# Unlocking the Potential of Poly(norbornene-dicarboximides): Synthesis, Applications, and Future Prospects

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# Unlocking the Potential of Poly(norbornene-dicarboximides): Synthesis, Applications, and Future Prospects

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**Abstract:** *This brief review focuses on the synthesis and diverse applications of poly(norbornene-dicarboximides) (poly-NDIs), shedding light on their versatile properties. and provides an overview of the simplicity of synthesizing norbornene derived-polymers via ring-opening metathesis polymerization (ROMP). The ROMP technique is described, elucidating the initiation, propagation, and termination steps with Grubbs' catalysts, which play pivotal roles. Synthetic routes to poly-NDIs were clarified, emphasizing their potential for customization through substituent modifications. In addition, it explores numerous uses of poly-NDIs, including gas separation membranes, drug delivery systems, energy storage devices, capacitors, and electro-optic devices. This emphasizes their excellent gas permeability, adjustable adsorption qualities, high dielectric constants, thermal stability, and ease of production. Furthermore, poly-NDIs with aggregation-induced emission (AIE) features have been recognized for their potential as chemical sensors, enabling sensitivity and selectivity in detecting various analytes.*

**Keywords:** Poly-NDIs; ROMP; EO materials; Gas separation; Drug delivery.

## 1. INTRODUCTION

Since Asrar's initial preparation of poly(norbornene-dicarboximides) (poly (NDI)s) in 1992, scholarly interest in these materials has grown significantly [1]. The most general and simplest technique for synthesizing 5,6-derivatives of norbornene is the Diels-Alder cycloaddition of dienophiles such as maleic anhydride or dialkyl maleates with dienes such as furan [2]. Norbornene monomers have recently attracted attention because of their ease of synthesis and strong reactivity in ring-opening metathesis polymerization (ROMP) [3]. They have various applications in optics because of their exceptional optical qualities [4] . Furthermore, it has been demonstrated that poly (NDI) has advantageous mechanical and thermal properties, significantly increasing its use [5]. These strained monomers can be easily and almost completely converted into high-molecular-weight polymers. These reactions typically occur without major byproducts or subsequent intramolecular cyclizations [6]. Furthermore, suitable catalysts have been demonstrated using ring-opening metathesis polymerization (ROMP) employing norbornene dicarboximides with linear aliphatic and phenyl substituents [7,8]. When cyclic monomers with substantial ring strains are used, ROMP can produce well-defined homopolymers, random copolymers, and block copolymers. In contrast to many other ROMP monomers, NDI monomers are simple to synthesize, making poly (NDIs) a suitable platform for tailoring polymers by substituent modification for various applications [9–16].

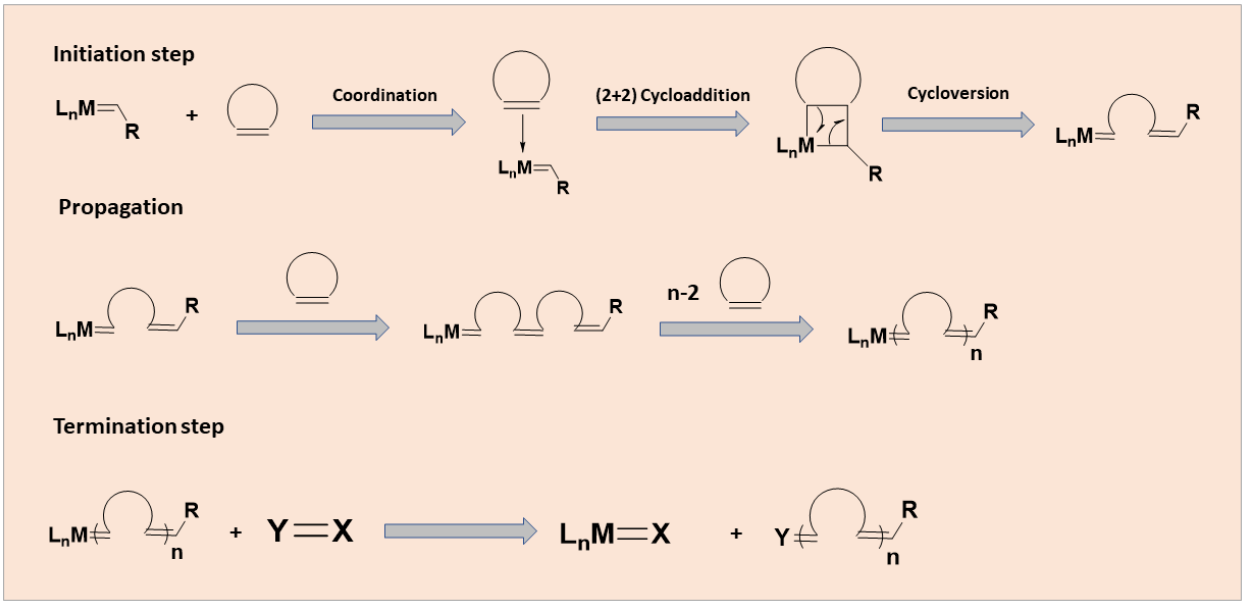
## 2. RING-OPENING METATHESIS POLYMERIZATION (ROMP)

Ring-opening metathesis polymerization (ROMP) has proved an essential technique for synthesizing poly(alkene)s with unique topologies, narrow dispersities, specified regioregularities, and controlled molecular weights since the discovery of olefin metathesis in the mid-1950s [17,18]. Currently, Grubbs catalyst-ruthenium complexes **(**Fig. 1**)**, for instance, are mostly employed to catalyze this process, which permits the synthesis of block copolymers as well as end functionalization [19]. ROMP is typically accomplished in three steps: First, initiation: the catalyst aligns with the double bond of the cyclic olefin monomer, resulting in the formation of a metal-carbene intermediate, which is then a [2+2] cycloaddition process to afford a four-membered metallacyclobutane intermediate, marking the start of a growing polymer chain. Second, propagation occurs when a cyclic olefin monomer molecule connects with the metal-carbene intermediate, opening the ring of the monomer and creating a new metal-carbene intermediate, to which the growing polymer chain is linked. Finally, termination: The transition metal from the growing polymer chain is removed and deactivated by a specific reagent that reacts with the metal-carbene intermediate. This produces a terminated polymer and a new metal-carbene intermediate that can start a new polymer chain [20,21]. **Scheme 1** illustrates the general mechanism of ROMP [22] .

## 3. SYNTHETIC PATHWAYS

In general, an exo/endo mixture of norbornene-5,6-dicarboxylic anhydride (NDA) is produced by the Diels–Alder reaction of dienophiles such as norbornene with maleic anhydride as a diene in o-dichlorobenzene under heating conditions. This exo-norbornene-5,6-dicarboxylic anhydride was then formed in acceptable

yields by further recrystallization in chlorobenzene [23]. The strained bicyclic system of norbornene-5,6-dicarboximides (NDIs), which are easy reactants for (ROMP), is made possible by the structural nature of the exo-form anhydride, which readily condenses with various amino group-containing compounds such as amines, hydrazine, and hydrazides. This produces functionalized unsaturated poly-NDIs that can be further derivatized to modify their physicochemical properties and applications [24]. A simple diagram of the synthetic pathway for these compounds is shown in **Scheme 2**.




Scheme 1. The general ROMP mechanism.

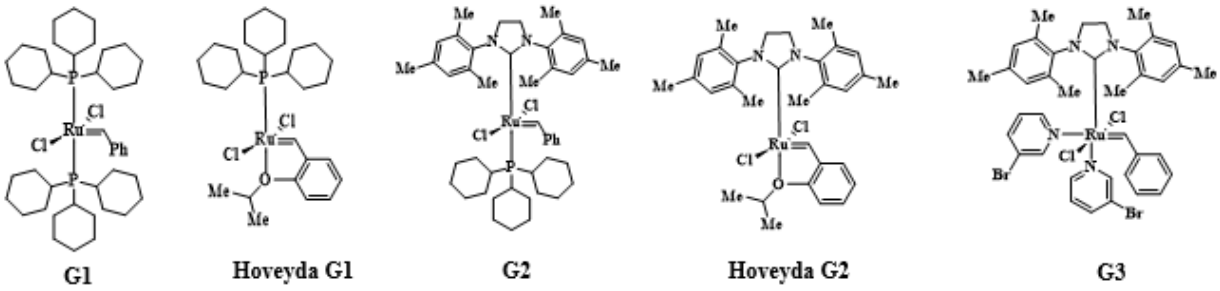
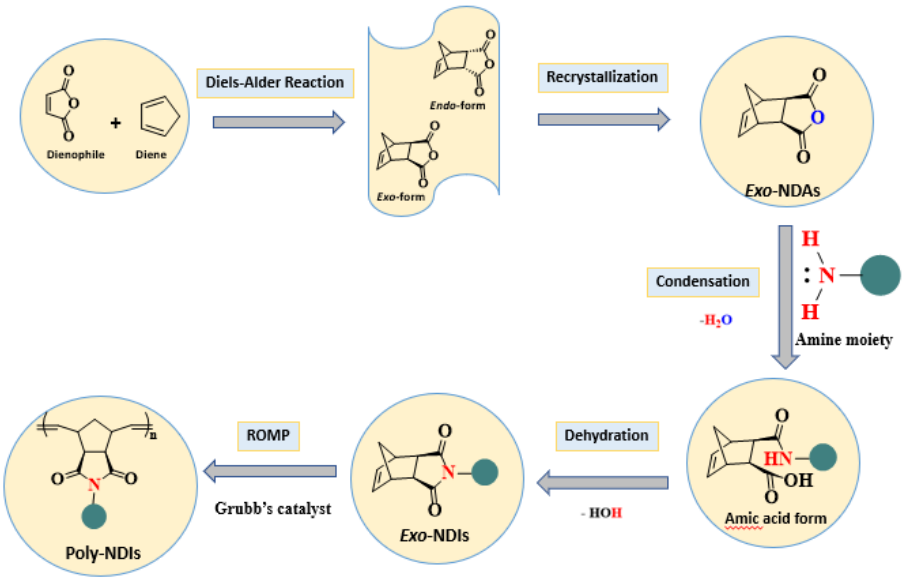



Fig. 1. Different types of Grubbs catalysts




Scheme 2. The synthetic approaches of poly-NDIs

## 4. APPLICATIONS OF POLY-NDIS

### 4.1 Poly-NDIs as potential materials for gas separation

Norbornene dicarboximides (NDIs) represent a promising category of monomers for the development of poly NDI-based membranes because of their straightforward synthesis using the ROMP technique [15]. NDIs, characterized by a rigid bicyclic backbone and two imide groups, offer an ideal framework for gas molecule binding via hydrogen bonding and π-π stacking, and the adsorption properties of NDIs can be finely tuned, allowing for the enhancement of selectivity and permeability in polymeric membranes employed in gas separation processes and an improvement in the separation efficiency of specific gas mixtures[25]. From 2000 to 2010, academics focused on metathesis poly-NDIs and identified limited gas permeability attributed to elevated interchain dipole-dipole interactions between imide moieties; despite this limitation, these polymers demonstrated favorable $CO_2/CH_4$, $H_2/C_3H_6$, and $CO_2/N_2$ selectivity [26]. Interestingly, the introduction of stiff and bulky carbocyclic substituents (e.g., adamantyl, cyclohexyl, and cyclopentyl groups) did not affect gas permeability [8]. In addition, the chemical composition of poly-NDIs facilitate modification by introducing fluorine-containing substituents, leading to significant enhancement in gas permeability [27]. Conversely, subjecting unsaturated poly-NDIs to comprehensive hydrogenation using Wilkinson's catalyst or diimide reduction yields saturated poly-NDIs characterized by diminished gas permeability and improved chemical stability [28]. Fig. 2 shows a simple illustration of membrane gas separation.

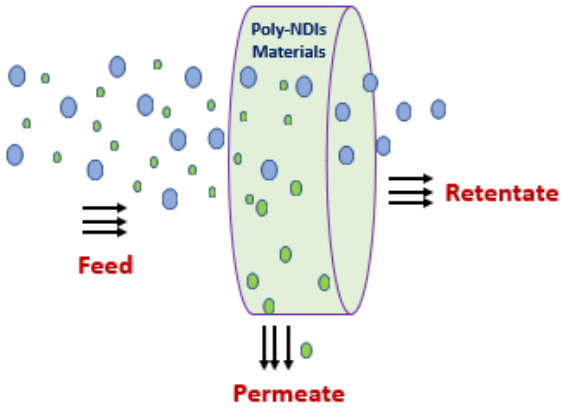



Fig. 2. The basic concept of membrane gas separation.

### 4.2 Poly-NDIs in drug delivery systems

Chemotherapy, which enhances cure and patient survival, is a widely used treatment for cancer. However, its effectiveness is limited by its lack of targeting specificity, which causes nonspecific accumulation and adverse effects on non-cancer cells. In addition, many anticancer compounds have low water solubility [29]. Polymeric micelles, which self-assemble from amphiphilic block copolymers, are a potential drug delivery platform because of their nanoscale size, fast synthesis, and variable solubilization/dispersion capabilities, which make them excellent for in vivo performance [30]. ROMP is a powerful method for creating finely structured amphiphilic block polymers from norbornene and enables molecular property control, culminating in the production of highly branched brush copolymers with specific self-assembly, drug delivery, and imaging capabilities [31]. Fig. 3A illustrates a study of amphiphilic brush copolymers, including poly-NDIs with cholesterol and PEG blocks, for potential use in delivering doxorubicin, an anticancer drug [32]. Sleiman et al. developed a new category of block copolymers containing transition-metal-containing monomers, biologically compatible monomers, macromonomers with oligoethylene glycol units, bioconjugatable monomers, and biorecognition units (Fig. 3B) [33]. Furthermore, Weak et al. reported a system containing norbornenes with a poly (ethylene glycol) methyl ether chain, an alkyl bromide chain, and/or a near-infrared (NIR) fluorescent cyanine dye. Post-polymerization transformations, including bromide-azide substitution and strain-promoted azide-alkyne cycloaddition, allow functionalization with the piplartine (PPT) moiety, and the self-assembly process of paclitaxel (PTX) can effectively encapsulate into a hydrophobic core, resulting in stable micelles with high loading capacities and encapsulation efficiencies (Fig. 3C) [34].

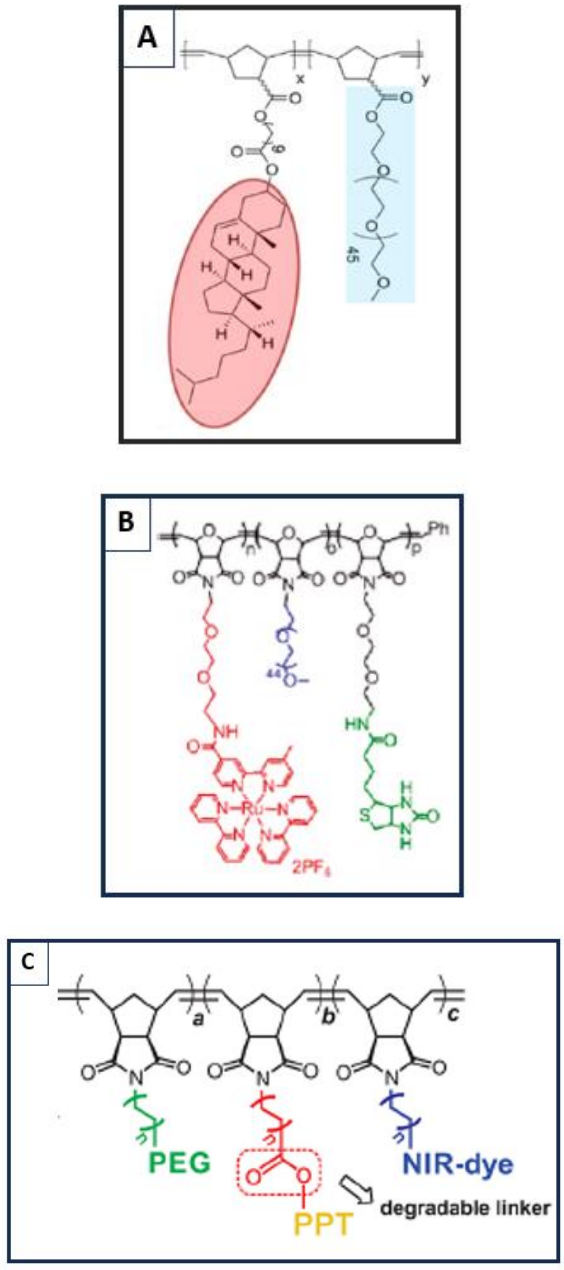
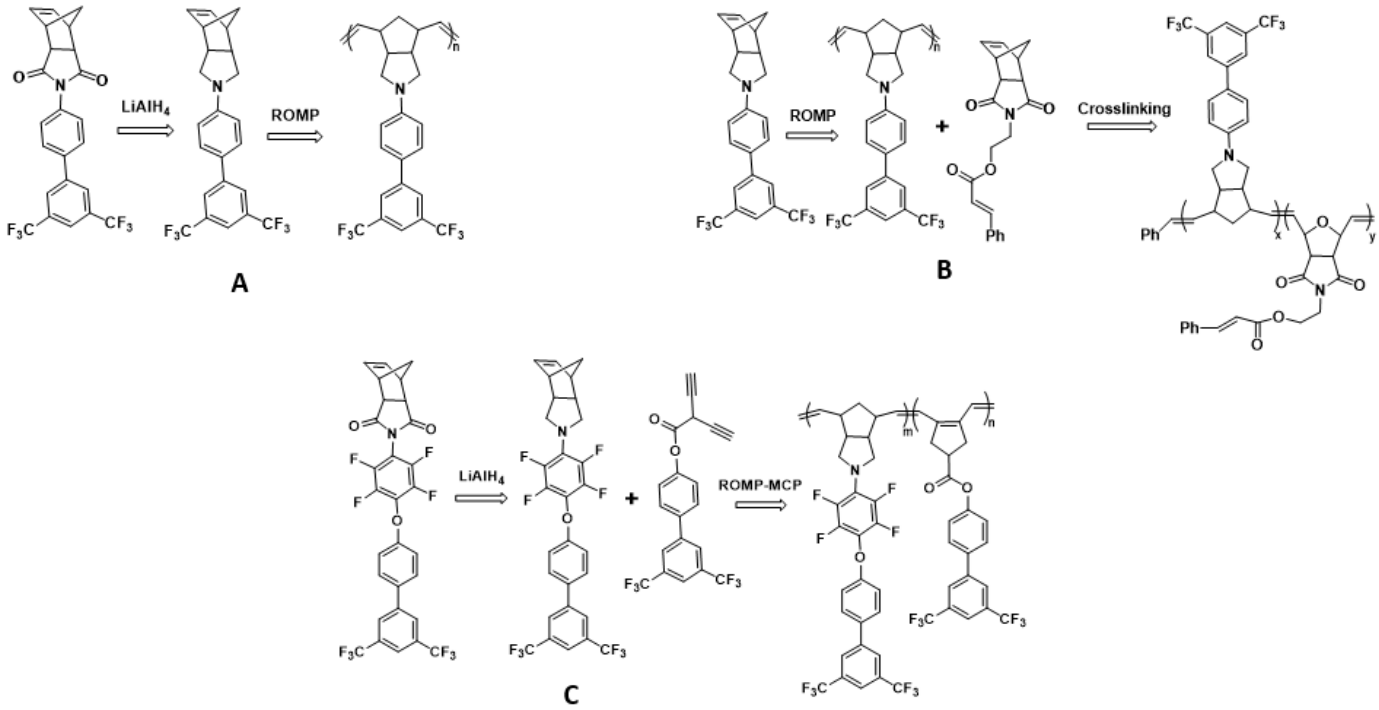



Fig. 3. Examples of norbornene copolymers as active species of drug delivery

### 4.3 Poly-NDIs for energy storage devices and capacitors

The focus is on developing materials with high dielectric constants, low dielectric losses, and high energy densities for energy storage devices and capacitor fabrication [35]. Ceramics such as silicon oxide and barium titanate have high dielectric constants but large dielectric losses [36]. Thin-film capacitors made from polymers such as polypropylene, polyester, and polyethylene are attractive for energy storage because of their lightweight, low cost,




Scheme 3. Synthetic diagram of high dielectric constant poly-NDIs

and safety properties. However, they often suffer from low energy densities and dielectric constants (2–3) [37]. The dielectric constant depends on the degree of polarization in the polymer matrix, which is associated with the presence or absence of more polarized dipole moment groups like (cyano, nitro, halogen, and perfluoro alkyl so on) on the side chain of the polymer blend. Despite having a low dielectric constant [38], poly-NDIs are useful materials for energy storage systems because of their ease of copolymerization, high Tg value, thermal stability, synthetic simplicity, available derivativity, and low cost. NDIs can be incorporated with other polarized species under the ROMP route to produce high-energy-density materials with a high dielectric constant. For instance, but not exclusively, Xie et al. created functional poly-NDIs with a high dielectric constant of 20 using ROMP, **Scheme 3A** [39]. Liao et al. reported a method for producing photocrosslinkable polynorbornene-based block copolymers with improved dielectric and thermal properties, **Scheme 3B** [40]. **Scheme 3C** illustrates a highly polarizable block copolymer consisting of insulating polynorbornene and conducting polyacetylene segments via ROMP-MCP with multifluorinated pendants, which had a reasonably high dielectric constant of 8 [41].

### 4.4 Poly-NDIs: Paving the way for efficient electro-optic devices

Electro-optic (EO) materials, a class of materials that change their refractive index when exposed to an electric field, are crucial for photonic and optical communication applications such as modulators, switches, and sensors [42]. The first EO devices were fabricated using inorganic crystalline materials such as lithium niobate [43]. Organic EO materials, known as chromophores, have similar properties to lithium niobate because of their non-centrosymmetric structure and strong delocalization, but are poorly suited for film formation [44]. To achieve excellent film formation, high thermal stability, and mechanical quality in EO materials, a non-conjugated polymer with a chromophore was incorporated. Poly-NDIs are the optimal non-conjugated polymers for this application because they dissolve easily in solvents and can be spin-coated onto the desired substrate. They produce thin films with excellent optical quality, uniformity, flatness, and large surface area [45]. Poly(NDI)s exhibit high thermal decomposition and glass transition temperatures [46]. The versatility of poly(NDI) is because groups can be easily attached to the backbone via the nitrogen atom [47]. Homopolymers and copolymers are produced with high reproducibility by the ROMP of poly(NDI)s, which also serves as the basis for complex macromolecular structures such as polymer brushes [48]. Spring et al. described trans-poly-NDIs containing adamantyl and carbazole as electro-optic chromophore hosts (Fig. 4A) [49]. The same author demonstrated a poly-NDI side chain system with an attached phenylvinylenethiophene chromophore with high electro-optic performance, as shown in Fig. 4B [50].

### 4.5 Poly-NDIs: Advancing chemical sensor frontiers

Aggregation-induced emission (AIE) is a remarkable phenomenon with considerable potential in chemical sensors. In contrast to conventional fluorescent molecules, which weaken when they aggregate, AIE increases when the molecules clump together. This

particular property makes AIE an excellent candidate for various sensing applications because it offers several advantages [51]. However, sensors based on traditional luminogens often face challenges because they exhibit strong emission in the solution state but suffer from self-quenching in the aggregate state [52]. This is attributed to the effects of the robust π-π interactions and dipole-dipole interactions between aromatic rings in traditional luminogens, leading to aggregation-induced quenching [53]. This limitation hinders the development and application of such sensors. In addition, luminescent materials are often poorly miscible in aqueous media, leading to the formation of precipitates and aggregates that cause quenching, limiting their usefulness in aqueous solutions. Poly-NDIs are a class of polymers with aggregation-induced emission (AIE), which makes them very promising for applications such as organic light-emitting diodes (OLEDs), chemical sensors, and bioimaging [54]. Poly-NDIs show weak fluorescence in dilute solutions but become strongly luminescent when they aggregate, which increases the radiative decay rate and leads to brighter emissions. The NDI moiety in PNDIs can be modified with different electron-donating or withdrawing groups so that the selectivity and sensitivity of the polymer to specific analytes can be customized. This versatility enables the development of PNDI sensors for various chemical targets. The binding of the analyte can quench the intrinsic fluorescence of the NDI unit, providing a sensitive optical readout for sensing. Poly NDIs are also stable and can withstand heat, light, and chemical degradation, making them suitable for long-term sensing applications, especially in challenging or harsh environments [55]. Organic amines are commonly used in the dye, material, chemical, medical, and food industries. However, because of their toxicity, they pose a risk to the environment and human health. To address these concerns, effective monitoring tools for amine concentrations in air and wastewater are required. Yu et al. used ring-opening metathesis polymerization to prepare well-defined homopolymers and block copolymers based on NDIs and integrated tetraphenylethylene or fluorinated tetraphenylethylene units for aniline detection, **Scheme 4** [56].

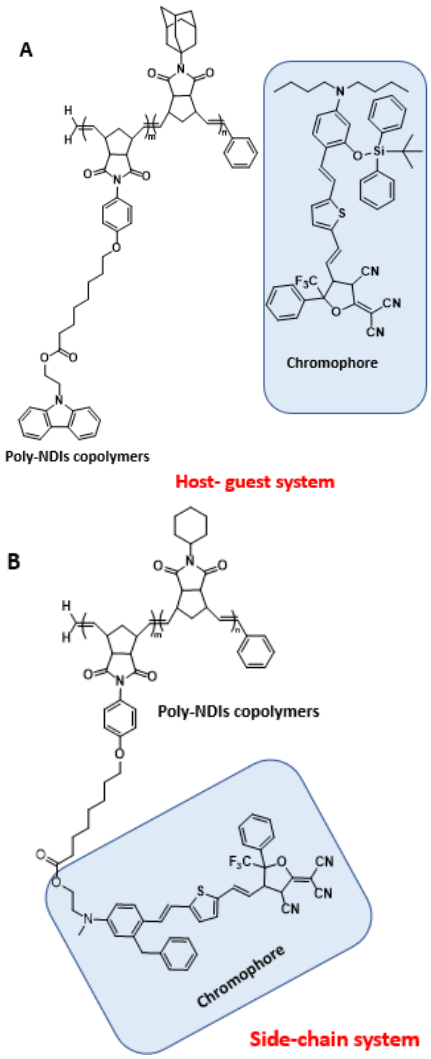
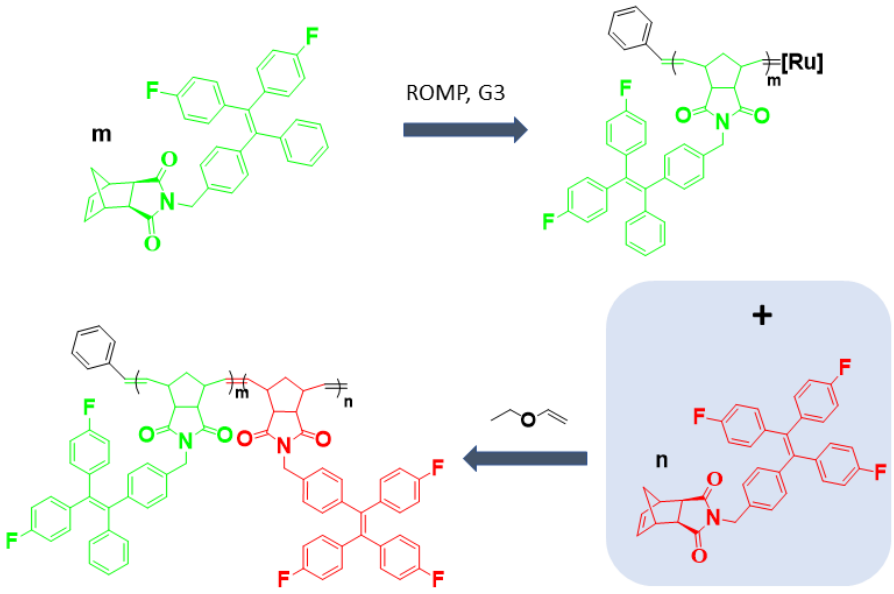



Fig. 4. (A) Host-guest system and (B) Side-chain system of poly-NDIs EO material




Scheme 4. Synthetic approaches of fluorinated tetraphenylethylene poly-NDIs

## 5. CONCLUSION

In conclusion, this review emphasizes the importance of poly-NDIs and diverse applications. Starting from their synthesis by Diels-Alder cycloaddition and the versatility of ring-opening metathesis polymerization (ROMP), the synthetic routes are explored and the ease of modification for tailored applications is highlighted. The applications discussed range from gas separation membranes, drug delivery systems, energy storage devices, electro-optical materials, and chemical sensors. Poly-NDIs exhibit unique properties such as high gas selectivity, the ability to self-assemble for drug delivery, suitability for energy storage with high dielectric constants, and efficiency in electro-optical devices. In addition, the role of poly-NDIs in advancing chemical sensors is emphasized, especially their aggregation-induced emission (AIE) properties, making them promising candidates for various sensing applications. Overall, poly-NDIs prove to be a versatile class of polymers with immense potential in various fields, emphasizing their importance in modern materials science.

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