Synthesis, Characterization, and Optical Properties of Carbazole-Functionalized Poly(norbornene-dicarboximide) by ROMP

Mahmoud Z. Basyouni
Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Mohammed F. Radwan
Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Mohamed E. Abdu
Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Andrew M. Spring
Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

https://doi.org/10.5109/7172257

出版情報：Evergreen. 11 (1), pp.207-213, 2024-03. 九州大学グリーンテクノロジー研究教育センター
バージョン：

EVERGREEN Joint Journal of Novel Carbon Resource Sciences & Green Asia Strategy, Vol. 11, Issue 01, pp207-213, March, 2024

Synthesis, Characterization, and Optical Properties of Carbazole-Functionalized Poly(norbornene-dicarboximide) by ROMP

Mahmoud Z. Basyouni[1,2*], Mohammed F. Radwan[1,3], Mohamed E. Abdu[1,4], Andrew M. Spring[1*]
[1]Interdisciplinary Graduate School of Engineering Sciences, Kyushu University
[2]Department of Chemistry, Faculty of Science, Benha University, Benha, 13518, Egypt
[3]Department of Chemistry, Faculty of Science, South Valley University, Qena, 83523, Egypt
[4]Department of Chemistry, Faculty of Science, Zagazig University, Zagazig, 44519, Egypt

*Corresponding author email:
spring@cm.kyushu-u.ac.jp
mahmoud.basiouny@fsc.bu.edu.eg

(Received December 12, 2023: Revised February 13, 2024: Accepted February 19, 2024)

Abstract: A novel norbornene-dicarboximide monomer functionalized with carbazole was synthesized and effectively polymerized using the Grubbs 3rd generation initiator. Extensive characterization through NMR, GPC, FT-IR, DSC, and UV-vis spectroscopy confirmed the polymer's characteristics. The polymer demonstrated the anticipated nearly 1:1 vinylene *cis-trans* microstructure, possessing a molecular weight of 26800 g/mol and a polydispersity index of 1.11. Its glass transition temperature, as determined by DSC, was 117 °C. UV-vis analysis confirmed the presence of the polymer-bound carbazole group, evidenced by a λ_{max} of 220 nm, compared to 222 nm for carbazole and 221 nm for the monomer.

Keywords: Organic Light-Emitting Diodes; Ring Opening Metathesis Polymerization; Grubbs Catalyst; Carbazole-Pendant Monomer

1. Introduction

Norbornene-dicarboximides (NDIs) are commonly used norbornene-derived monomers in living ring-opening metathesis polymerization (ROMP) to create polymers with customizable sizes, shapes, and functional derivatives exhibiting unique topologies, narrow dispersity, precise regioregularity, and controlled molecular weights[1-5]. Studies have confirmed that employing the Grubbs 1st generation initiator (G1) predominantly yields a *trans* vinylene microstructure, whereas using the G2 or G3 initiators results in an equal distribution of trans and cis vinylene units. Moreover, the G3 initiator is deemed more suitable for polymerizing sterically demanding aromatic substrates [6-9]. The facile functionalization of the dicarboximide nitrogen with desired units of interest has rendered poly (NDI)s valuable active materials across various physical sciences [10-14].

Electro-optic (EO) materials, which change their refractive index under an electric field, are crucial in photonics and optical communication[15]. Poly-NDIs are the top non-conjugated polymers for these applications due to their ability to dissolve in solvents and spin-coat onto substrates. These thin films have excellent optical properties, uniformity, flatness, and large surface area. Additionally, they exhibit high thermal decomposition and glass transition temperatures [16, 17]. Carbazole pendant polymers, which attach a carbazole unit to a non-conjugated polymer backbone like PVC, are popular due to their unique physical properties. They exhibit photoconductivity and resistance to high temperatures, making them versatile materials used in electrical insulators, hole-transport materials, OLED components, photovoltaic devices, and electro-optics [18-25]. They also serve as hole-transporting and electron-blocking layers in OLEDs. Their high glass transition temperatures and thermal decomposition temperatures further expand their potential applications [26-35].

In forthcoming research, it is envisioned that the polymer could serve as a suitable host material for EO chromophore guests with high polarizability. So, in this study we synthesized a novel carbazole-pendant norbornene-dicarboximide monomer (CA-NDI) through a cost-effective and commercially available amino-acid precursor route in a few synthetic steps. Subsequently, we subjected this monomer to polymerization under mild room-temperature conditions in dry chloroform, employing the Grubbs 3rd generation initiator G3. This process yielded the well-controlled and monodispersed carbazole-pendant polymer, poly (CA-NDI), as illustrated in the scheme. The characterization of the polymer involved NMR, GPC, FT-IR, DSC, and UV-vis analyses.

2. Materials and Technique*s*

2.1. Materials and Technique*s*

Laboratory reagents and solvents were sourced from TCI or Kanto Chemical Co. and were utilized without further purification. The Grubbs 3rd generation initiator was sourced from Sigma-Aldrich and utilized in its original condition. 2-(9H-carbazol-9-yl)ethan-1-ol was prepared according to our previous work2).

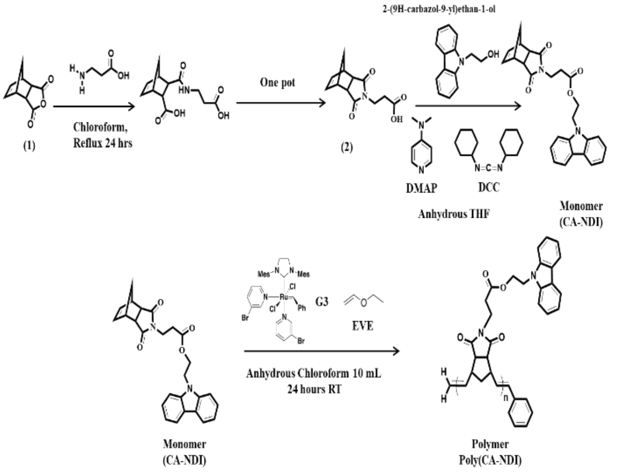
NMR spectra were acquired using a JEOL Inc. ECZ400 spectrometer in $CDCl_3$, with TMS serving as an internal standard. MS analyses were conducted utilizing a JEOL MStation JMS700 instrument. DSC was conducted at a rate of heating of 10 °C/min in the presence of air using an SII-DSC 6220 instrument. For consistency in DSC measurements, the sample underwent two consecutive runs. SEC measurements were carried out employing a Shodex GPC K-805L column on a JASCO LC2000 LC system, with THF used as the eluent. The system underwent calibration using narrow PDI Shodex SM-105 polystyrene standards. UV-vis spectra were acquired using a JASCO V-670 UV-vis Spectrophotometer in a THF solution placed in a quartz cell. CHN elemental analysis was conducted with a Yanako CHN corder MT-6. FTIR spectra were obtained using a Shimadzuo FTIR-8400S Infrared Spectrophotometer, with the sample deposited onto KBr plates from a DCM solution.

2.2. Synthesis of precursor (1)

The synthesis of *exo*-norbornene-5,6-dicarboxylic anhydride (1) proceeded as follows: Maleic anhydride MA (188.20 g, 1.92 mol) was dissolved in 200 ml of o-dichlorobenzene. The solution was raised to a temperature of 200 °C. Simultaneously, dicyclopentadiene was warmed in a water bath at 45 °C to facilitate melting, enabling easy pouring. The melted dicyclopentadiene (128.60 g, 0.97 mol) was then gradually introduced into the pre-stirred solution using a funnel. following the complete addition, the product was additionally heated to 200 °C. for an extra two hours. The heated mixture was transferred into a beaker and left to gradually cool to room temperature. The obtained crystals were filtered and rinsed with 100 ml *o*-dichlorobenzene. To obtain the desired exocyclic isomer, the crystals were recrystallized from chlorobenzene two or three times as required to obtain a high purity in a yield of around 40%.^{1}H NMR (400 MHz, $CDCl_3$): 1.42 (d, J=11Hz, 2H), 1.64 (d, J=10Hz, 2H), 2.99 (s, 2H), 3.43 (s, 2H), 6.31 (s, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 44.20, 46.96, 48.85, 138.04, 171.71 ppm. LRMS (EI+) computed for $C_9H_8O_3$: m/z 164; Determined m/z 164. EA computed for $C_9H_8O_3$: C% 65.85, H% 4.91, N% 0.00. Determined C% 65.80, H% 4.78, N% 0.02.

2.3. Synthesis of precursor (2)

Precursor (1) (10.00 g, 0.061 mol) was dissolved in 100 mL of $CHCl_3$ at room temperature, and beta-alanine (5.44 g, 0.061 mol) was gradually introduced into the stirred solution under a nitrogen atmosphere. The mixture underwent reflux for 24 hours. Removal of the solvent by rotary evaporator gave the crude product a clear viscous oil. The pure product was obtained by column chromatography in 90% $CHCl_3$ and 10% CH_3OH. The white solid was then recrystallized from hexane and the minimum amount of tetrahydrofuran in a yield of 57%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.21 (d, J=9.6Hz, 2H), 1.48 (d, J=10.1Hz, 2H), 2.62 (t, J=8Hz, 2H), 2.66 (s, 2H), 3.23 (s, 2H), 3.74 (t, J=7Hz, 2H), 6.25 (s, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 31.80, 34.15, 42.82, 45.26, 47.91, 137.92, 176.40, 177.97 ppm. LRMS (EI+) computed for $C_{12}H_{13}NO_4$: m/z 236; Determined m/z 236. EA computed for $C_{12}H_{13}NO_4$: C% 61.26, H% 5.56, N% 5.94. Determined C% 61.32, H% 5.60, N% 5.94.



Scheme: The preparation of the carbazole pendant NDI monomer CA-NDI and polymer poly(CA-NDI)

2.4. Synthesis of Monomer (CA-NDI)

A mixture of 2-(9H-carbazol-9-yl) ethan-1-ol (4.49 g, 0.021 mol), DMAP (2.59 g, 0.021 mol), DCC (4.38 g, 0.021 mol), and precursor (2) (5.00 g, 0.021 mol) was mixed and chilled to -5 °C under a nitrogen atmosphere. Cooled THF (50 ml) was then rapidly injected into the reaction vessel. After 2 hours of Stirring at this temperature initiated the formation of a white precipitate. The mixture underwent an additional 48 hours of stirring at -5 °C, following which the tetrahydrofuran was evaporated. The unrefined material underwent purification through column chromatography, employing a solvent blend of 20% THF and 80% Hex. Subsequently, it underwent drying in a vacuum oven at 45 °C for 24 hours. the material transformed into a white solid, yielding 43%.^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.16 (d, J=10Hz, 1H), 1.43 (d, J=10Hz, 1H), 2.47 (t, J=7Hz, 2H), 2.52 (s, 2H), 3.20 (s, 2H), 3.67 (t, J=1Hz), 4.45 (m, 2H), 4.54 (m, 2H), 6.23 (s, 2H), 7.25 (m, 2H), 7.45 (m, 2H), 8.08 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 34.33, 41.59, 42.78, 45.22, 47.82, 62.59, 108.61, 119.42, 120.51, 123.10, 125.99, 137.87, 140.45, 170.65, 177.65 ppm. LRMS (EI+) computed for $C_{26}H_{24}N_2O_4$: m/z 428; computed m/z 428. EA computed for $C_{26}H_{24}N_2O_4$: C% 72.89, H% 5.64, N% 6.55. computed C% 70.33, H% 5.54, N% 6.26. UV-vis: λ_{max}: 221nm.

2.5. Synthesis of Polymer poly(CA-NDI)

The carbazole-pendant monomer (CA-NDI) (0.50 g, 0.00116 mol) was moved to a Schlenk tube, which was then flushed with nitrogen. Subsequently, 10 ml of dry chloroform was injected using a syringe. After approximately 10 minutes of stirring to ensure the solid completely dissolved, the Grubbs 3rd generation initiator (10.32 mg, 1.16 x 10^{-5} mol) dissolution in 2 ml of dry $CHCl_3$ was swiftly injected. The polymerization proceeded for 12 hours at room temperature to ensure full conversion of the monomer. To terminate the living polymerization, 4 ml of degassed EVE was injected. The quenching reaction was allowed to progress for one more hour, following which the polymer was isolated through multiple reprecipitations into stirred methanol, subsequent filtration, and drying in a vacuum oven at 45 °C for 24 hours, resulting in a pure polymer with a yield of 90%.^{1}H NMR (400MHz, $CDCl_3$) δ: 1.23-1.51 (1H, m), 1.79-2.19 (1H, m), 1.20-3.25 (6H, m), 3.38-3.77 (2H, m), 4.12-4.62 (4H, m), 5.22-5.64 (2H, m), 7.09-7.64 (9H, m), 7.91-8.14 (m, 2H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 31.97, 34.26, 45.52, 50.67, 62.59, 108.66, 118.87, 120.47, 123.03, 126.11, 140.43, 170.96, 177.63 ppm. DSC (T_g): 117 °C. FTIR: 3456, 3124-2740, 2414-2260, 1828-1633, 1600, 1506-923 and 758 cm^{-1}. GPC: M_n: 26800 g/mol, M_w: 29,905 g/mol, PDI: 1.11. UV-vis: λ_{max}: 220 nm.

3. Results and Discussion

3.1. Monomer Synthesis and Characterization

Organic photorefractive materials have been known for several decades and are unique in that they are able to undergo a temporary change in their refractive index after being exposed to certain wavelengths of light. Such a phenomenon has proved useful in the development of holographic images etc. As in many areas of organic electronics, organic materials have been a research focus due to their inherent tunability of properties and ease of processing compared with inorganic alternatives. Non-conjugated polymers with pendant carbazole groups such as poly(vinyl carbazole) (PVC) have been extensively investigated. ROMP technique is an excellent method for the production of well controlled homo, block and random copolymers. For the preparation of non-conjugated materials, norbornene-dicarboximides (NDI)s are an excellent and easily functionalized monomer. Hence, the synthesis of carbazole-pendant NDI monomers proves particularly valuable for integration into more intricate systems. The preparation of the carbazole-pendant NDI monomer CA-NDI initiated with the synthesis of compound (1) through the condensation of cyclopentadiene and MA. Subsequent recrystallizations from chlorobenzene yielded the desired exocyclic isomer in high purity in addition to the ^{1}H and ^{13}C as observed in Fig.1. Precursor (2) was then generated through the reaction of this molecule with the cost-effective and readily available amino acid beta-alanine in a convenient one-pot reaction in chloroform, resulting in a precursor (2) and the ^{1}H and ^{13}C as showed in Fig. 2.

The linking of the acid group of precursor (2) with the alcohol group in carbazole moiety facilitated by DCC and DMAP, resulted in the formation of the desired monomer CA-NDI, achieving a satisfactory yield. Purification was achieved by column chromatography the annotated ^{1}H-NMR and ^{13}C-NMR spectra of the monomer CA-NDI can be observed in Fig. 3. The NMR spectra were obtained

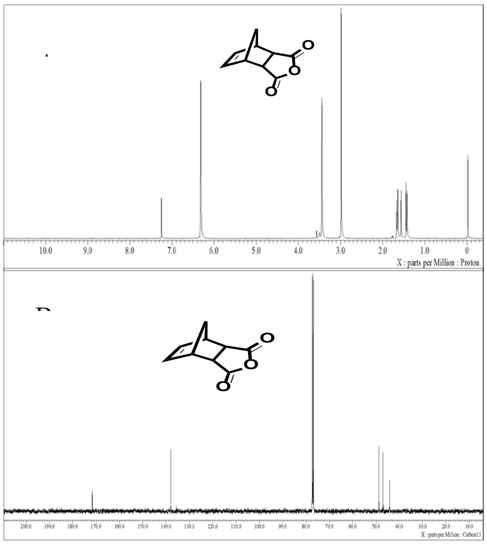


Fig. 1: The annotated ^{1}H NMR (A) and ^{13}C NMR (B) spectra of the precursor (1).

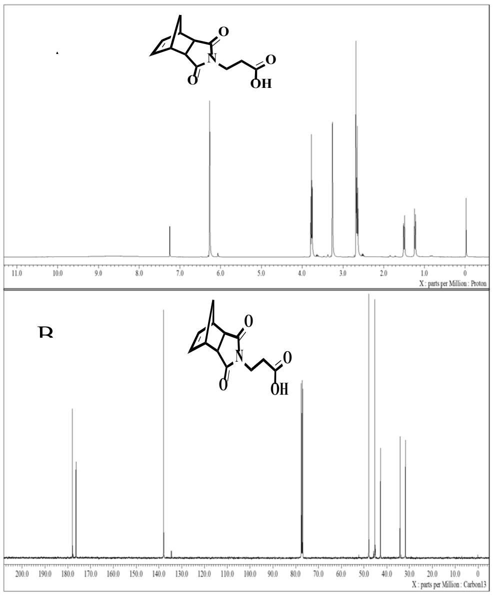


Fig. 2: The annotated ^{1}H NMR (A) and ^{13}C NMR (B) spectra of the precursor (2).

in $CDCl_3$ with TMS as the internal standard. The ^{1}H NMR spectrum of CA-NDI affirms the presence of 11 distinct proton environments, denoted as a to k in Fig. 3A. A few signals of note are the three carbazole peaks of (a), (b) and (c). The two protons of (a) being responsible for the pronounced doublet at 8.07 ppm. The two alkenic protons of the NDI monomer are associated with the prominent singlet at 6.24 ppm. The four protons of the carbazole linking group (e) are designated to the adjacent multiplets at 4.55 ppm and 4.45 ppm, respectively. Meanwhile, the NDI linking group protons (f) and (i) are assigned to the triplets at 3.67 ppm and 2.47 ppm. The ^{13}C-NMR spectrum verifies the existence of 17 distinct carbon environments, as illustrated in Fig. 3B. A few signals worthy of mention are the peak at 170.64 ppm which has been assigned to the carbon (2) of the ester linking group. The noticeable peak at 137.86 ppm is attributed to the two carbons (4) of the NDI alkene. Carbazole carbons (7), (8) and (9) have been assigned to the peaks at 120.51, 119.42 and 108.60 ppm respectively. Carbazole linking group carbons (10) and (11) have been attributed to the single peak at 62.57 ppm. Low resolution (EI) mass spectrometry revealed a strong peak at 428 confirming the correct molecular composition of $C_{26}H_{24}N_2O_4$.

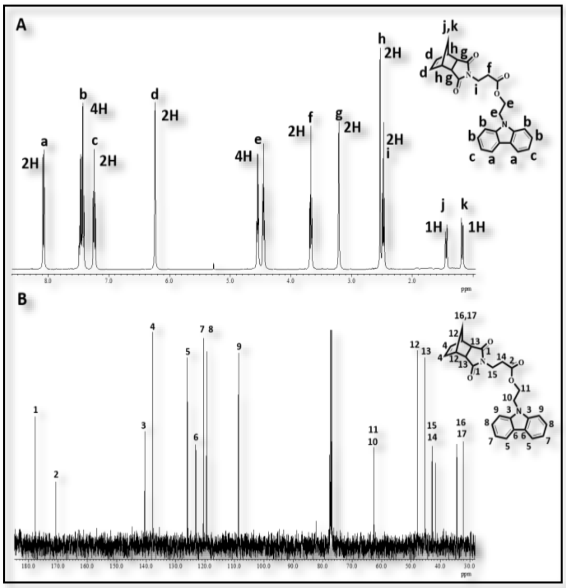


Fig. 3: The annotated ^{1}H NMR (A) and ^{13}C NMR (B) spectra of the monomer CA-NDI

3.2. Polymer (poly(CA-NDI)) Synthesis and Characterization

The polymerization of the CA NDI monomer in its pure form occurred at room temperature for a duration of 12 hours under a nitrogen atmosphere. Previous experimentation suggested that achieving full polymerization of NDI monomers typically took place in around an hour when employing the Grubbs 1st generation initiator G1.

The G3 initiator is recognized for demonstrating similar kinetics, displaying tolerance to bulky substituents, and leading to a *cis-trans* vinylene configuration. The prolonged reaction period of 12 hours was chosen to ensure complete consumption of the sizable and sterically hindered CA-NDI monomer. Additionally, at room temperature, occurrences of backbiting are believed to be minimal, resulting in a few disadvantages associated with an extended reaction time. The ^{1}H NMR and ^{13}C NMR spectra of the polymer (poly(CA-NDI)) were obtained in deuterated chloroform and are annotated in Fig. 4.

As can be observed in Fig. 4A, there are 12 proton environments, however, due to the broad nature of most peaks as can be expected from an NMR spectrum of a polymer it is difficult to assign precisely.

Peaks of note include the broad but sharp multiplet at 8.00 ppm corresponding to the carbazole protons (l). Carbazole protons (i), (j) and (k) are designated to the broad multiplet in the range of 7.65-7.08 ppm. The NDI alkenic protons (h) are clearly visible as a broad doublet at 5.62-5.28 ppm. The doublet corresponds to both *cis* and *trans* vinylene linkages which are in an approximately 1:1 ratio as is expected from the G3 initiator. Carbazole linking group protons (f) and (g) have been assigned to the multiplet at 4.40 ppm.

The ^{13}C-NMR spectrum confirms there are 14 distinct carbon environments. Some noteworthy peaks are the short peak at 177.82 ppm which has been assigned to the NDI carbonyl carbon (14). The adjacent short peak at 170.75 ppm has been assigned to the ester carbon (13) respectively. The vinylene carbon (12) is clearly visible at 140.43 ppm. Carbazole carbon (7) is notably discernible and has been assigned to the peak at 108.66 ppm, as indicated in Fig. 4B.

The GPC data for poly(CA-NDI) were acquired employing a JASCO LC2000 liquid chromatography system equipped with a TSKgel G2000Hxl column, RI2031plus IR detector, and UV 2060plus UV detector. THF served as the eluent at rate of flow 1 mL/min. The calibration of the system utilized narrow PDI Shodex SM-

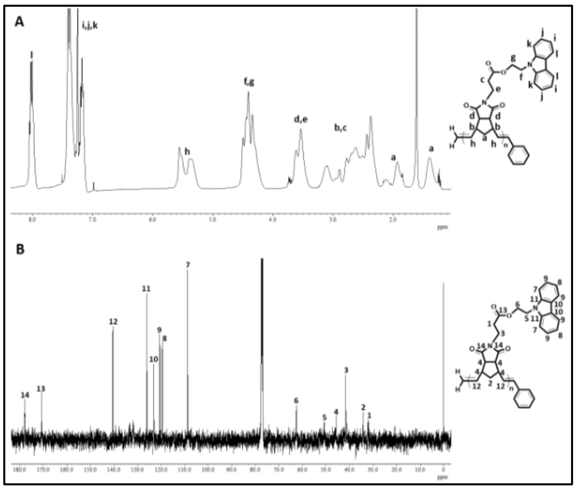


Fig. 4: The annotated ^{1}H NMR (A) and ^{13}C NMR (B) spectra of poly CA NDI

105 polystyrene standards. Results obtained by this system are not absolute values. A plot of D.MWD vs Log M can be observed in Fig. 5A. The molecular weight (M_n) measured was 26800 g/mol with a very narrow PDI of 1.11 confirming the well-controlled polymerization at room temperature. Figure 5B shows the DSC measurement of the polymer, analysis revealed a T_g of 117 °C. This relatively low T_g may be attributed to the flexible linker group between the NDI unit and the carbazole. Shortening of this linker may allow the T_g to be raised, if the application so required.

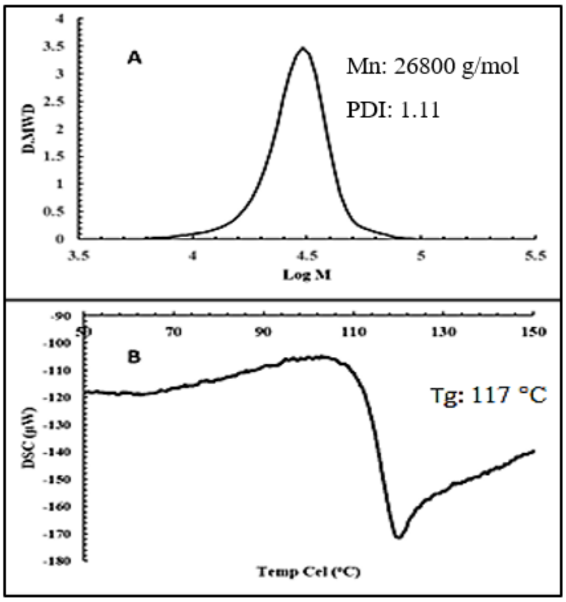


Fig. 5: The marked GPC (A) & DSC (B) analysis of Poly CA NDI

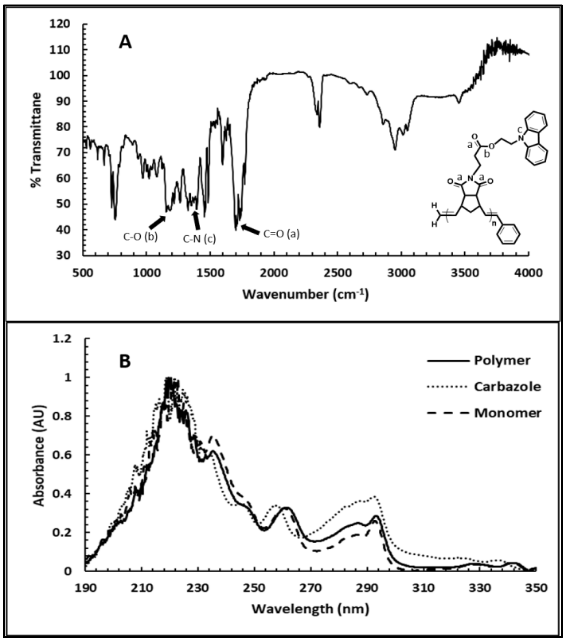


Fig. 6: The marked FTIR (A) and UV-vis (B) analysis of Poly CA NDI

The FTIR spectrum of poly CA NDI is shown in Fig. 6A. There are three main stretching modes of poly(CA-NDI) that can be observed in the spectrum. These are the C=O (a) of the imide unit at approximately 1700cm^{-1}. The C-O (b) of the ester moiety at approximately 1100 cm^{-1} and the C-N (c) of the carbazole which is present at approximately 1300 cm^{-1}. The UV-vis spectrum of poly (CA-NDI) was measured in dilute THF solution as is shown in Fig. 6B by the solid line. The λ_{max} was observed to be 220 nm. The UV-vis spectrum of carbazole was also acquired in dilute THF solution (fine dashed line). In this case, the λ_{max} was observed to be 222 nm, while the monomer had a λ_{max} of 221 nm.

4. Conclusion

A novel carbazole-appended NDI monomer (CA-NDI) was produced with exceptional purity using a concise and straightforward amino acid precursor method, serving as a promising host material for electro-optic chromophore guests possessing high polarizability. This monomer was then successfully polymerized in a well-controlled living manner in dry chloroform solution utilizing the Grubbs 3rd generation initiator at room temperature. The resulting poly CA-NDI had a measured Mn of 26800 g/mol and a PDI of 1.11, confirming a well-controlled polymerization. ^{1}H-NMR analysis showed an approximately 1:1 *cis-trans* vinylene units as was expected from the G3 initiator. DSC confirmed that the polymer T_g was 117 °C, the relatively low value being attributed to the flexible linker group. FTIR analysis confirmed the presence of key functional groups such as C=O at approximately 1700 cm^{-1}, C-O at approximately 1100cm^{-1} and a C-N at approximately 1300 cm^{-1}. UV-vis spectrum of the polymer in THF solution confirmed the presence of the carbazole group. The λ_{max} of the polymer was 220 nm, this compared to a Carbazole λ_{max} of 222 nm and a monomer λ_{max} of 221 nm. This useful and easily prepared NDI monomer (CA-NDI) has been shown to exhibit a smooth and easily controlled polymerization profile, thus providing a viable means of introducing carbazole into more complex ROMP polymers for the aforementioned photorefractive applications. The polymer poly(CA-NDI) exhibited a relatively high T_g, presence of carbazole was confirmed by NMR and UV-vis and a had a good solubility in THF and chloroform. The polymer is now being investigated as a potential host for EO chromophores in a host-guest configuration.

References

1) A.M. Spring, F. Qiu, J. Hong, A. Bannaron, X. Cheng, S. Yokoyama, Adamantyl and carbazole containing trans-poly(norbornene-dicarboximide)s as electro-optic chromophore hosts, Polymer (Guildf). 172 (2019) 382–390. https://doi.org/10.1016/j.polymer.2019.04.015.

2) A.M. Spring, F. Qiu, J. Hong, A. Bannaron, T.

Kashino, T. Kikuchi, M. Ozawa, H. Nawata, K. Odoi, S. Yokoyama, Crosslinked poly(norbornene-dicarboximide)s as electro-optic chromophore hosts, Eur. Polym. J. 97 (2017) 263–271. https://doi.org/10.1016/j.eurpolymj.2017.10.022.

3) W.J. Wolf, T.P. Lin, R.H. Grubbs, Examining the Effects of Monomer and Catalyst Structure on the Mechanism of Ruthenium-Catalyzed Ring-Opening Metathesis Polymerization, J. Am. Chem. Soc. 141 (2019) 17796–17808. https://doi.org/10.1021/jacs.9b08835.

4) S.J. P'Pool, H.J. Schanz, Reversible inhibition/activation of olefin metathesis: A kinetic investigation of ROMP and RCM reactions with Grubbs' catalyst, J. Am. Chem. Soc. 129 (2007) 14200–14212. https://doi.org/10.1021/ja071938w.

5) D. Mäker, U.H.F. Bunz, Fourfold alkoxy-substituted [2.2.2] paracyclophane-1,9,17-trienes-ROMP into PPVs with unusual topologies, Macromol. Rapid Commun. 35 (2014) 2096–2100. https://doi.org/10.1002/marc.201400515.

6) Y. Janpatompong, A.M. Spring, V. Komanduri, R.U. Khan, M.L. Turner, Synthesis and Ring-Opening Metathesis Polymerization of o-Dialkoxy Paracyclophanedienes, Macromolecules. 55 (2022) 10854–10864. https://doi.org/10.1021/acs.macromol.2c02111.

7) D.R. Kumar, B.J. Lidster, R.W. Adams, M.L. Turner, Mechanistic investigation of the ring opening metathesis polymerisation of alkoxy and alkyl substituted paracyclophanedienes, Polym. Chem. 8 (2017) 3186–3194. https://doi.org/10.1039/c7py00543a.

8) V. Joseph, K.R.J. Thomas, S. Sahoo, M. Singh, J.H. Jou, Simple carbazole based deep-blue emitters: The effect of spacer, linkage and end-capping cyano group on the photophysical and electroluminescent properties, Dye. Pigment. 151 (2018) 310–320. https://doi.org/10.1016/j.dyepig.2017.12.061.

9) C.C. Wang, C.Y. Yu, Synthesis, characterization and nanoaggregates of alkyl and triethylene glycol substituted 3,6-carbazolevinylenes homopolymers and block copolymers, Polymer (Guildf). 166 (2019) 123–129. https://doi.org/10.1016/j.polymer.2019.01.070.

10) B.E. Lynde, R.L. Maust, P. Li, D.C. Lee, R. Jasti, A.J. Boydston, Ring-opening metathesis polymerization of a strained stilbene-based macrocyclic monomer, Mater. Chem. Front. 4 (2020) 252–256. https://doi.org/10.1039/c9qm00604d.

11) H.I. Mohamed, M.Z. Basyouni, A.A. Khalil, K.A. Hebash, A.H. Tantawy, Petroleum-dispersing and antimicrobial activity of newly synthesized polymeric surfactants tethering tetrachlorophthalimide moiety, J. Iran. Chem. Soc. (2020). https://doi.org/10.1007/s13738-020-02023-9.

12) V. Komanduri, D.R. Kumar, D.J. Tate, R. Marcial-Hernandez, B.J. Lidster, M.L. Turner, Bidirectional ROMP of paracylophane-1,9-dienes to tri- and penta-block: P -phenylenevinylene copolymers, Polym. Chem. 10 (2019) 3497–3502. https://doi.org/10.1039/c9py00147f.

13) A.M. Spring, F. Qiu, S. Yokoyama, High stability poly(N-adamantyl-exo-norbornene-5,6-dicarboximide) and phenyl vinylene thiophene electro-optic host-guest system, Eur. Polym. J. 84 (2016) 89–99. https://doi.org/10.1016/j.eurpolymj.2016.09.012.

14) A.H. Tantawy, H.I. Mohamed, A.A. Khalil, K.A. Hebash, M.Z. Basyouni, Novel bioactive imidazole-containing polymeric surfactants as petroleum-collecting and dispersing agents: Synthesis and surface-active properties, J. Mol. Liq. 236 (2017) 376–384. https://doi.org/10.1016/j.molliq.2017.04.040.

15) R.S. Jacobsen, K.N. Andersen, P.I. Borel, J. Fage-Pedersen, L.H. Frandsen, O. Hansen, M. Kristensen, A. V. Lavrinenko, G. Moulin, H. Ou, C. Peucheret, B. Zsigri, A. Bjarklev, Strained silicon as a new electro-optic material, Nature. 441 (2006) 199–202. https://doi.org/10.1038/nature04706.

16) F. Qiu, A.M. Spring, F. Yu, I. Aoki, A. Otomo, S. Yokoyama, Thin TiO2 core and electro-optic polymer cladding waveguide modulators, Appl. Phys. Lett. 102 (2013) 1–4. https://doi.org/10.1063/1.4809818.

17) A. Pineda Contreras, M.A. Tlenkopatchev, M. Del Mar López-González, E. Riande, Synthesis and gas transport properties of new high glass transition temperature ring-opened polynorbornenes, Macromolecules. 35 (2002) 4677–4684. https://doi.org/10.1021/ma011959p.

18) Y.J. Lin, M. Horie, Dithienylethene-containing cyclic and linear conjugated molecules: Synthesis, photochromism, and photoluminescence, Dye. Pigment. 195 (2021) 109700. https://doi.org/10.1016/j.dyepig.2021.109700.

19) J. Guo, E.J. Park, Y.C. Teo, A. Abbas, D. Goh, R.A.A. Smith, Y. Nie, H.T.L. Nguyen, J.P.S. Yeong, S. Cool, H. Makio, P. Teo, Bioactive polyethylene synthesized by ring opening metathesis polymerization for potential orthopaedic applications, Polym. Chem. 14 (2023) 1743–1751. https://doi.org/10.1039/d2py01545e.

20) Y. Janpatompong, V. Komanduri, R.U. Khan, M.L. Turner, Synthesis and ring-opening metathesis polymerisation of o-alkoxy benzothiadiazole paracyclophane-1,9-dienes, Org. Biomol. Chem. 21 (2023) 3245–3250. https://doi.org/10.1039/d2ob01989b.

21) Y. Janpatompong, K. Suwada, M.L. Turner, G. De Bo, Mechanical stability of cis, trans-poly(p-phenylene vinylenes), Polym. Chem. 14 (2023) 1978–1982. https://doi.org/10.1039/d3py00021d.

22) A. Mann, M.D. Hannigan, M. Weck, Cyclophanediene and Cyclophanetriene-Based Conjugated Polymers, Macromol. Chem. Phys. 224 (2023) 1–17. https://doi.org/10.1002/macp.202200397.
23) T. Mehreen, S.I. Vagin, V. Kumar, X. Liu, L. Eylert, B. Rieger, A. Meldrum, A Phenylene-Based Light-Emitting Polymer: Atums Green, Macromol. Chem. Phys. 224 (2023) 1–10. https://doi.org/10.1002/macp.202200294.
24) A.R. Nurohmah, M. Ayuningtyas, C.S. Yudha, A. Purwanto, H. Widiyandari, Synthesis and Characterization of NMC622 Cathode Material Modified by Various Cheap and Abundant Transition Metals for Li-ion Batteries, Evergreen. 9 (2022) 427–437. https://doi.org/10.5109/4794168.
25) N. Nurwidiana, B.M. Sopha, A. Widyaparaga, Modelling photovoltaic system adoption for households: A systematic literature review, Evergreen. 8 (2021) 69–81. https://doi.org/10.5109/4372262.
26) G. Gupta, R.K. Tyagi, S.K. Rajput, A statistical analysis of sputtering parameters on superconducting properties of niobium thin film, Evergreen. 8 (2021) 44–50. https://doi.org/10.5109/4372259.
27) S. Silviana, A.G. Hasega, A.R. Nur Hanifah, A.N. Saadah, Synthesis of Silica Coating Derived from Geothermal Solid Waste Modified with 3-Aminopropyl Triethoxysilane (APTES) and Silver Nano Particles (AgNPs), Evergreen. 9 (2022) 1224–1230. https://doi.org/10.5109/6625733.
28) L. Wang, Y. Xu, Q. Zuo, H. Dai, L. Huang, M. Zhang, Y. Zheng, C. Yu, S. Zhang, Y. Zhou, Visible light-controlled living cationic polymerization of methoxystyrene, Nat. Commun. 13 (2022) 1–11. https://doi.org/10.1038/s41467-022-31359-4.
29) E. Witkowska, I. Glowacki, T.H. Ke, P. Malinowski, P. Heremans, Efficient OLEDs Based on Slot-Die-Coated Multicomponent Emissive Layer, Polymers (Basel). 14 (2022) 1–16. https://doi.org/10.3390/polym14163363.
30) J. Poisson, C.J. Christopherson, Z.M. Hudson, Cationic bottlebrush brush polymers via sequential SI-ROMP and SI-ARGET-ATRP, Polym. Int. (2022). https://doi.org/10.1002/pi.6482.
31) X. Chen, S. Hussain, A. Abbas, Y. Hao, A.H. Malik, X. Tian, H. Song, R. Gao, Conjugated polymer nanoparticles and their nanohybrids as smart photoluminescent and photoresponsive material for biosensing, imaging, and theranostics, Springer Vienna, 2022. https://doi.org/10.1007/s00604-021-05153-w.
32) M.D.M. Faure, B.H. Lessard, Layer-by-layer fabrication of organic photovoltaic devices: Material selection and processing conditions, J. Mater. Chem. C. 9 (2021) 14–40. https://doi.org/10.1039/d0tc04146g.
33) Y.J. Lin, H.Y. Chiang, O. Oki, S. Kushida, S.W. Chang, S.T. Chiu, Y. Yamamoto, T. Hosokai, M. Horie, Conjugated Copolymers of Poly(arylenevinylene)s: Synthesis by Ring-Opening Metathesis Polymerization, Film Morphology, and Resonant Luminescence from Microspheres, ACS Appl. Polym. Mater. 1 (2019) 2240–2248. https://doi.org/10.1021/acsapm.9b00549.
34) J. Freudenberg, D. Jänsch, F. Hinkel, U.H.F. Bunz, Immobilization Strategies for Organic Semiconducting Conjugated Polymers, Chem. Rev. 118 (2018) 5598–5689. https://doi.org/10.1021/acs.chemrev.8b00063.
35) C.A. Young, A. Hammack, H.J. Lee, H. Jia, T. Yu, M.D. Marquez, A.C. Jamison, B.E. Gnade, T.R. Lee, Poly(1,4-phenylene vinylene) Derivatives with Ether Substituents to Improve Polymer Solubility for Use in Organic Light-Emitting Diode Devices, ACS Omega. 4 (2019) 22332–22344. https://doi.org/10.1021/acsomega.9b02396.