NiFe$_2$O$_4$/Poly(1,6-heptadiynes) Nanocomposite Energy-Storage Device for Electrical and Electronic Applications

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ABSTRACT: In present study, we have synthesized intrinsically conductive poly(1,6-heptadiynes) via cyclopolymerization technique, and further it is composited with the NiFe$_2$O$_4$ to fabricate pellet for electrical and electronic applications. The synthesized polymer $I$–$V$ characteristics were obtained by two-probe measurement technique. The results suggest that the high current density of the synthesized polymer was in the range of $1.2 \times 10^{-5}–3.1 \times 10^{-5}$ S/cm, which attributes to the potentially induced hoping charge-carrier mechanism within the conjugated poly(1,6-heptadiynes). NiFe$_2$O$_4$ and NiFe$_2$O$_4$/poly(1,6-heptadiynes) composite pellets were fabricated by utilizing hydraulic pelletizer. The sample’s electrical measurements were performed via broad-band dielectric impedance spectroscopy, wherein the composite permittivity was about $\varepsilon = 45$ (100 Hz to 10 kHz), which attributes to the NiFe$_2$O$_4$ and poly(1,6-heptadiynes) phases; further, this describes the capacitance, which improved from 0.3 to 0.1 pf at 1 kHz. Also, these results suggest the reduced equivalent series resistance (72.1–1 MHz), which attributes to the incorporated intrinsically conducting poly(1,6-heptadiynes). Thus, the reduced dissipation factor (DF = 0.0032) was observed from impedance characteristics of a nanocomposite. Moreover, the improved $Q$-factor was observed, which was about 8.1–310 at 1 kHz. The resistance and capacitance time constant was also computed to be about 0.29 $\mu$s at 1 kHz for NiFe$_2$O$_4$/poly(1,6-heptadiynes) nanocomposite. Furthermore, the nanocomposite-enabled capacitor gravimetric energy density and power densities were calculated to be about 0.00575 mJ/g and 9.91 W/g, respectively. Additionally, thermal threatening, that is, heat generated within the capacitor, $P_{\text{loss}}$ is also estimated for the nanocomposite capacitor, which improved from 0.0006 to $8.9 \times 10^{-6}$, and these results suggest improved nanocomposite thermal stability. Further, the delineated quantities were compared to the commercially available configurations of tantalum hybrid capacitors and Al and Ta electrolytic capacitors, including carbon electrochemical capacitors, which suggest that the reported nanocomposites could be a suitable candidate for electrical and electronic applications.

INTRODUCTION

In active and passive components consisted of modern electronics, passive elements (resistors, inductors, and capacitors) occupy 80% of circuit board area.$^{1,2}$ Among them, capacitors can be a useful component for tuning and filtering, bypassing, decoupling, and noise suppression.$^{3,4}$ High area occupied by the integration of passive components leads to parasitic effects and thus to lower reliability.$^{3,4}$ Therefore, increased fabrication emphasizes on miniaturized electronic components and their devices fascinate the demands of electronic technology. Although electronic miniaturization facilitates reduction of energy consumption, lightweight and economically stable miniaturization of passive embedded technology has anomalous effects on the electronic components, probably due to the stray capacitance and short-circuit-effect-induced insulation failure.$^5$ Parasitic effects of integrated passive elements hinder the adequate power supply in electronic integrated circuit (IC) technology.$^6$ Simultaneous switching noise is one of the common manifestations of parasitic effects, which could be attributed to the distributed power network, and passive inductance prevents rapid changes in currents as required by the higher-frequency ICs of today’s technology.$^6$ Moreover, the potential drop from the change in inductance causes glitches on the power supply, which could facilitate false switching current. To overcome these abnormalities in current electronic industry and to improve...
the reliability and performance of electronic devices, the miniaturization with functional material properties is keenly required while maintaining reduced sizes such as higher dielectric constant, frequency, and temperature stability. Recently, researchers have revealed the essential factors for efficient functional electronics, which are high dielectric constant, proper dielectric dispersion at higher frequency, and good interfacial dispersion between the polymer and matrix. Tummala et al. reported the dielectric constant (20–30) of organically facilitated process enabled ceramic composites to meet electronic high frequency miniaturized decoupling components. Although the high dielectric constant with functional properties induces the improved performance of miniaturized electronics, in some electronic applications, the lower dielectric permittivity is essentially required, which permits the varactors (a semiconductor diode with capacitance) to be fabricated with picofarad capacitance for microwave circuits, which are being tuned with the direct-current (DC) voltage level <200 V. These developments facilitate low-cost phase shifters for phased array antennae as well as tunable oscillators and tunable filters for wireless applications such as cellular and personal communication service. The challenges could be high dielectric loss and picofarad operating voltage of capacitors, lower Q-quality factor at required frequencies, and insufficient power-handling capabilities of tuning elements.

Recently, high energy storage materials have attracted attention to meet the demand for large-scale practical applications. Inorganic polymer composites are to be considered as promising energy-storage materials due to their dielectric permittivity with low loss, dielectric strength, and high processability. For example, BaTiO$_3$@TiO$_2$ core–shell materials in a polyvinylidene matrix composite exhibit improved permittivity (66.2) and low loss (0.048); further, the results suggest that the discharge energy density 20 J/cm$^3$ was attained at an applied electric field of 646 kV/mm. Zhang et al. reveal that the energy density relates to the applied electric field (either directly or inversely); for example, synthesized titanium dioxide/lead zirconate titanate nanowire arrays exhibit an energy density of 6.9 J/cm$^3$ at a lower intensity of applied electrical fields 143 kV/mm, which is attributed to the high relative permittivity at 1 kHz. Further, the applied fields increase, for example, 400–600 kV/mm, which may bring more challenges relating to the failure probability. According to some researchers, such type of organopolymer composites enabled that high energy density with low power loss and high dielectric strength characteristics are desirable candidates for electrical and electronic applications such as embedded capacitors for power systems, multilayer capacitors, piezoelectrical devices, and gate insulators to meet the current demands.

In this context, we have attempted to explore poly(1,6-heptadiynes), which was synthesized via cycopolimerization (CP) technique. The $I$–$V$ characteristics of synthesized poly(1,6-heptadiynes) were scrutinized via two-probe conductivity technique. The pellets’ (NiFe$_2$O$_4$ and NiFe$_2$O$_4$/poly(1,6-heptadiynes) nanocomposite pellets’) dielectric permittivity ($\varepsilon$), dissipation factor (DF), impedance ($Z$), capacitance ($C$), and quality factor ($Q$) were reported for the first time. Also, the reduced equivalent series resistance (ESR), resistance and capacitance (RC) time constant, gravimetric energy density, and power density of a nanocomposite-enabled capacitor were quantified and then compared to those of the commercially available tantalum hybrid capacitors and the Al and Ta electrolytic capacitors, including carbon electrochemical capacitors. In addition, electronic application assistive capacitor $P_{\text{loss}} = \text{power loss}$ and charge discharge is discussed in this work.

### MATERIALS AND METHODS

**Materials.** Raw materials (nickel ferrites (NiFe$_2$O$_4$) (particle size ca. 30–70 nm and density $\sim$5.13 g/cc)) were purchased from Sigma-Aldrich Corp., India. Malonic ester was procured from Alfa Aesar. Sodium hydroxide, propargyl bromide, Hoveyda-Grubbs’ second-generation catalyst, and ethyl vinyl ether were purchased from Sigma-Aldrich, India. Diethyl ether, tetrahydrofuran (THF), ethyl acetate, hexane, chloroform, acetonitrile, and anhydrous sodium sulfate were acquired from Merck India Ltd. Ethanol (purity $\sim$99%) was purchased from Sigma-Aldrich, India. All of the solvents were dried over calcium hydride before use, and all raw materials and solvents were used as received without any further purification.

**Characterization Techniques.** Two-probe measurement (Keithley Instruments, U.K.) technique was used to analyze the DC conductivity of synthesized poly(1,6-heptadiynes). The room-temperature broad-band dielectric impedance characteristics (dielectric permittivity, impedance, and capacitance) were measured according to the standard ASTM-D150 over the 1–10 MHz frequency range via a broad-band impedance analyzer (Novocontrol Alpha, Germany).

**Need and Necessity of NiFe$_2$O$_4$ and Poly(1,6-heptadiynes) for Electrical and Electronic Applications.** Researchers have implemented various kinds of shielding materials for electrical and electronic devices to shield abnormal radiations. Although the shielding materials were extensively explored, in modern television receiving equipment and other high-frequency military and commercial devices, it is customary to shield generators in metallic shields so that the electromagnetic interference generated by the radiations near the adjacent devices can be prevented. During filament heating supplying low frequency of alternative currents, for example, in supplying DC potentials for grid circuits or for plates, considerable high-frequency current will leave the shielding enclosures by traveling along the supply leads, as a result, spurious radiation. To avoid this problem, researchers have fabricated capacitors that form low reactance at high frequency to the ground at the shielding enclosures. The capacitors are essentially required to be employed at the shield boundaries to prevent high-frequency current-induced spurious radiations. Nanonickel and its ferritic compounds were widely utilized in electrodes for ceramic capacitors. Reports on the manufacture of electrodes for capacitors using ultrafine nickel powder and the manufacture of microwave absorption of nickel ferritic compound suggest that nickel powder and its compounds are not limited to this application, which can be used as an electrode material for secondary cell, fuel cell, and others such as thin-layer laminated ceramic capacitors due to their reduced electrical resistance and it prevents the delamination or cracks of thin multilayered capacitor when the capacitor is under stress. Furthermore, easy preparation and high corrosion resistance, saturation magnetization, superior antioxidation, magnetocrystalline anisotropy, and application-desired structural compatibility are important characteristics of nickel-based compounds that can be used in electrical and electronic applications.
The advantages and disadvantages of NiFe₂O₄ for electrical and electronic applications are provided in Table 1.

| advantages | disadvantages |
|------------|---------------|
| wide range of frequency stability | loss (tan δ) |
| large magnetic saturation | density (5.33 g/cc) |
| high magnetocrystalline anisotropy | poor thermal conductivity |
| oxidation and temperature stability | brittle material |

The preparation of soluble polymers via cyclopolymerization can now be effectively extended to avoid the difficulty associated with the formation of insoluble intractable conducting polymers when synthesized through conventional methods. Cyclopolymerization-derived poly(1,6-heptadiynes) and their derivative are intrinsically conjugated polymers, which facilitate the conductivity via electron hopping and tunneling mechanism. Although the activation energy of cyclopolymerized poly(1,6-heptadiynes) (13 kcal/mol (0.6 eV)) is similar to that of trans-polyacetylene (13.8 kcal/mol (0.579 eV)), the rate of oxidation of poly(1,6-heptadiynes) is more than 10 times that of polyacetylene, which leads to the higher oxidative stability of poly(1,6-heptadiynes) than polyacetylene. Moreover, poly(1,6-heptadiynes) and their derivative polymers were mostly soluble in organic solvents, as well as stable to air oxidation and thermal stresses without losing intact and attractive mechanical properties and film-processable characteristics. These properties are essentially desirable and facilitate the probability of electrical and electronic components or devices fabrication, which further enhance the efficiency and the life cycle stability under influenced force-field conditions.

Our invention relates to the capacitors for high frequencies and particularly used as shielding head to prevent high-frequency currents generated by spurious radiation by enabling low reactive and resistive component to the ground when the supply leads are superimposed. For frequency stability at higher frequencies and due to the electrical and electronic application compatibility, we used nickel ferrites composited with poly(1,6-heptadiynes), which further facilitates the reduction of intrinsic resistance of nickel ferrite composite to enable low resistance path to the ground.

Synthesis of Diacetylene (DA) and Poly(1,6-heptadiynes). The monomer and poly(1,6-heptadiynes) polymer were synthesized according to the previously reported protocol by Shunmugam et al. We have used THF as a solvent to dissolve diacetylene monomer under inert conditions (Synthesis of Diacetylene (DA) Monomer, Supporting Information (Figure S1a,b)). Then, the reaction was carried out for 2 h, followed by the addition of second-generation Hoveyda-Grubbs’ catalyst. Finally, the reaction was quenched by ethyl vinyl ether simultaneously precipitated in diethyl ether. The as-obtained synthetic compound was confirmed by NMR spectroscopy and gel permeation chromatography (GPC) (Poly(1,6-heptadiynes) H NMR and GPC Characterization, Supporting Information (Figure S1a,b)).

Sample Fabrication for Electrical Measurements. To prepare the pellet for electrical measurements as per the ASTM-D150, we have implemented the pellet-pressing technique using Atlas hydraulic pellet press. First, nanosized nickel ferrite granules were mixed with poly(1,6-heptadiynes) (Confirmation by NMR and GPC, Supporting Information (Figure S1a,b)) under an agitate mortar for segregating the particles. The nanocomposite mass ratio was about 1:20 (poly(1,6-heptadiynes)/NiFe₂O₄), which was mixed under vacuum environment to avoid additional moisture absorption from the ground and smaller oxide particles. Then, 0.6 g of the nanocomposite was pressed in a ø10 mm high-end evacuated die (Atlas: GS03100) under an applied load of 15 tons for 30 s by a microprocessor-controlled hydraulic press. It facilitated a dense pellet of thickness 1.5 mm and diameter 10 mm with weight 0.6 g, which is illustrated in Figure 1.

Field emission scanning electron microscopy (FESEM) images of fabricated NiFe₂O₄ and NiFe₂O₄/poly(1,6-heptadiynes) nanocomposite pellets are illustrated as shown in Figure 2. These images describe the surface morphology, in which we can observe nanoparticle distribution in NiFe₂O₄/poly(1,6-heptadiynes) nanocomposite. Further, this significance can be elucidated by the polymer filling factor. The nickel ferrite pellet micrograph demonstrates porous morphology, whereas in the case of nanocomposite surface morphology changes due to the addition of poly(1,6-heptadiynes), the presence of pores is not observed in the micrograph. Thus, it suggests that most of the pores were filled by the poly(1,6-heptadiynes) filling factor and it is also observed that some of the nickel particles form agglomerations on the surface.

Investigation of Electrical Properties. I−V Characteristics of Poly(1,6-heptadiynes) Polymer. The poly(1,6-heptadiynes) sample was coated on a dry glass substrate to evaluate the electrical DC conductivity via a two-probe technique under laboratory conditions. The dissimilar materials (electrode material and sample) are put in intimate contact, where the energy barrier could attribute to an interface between two dissimilar materials due to their impedance

Figure 1. Representation of NiFe₂O₄/poly(1,6-heptadiynes) nanocomposite pellet.
mismatch, which probably prevents easy electron injection.\textsuperscript{35,36} Minimizing the contact resistance at the interface for accurate measurement is an essential requirement.\textsuperscript{36} Hence, we have introduced highly conductive silver ink electrode contacts, which result in uninterrupted electron conduction between metal–polymer and polymer–metal interfaces. To measure the conductivity under low-energy and bias-voltage conditions, a voltage ramp was applied across split electrodes in two-probe measurement technique using a source voltmeter. Then, the steady-state electronic current at each voltage was measured. The load-line mapping approach was utilized to measure the conductivity.\textsuperscript{35} The polymer film current density value was about $1.2 \times 10^{-5} - 3.1 \times 10^{-5}$ S/cm (Figure 3) over the range of applied voltages ($20-60$ V) of the sample thickness $\sim$30 μm. These results are comparable to the conductivity of iodine-doped poly(1,6-heptadiynes) demonstrated by Gibson et al.,\textsuperscript{37} who demonstrated the electrical conductivity of poly(1,6-heptadiynes) changes by a factor of $10^{10}$ from $10^{-12}$ to $10^{-2}$ Ω$^{-1}$ cm$^{-1}$ over a period of 60 min. Also, the results show analogous conductivity of freestanding stability of blended poly(1,6-heptadiynes)/poly(vinylethyleimidozolium dicyanamide) films reported by Buchmeiser et al.\textsuperscript{38} The conductivity of blended poly(1,6-heptadiynes)/poly-(vinylethyleimidozolium dicyanamide) thin film was measured via Novocontrol and dielectric spectrometer equipped with alpha analyzer. The obtained conductivity was about $10^{-3}$ S/cm at 10$^7$ Hz, which attributes to $\pi-\pi^*$ electron transfer by the conjugated polymer backbone.\textsuperscript{35} These results indicate that the conductivity of the present system was probably due to the highly specific backbone structure.

The current density $J$ can be expressed as $J \propto \exp^{-\beta d}$, where $d$ is the barrier width and $\beta$ is the tunneling decay coefficient. In Figure 3, the current density $J$ explains an exponential state to the applied voltages; this is probably due to potentially induced charge transfer in poly(1,6-heptadiynes)-conjugated chain length.\textsuperscript{36} Moreover, $J$ probably demonstrates the non-resonant bond tunneling in poly(1,6-heptadiynes), which is one of the charge-transport mechanisms in the metal–polymer–metal junction.\textsuperscript{39} This can be interpreted with the aid of $\beta$ the tunneling decay coefficient, and it can be attained by the slope of linear fit. The quantified tunneling decay coefficient values are listed in Table 2, wherein we observe the increase in bias voltages, while $\beta$ value decreases, which would reveal incremental current density.\textsuperscript{39} Additionally, this consequence concerns the molecular junction exhibiting voltage-dependent current density (Figure 3), which is in good agreement with the results reported by Salomon et al.\textsuperscript{40} The two-probe measurement approximation of $I-V$ characteristics suggests that poly(1,6-heptadiynes) can behave as a conducting polymer, wherein the polymer’s conjugation structure instigates the charge-transport mechanism. The charge transport in five-membered ring poly(1,6-heptadiynes) is different from that in the six-membered ring structure of a polymer chain. These ring sizes are the direct consequences of the addition mode of the monomer to the initiator. Usually, the five-membered ring structure is prominent for the most electronic applications due to their bathochromic shift and higher conductivity.\textsuperscript{41} This was the significant characteristic of

| Table 2. Tunneling Decay Coefficient $\beta$ at Different Bias Voltages |
|-----------------------------|
| bias voltage (V) | $\beta$ |
| 20–30 | 0.3803 |
| 30–40 | 0.6643 |
| 40–50 | 0.2643 |
| 50–60 | 0.2357 |

Figure 2. FESEM images of (a) NiFe$_2$O$_4$ and (b) NiFe$_2$O$_4$/poly(1,6-heptadiynes) nanocomposites.

Figure 3. $I-V$ characteristics of poly(1,6-heptadiynes).
the as reported poly(1,6-heptadiynes); hence, higher conductivity was attained.

**Electrical Properties of NiFe₂O₄/Poly(1,6-heptadiynes) Nanocomposite.** The capacitors are dielectric material-dependent passive components, wherein the polarization-induced dielectric permittivity stores the electric charge. The electric field-induced polarization “P” contributes electronic, atomic, and dipolar polarization mechanisms and consequently intrinsic dielectric permittivity. Further, these features can be explained efficiently with the aid of Clausius–Mossotti relation, as shown in eq 1:<ref>22</ref>

\[
\frac{K M}{d} = P = P_e + P_a + P_d
\]

where \( P_e \) is the electronic polarization, \( P_a \) is the atomic polarization, \( P_d \) is the dipolar polarization, \( K \) is the total dielectric constant, which is expressed as \( K = (\varepsilon - 1)/\varepsilon + 2 \), \( M \) is the molecular weight, \( \varepsilon \) is the dielectric constant, and \( d \) is the density. The net \( K \) is an analytical interpretation that reveals the dielectric permittivity of a mixture of two materials, which is further in proportion to the masses. The same can be analyzed with the aid of the Clausius–Mossotti relation and is shown in eq 2:<ref>22</ref>

\[
(e_2 - 1)/(e_2 + 2) = \frac{M_a}{M_e} (e_1 - 1) /

\epsilon_1 + 2
\]

In dielectric composite materials, the external field-induced polarization arises from the finite displacement of dipoles and their rotations.<ref>54</ref> In the atomic scale, distribution of electron cloud distortion is pre-eminent for the dipole-induced polarization. Likewise, in the molecular scale, non-bond interactions and/or physical rotation of molecular dipoles are dominant for polarization mechanism.<ref>45</ref> Such type of molecule-induced polarization in gases and liquids is due to the free rotation of the molecular dipoles, which is probably due to the free dipole angular momentum. However, in the case of solids (e.g., in polymers), the molecular dipole rotations are restricted and therefore the dipoles do not significantly contribute to the quantitative dielectric permittivity.<ref>46</ref> Hence, in Figure 4, the observed dielectric permittivity response value is only due to the nickel ferrite oxides and its ferromagnetic resonance attributed relaxation phenomena, which is consistent with the results obtained by Ahmed et al.<ref>47</ref> However, permittivity is a frequency-dependent hypothesis; hence, an exponential decay was observed in Figure 4, as the applied electric fields increase from 10⁴ to 10⁵ Hz.<ref>36</ref> These permittivity characteristics are attributed to the space charge and dipolar polarization mechanisms in NiFe₂O₄ as well as in NiFe₂O₄/poly(1,6-heptadiynes) nanocomposite,<ref>48</ref> where the polarization-dependent typical relaxation times are in the range of ca. 10⁻¹⁵–10⁻¹⁰ s. Figure 4 shows the low permittivity of NiFe₂O₄/poly(1,6-heptadiynes) nanocomposite compared to NiFe₂O₄ alone, which is probably due to the conducting properties of the conjugated poly(1,6-heptadiynes).<ref>52</ref> The permanent dipoles existing in a poly(1,6-heptadiynes) polymer are unable to follow over the applied frequency range, which is probably due to the polymer in the vicinity of nickel ferrite nanoparticles restricting the molecule-induced dipole angular momentum;<ref>55</ref> consequently, charge transport is high throughout the polymer (between nickel ferrite particles, where the polymer can act as a medium for charge transport) and hence the non-resonant (frequency-independent) permittivity characteristics over the frequency range (10⁴–10⁵ Hz) was observed. Further, the non-resonant permittivity-influenced polymer conducting properties can be elucidated via diffusing coefficient of the polymer, if the self-diffusing coefficient of the polymer is low, which results in high conductivity of the polymer due to more number of nonbond interactions induced by the hoping charge carrier mechanism.<ref>54</ref> This, in turn, depends on molecule density in accordance with the Clausius–Mossotti relation and intermolecular forces.<ref>52</ref> Moreover, in NiFe₂O₄/poly(1,6-heptadiynes) nanocomposite, the polymer molecule behaves qualitatively like a polar substance, which connects the two nickel ferrite nanoparticles and consequently has higher charge-transport capability. Also, this can help in the reduction of τ = RC time constant by reducing “R” of the composite medium.<ref>57</ref> Further, this consequence can be elucidated with the aid of loss and impedance characteristics, which were obtained from impedance spectroscopy measurement.

The loss characteristics of a dielectric are also known as dissipation factor (DF). The dissipation factors (DFs) of the NiFe₂O₄ and NiFe₂O₄/poly(1,6-heptadiynes) nanocomposites are illustrated in Figure 5. The decreased DF of the NiFe₂O₄/poly(1,6-heptadiynes) nanocomposite is apparent over a wide frequency range of 10 Hz to 10 MHz (Table 3). This might be explained as the fact that the conduction of a polymer, which is further related to the DC electrical conductivity of poly(1,6-heptadiynes) (Figure 3), contributes to the change in DF value less significantly as the frequency increases.<ref>58</ref> Such a consequence further can be elucidated with the aid of mathematical relation \( \tan(\delta) = e''/e' \) where \( e' \), \( e'' \), \( \sigma \), and \( \omega \) are the imaginary and real dielectric permittivity, electrical conductivity and frequency of the materials, respectively.<ref>58</ref> However, in nanocomposite, change in losses is more significant at lower frequencies, which is due to the reduction in the contact resistance and intrinsic resistivity of that medium.<ref>59,60</ref>

In current electronic technology, the motivation to use capacitors in interdigital electronics and electrical appliances are based on their loss factor value; hence, it is essential to
analyze the Q-factor. Dissipation factor (DF) is used to extract the Q-factor value, which is an inverse relation to the DF. Table 3 shows the quantified quality factor “Q” of the NiFe$_2$O$_4$ and NiFe$_2$O$_4$/poly(1,6-heptadiynes) nanocomposite. The nanocomposite quality factor was >20 from 200 to $10^5$ Hz and 310 at $10^4$ Hz, which is ~37 times higher than that of the NiFe$_2$O$_4$ alone. In general, the Q-quality factor can be defined as the ratio of resistance to reactance. Nanocomposite results suggest that the high Q-factor attributes to the reduced intrinsic resistance of that medium. These characteristics are in good agreement with the impedance characteristics that were obtained from the broad-band impedance spectroscopy measurement (Figure 6). Therefore, higher Q-factor in addition to the dielectric tunability facilitates the NiFe$_2$O$_4$/poly(1,6-heptadiynes) nanocomposite for capacitor.

The impedance ($Z = Z’ + Z”$) characteristics are illustrated in Figure 6a, where $Z’$ gives the resistance value and $Z”$ gives the reactance value. The NiFe$_2$O$_4$ and NiFe$_2$O$_4$/poly(1,6-heptadiynes) nanocomposite shows higher impedance values at lower frequency (<$10^2$ Hz), wherein the higher resistance $Z’$ of the NiFe$_2$O$_4$ sample at lower frequencies (<$10^2$ Hz) is due to the contact resistance between electrodes and dielectric material, and the intrinsic material resistance. However, in the case of NiFe$_2$O$_4$/poly(1,6-heptadiynes) composite, the $Z’$ resistance elucidates the frequency-independent value, which is due to the conducting properties of the conjugated poly(1,6-heptadiynes) as an intermediate medium located between the nickel ferrite particles. Further, the equivalent series resistance (ESR) quantifications of pellets elucidate these characteristics, where the nanocomposite pellet exhibits ESR 72 times lower resistance compared to the NiFe$_2$O$_4$ sample. The quantified resistance values for the NiFe$_2$O$_4$ and NiFe$_2$O$_4$/poly(1,6-heptadiynes) nanocomposite pellets are shown in Table 4.

### Table 3. Dissipation Factor and Quality Factor at Different Frequencies

| frequency (Hz) | NiFe$_2$O$_4$ DF | nanocomposite DF | NiFe$_2$O$_4$ Q | nanocomposite Q |
|----------------|-----------------|-----------------|----------------|----------------|
| $10^1$         | 0.1725          | 0.254           | 0.5797         | 3.9730         |
| $10^2$         | 0.324           | 0.0845          | 3.0864         | 11.8343        |
| $10^3$         | 0.132           | 0.0096          | 7.5757         | 104.1667       |
| $10^4$         | 0.0119          | 0.00322         | 8.4033         | 310.559        |
| $10^5$         | 0.0185          | 0.00492         | 5.4054         | 20.325         |
| $10^6$         | 0.0347          | 0.0202          | 2.8818         | 4.9504         |
| $10^7$         | 0.416           | 0.307           | 2.4038         | 3.2573         |

### Table 4. Equivalent Series Resistances (ESR) and Capacitance at Different Frequencies

| frequency (Hz) | NiFe$_2$O$_4$ ESR (MΩ) | nanocomposite ESR (MΩ) | NiFe$_2$O$_4$ C (pF) | nanocomposite C (pF) |
|----------------|-------------------------|------------------------|----------------------|----------------------|
| $10^1$         | 2.608 $\times$ $10^3$  | 39.736                 | 0.960                | 0.432                |
| $10^2$         | 220.8311                | 39.736                 | 0.486                | 0.311                |
| $10^3$         | 92.155                  | 1.612                  | 0.394                | 0.184                |
| $10^4$         | 72.140                  | 1.0                    | 0.340                | 0.159                |
| $10^5$         | 66.422                  | 1.0                    | 0.370                | 0.117                |
| $10^6$         | 66.422                  | 1.0                    | 0.777                | 0.777                |

Figure 5. NiFe$_2$O$_4$ and nanocomposite’s dissipation factor (DF) as a function of frequency.

Figure 6. NiFe$_2$O$_4$ and nanocomposite’s impedance ($Z’$ and $Z”$) as a function of frequency: (a) $Z’$ = resistance; (b) $Z”$ = reactance.
frequency-dependent parameter, which is in good agreement with the mathematical relation \( C = \frac{1}{2\pi f Z''} \), as described by Miller et al., where \( C \) is the capacitance and \( Z'' \) is the reactance.\(^{66}\) The capacitance can be computed by using the above mathematical relation; the computed capacitance values at different frequencies are reported in Table 4.\(^{63,67}\) These quantified capacitance values are in good agreement with the frequency-dependent capacitance characteristics illustrated as shown in Figure 7.

![Figure 7. NiFe\(_2\)O\(_4\) and nanocomposite’s capacitance as a function of frequency.](image)

The resistance and capacitance (RC) product is a measure of capacitor time constant, which is a pre-eminent parametric feature for estimating the minimum time required to charge and discharge stored energy.\(^{65,67}\) The time constant can be attained by the combination of resistance and capacitance (Figures 6 and 7) of NiFe\(_2\)O\(_4\) as well as NiFe\(_2\)O\(_4\)/poly(1,6-heptadiynes) nanocomposite at different frequencies. According to the impedance characteristics, the total impedance of a capacitor can be represented as \( Z = \sqrt{ESR^2 + (X_C - X_L)^2} \), which includes the reactive \((X_C = \text{capacitive and } X_L = \text{inductive})\) and resistive components. The self-resonance frequency \( f_r \) is an important observation attained from the impedance characteristics. The resonance frequency can be calculated in accordance with the equation \( f_r = \frac{1}{\sqrt{2\pi \times \sqrt{ESR}}} \) at this frequency, the impedance is equal to the equivalent series resistance (ESR).\(^{68}\) Below the self-resonance \( f_r \), the capacitive component “\( X_C \)” is dominant and hence the component behaves like a capacitor. Likewise, the self-resonance frequency-inductive component “\( X_L \)” is dominant and hence the component behaves like an inductor.\(^{68}\) Therefore, the \( R \) and \( C \)-induced time constant for a NiFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\)/poly(1,6-heptadiynes) nanocomposite capacitor can be calculated at 1 kHz or 1 Hz frequency since their capacitance and resistance values are insensitive at that frequency.\(^{67}\) The calculated RC values were about 3.19 ms at 1 Hz and 36.30 \( \mu \)s at 1 kHz for a NiFe\(_2\)O\(_4\) sample, and about 20.26 \( \mu \)s at 1 Hz and 0.29 \( \mu \)s at 1 kHz for a NiFe\(_2\)O\(_4\)/poly(1,6-heptadiynes) nanocomposite. These results are in comparable agreement with the commercially available tantalum hybrid capacitors and are at least 3 orders of magnitude smaller than the commercially available Al and Ta electrolytic capacitors, including carbon electrochemical capacitors.\(^{67}\) The maximum storage energy capacity of a nanocomposite capacitor can be calculated using the equation \( E_{\text{max}} = \frac{1}{2} CV^2 \), where \( C \) is the DC capacitance and \( V_M \) is the rated voltage.\(^{67}\) Further, the gravimetric energy density can be obtained by dividing \( E_{\text{max}} \) by weight of a composite, wherein the nanocomposite DC capacitance \((C_{\text{DC}} = 1.1 \text{ and } 0.51 \text{ pF at } 50 \text{ V})\) was used to compute the gravimetric energy density, and the calculated energy density values were about 0.0159 and 0.00575 mJ/g, respectively.

Moreover, the capacitor power density can be obtained from the alternating current (AC) impedance “\( Z \)” measurements by assuming the load resistance condition \( R_{\text{load}} = R \), at which the maximum power can be expressed by the mathematical relation \( P_{\text{max}} = \frac{V_M^2}{4R} = \frac{E_{\text{max}}}{2RC} \).\(^{67}\) From the above relation, the ratio of energy density to time constant (RC) gives the power density, which is a gravimetric power density and is about 0.019 kW/g. These quantifications are in comparable agreement with the hybrid capacitors, Al and Ta electrolytic capacitors, as reported by Zheng et al.\(^{67}\)

**Thermal Stability Parameters of a Composite for Capacitor Application.** Besides the dielectric properties, harsh environments such as high-temperature capability, aggressive media, and radiation exposure are the primary concerns for the capacitor applications. A clear future requirement is to save weight, volume, and low energy loss in unfriendly environments like high temperatures.\(^{70}\) In the current system of electronic components, for example, temperature rise in capacitor core, failure occurs probably due to temperature-induced losses. The degradation and early failure of electronic components are also due to the utilization of self-heat generated materials. The mechanisms that are prominently responsible for the losses in a capacitor include the dielectric material and its inherent power losses and heat retention properties, electrode system and ohmic losses, end connection scooping, and termination method (wire, tab, or terminals). To overcome these thermal impediments and losses in the capacitor, it is needed to choose high-temperature-stabilized low-loss dielectric materials for new capacitor design. Researchers have reported various high-
temperature dielectric composites for the capacitors to meet the higher-temperature operation. However, for applications at >200 °C, insufficient number of materials are available to offer high energy density. In this context, we have used the (NiFe$_2$O$_4$/poly(1,6-heptadiynes)) nanocomposite system consisting of NiFe$_2$O$_4$ (high dielectric material) and poly(1,6-heptadiynes) (conducting polymer), where the thermal stability of NiFe$_2$O$_4$ was around >250 °C and the thermal stability of poly(1,6-heptadiynes) was around ∼180 °C. The power loss of a capacitor can be computed with the aid of mathematical relation $P_{\text{loss}} = \omega* C*V_{\text{RMS}}^2 \tan \delta$. The computed $P_{\text{loss}}$ values for a NiFe$_2$O$_4$ and NiFe$_2$O$_4$/poly(1,6-heptadiynes) nanocomposite are reported in Table 5. The quantified results suggest that the nanocomposite capacitor $P_{\text{loss}}$ is low (×10$^2$ order at 1 kHz) compared to that of the NiFe$_2$O$_4$ capacitor; furthermore, this nanocomposite probably demonstrates low heat generation in comparison to the commercially available electrolytic capacitors; hence, the thermal threatening in miniaturized electronics could be reduced with this nanocomposite usage.

**Table 5. Equivalent Series Resistances (ESR) and Capacitance at Different Frequencies**

| frequency | NiFe$_2$O$_4$ $P_{\text{loss}}$ | NiFe$_2$O$_4$/poly(1,6-heptadiynes) $P_{\text{loss}}$ |
|-----------|-------------------------------|-----------------------------------------------|
| 10$^2$ | 2.5 × 10$^{-5}$ | 1.7 × 10$^{-4}$ |
| 10$^3$ | 2.3 × 10$^{-5}$ | 3.7 × 10$^{-4}$ |
| 10$^4$ | 8.0 × 10$^{-5}$ | 3.0 × 10$^{-4}$ |
| 10$^5$ | 0.0006 | 8.9 × 10$^{-5}$ |
| 10$^6$ | 0.0081 | 0.0011 |
| 10$^7$ | 0.01024 | 0.0387 |
| 10$^8$ | 0.7837 | 0.4197 |

Figure 9. Fabricated capacitor compared to conventional capacitors.
and 9.91 W/g, respectively. Furthermore, the improved
Subsequently, the nanocomposite-enabled capacitor gravimet-
ized capacitor are illustrated in Table 6.

Table 6. Advantages of Nanocomposite Capacitor over Commercially Capacitors

| electrolytic capacitor | nanocomposite capacitor |
|------------------------|-------------------------|
| lower dielectric constant compared to nanocomposite capacitor | dielectric constant (mean value = 60) |
| larger in size as the capacity increases (10 mm diameter; 20 mm length) | 13 times smaller compared to the electrolytic capacitor |
| weight 2.82 g | lightweight (~5 times lower than electrolytic capacitor) |
| material instability | material stability in harsh environment (oxidation stability) |
| temperature stability (40–105 °C) | temperature stability (>200 °C) |
| frequency instability | frequency stability (up to 10 MHz) |
| high dissipation factor dissipation factor (~0.02) | dissipation factor is 0.00032 at 1 kHz |
| low quality factor | quality factor is around 310.55 at 1 kHz |

The advantages of the nanocomposite capacitor over the commercially available electrolytic capacitor are illustrated in Table 6.

### Conclusions

In the present study, we have synthesized intrinsically conductive poly(1,6-heptadiynes) via cyclopolymerization (CP) technique, and further poly(1,6-heptadiynes) was composites with NiFe2O4. Two-probe measurement was utilized to reveal I–V characteristics of synthesized poly(1,6-heptadiynes). The results suggest that the conductivity was in the range of 1.2 × 10^{-5}–3.1 × 10^{-5} S/cm. NiFe2O4 and NiFe2O4/poly(1,6-heptadiynes) pellets were fabricated by utilizing hydraulic pelletizer. Electrical measurements of the fabricated pellets were performed with the aid of broad-band impedance spectroscopy. The attained dielectric permittivity ε = 45 (100 Hz to 10 kHz) was attributed to the NiFe2O4 phase as well as poly(1,6-heptadiynes). The nanocomposite dissipation factor (DF) reduced (DF = 0.0032) due to the intrinsic conducting properties of conjugated poly(1,6-heptadiynes) embedded in the nanocomposite. Further, this reveals that the reduced equivalent series resistance (ESR) (72 times) was observed from the impedance characteristics of a nanocomposite. Moreover, improved Q-factor was observed, which was about 310 at 1 kHz. Also, the nanocomposite RC constant was calculated, which was about 0.29 μs at 1 kHz. Subsequently, the nanocomposite-enabled capacitor gravimetric energy density and power density were about 0.00575 mJ/g and 9.91 W/g, respectively. Furthermore, the improved thermal threatening P_{loss} of the nanocomposite capacitor was about 8.9 × 10^{-6}. All of the results of a nanocomposite-enabled capacitor were compared with the commercially available configuration of tantalum hybrid capacitors, Al and Ta electrolytic capacitors, including carbon electrochemical capacitors. These results suggest that the nanocomposite could be a possible candidate for electrical and electronic applications.

### Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02306.

Syntheses of diacetylene monomer and diacetylene monomer; H NMR and GPC characteristics (PDF)

Electrolytic capacitor charging and LED illuminating (MPG)

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Notes

The authors declare no competing financial interest.

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### References

1. Tummala, R. R.; Chahal, P.; Bhattacharya, S. In Recent Advances in Integral Passives in PWB, International Microelectronic and Packaging Society Nordic Conference, 1998.
2. Rao, Y.; Wong, C. P. Material Characterization of a High-Dielectric-Constant Polymer-Ceramic Composite for Embedded Capacitor for RF Applications. J. Appl. Polym. Sci. 2004, 92, 2228–2231.
3. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. Light-Emitting Diodes Based on Conjugated Polymers. Nature 1990, 347, 539–541.
4. Tang, C. W.; VanSlyke, S. A. Organic Electroluminescent Diodes. Appl. Phys. Lett. 1987, 51, 913–915.
5. Ulrich, R. A. In Web-Based Course on Integrated Passive Component Technology, 53rd Electronic Components and Technology Conference, 2003; pp 493–494.
6. Bhattacharya, S. K.; Tummala, R. R. Next Generation Integral Passives: Materials, Processes, and Integration of Resistors and Capacitors on PWB Substrates. J. Mater. Sci. Mater. Electron. 2000, 11, 253–268.
7. Grannan, D. M.; Garland, J. C.; Tanner, D. B. Critical Behavior of the Dielectric Constant of a Random Composite near the Percolation Threshold. Phys. Rev. Lett. 1981, 46, 375–378.
PbZrTiO₃ ferroelectric ceramics under cyclic electric loading. Adv. Mater. Sci.: Mater. Electron. 2016, 2016 RSC Adv.

RSC Adv. dielectric properties and charge transport mechanism of \(2016\) ACS Omega

Ceramic Sensors for Underwater Transducer Application. Technol. 2015, 2015 Adv. Mater. 2015, 27, 819–824.

Zhang, D.; Liu, W.; Guo, R.; Zhou, K.; Luo, H. High discharge energy density at low electric field using an aligned titanium dioxide/lead zirconate titanate nanowire array. Adv. Sci. 2018, 5, No. 1700512.

Luo, H.; Wu, Z.; Zhou, Z.; Yan, Z.; Zhou, K.; Zhang, D. Enhanced performance of P(VDF-HFP) composites using two-dimensional BaTiO₃ platelets and graphene hybrids. Compos. Sci. Technol. 2018, 160, 237–244.

Luo, H.; Ma, C.; Zhou, Z.; Chen, S.; Zhang, D. Interfacial design in dielectric noncomposites using liquid-crystalline polymers. Macromolecules 2017, 50, 5132–5137.

Luo, H.; Zhang, D.; Jiang, C.; Yuan, X.; Chen, C.; Zhou, K. Improved dielectric properties and energy storage density of poly(vinylidene fluoride-co-hexafluoropropylene) noncomposite with hydantoin epoxy resin coated BaTiO₃. ACS Appl. Mater. Interfaces 2015, 7, 8061–8069.

Lonkar, C. M.; Kharat, D. K.; Kumar, H. H.; Prasad, S.; Balasubramanian, K. Effect of La on piezoelectric properties of Pb(Ni₁₈,75,25)(Sn₀,75,25)O₃–Pb(Zr,Ti)O₃ ferroelectric ceramics. J. Mater. Sci.: Mater. Electron. 2013, 24, 411–417.

Kumar, H. H.; Lonkar, C. M.; Balasubramanian, K. Harvesting Power Through Random Vibrations of Aerospace Vehicles from Nanostructured La-Pb(Ni₁₈,75,25)(Sn₀,75,25)O₃–PbZrTiO₃ Ferroelectric Composites. Def. Sci. J. 2016, 66, 353–359.

Lonkar, C. M.; Kharat, D. K.; Kumar, H. H.; Prasad, S.; Balasubramanian, K.; Prasad, N. S. Pb(Ni₁₈,75,25)(Sn₀,75,25)O₃–Pb(Zr,Ti)O₃ Ceramic Sensors for Underwater Transducer Application. Def. Sci. J. 2012, 62, 269–273.

Lonkar, C. M.; Premkumar, S.; Kharat, D. K.; Kumar, H. H.; Prasad, S.; Balasubramanian, K. Behaviour of Pb(Ni₁₈,75,25)(Sn₀,75,25)O₃–PbZrTiO₃ ferroelectric ceramics under cyclic electric loading. J. Mater. Sci.: Mater. Electron. 2013, 24, 1959–1993.

Tahalyani, J.; Rahangdale, K. K.; Aepuru, R.; Kandasubramanian, B.; Datar, S. Dielectric investigation of a conducting fibrous nonwoven porous mat fabricated by a one-step facile electrospinning process. RSC Adv. 2016, 6, 36588–36598.

Tahalyani, J.; Rahangdale, K. K.; Balasubramanian, K. The dielectric properties and charge transport mechanism of \(\pi\)-conjugated segments decorated with intrinsic conducting polymer. RSC Adv. 2016, 6, 69733–69742.

Tahalyani, J.; Datar, S.; Balasubramanian, K. Investigation of dielectric properties of free standing electrospun nonwoven mat. J. Appl. Polym. Sci. 2018, 135, 46121.

Magisetty, R. P.; Shukla, A.; Kandasubramanian, B. Dielectric, Hydrophobic Investigation of ABS/NiFe₂O₄ Nanocomposites Fabricated by Atomized Spray Assisted and Solution Casted Techniques for Miniaturized Electronic Applications. J. Electron. Mater. 2018, 47, 5640–5656.

Magisetty, R. P.; Khanale, M.; Kandasubramanian, B. Handbook of Nanomaterials for Industrial Application. Dielectric Polymeric Compositions for Improved Electrical Properties of Flexible Electronics; Elsevier Publishers, 2018; pp 430–467.

Magisetty, R. P.; Shukla, A.; Kandasubramanian, B. Magneto-dielectric Microwave Radiation Absorbent Materials and Their Polymer Composites. J. Electron. Mater. 2018, 47, 6335.
Dielectric and Electrical Anisotropy. RSC Adv. 2016, 6, 32272–32285.
(49) Stuerger, D. Microwave-Material Interactions and Dielectric Properties. In Key Ingredients for Mastery of Chemical Microwave Processes; Loupy, A., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2006; pp 1–59.
(50) Hummel, R. E. Electronic Properties of Materials; Springer: Berlin, 2001; pp 1–438.
(51) Kreuer, K. D.; Fuchs, A.; Ise, M.; Spazeth, M.; Maier, J. Imidazole and Pyrazole-Based Proton Conducting Polymers and Liquids. Electrochim. Acta 1998, 43, 1281–1288.
(52) He, P.; Lau, S.; Chan, H. L.; Fan, J. High Dielectric Permittivity and Low Percolation Threshold in Nanocomposites Based on Poly(Vinylidene Fluoride) and Exfoliated Graphite Nanoplates. Adv. Mater. 2009, 21, 710–715.
(53) De Gennes, P. G. Simple Views on Condensed Matter, Expanded Edition; World Scientific: Singapore, 1992; pp 1–498.
(54) Zhao, K.; Khan, H. U.; Li, R.; Su, Y.; Amassian, A. Entanglement of Conjugated Polymer Chains Influences Molecular Self-Assembly and Carrier Transport. Adv. Funct. Mater. 2013, 23, 6024–6035.
(55) Liu, J.; Wu, Y.; Shen, J.; Gao, Y.; Zhang, L.; Cao, D. Polymer–nanoparticle Interfacial Behavior Revisited: A Molecular Dynamics Study. Phys. Chem. Chem. Phys. 2011, 13, 13058.
(56) Kropka, J. M.; Putz, K. W.; Pyramitsyn, V.; Ganesan, V.; Green, P. F. Origin of Dynamical Properties in PMMA–C60 Nanocomposites. Macromolecules 2007, 40, 5424–5432.
(57) Gabriel, C.; Gabriel, S.; Grant, E. H.; Grant, E. H.; Halstead, B. S. J.; Mingos, D. M. P. Dielectric Parameters Relevant to Microwave Dielectric Heating. Chem. Soc. Rev. 1998, 27, 213.
(58) Lu, J.; Moon, K.-S.; Xu, J.; Wong, C. P. Synthesis and Dielectric Properties of Novel High-K Polymer Composites Containing In-Situ Formed Silver Nanoparticles for Embedded Capacitor Applications. J. Mater. Chem. 2006, 16, 1543.
(59) Lu, J.; Wong, C. P. Recent advances in high-k nanocomposite materials for embedded capacitor applications. IEEE Trans. Dielectr. Electr. Insul. 2008, 15, 1322–1328.
(60) Amaral, A. M. R.; Cardoso, A. J. M. In An Experimental Technique for Estimating the ESR and Reactance Intrinsic Values of Aluminum Electrolytic Capacitors, 2006 IEEE Instrumentation and Measurement Technology Conference Proceedings; IEEE, 2006; pp 1820–1825.
(61) Tahalyani, J.; Datar, S.; Balasubramanian, K. Investigation of Dielectric Properties of Free Standing Electrospun Nonwoven Mat. J. Appl. Polym. Sci. 2018, 135, 46121.
(62) Liu, A.; Jones, R.; Liao, L.; Samara-Rubio, D.; Rubin, D.; Cohen, O.; Nicolaeasuc, R.; Paniciuc, M. A High-Speed Silicon Optical Modulator Based on a Metal–oxide–semiconductor Capacitor. Nature 2004, 427, 615–618.
(63) Evans, D. A. In Tantalum Hybrid Button Cell Capacitor, CARTS-Conference; Components Technology Institute Inc., 2004; p 182.
(64) Kirchmeyer, S.; Reuter, K. Scientific Importance, Properties and Growing Applications of Poly(3,4-Ethylendioxythiophene). J. Mater. Chem. 2005, 15, 2077.
(65) Snoek, G. A.; Kao, P.; Best, A. S. Conducting-Polymer-Based Supercapacitor Devices and Electrodes. J. Power Sources 2011, 196, 1–12.
(66) Miller, J. R.; Outlaw, R. A.; Holloway, B. C. Graphene Double-Layer Capacitor with Ac Line-Filtering Performance. Science 2010, 329, 1637–1639.
(67) Chang, T. Y.; Wang, X.; Evans, D. A.; Roberson, S. L.; Zheng, J. P. Characterization of Tantalum Oxide–Ruthenium Oxide Hybrid Capacitors. IEEE Trans. Ind. Electron. 2004, 51, 1313–1317.
(68) Fiore, R. ESR Losses in Ceramic Capacitors; American Technical Ceramics Corporation, 1999.
(69) Stephen, N. G. On Energy Harvesting from Ambient Vibration. J. Sound Vib. 2006, 293, 409–425.
(70) Werner, M. R.; Fahrner, W. R. Review on Materials, Microsystems, Systems and Devices for High-Temperature and Harsh-Environment Applications. IEEE Trans. Ind. Electron. 2001, 48, 249–257.
(71) Šepelák, V.; Baake, D.; Mienert, D.; Schultze, D.; Krumreich, F.; Litterst, F. J.; Becker, K. D. Evolution of Structure and Magnetic Properties with Annealing Temperature in Nanoscale High-Energy-Milled Nickel Ferrite. J. Magn. Magn. Mater. 2003, 257, 377–386.
(72) Anders, U.; Nuyken, O.; Buchmeiser, M. R.; Wurst, K. Stereoselective Cyclopolymerization of 1,6-Heptadiynes: Access to Alternating cis-Trans-1,2-(Cyclopent-1-Enylene)Vinylene by Fine-Tuning of Molybdenum Imidoalkylidene. Angew. Chem., Int. Ed. 2002, 41, 4044–4047.
(73) Krause, J. O.; Wang, D.; Anders, U.; Weberskirch, R.; Zarka, M. T.; Nuyken, O.; Jäger, C.; Haarer, D.; Buchmeiser, M. R. Stereoselective Cyclopolymerization of Dynes: Smart Materials for Electronics and Sensors. Macromol. Symp. 2004, 217, 179–190.