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Dielectric polymers with novel chemistry, compositions and architectures

Yali Qiao [a], Xiaodong Yin [a], Tianyu Zhu [a], Hui Li [b], Chuanbing Tang [a],*

[a] Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, United States
[b] School of Chemistry and Chemical Engineering, Shandong Key Laboratory of Fluorine Chemistry and Chemical Materials, University of Jinan, Jinan, 250022, Shangdong, China

ABSTRACT

Dielectric capacitors have attracted ever-increasing interest in recent decades for numerous applications in modern electronic and electrical power systems due to their fast charge/discharge speed and high energy density. Novel dielectric materials are highly sought for these capacitive applications. Polymer dielectrics are attractive as they can offer high dielectric strength, low dielectric loss, and light weight, however, a few challenges still exist. For examples, the state-of-the-art polymer dielectric, biaxially oriented polypropylene (BOPP), has low dielectric permittivity, while polyvinylidene fluoride (PVDF) has high dielectric loss. These hurdles require developing next-generation polymers as dielectric materials with new chemistry and unique architectures that are tunable in compositions, flexible in mechanical properties and stable at high temperature. In this short review, we begin with some theoretical considerations for the rational design of dielectric polymers with high performance. In the guidance of these theoretical considerations, we review recent progress toward dielectric polymers based on two major approaches, in terms of macromolecular architectures, namely main-chain and side-chain dielectric polymers, and various chemistry and compositions are discussed within each approach.

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1. Introduction

Novel dielectric materials are highly desirable due to their applications in a broad range of advanced energy harvesting and storage systems, such as portable electronic devices, hybrid electric vehicles (HEVs), and pulse power systems [1–5]. Compared to inorganics, polymers are attractive materials as dielectrics [6–12] as they allow for easier processing techniques and lower densities, leading to the formation of lightweight, flexible films suitable for devices with limited size and space. One of the state-of-the-art polymer dielectrics, biaxially oriented polypropylene (BOPP), exhibits a high breakdown strength ($E_b > 600\,MV\,m^{-1}$) and an inherently low dielectric loss (tanδ $\sim$ 0.0002). However, its energy density is limited by a low dielectric constant ($\varepsilon_r = 2.2$) and an operating temperature below 100 °C ($T_m < 140$ °C) [13]. The other benchmark polymer dielectric, polyvinylidene fluoride (PVDF), possesses high dielectric constant ($\varepsilon_r > 10$), which can be significantly enhanced ($\varepsilon_r > 50$) by proper defect modification, and achieve a very high energy density ($>20\,J\,cm^{-3}$) [8,14–16]. However, PVDF-based ferroelectric poly-

mers suffer from large polarization hysteresis loss due to the strong dipole–dipole interactions and limited operating temperature below 125 °C ($T_m < 140$ °C).[13,17] Therefore, next-generation polymer dielectrics simultaneously possessing high dielectric constant (>5–10), low loss, high efficiency as well as high operating temperature (>150 °C) are highly sought.

A capacitor with a dielectric layer (area A, dielectric thickness d) between two metallic electrodes is applied a voltage V to store energy, which can be described with volumetric energy density by:

$$W = \frac{1}{Ad}\int V dq = \int E dD \tag{1}$$

where E, D, and $q = DA$ are the electric field, electric displacement, the free surface charge, respectively. Eq. (1) shows that the increase of E to some reasonable fractions of the breakdown field E_b can maximize the stored energy density. Moreover, since the electric displacement is related to the polarization P by $D = P + \varepsilon_0 E$, high polarization favors high displacement, ultimately leading to enhancement of the stored energy density. For linear dielectric materials with $D = \varepsilon_0\varepsilon_r E$, the energy density is changed to:

$$W = \frac{1}{2}\varepsilon_r\varepsilon_0 E^2 \tag{2}$$

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* Corresponding author.
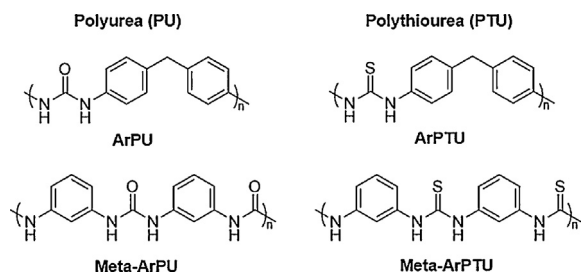 *E-mail address:* tang4@mailbox.sc.edu (C. Tang).

Fig. 1. Chemical structures of (meta)aromatic polyurea and polythiourea.

where ε_r is the dielectric material's relative permittivity, and $\varepsilon_0 = 8.85 \times 10^{-12}\,\mathrm{F\,m^{-1}}$ is the vacuum permittivity. Eq. (2) indicates that materials with large relative permittivity and breakdown field strength can achieve high energy density.

At present, in order to achieve high energy density in polymer dielectrics, one typical strategy is to develop PVDF-related ferroelectric polymers [8,18–29]. Nevertheless, experimental results showed that these modifications to PVDF-based copolymers and terpolymers cannot fully suppress the polarization coupling in these ferroelectric polymers, especially at high electric fields. Therefore, it is still of great challenge to further reduce the ferroelectric loss and high field conduction loss in those ferroelectric polymers. Recently, efforts have started to be devoted to improving the energy density of linear polymers by introducing highly polar molecular groups, which is another promising approach toward novel high-performance polymer dielectrics [6,7,10,30,32–34]. In general, the dielectric permittivity in a linear dielectric polymer can be estimated by using the Fröhlich model [35]:

$$\frac{(\varepsilon_{rs} - \varepsilon_{r\infty})(2\varepsilon_{rs} + \varepsilon_{r\infty})}{\varepsilon_{rs}(\varepsilon_{r\infty} + 2)^2} = \frac{Ngu^2}{9\varepsilon_0 kT} \tag{3}$$

which implies $\varepsilon_r \sim Ngu^2$. Here ε_{rs} and $\varepsilon_{r\infty}$ are the dielectric constants at low frequency and optical frequency, respectively; N is the volumetric dipole density; g is the correlation factor; u is the dipole moment; k is the Boltzmann constant; and T is the temperature. Therefore, high volumetric density of highly polar molecular groups with proper dipolar coupling is highly beneficial to the achievement of higher dielectric constant, maintenance of relatively low loss, in turn leading to high energy density in such linear dielectric polymers. In this short review, we intend to explore the recent progress on approaches to developing novel dielectric polymers. In particular, we focus on linear dielectric polymers, based on incorporation of highly polar functional groups and/or molecules via two major approaches, in terms of macromolecular architectures, namely main-chain and side-chain dielectric polymers, and various chemistry and compositions are discussed within each approach.

This short perspective is certainly not inclusive for all interesting development over last two decades. For work on dielectric polymeric composites, readers are referred to publications cited herein [11,36–64].

2. Polymers containing dipolar groups in main-chain architectures

2.1. Main-chain (aromatic) urea- and thiourea-functionalized polymers

Polyurea and polythiourea, as highly polar polymers, have been well-known for their interesting dielectric, pyroelectric, piezoelectric, and ferroelectric properties [65–68]. The dipole moments of urea and thiourea [69] are 4.56 Debye and 4.89 Debye, respectively, which are much larger than most polymer materials, such as PP, PET, PC, and PVDF (2.1 Debye). The Zhang group initially

investigated aromatic polyurea (ArPU) (Fig. 1) as dielectric thin films for possible high-temperature, high-energy density capacitor applications. Relatively high dielectric constant ($\sim$4.2), high breakdown strength (690 MV m^{-1}), and very low leakage current have been demonstrated in high-quality aromatic polyurea thin films fabricated through vapor deposition polymerization of monomers 4,4′-diamino-diphenylmethane (MDA) and 4,4′-diphenylmethane-diisocyanate (MDI) [70,71], resulting in a high energy density (9 J cm^{-3}) and very high charge-discharge efficiency (>95%). These values decrease only slightly from room temperature to 180 °C. The design of direct connection of highly polar urea functional group with highly hydrophobic aromatic rings not only favors the formation of delocalized electrons to enhance the dielectric response, but also suppresses the dipole–dipole coupling to maintain relatively low loss, making aromatic polyurea a polar linear dielectric exhibiting higher dipole moment than PVDF without ferroelectricity.

Shortly, the same group reported the development of aromatic polythiourea (ArPTU) (Fig. 1) with greatly improved dielectric performance, especially at high electric fields. ArPTU was synthesized via microwave-assisted polycondensation of 4,4′-diphenylmethanediamine (MDA) with thiourea in N-methyl-2-pyrrolidone (NMP) with p-toluenesulfonic acid (p-TSOH) as a catalyst [72]. Due to slightly higher dipole moment of thiourea than that of urea, ArPTU exhibits a moderate increase in dielectric constant ($\sim$4.5 in ArPTU versus $\sim$4.2 in ArPU). Additionally, ArPTU films demonstrate an extremely high dielectric breakdown strength (>1.1 GV m^{-1}), resulting in a maximum electrical energy density up to 24 J cm^{-3} and very high charge-discharge efficiency of 92.5% at 1 GV m^{-1}. The dielectric properties do not change significantly with temperature up to 150 °C. Unlike the strongly coupled dipolar polymers such as PVDF that are semicrystalline, ArPTU is an amorphous, glass-phase polymer ($T_g > 200$ °C), eliminating band conduction and avoiding ferroelectric loss even at the highest measured electric field (1.1 GV m^{-1}). The large dipole moments of thiourea functional groups can provide strong scattering to the electrons and ions, thereby further reducing the conduction loss. The weak coupling among the dipoles due to the separation of thiourea groups via aromatic rings is favorable to achieving low dielectric loss. Moreover, the ultrasmooth surface plays a great role in ensuring very high breakdown strength while maintaining low loss [73,74].

They further investigated meta-aromatic polyurea (meta-ArPU) [75] and corresponding meta-aromatic polythiourea (meta-ArPTU) [76] (Fig. 1) with a higher volumetric dipole density and thus
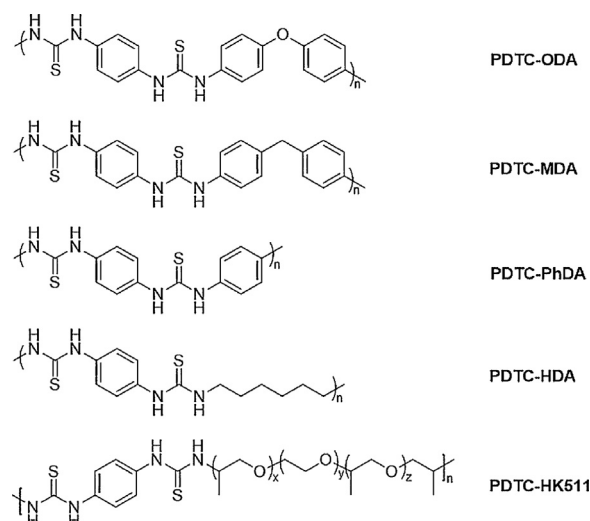

Fig. 2. Chemical structures of a series of polythiourea with long and flexible chains.