride-chlorotrifluoroethylene) [P(VDF-CTFE)] and a low dielectric loss

poly(ethylene-chlorotrifluoroethylene) (ECTFE). Both the blend and crosslinked blend films exhibit a dielectric constant of 7 and low loss ( $\sim 1\%$ ), as expected from the classical composite theory. Specially, they found that introducing crosslinking in the blends can lead to a marked reduction of losses in blend films at high fields while maintaining a high energy density, which was attributed to the improved mixing at nanoscale in the crosslinking blend.

## 5. HIGH-k POLYMER COMPOSITES

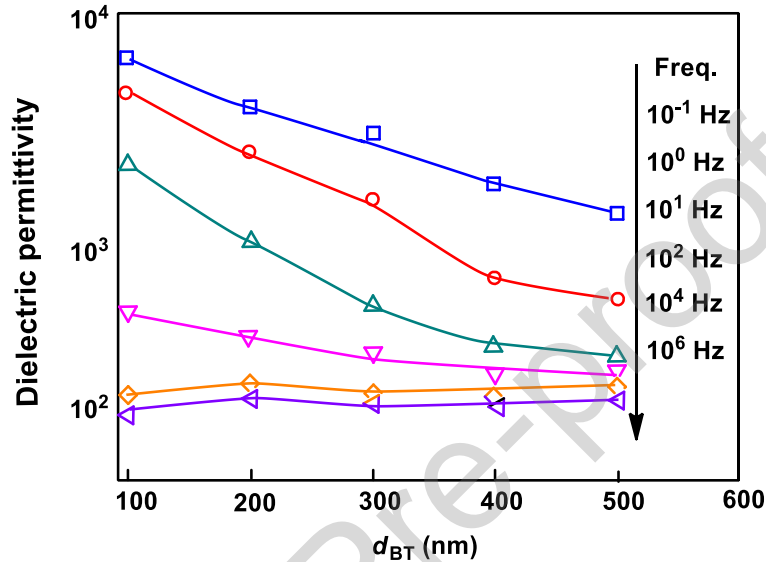
In order to further increase the permittivity of polymer systems to meet the requirements of the electronic industry, researchers have focused on the polymer composites since the composite approach is relatively simple. Various kinds of particles are employed as fillers dispersed into the polymer matrix to prepare high permittivity polymer composites. [233-248] Based on the strategy of combining advantages of high- $k$  inorganic materials and organic insulation material, polymer composites will exhibit high permittivity, excellent temperature stability and frequency characteristics to achieve the effect of “ $1+1>2$ ”. Generally speaking, two general types of fillers have frequently been utilized. One is high- $k$  ceramic particles; the other is electrical conducting fillers such as metals or electrically conducting carbon particles. These two types of fillers play different roles in improving the permittivity of polymer composites. It should be noted that the poor compatibility between inorganic fillers and organic polymer matrix, as well as the agglomeration of nanofillers, hinders the development of composites; Besides, for the high- $k$  polymer system, the leakage current and dielectric loss of the composites will increase with the addition of fillers; Finally, under the applied electric field, the electric field inside the composites will be distorted due

to the significant difference of permittivity between fillers and the polymer matrix, which causes high probability breakdown. [248]

### 5.1 Dielectric/Dielectric Polymer Composites

For ceramic composites the goal is to disperse ceramic particles with a high dielectric constant into the polymer matrix to produce a large interfacial area in the polymer composites, and the interfacial polarization increases the permittivity of the composites. Ferroelectric ceramic materials, such as BaTiO<sub>3</sub> (BT), PZT [Pb(Zr,Ti)O<sub>3</sub>] and lead magnesium niobate (PMN) have received much attention because of their high dielectric constants.[233] Among this group, BT may be one of the most important fillers, because its permittivity is about 2000. BT is commercially available and environment friendly since it is lead-free. Cherqaoui et al. have first studied BT particles in a PVDF matrix.[234] Muarlidhar et al. found variation of  $k'$  and  $k''$  of the BT/PVDF composites with frequency produced by changing the weight fraction of BT, and the permittivity of the composite with 70 wt % fraction increased to 133 at 10 Hz and 30 °C.[237] Here nano-sized BT particles with a huge specific surface area were used to increase the interfacial interaction of the composites. In addition, Hao and her coworkers found ultrafine nanocrystals with a diameter less than 10 nm could effectively improve the breakdown strength and the electrical displacement of the composite simultaneously due to larger interfaces than conventional nanofillers.[236] Moreover, smaller size of fillers is beneficial for the thinner film which is a tendency of practical applications, because the thinner dielectric film represents higher capacitance per unit volume. Dang et al. compared the dielectric properties of BT/PVDF with different particle sizes of BT fillers over a wide frequency ranges from 10<sup>-1</sup> Hz to 10<sup>7</sup> Hz and found a significant enhancement of the dielectric constant in the

BT/PVDF composites with nano-sized fillers. They proposed that the high interfacial surface area and dipole polarization of the particle result in a significant increase in permittivity at low frequency, as is shown in Figure 10. [238]

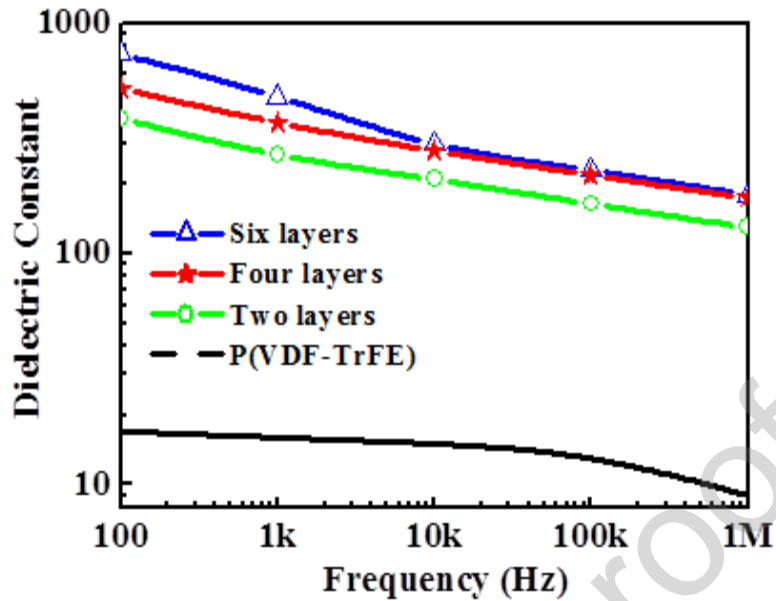


**Figure 10.** Dependence of dielectric permittivities of the BT/PVDF composites on the BT particle sizes at different frequencies, from top to bottom,  $10^{-1}$ ,  $10^0$ ,  $10^1$ ,  $10^2$ ,  $10^4$ , and  $10^6$  Hz. Reprinted with permission from ref. 238. Copyright 2007 American Institute of Physics.

However, at high volume fractions, the nano-sized particles exhibit aggregation and uniformity issues in polymer matrix because of the high surface energy, which leads to undesirable dielectric properties, such as a decreased electrical breakdown strength and a reduced permittivity of the composites. To reduce the effect of filler aggregation, Kim et al. modified the surface of BT nanoparticles to produce a uniform dispersion of nanosized fillers. [239, 240] For this, they used phosphoric acid to modify the surface of BT particles, obtaining the surface modified BT using pentafluorobenzyl phosphonic acid (PFBPA) as the surface agent. However, there are obviously voids in the PFBPA-BT/poly(vinylidene fluoride-hexafluoropropylene) [P(VDF-HFP)] composites.

They further improved the dispersion of the filler in the composite, and predicted the dielectric constant of the composites by a self-consistent effective medium treatment. The energy density of the composite increased to a value of  $3.2 \text{ J/cm}^3$  as the nanoparticle volume fraction reached 50 vol%.

Calcium copper titanate (CCTO), a non-perovskite structure ceramic with a huge dielectric constant, has received much attention in recent years.[23] Though there is not consistent agreement regarding its huge dielectric constant, a widely accepted mechanism is that the peculiar dielectric properties should be ascribed to its internal barrier layer capacitor structure, in which the core is semiconductive and the boundary layer is just electrical insulation.[23] Arbatti et al. studied the effect of sample architecture on the dielectric constant of the CCTO/P(VDF-TrFE) composite.[241] They prepared the composite film samples using a layer by layer hot press method. The permittivity of the CCTO/polymer composites can be further increased with more layers hot-pressed together, as shown in Figure 11. Annealing the composites at high temperature could increase the dielectric constant of the composites. They achieved the composite with a permittivity of about 610 at  $10^2 \text{ Hz}$  at 50 vol% CCTO loading. CCTO with different states was also proved to exhibit different impact in polymer matrix. CCTO fabricated through the sol-gel method (CCTO-sg) and solid-state method (CCTO-ss) was introduced into PVDF respectively. Because CCTO-sg particles showed narrower distribution size and smaller size than that of CCTO-ss particles, the CCTO-sg/PVDF composites exhibited better dielectric properties than CCTO-ss/PVDF composites. For example, the permittivity of CCTO-sg/PVDF composites with 50 vol% filler loading reached up to 62.3, which was 2 times higher than that of 50 vol% CCTO-ss/PVDF composites.

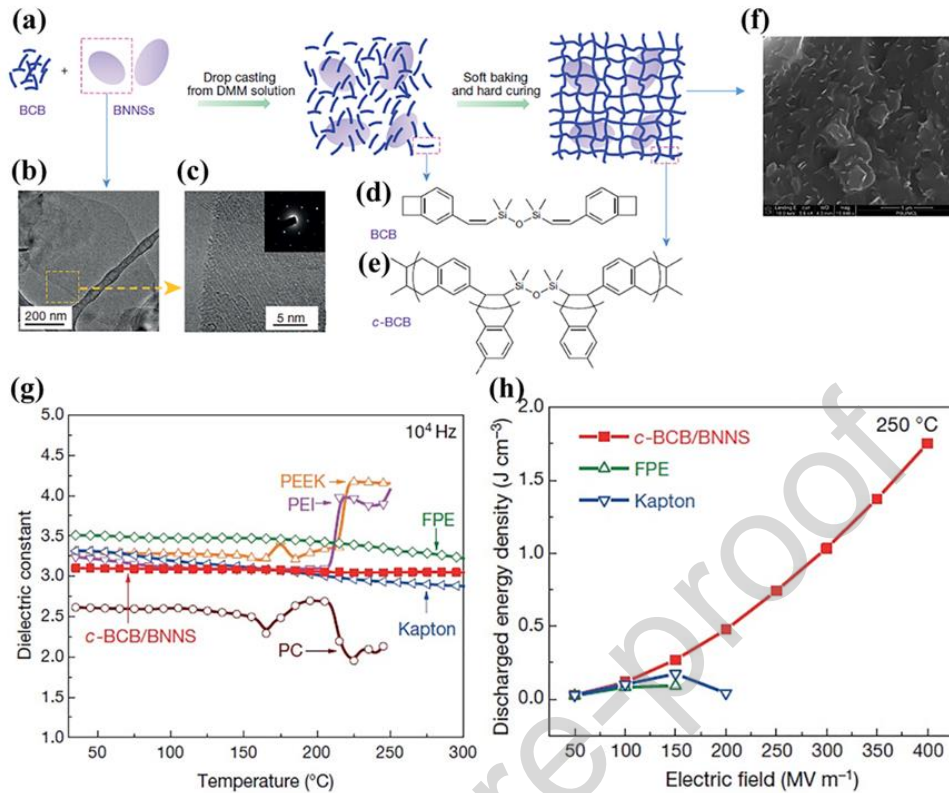


**Figure 11.** Dielectric constant vs. frequency from 100 Hz to 1 MHz for the CCTO/P(VDF-TrFE) composites with 50 vol% CCTO loading at room temperature after thermal annealing. Reprinted with permission from ref. 241. Copyright 2007 WILEY.

Besides the ferroelectric polymers, various epoxy resins and polyimides (PI) were employed as the matrix in many studies because of their excellent thermal stability and promising application as printed circuit boards (PCB). Cho et al. have studied the preparation and dielectric properties of BT/epoxy composites. [242] A high throughput roll coating method was used for obtaining the embedded film with a large area and uniform thickness. The dielectric properties of the composite at high frequency range (0.5-3 GHz) were reported. The dielectric constant of a capacitor containing about 50 vol% BT powder was estimated to be about 63 at 100 kHz. Dang et al. have utilized an in-situ polymerization approach to prepare the BT/PI composite.[26] They found the BT filler could be well dispersed in the PI matrix by the in-situ polymerization method and there is core-shell structure in the BT/PI composite. With this structure, BT/PI composites with a permittivity as high as 20 and



a high break breakdown strength of 67 MV/m were obtained. Moreover, the permittivity of the BT/PI composites have a weak temperature dependence, and it meets the X7R EIA specification (EIA=Electronic Industries Association). Furthermore, they studied the dielectric properties of the CCTO/PI composites prepared in the same fashion, and measured a dielectric constant of about 50 at  $10^2$  Hz at room temperature, which is about 14 times higher than that of the pure PI. [25] Xiong and Zhu demonstrated that the CCTO/PI system fitted well with the percolation theory, and a high permittivity over 171 and low dielectric loss less than 0.45 at 100 Hz were obtained near the percolation threshold. [247] Recently, Wang created a new polymer nanocomposite by adding nanometer-scale sheets of boron nitride to a conventional polymer as shown in Figure 12, which showed the energy density was increased by 400 percent. Moreover, the newly polymer composites was able to remain stable at temperatures as high as 300 °C, and preserve excellent dielectric and capacitive performance after intensive bending cycles.[2] As shown in Figure 12h, the high-field capacitive energy storage properties of c-BCB/BNNS is up to 400 MV m<sup>-1</sup> with a discharged energy density of 1.8 J cm<sup>-3</sup> at 250 °C, while none of the high- $T_g$  polymer dielectrics can operate at more than 150 MV m<sup>-1</sup>.



**Figure 12.** Schematic of the preparation of c-BCB/BNNS films (a). Transmission electron microscopy images of BNNSs (b, c). Inset to c is an electron-diffraction pattern of BNNSs. Chemical structure of the BCB monomer (d). The repeating unit of c-BCB (e). SEM image (scale bar of 5  $\mu\text{m}$ ) of cross-section of c-BCB/BNNS with 10 vol.% of BNNSs. The c-BCB/BNNS with 10 vol.% of BNNSs and high- $T_g$  polymer dielectrics for (g) temperature dependence of dielectric constant and (h) discharged energy density measured at 250  $^{\circ}\text{C}$ . Reprinted with permission from ref. 2. Copyright 2015 Macmillan Publishers Limited.

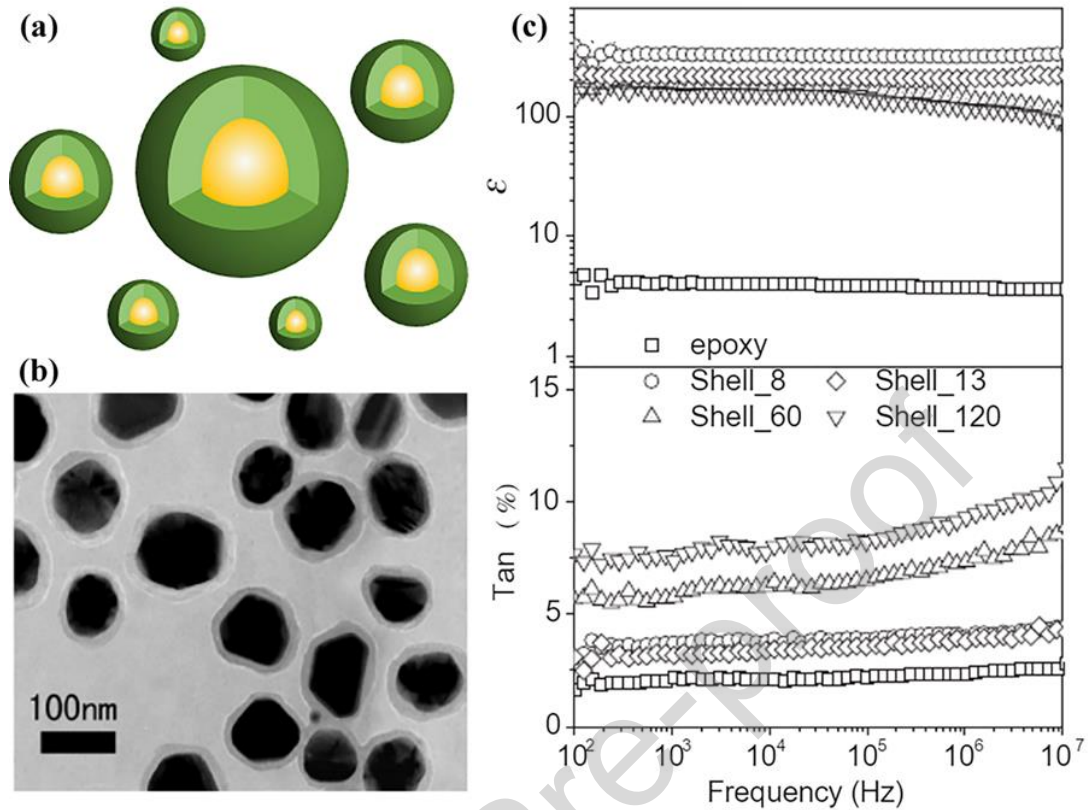
Wang et al. fabricated three-phase P(VDF-CTFE) nanocomposites using  $\text{BaTiO}_3$  nanoparticles as the dielectric filler and boron nitride nanosheets (BNNs) as the insulating filler, which resulted in excellent dielectric properties, high breakdown strength and a resultant high energy density. [234] What's more, the introduction of BNNs greatly improved dispersion state of  $\text{BaTiO}_3$  nanoparticles in polymer matrix. The breakdown strength reached 649 MV/m at 12 wt% BNNs, which was 1.7 times higher than the pure P(VDF-CTFE). The maximum energy density was as high as 21.2  $\text{J}/\text{cm}^3$  (5.9 wh/L) and a power density was up to 850 MW/L, which were much better than those of BOPP.

Tanaka et al. proposed a “multi-core” model to explain the various properties of the dielectric polymer nanocomposites. [244] They define an “interaction zones” area. This interface layer is about of several nanometers which in turn was divided into three layers: bonded layer, a bound layer, and a loose layer looking from the inside out, with a diffuse Gouy-Chapman layer superimposed upon the above three layers. They found the three kinds of layers each play different roles on the dielectric properties of the composites, and they used the multi-core model to explain the partial discharge phenomena in the polymer composites.

## **5.2. Core-shell Structure Nanofiller/Dielectric Polymer Composites**

Many reports have shown the high permittivity of composites by using conductive fillers. However, the large increase in dielectric constant is usually accompanied by a dramatic increase in loss tangent, which makes the composites unacceptable for practical application. [248] Because the conducting fillers play a negative impact on the breakdown strength, core-shell structure turns out to be an effective way of balancing the dielectric and energy storage properties.

For instance, Shen et al. employed one kind of core-shell filler, with a Ag particle as the core and organic dielectric component as the shell, as shown in Figure 13(a)(b). [15,16] They believed these kinds of structures could prevent direct electrical contact of the Ag particles.



**Figure 13.** (a) Schematic diagram of core-shell structure. (b) TEM of the Ag@C core/shell particles with thinner shells. (c) Dependencies of dielectric constant and dielectric loss on frequency, where the data were obtained for the nanocomposites Ag@C nanoparticles. Reprinted with permission from ref. 15. Copyright 2007 WILEY.

The resultant Ag@C/epoxy composite with a dielectric constant about 400 showed a loss factor about 0.04 at  $10^2$  Hz. Moreover, the well dispersed fillers resulted in a dielectric constant of the Ag@C/epoxy composites independent of frequency over the range of  $10^2$ - $10^7$  Hz, as shown in Figure 13(c). Similarly, Kohlmeyer et al. hydroxylated MWNTs to lower the conductivity of its surface and impact a core-shell structure of fillers. With the above filler, the shelled MWNTs/PVDF composite with higher dielectric constant and lower loss tangent was prepared. Zhou et al. synthesized core-shell structured Al@Al<sub>2</sub>O<sub>3</sub> nanoparticles by a calcination process, and prepared

Al@Al<sub>2</sub>O<sub>3</sub>/PVDF nanocomposites, which showed excellent dielectric properties due to the enhanced intra-particle polarization and suppressed inter-particle polarization. [246]

Some polymer composites with different compositions and dielectric properties are summarized in Table 3.

**Table 3.** Dielectric permittivities of different polymer composites

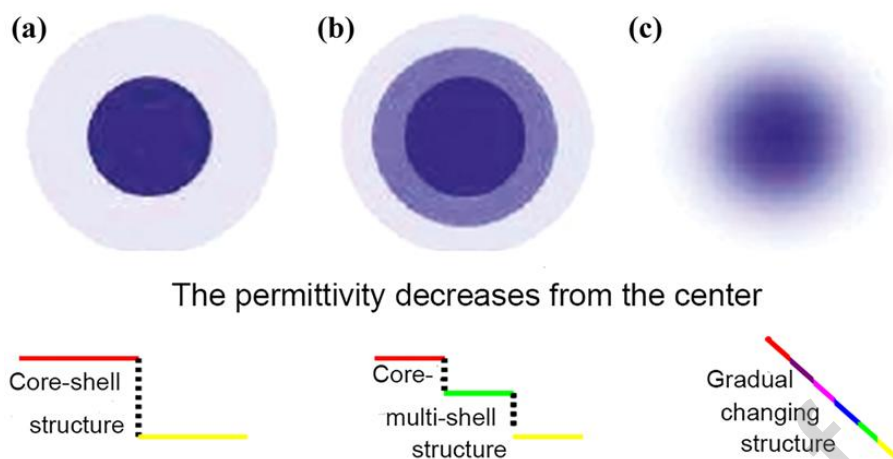
Type	Sub-type	Composite systems	Dielectric permittivity
Ceramic particles /polymer composites	Ferroelectric ceramic particles	BT/PVDF system	133 at 10 Hz
		BT/PVDF system	380 at 100 Hz
		BT/epoxy system	63 at 100 Hz
	Nonferroelectric ceramic particles	BT/PI system	20 at 100 Hz
		PFBPA-BT/P(VDF-HFP) system	80 at 100 Hz
		CCTO/P(VDF-TrFE) system	610 at 100 Hz
Conducting particles /polymer composites	Spherical metal particles	CCTO/PI system	20 at 100 Hz
		BT/PVDF system	400 at 100 Hz
		BT/PVDF system	300 at 100 Hz
		BT/epoxy system	400 at 100 Hz
	1-dimension particles	BT/PI system	225 at 1 Hz
		MWNT/PVDF system	4000 at 1000 Hz
		MWNT/PVDF system	300 at 1000 Hz
2-dimension particles	xGnP/PVDF system	107 at 1000 Hz	

The conductive filler is harmful for the energy storage application because of the high dielectric loss and the decreased breakdown strength from the conductive network. According to the examples discussed above, we propose that the core-shell structure is an effective strategy for the energy storage application due to the obstruction of conductive path.

Jiang and Huang used kinds of reagents as the shell to modify BT nanoparticles such as 1H,1H,2H,2H-heptadecafluorodecyl acrylate (HFDA), trifluoroethyl acrylate (TFEA), styrene (St), methyl methacrylate (MMA), hydroxyethyl methacrylate (HEMA), and glycidyl methacrylate

(GMA) and hyperbranched aromatic polyamide (HBP).[256-261] The effects of interfacial region for the dielectric properties and energy density of nanocomposites was carefully discussed through three types of core-shell structured polymer@BT nanoparticles in PVDF matrix. [258] The MMA, HEMA, and GMA monomers were grafted onto the surface of BT via reversible-addition-fragmentation chain transfer (RAFT) polymerization. It was demonstrated that the core-shell nanoparticle filler should have both high dielectric constant and low electrical conductivity to achieve high energy density of nanocomposites. And the breakdown strength of nanocomposites is highly affected by the electrical properties of the polymer shells. They also successfully fabricated a core@double-shell structure BT nanoparticles, in which the outside shell is PMMA and the inner shell is HBP. The double shell of BT nanoparticles resulted in superior dielectric properties of nanocomposites. [259]

Just like the core@double-shell structure discussed above; we propose a kind of rational design as shown in Figure 14. The core-shell structure still endures a sharp decrease of permittivity, which will result in severe electric field distortion in the interphase when the external electric field is applied on the composites. The electric field distortion increases the breakdown possibility at the interphase, and this is very harmful for the breakdown strength of nanocomposites. The core-multi-shell structure can decrease the distortion due to the buffer shells, which retards the great change of permittivity. Figure 14c is the optimized design because of the gradual reduction of permittivity that can minimize the electric field distortion.

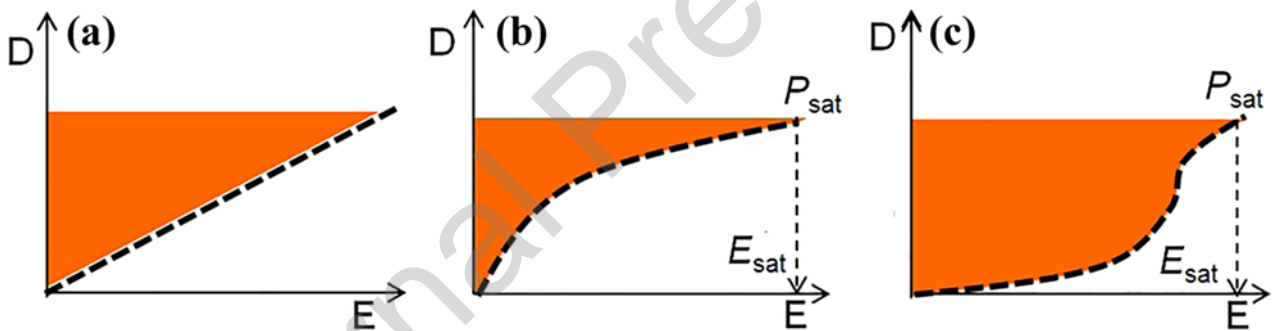


**Figure 14.** Schematic images of a rational design: (a) core-shell structure; (b) core-multi-shell structure and (c) gradual changing structure.

Tang also made impressive progress on the core-shell structure nanoparticles for dielectric nanocomposites. [262,263] An oligothiophene monomer was successfully grafted onto the surface of BT nanoparticles through RAFT polymerization. The oligothiophene shell was beneficial for the compatibility between BT nanoparticles and oligothiophene polymer matrix. It was demonstrated that the nanocomposites system promoted the permittivity and lower dielectric loss over a wide range of frequency.

As mentioned above, a low dielectric loss of materials is critical when the materials with high- $k$  are used as energy storage films in capacitors. [264] It should be noticed whatever pure polymers, polymer blends or polymer-matrix composites with high- $k$  values must have a low dielectric loss. Otherwise, part of power energy translates into thermal energy due to the high dielectric loss of materials. In addition, though ferroelectric components including inorganic fillers and polymer matrix are used in most present studies, an inevitable disadvantage is their ferroelectric memory

effects (large hysteresis loops, see Figure 15(b) so that the stored energy density of these materials with high- $k$  values is not enough large as we expect. And the stored energy density is not a linear variation with the composition of materials or the applied field. Therefore, it should be encouraged that nonferroelectric and antiferroelectric materials should be given more attention in future work in order to meet the use of film capacitors as shown in Figure 15 (see Figures 14(a) and 14(c)). [265] Furthermore, the maximal stored energy density should not be estimated based on the breakdown field values of materials because the electrical field at the saturation polarization might be lower than the breakdown field of dielectric materials.



**Figure 15.** Schematic images showing dependences of stored electric energy density ( $D$ ) of different dielectric materials including (a) linear, (b) ferroelectric and (c) antiferroelectric dielectrics on applied electric field. The shaded area is the stored energy density of different dielectric materials. Reprinted with permission from ref. 265. Copyright 2013 WILEY.

In brief, there is a great challenge to design and synthesize novel dielectric polymers with outstanding properties which can meet the practical requirements for applications. At present, polymer blending and an inorganic/polymer composite are favorable approaches to realize the high-



$k$  polymer materials. However, the polymer composites must deliver a high permittivity and a high breakdown field for high-density energy storage in capacitor applications. Therefore, it is still crucial to generate the materials with both excellent permittivity and high breakdown fields simultaneously.

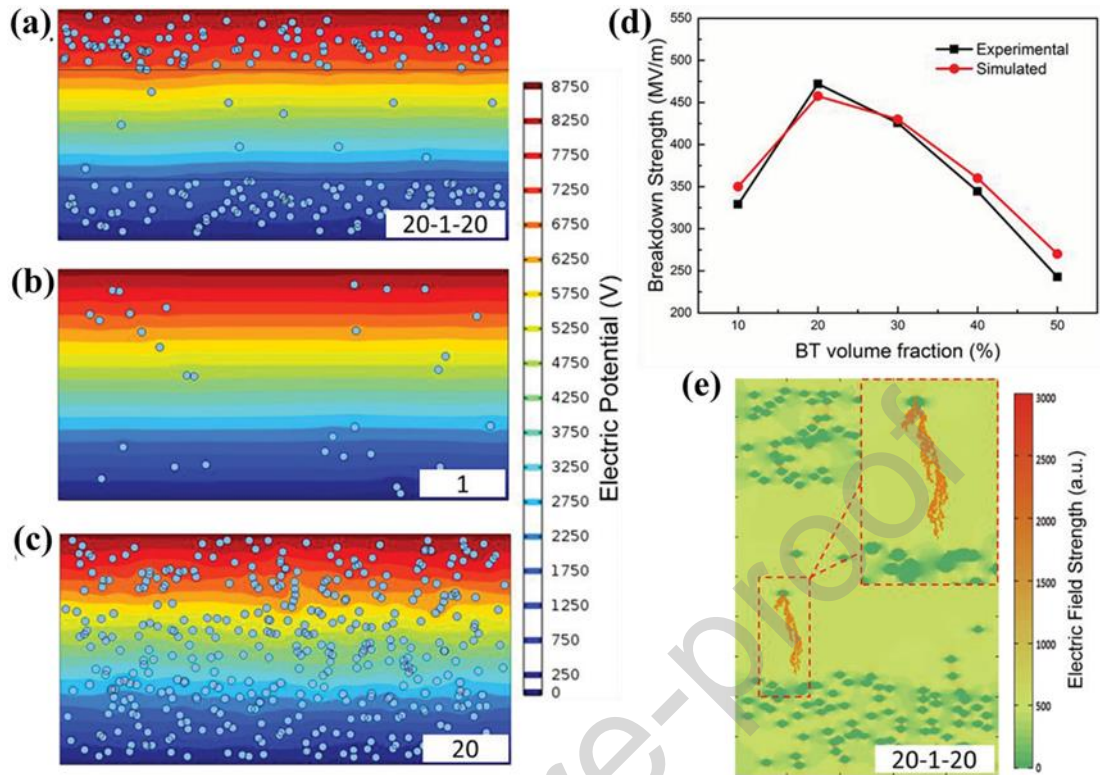
## 6. Multilayer structured polymers

Multilayer coextrusion is a process in which polymers can be extruded and joined together in a feedblock or die to form a single structure but with multiple layers. The number of layers in a multilayered film can be increased by placing two-channel interfacial surface generators in series. In a multilayer structured film, each layer normally has a uniform thickness [266,267]. The individual layer thickness in the multilayer film can be as low as 10 nm, and consequently the nano-confinement effect should be considered as a major factor on dielectric properties. It should be pointed out that not all polymer pairs can be stacked together to form multilayered film. The polymers for individual layers must “stick” to each other to avoid delamination but must be simultaneously immiscible [268]. Moreover, as reported by Bironeau et al. [269], the selected polymer pair needs to meet the requirement of rheological match; e.g., a ratio of viscosity in the range from 0.6 to 0.8 and a ratio of elasticity in the range from 0.2 to 0.5 in order to assure the mechanical quality of the film. Thus, in some cases of multilayer films, a tie layer polymer will be necessary to introduce for modifying the interfacial adhesion, and the tie layer polymer is usually miscible with one layer and compatible with another.

For example, the work in Baer showed an effect of tie polymer materials on dielectric properties in three-component polycarbonate/tie/poly(vinylidene fluoride-co-hexafluoropropylene) [PC/tie/P(VDF-HFP)] multilayer films.[223] When different polymers including poly(methyl methacrylate), styrene-co-acrylonitrile copolymer with 30% acrylonitrile content (SAN30), and poly(ethylene terephthalate-co-1,4-cyclohexanedimethylene terephthalate) (PETG) as tie materials, the 65-layer PC/PMMA/P(VDF-HFP) films exhibited a 25% enhancement in breakdown properties, 50% higher energy density, 40% smaller hysteresis loop areas, and orders of magnitude slower ion migration relative to the 33-layer PC/P(VDF-HFP) control. Baer et al. suggest that these property improvements are mainly attributed to the localized interactions at PMMA/P(VDF-HFP) and PMMA/PC interfaces, forming interphase regions. The modified PMMA/P(VDF-HFP) interphase region can effectively hinder the migration of impurity ions in P(VDF-HFP), reducing their mobility within the layer. Additionally, a small fraction of PMMA can lead to slightly increased dielectric constant of the composite films owing to strong interaction between PMMA and P(VDF-HFP). The other two systems with PETG and SAN30 as tie layers exhibited marginal improvements in dielectric properties owing to their weaker interactions with the P(VDF-HFP) layers.

The multilayered structure can be the pair of polymers and it can also be the combination of nanocomposites.[270-277] Hu et al. investigated a PVDF/BT nanocomposite film by introducing spherical BT nanoparticles and BT nanofibers to fabricate a sandwich structure film.[270] In the nanocomposite film, two out-layers had 10 vol % BT nanofillers as a layer with high dielectric constant and the middle-layer had 2 vol % BT nanofibers as a layer with high dielectric strength. As a result, the optimally tailored topological structure with good permittivity and its maximum energy

density can reach  $9.72 \text{ J/cm}^3$ . Wang and her coworkers [271] investigated BT/PVDF nanocomposites film but with an opposite arrangement. They combined two out-layers with 20 vol % BT to provide a higher permittivity and a inter-layer with 1 vol % BT to offer a higher breakdown strength. The nanocomposite with the permittivity of 17 and the breakdown strength of 470 MV/m was obtained, which eventually caused higher energy density ( $18.8 \text{ J/cm}^3$ ). A finite element simulation was used to analyze the breakdown route and the results found that the enhanced dielectric performances resulted from the heterogeneous distribution of the electric field in the nanocomposite film. The interface of the multilayered structure could block the growth of electrical trees as shown in Figure 16. They also prepared a kind of gradient-layered polymer nanocomposites inspired by the hierarchical structure of bamboo culms, in which the contents of  $\text{BaTiO}_3$  NWs raised gradually from the upper to bottom layers. [272] The designed buffer layer and gradient change of electric field at the interfaces served as efficient barriers against charge injection and electrical conduction to prevent early dielectric breakdown. Finally, the maximum energy density of gradient-layered nanocomposite with the optimized filler content was as high as  $17.6 \text{ J/cm}^3$  at 510 MV/m with a high charge-discharge efficiency up to 71%.



**Figure 16.** The distribution of electric field in: (a) sandwiched BT/PVDF nanocomposites with 20 vol% BT in “soft layers” and 1 vol% BT in “hard layer,” (b) single layer BT/PVDF nanocomposites with 1 vol% BT, and (c) single layer BT/PVDF nanocomposites with 20 vol% BT, simulated by finite element methods. (d) The experimental and simulated breakdown strength of sandwich BT/PVDF (e) The incomplete breakdown in sandwiched BT/PVDF with 20 vol% BT in the “soft layer” at the applied voltage of 9 kV simulated by finite element method. Copyright 2015, Reproduced with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. [271]

Boron nitride nanosheet (BNNS), as an insulating material with a wide band gap (6 eV) [278-281], has been introduced in nanocomposites with multilayered structure recently. Liu et al. [273] prepared a PVDF matrix nanocomposite with a multilayered structure combined by BNNS and barium strontium titanate (BST) nanowires. The out-layers loaded by 10 vol% BNNS provided high

breakdown strength, and the middle-layer contained 8 vol% BST nanowires enhanced the permittivity of the composite. Finally, the prepared multilayered composites displayed impressive energy density of  $20.5 \text{ J/cm}^3$  at 588 MV/m.

## 7. SUMMARY AND OUTLOOKS

In summary, this review has introduced some of the recent progress and perspective in the area of Polymer-based dielectrics, especially the high- $k$  polymer materials. It should be noted that the configuration/conformation of the polymer chains and the morphology of polymer composites play critical roles in determining the final dielectric properties. The concluding remarks are as follow:

(1) It is still an important challenge how to design and synthesize the polymers with suitable configuration of the substituting conformation of the polymer chains and the morphology of polymer composites. For pure polymer materials, they should be awarded the required permittivity, low dielectric loss and high breakdown. In addition, it is suggested that studies on nonferroelectric materials including polymers and inorganic fillers are encouraged since they make a linear correlation between the concentration of fillers and energy storage. These materials are very useful as dielectric films in future capacitors.

(2) The physical/chemical characteristics of nanoparticles play a crucial role in determining the final dielectric properties of polymer materials. However, due to the complexity of the interaction between nanoparticles and polymers, existing theoretical models cannot give an accurate prediction to the dielectric properties of polymer materials when nanoscale particles are added to form the polymer-matrix composites.

(3) The interfaces between inorganic fillers and polymers are critical and appropriate surface modification of inorganic fillers can improve their compatibility with the polymers. Core-shell structure fillers is an important way to promote the interfacial interactions between filler and polymer and the uniform dispersion of the fillers in the polymers.

(4) Reasonable designing composite structure turns out to be an effective strategy of realizing high- $k$  goal. Multilayered structure could ameliorate the dielectric performances by hierarchical structures and combinations. And accurate architectures for functional layer or filler structure of composite film are helpful to balance various dielectric characteristics, which should draw more attention and needs further study.

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGEMENTS

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**[282] Declaration of interests**

[283]  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

[284]  The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

[285]

## Highlights

- Some representative structure characteristics of high-k polymers are introduced.
- To realize the high-k polymer materials by employing different routes is illustrated
- Guidance on achieving polymer based materials with high permittivity is provided.

## Graphical abstract

