

High Dielectric Constant Polyimides Containing Nitrile Groups

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Abstract: A facile strategy for achieving polyimides with high dielectric constant and quite low dielectric loss using nitrile groups was developed. The dielectric constant of 2CN-BTDA can reach 4.80 with a low dielectric loss of 0.00157 at 1 kHz. Theoretical calculation was carried out to study the relationship between the molecular structure and dielectric properties of polymers, which is beneficial for the design of high dielectric polymers.

1. INTRODUCTION

Recently, materials with high dielectric constant, low dielectric loss and excellent temperature tolerance are highly desirable for next-generation power and electrical application, such as film capacitors for advanced power electronics and gate dielectrics. According to previous reports [1-3], polymer composites are suitable for these flexible capacitors by maximizing the dielectric constant and at the same time, managing the dielectric loss to an acceptable level. From the matrix materials standpoint, it is clear that the pure polymers with high dielectric constant are urgently needed for fabricating composites.

Although ferroelectric polymers such as polyvinylidene fluoride (PVDF) possess high dielectric constant ($k > 6$), however, the high crystalline and amorphous dipole mobility promote the ionic and electronic mobility, resulting in high dielectric loss. Besides, PVDF is also limited by low operating temperatures because of the low melting points (175 °C), which cannot be used under a more severe aerospace environment, for example, near aircraft engine. Among numerous polymer materials, polyimide (PI) is considered as the best candidate for these special dielectrics owing to its high glass transition temperature, great flexibility and outstanding resistance to solvents, which are definitely crucial for extreme conditions. However, polyimide is a kind of linear dielectric without spontaneous polarization capacity, so that it is hard to enhance the dielectric constant. In theory, there are four types of polarization in dielectrics: electronic, atomic, orientational (or dipolar) and space charge polarization [4]. Electronic and atomic polarizations belong to the resonance regime, and they happen in the optical (10^{14} to 10^{16} Hz) and infrared frequencies (10^{11} to 10^{14} Hz), respectively. Besides, orientational polarization, taking place in 10^4 to 10^{11} Hz, is able to induce the dielectric dipole turning to the direction of external electric field. Unlike the others, space-charge polarization is mainly happened on polymer composites at low frequencies ($< 10^4$ Hz). Therefore, the mainly polarization behavior occurred for pure polyimide in our test frequencies ($10^2 \sim 10^6$ Hz) is orientational polarization (including permanent dipole and induced dipole polarization). Though the glass transition temperature of polyimide is so high that hinders the dipole orientation, introducing some strong polar groups to polyimide structure is still effective for enhancing dielectric properties [2].

Herein, a diamine monomer with two nitrile groups was designed and synthesized. Unlike the previous report [3], these two nitrile groups were ortho in a benzene ring to ensure the same dipole moment direction. A diamine monomer without nitrile groups was also prepared as comparison. After that, the as-prepared diamine monomers were polymerized with five different types of commercial dianhydride monomers to obtain polyimide films. The results show that all the polyimides with nitrile groups exhibit enhanced dielectric constant comparing with those without nitrile groups, and the dielectric loss of all the polyimide films can be controlled below 0.01(1 kHz), which show great potential for using in film capacitors. Moreover,

we investigated the essence of designing high- k polymer materials through electromagnetic theory, which can be expected to provide ideas for similar studies.

2. EXPERIMENTAL

Monomer synthesis

The diamine monomer with two nitrile groups (2CN) was one-pot synthesized through Williamson etherification by using 4,5-dichlorophthalonitrile, 4-aminophenol and potassium carbonate (K_2CO_3). The diamine monomer without nitrile groups (0CN) was also synthesized through the same reaction by using catechol, 4-nitrochlorobenzene and potassium carbonate (K_2CO_3). Then the products were reduced to diamines by Pd/C and hydrazine hydrate. All the chemical structures mentioned above were confirmed by the 1H NMR, ^{13}C NMR spectra and the high resolution mass spectrum.

Polymer synthesis

These two as-prepared diamine monomers were respectively polymerized with five commercial dianhydride monomers: pyromellitic anhydride (PMDA), 4,4'-bipthalic anhydride (BPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic anhydride (ODPA) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) in a conventional two-steps procedure. All the details are shown in Figure 1.

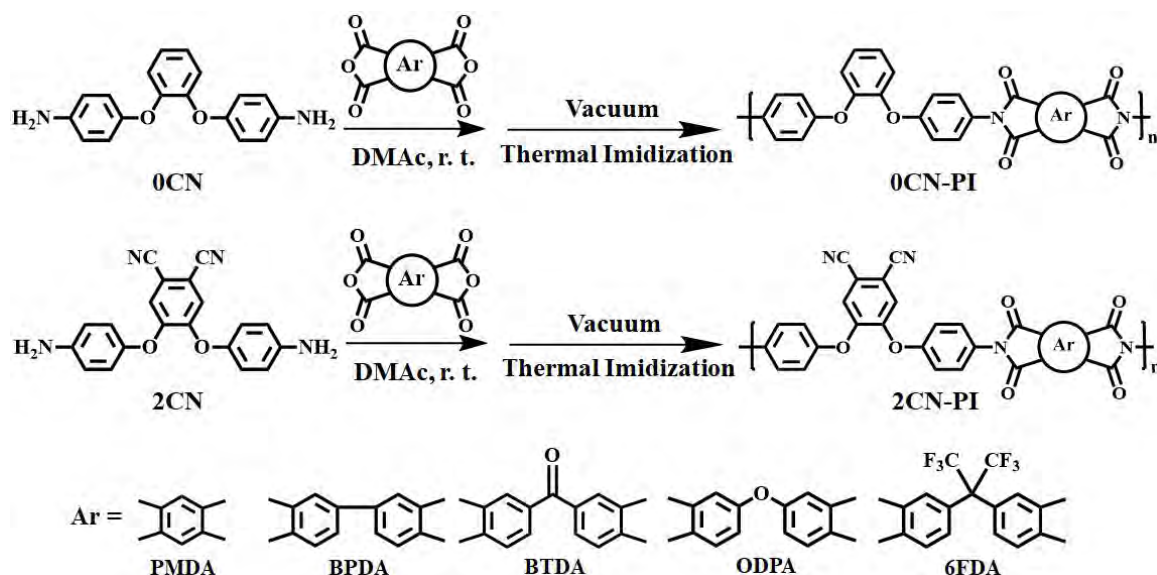


Figure 1. The detail routes of synthesizing polyimide with or without nitrile groups

3. RESULTS AND DISCUSSION

The dielectric properties of the polyimide films were measured at the frequencies ranged from 100 Hz to 1 MHz at room temperature using a Solartron SI 1260 impedance/gain phase analyzer (Solartron Group Ltd., U.K.). Firstly, a capacitance measurement was carried out, and then the dielectric constant of the polyimide films was calculated using equation (1):

$$C = \epsilon_0 \epsilon \frac{S}{d} \quad (1)$$

where ϵ_0 is the vacuum permittivity ($\epsilon_0=8.85 \times 10^{-12}$ F m $^{-1}$), ϵ is the permittivity of dielectric material; S and d represent the areas and distances of polar plates, respectively. The results are shown in Figure 2, Table 1 and Table 2.

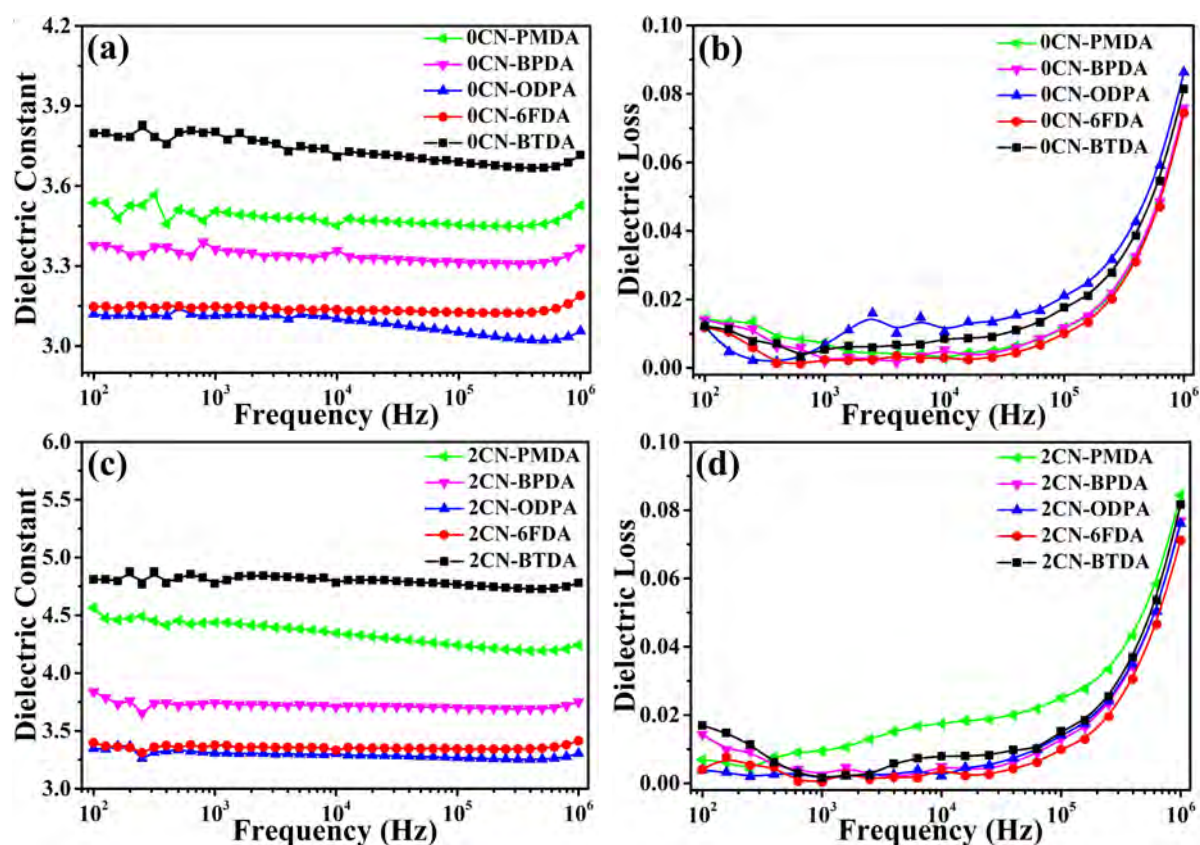


Figure 2. Frequency dependence of the (a) dielectric constant, (b) dielectric loss ($\tan \delta$) of 0CN-PI and (c) dielectric constant, (d) dielectric loss ($\tan \delta$) of 2CN-PI films measured at room temperature from 100 Hz to 1 MHz.

Table 1. Dielectric constant of 0CN-PI and 2CN-PI films measured at room temperature (1 kHz)

	PMDA	BPDA	BTDA	ODPA	6FDA
0CN	3.50	3.36	3.80	3.11	3.14
2CN	4.44	3.74	4.80	3.31	3.37

Table 2. Dielectric loss ($\tan \delta$) of 0CN-PI and 2CN-PI films measured at room temperature (1 kHz)

	PMDA	BPDA	BTDA	ODPA	6FDA
0CN	0.00740	0.00201	0.00538	0.00672	0.00233
2CN	0.00946	0.00236	0.00157	0.00119	0.00286

As shown in **Figure 2**, **Table 1** and **Table 2**, due to the introduce of nitrile groups, the dielectric constant of 2CN-PI films are greatly increased comparing with these 0CN-PI films when using the same dianhydride monomer. It can also be observed that different types of dianhydride monomer will affect the dielectric properties for both 2CN-PIs and 0CN-PIs on account of the essence of dielectric polarization. The dielectrics with more polar groups and molecules are easier to be polarized, which leads to higher dielectric constant. Therefore, on the one hand, the nitrile groups are supposed to help increase the dielectric constant. On the other hand, when using the same diamine monomer, BTDA with a polar carbonyl group, is beneficial to increase the dielectric constant of the resulted polyimides. Thus the k value of 0CN-BTDA, 2CN-BTDA are 3.70 and 4.80 at 1 kHz respectively. Besides, PMDA is considered as the smallest structure comparing with other dianhydride monomers, such as BPDA, ODPA and 6FDA, which may increase the density of nitrile groups to achieve higher k value. As a result, the k value of 2CN-PMDA can rise to 4.44. Moreover, ODPA has an ether bond in the structure, which may lead to loose packing in polyimide structure comparing with

using other dianhydride monomers, like PMDA, BPDA and BTDA. In other words, the free volume of polyimide with ODPA may be bigger than these with PMDA, BPDA and BTDA. Thus the k value will be decreased as expected. For 6FDA, things may be more complex. Even though 6FDA has C-F bond with large dipole moment, it was reported that C-F bond has weak polarization ability because of low electron delocalization cause by high electronegativity of fluorine atom. More importantly, the large volume of trifluoromethyl groups may help to increase the free volume of polyimide and the k value is more likely to drop. Unlike PVDF, the molecular chains of these polyimides are frozen at room temperature, which means the dielectric loss can be quite low (<0.01 , 1 kHz).

According to Clausius-Mossotti equation (2), the dielectric constant of materials can be calculated as below:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N}{3\varepsilon_0} \alpha \quad (2)$$

where ε_0 is the vacuum permittivity ($\varepsilon_0=8.85 \times 10^{-12}$ F m⁻¹), ε is the permittivity of dielectric material; N is the repeat unit density and α represents the polarizability of dielectric. Generally, the N reflects number of molecules per volume and can be calculated as equation (3):

$$N = \frac{\rho}{M_{RU}} N_A \quad (3)$$

where ρ is the density of the polymer, M_{RU} is the molar mass of a repeat unit, and N_A is the Avogadro number. Therefore, the equation (2) can be expanded to equation (4):

$$1 - \frac{3}{\varepsilon + 2} = \frac{\rho N_A}{3M_{RU}\varepsilon_0} \left(\alpha_e + \alpha_a + \alpha_\mu + \frac{\mu^2}{3k_B T} + \alpha_s \right) \quad (4)$$

where μ is the permanent dipole moment of polymer, k_B is Boltzmann constant ($k_B=1.38 \times 10^{-23}$ J K⁻¹), T is the ambient temperature; α_e , α_a , α_μ and α_s represent the polarizability of electronic, atomic, induced dipole and space-charge polarization, respectively. Obviously, the density of polymer can be measured by a densimeter. Furthermore, in our test frequencies ($10^2 \sim 10^6$ Hz) at room temperature, α_e and α_a are not the main component of the polarizability. For pure polyimide, α_s doesn't exist and α_μ is tiny because of the freeze of polymer chains. As a result, the value of N can be calculated and μ of polymers can be approximate calculated using the structures of repeat unit by DFT/B3LYP/6-31G (2d, p) with the Gaussian 09 program. The above results are shown in **Table 3**.

Table 3. The ρ , N , M_{RU} and μ value of 0CN-PI and 2CN-PI films

	ρ (g cm ⁻³)	N (cm ⁻³)	M_{RU} (g mol ⁻¹)	μ (Debye)
0CN-PMDA	1.4961	1.8997×10^{21}	474.09	2.7898
0CN-BPDA	1.4129	1.5461×10^{21}	550.12	1.7215
0CN-BTDA	1.4493	1.5092×10^{21}	578.11	3.0678
0CN-ODPA	1.3918	1.4800×10^{21}	566.11	1.4895
0CN-6FDA	1.3786	1.1854×10^{21}	700.11	3.1574
2CN-PMDA	1.5556	1.7869×10^{21}	524.08	7.8824
2CN-BPDA	1.4790	1.4836×10^{21}	600.11	7.4992
2CN-BTDA	1.5175	1.4544×10^{21}	628.10	9.9816
2CN-ODPA	1.4484	1.4152×10^{21}	616.10	7.3656
2CN-6FDA	1.4188	1.1387×10^{21}	750.10	7.7684

Combining with the previous discussion, it is evident to find that the introducing of nitrile groups to polyimide structures is truly an effective way for enhancing the permanent dipole moment. Although the N value of 2CN-PI is slightly smaller than 0CN-PI when using the same dianhydride monomers, the great difference in μ value will lead to the improvement of dielectric constant. In addition, the polyimide with PMDA owns tight chain packing and the highest levels of density, which obtain higher N value to enhance k value. We believe that BTDA is surely suitable for preparing high- k polyimide due to the relatively high N value and the highest μ value. As for 6FDA, though C-F bond has large dipole moment, the low value of α_μ and the lowest N value will help to decrease the dielectric constant of polyimide containing 6FDA. That is the reason why we always use 6FDA as dianhydride monomer for low- k polyimide. Apparently, the theoretical results match well with our experimental results, whereas the value of α_e , α_a and α_μ can't be calculated accurately. More importantly, the value of N and μ are still approximate and the sense of T in equation (4) is still remaining to be discussed.

4. CONCLUSION

In summary, we develop a facile strategy for achieving polyimide with high dielectric constant and quite low dielectric loss using nitrile groups. Even though the theoretical model we constructed is not able to obtain the accurate k value, it still can explain our design thought and qualitatively analyze the essence of polymer dielectric, which offers guidance for preparing high- k polymer materials.

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