



NMR-based structural characterization of common aromatic poly(amic acid) polymers

İdris Yazgan¹

Received: 15 October 2018 / Revised: 6 March 2019 / Accepted: 22 April 2019 / Published online: 29 April 2019
© Springer-Verlag GmbH Germany, part of Springer Nature 2019

Abstract

Polyamic acid (PAA) has been widely synthesized as the precursor of polyimide for over 50 years. PAA has had recent attention when used as a final polymer in a variety of applications including sensors, flexible electronics, drug delivery and food packaging. In all cases, structural modifications are sought to advance usability of PAA polymers, where chemistry of the polymers plays a key role for further modifications. However, there is a gap in literature that would discuss structural and cis-/trans-isometric characterizations of the PAA polymers. In this study, common PAA polymers synthesized from the couples of (1) pyromellitic dianhydride and 4,4'-oxydianiline, (2) pyromellitic dianhydride-4-sulfonyldianiline, (3) 4,4'-carbonyldiphtalic dianhydride and 4,4'-oxydianiline and (4) pyromellitic dianhydride and 4,4'-ethylenedianiline were characterized with 1D and 2D NMR and supported with ATR-FTIR techniques. The findings revealed that both diamine and dianhydride sources along with the solvent choice are crucial for cis-/trans-binding of diamine to dianhydride monomers, average molecular weight and intramolecular interactions. The current study, to the best of our knowledge, is the first report on structural annotation of common PAA polymers along with the effect of the solvent on the isomers and average molecular weight.

Keywords Polyamic acid · Monomer · Isomerization · NMR · IR

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s00289-019-02793-0>) contains supplementary material, which is available to authorized users.

✉ İdris Yazgan
iyazgan@kastamonu.edu.tr

¹ Department of Biology, Center for Biosensors and Material Science, Faculty of Science and Art, Kastamonu University, Kastamonu, Turkey

Introduction

Poly(amic acid), PAA, is a generic name for the copolymers synthesized from dianilines and dianhydrides [1, 2]. PAA-derived polymers, including polyimide (PI), has been utilized in a variety of applications such as adhesive, separation, conducting or insulating material due to their good chemical and physical properties [3–7]. PAA as a final product has also been extensively studied in the last decade. It is electroactive, biodegradable [8] and has free carboxyl and amide groups that act as functional groups for further modifications [9, 10]. PAA has also been proved to have excellent catalytic capabilities [11] and acts as a semiconductor [8] and a reducing agent with an excellent stabilizing capability [12].

Biomedical and flexible electronic applications of PAA and PI from different formulations have been reported. They include drug delivery [13, 14], regenerative medicine [15], conducting polymers in electronics [16], sensors [2, 13] and tissue scaffold [17], and all further modifications of PAA and PI polymers are required to advance their successful applications. The modifications including functional group substitutions [18], salt formation and grafting via EDC/NHS [14], glutaraldehyde [10], imidazole [8], ethanolamine [19] and ethylamine [20], aminopropyl methacrylate [15] and aminopyridines [17] have been reported. In order to perform a successful activation of the functional groups and design the polymers based on application need, it is critical to know the exact chemistry. Similarly, three-dimensional structure of polymers and functional groups substituted in polymeric networks plays crucial roles to reveal their performance including optical (i.e., fluorescence and UV–vis) and thermomechanical performance and thermodynamic stability [21–23]. Therefore, controlling cis-/trans-isomerization and intramolecular interactions of the polymers in addition to their primary structure is critical to tailor the desired properties [21]. Type of monomers, heat and monomer ratio and solvent choice are the main elements to control cis-/trans-isomerism of the final polymer [21, 22]. Even though formation of polyimide closes the ring which eliminates the possible differences resulted from cis-/trans-isomerism, there are no studies available to discuss how the differences in PAA will alter the performance of the polyimide formation. Therefore, it is critical to find out the isomerism of PAA polymers beforehand.

Previous structural characterization studies done on PAA polymers from aromatic monomers were confined to group characterization, average molecular weight and peak assignments [1, 2, 8, 10, 12, 16, 18, 20, 24, 25], while detailed NMR and IR groups assignments can be found elsewhere [3]. Some of the data presented in the literature show contradiction to each other, which is probably related to the key differences in the experimental conditions and wrong assignments of the groups. In this study, two dianhydride sources and four dianiline sources were used to synthesize five different aromatic PAA polymers. NMR- and IR-based structural characterization revealed that the monomers and reaction media play a key role in cis-/trans-isomerization of dianiline–dianhydride condensation, intramolecular interactions, end-group differences and average molecular weight. This study is the first report on fully structural annotation of common

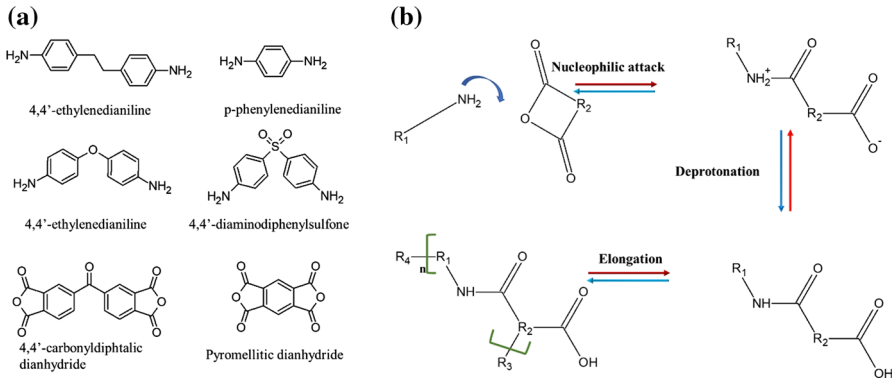


Fig. 1 **a** Common aromatic monomers used in the synthesis of polyamic acid polymers. **b** Polycondensation mechanism of poly(amic acid) polymer formation in an anhydrous polar aprotic solvent. R_1 and R_2 represent monomeric units, while R_3 and R_4 represent polymeric units. Synthesis of poly(amic acid) polymers from the monomer couples of PMDA-ODA, PMDA-DPS, PMDA-EDA and CPDA-ODA (structures shown in Fig. 1a) followed the mechanism shown in Fig. 1b

polyamic acid polymers, which will contribute to the biomedical and material science applications of polyamic acid polymers that need further modifications.

Experimental

Materials

Pyromellitic dianhydride (PMDA), 4,4'-carbonyldiphtalic dianhydride (CPDA), 4,4'-oxydianiline (ODA), 4,4'-diaminodiphenylsulfone (DPS), 4,4'-ethylenedianiline (EDA), *N,N'*-dimethylacetamide (DMAC), tetrahydrofuran (THF), *N,N'*-dimethylformamide were obtained from Sigma-Aldrich [Ankara, Turkey]. All the monomers and solvents were used as they were purchased from the vendors.

Synthesis of PAA polymers

Polyamic acid polymers, PAA, were synthesized via a polycondensation reaction (Fig. 1b), where the diamine source was dissolved in anhydrous organic polar aprotic solvent, followed by a dianhydride source being introduced to the media for polymerization [8]. In all cases, molar ratio of diamine and dianhydride sources was used as 1:1 at room temperature. A total of 0.16 M of PAA samples were prepared in 50-mL beaker under a hood. The reaction chamber was closed with an airtight plastic cover to prevent further vapor interference to the reaction system. The mixture was then left stirring for 18 h. The synthesized PAA polymers were not purified, and the polymers underwent phase inversion in 18.2 MΩ pure water to eliminate residual solvent. This was followed by rinsing three times with 18.2 MΩ pure water. Figure 1a reveals the structure of the monomers commonly used in PAA polymer synthesis. Polymers from the couples of (1) pyromellitic dianhydride

and 4,4'-oxydianiline (PAA1), (2) pyromellitic dianhydride-4,4'-sulfonyldianiline (PAA2) and (3) 4,4'-carbonyldiphtalic dianhydride and 4,4'-oxydianiline (PAA3) were synthesized from dimethylacetamide, and (4) pyromellitic dianhydride and 4,4'-ethylenedianiline (PAA4) and only one sample of (5) pyromellitic dianhydride and 4,4'-oxydianiline (PAA5)-based PAA polymers were synthesized from tetrahydrofuran.

Structural characterization

^1H , ^{13}C , ^1H COSY, ^1H ^{13}C HSQC/HMBC, 2D DOSY and 2D NOESY NMR were utilized to characterize the PAA polymers. All the phase-inverted PAA membranes were dissolved in DMSO- d_6 [Sigma-Aldrich, Ankara]. A total of 600/400 MHz Bruker instrument run by Top Spin 3.5pl7 software was used to collect NMR spectra. Top Spin 3.5pl7 software and ACD/Spectrus Processor 2017 were used to analyze the results. Functional group analyses were performed via Multireflection-ATR-FTIR (Bruker Alpha II FTIR Spectrometers). All the chemical formulas were drawn using *ACDLab Freeware 2016*.

Results and discussion

The two graphical insets are the cis- and trans-form of two ODA molecule binding to one PMDA (Fig. 2a, b). As seen from Fig. 2c, there are two adjacent peaks at 7.74 and 7.71 ppm which are labeled in Fig. 2a as “1” and “3.” Integrals, in Fig. 2a, of “4,” “5,” “3+1” and “2” are 1, 2, 8.8 and 7.9, respectively. Since “1” and “2” are equal under cis- and trans-conditions, “3” can be accepted as “1” equivalent to “4” since “3” is only possible in the presence of “4.” Cis- and trans-ratio can be accepted as 4/5, which reveals that the trans-form is more common under the experimental conditions. In contrast to this, a detailed study done on PMDA-ODA-based PAA polymer synthesis in water and ethanol-containing DMAC solvent systems, cis-isomer, was shown more preferable in the case of ethanol/DMAC and water/ethanol/DMAC solvent systems, where temperature did not alter the cis-/trans-preference [8]. ^1H NOESY reveals that a strong coupling occurs at the ODA residue, while only a slight long-range coupling occurs between amino proton and the proton on PMDA residue as labeled “3,” and the possibility of the interaction was further observed in ^1H ^{15}N HMBC (data not shown). ^1H NMR spectrum of ODA-PMDA polymer dissolved in DMSO- d_6 -containing 5% D_2O did not eliminate the peaks observed at around 10 ppm, which shows that the peaks are from $-\text{COH}-$. This reveals that the end group of ODA-PMDA-based polymer is carbonyl, which is against the common understanding [8].

Synthesis of ODA-PMDA-based polyamic acid in tetrahydrofurane resulted in formation of overwhelmingly (if not all) cis-form of PAA, whose amino peak was observed further downfield (from 10.6 to 12.0 ppm). However, tetrahydrofurane was observed as weak solvent to obtain highly viscous PAA polymers which can be applied to different fields. Similarly, acetone was shown as weak solvent to obtain

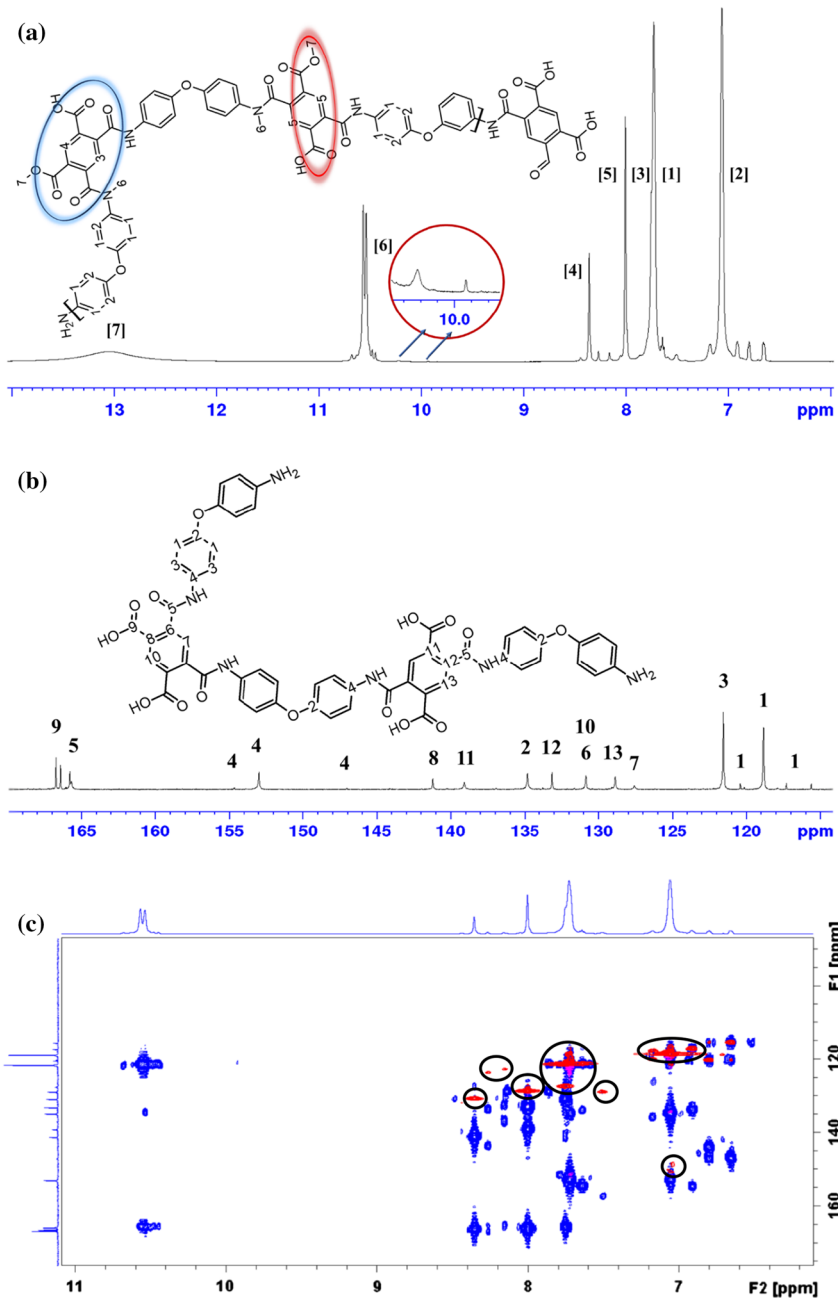


Fig. 2 **a** ^1H spectrum of ODA-PMDA-based PAA polymer synthesized in an anhydrous DMAC. Numbers refer to corresponding proton atoms. Left and medium circles show cis-/trans-isomerism while right circle depicts carbonyl groups. **b** ^{13}C assignments of ODA-PMDA-based PAA polymer synthesized in DMAC. Numbers refer to corresponding carbon atoms. **c** Merged NMR spectra for ^1H ^{13}C HMBC and ^1H ^{13}C HSQC (circled) of ODA-PMDA-based PAA polymer synthesized in DMAC

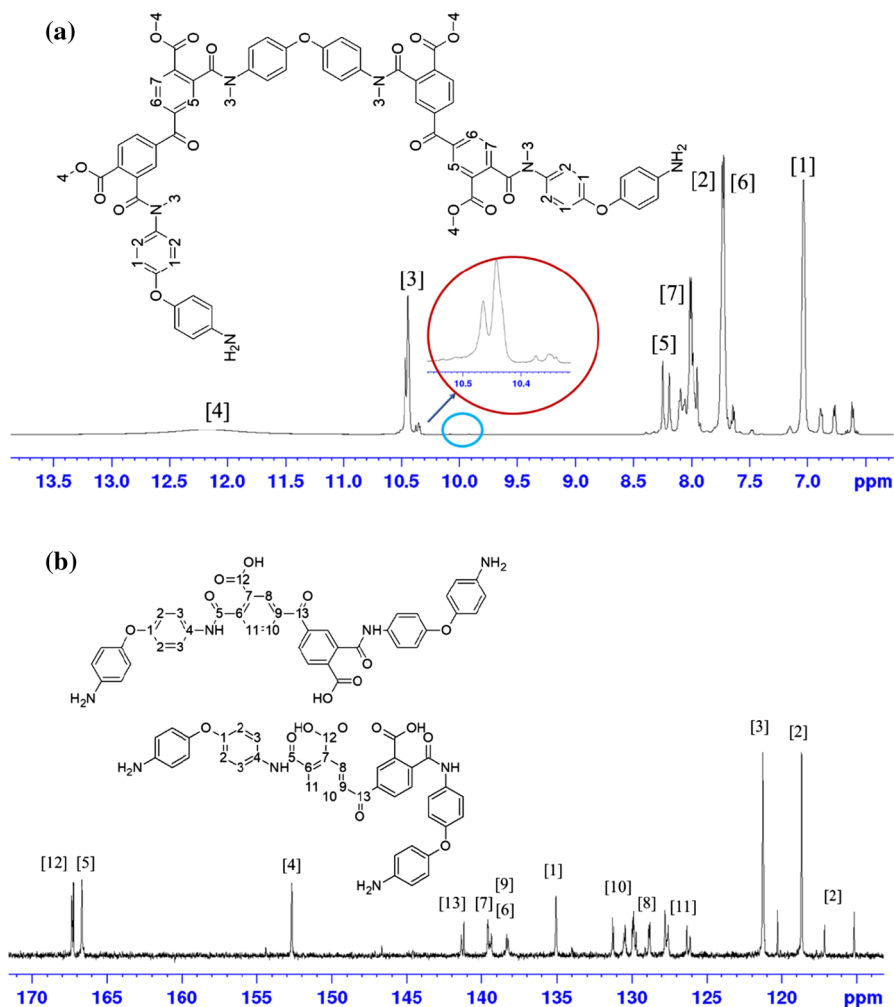


Fig. 3 **a** ^1H spectrum of ODA-CPDA-based PAA polymer synthesized in anhydrous DMAC. Numbers refer to corresponding proton atoms. Bottom circle depicts the carbonyl groups while top circle highlights the amino groups. **b** ^{13}C spectrum of ODA-CPDA-based PAA polymer synthesized in anhydrous DMAC. Numbers refer to corresponding carbon atoms

high molecular weight ODA-PMDA-based PAA polymers [8]. However, warming THF up to 50 °C before PMDA addition, dramatic structural changes became apparent as discussed in Supplementary Material. Briefly, the resulting PAA polymer gave 1:1 cis-/trans-isomerism, which could be related to the fact that heat can advance speed of the reaction and solubility of the forming PAA polymers.

As shown in Fig. 3a and b, CPDA-ODA-based PAA polymers were obtained in cis- and trans-forms. Cis- and trans-binding of ODA monomers to CPDA monomers will not bring about much difference to the environment of the protons labeled as “5,” “6” and “7” as shown in Fig. 3a. However, merging ^1H ^{13}C HMBC and ^1H ^{13}C

HSQC revealed that there is both cis- and trans-forms, which was calculated as 5/4 for cis-/trans-ratio based on the integral of “5,” “6,” “7,” “2” and “1.”

To characterize the end groups, 5% D₂O was added to the DMSO-d₆ to dissolve CPDA-ODA polymer, which revealed that both carbonyl (blue inset in Fig. 3a) and amino groups can be the end group of the polymer based on the preparation conditions. In the case of anhydrous DMAC, the end group is a carbonyl while regular pure DMAC gave amino as the end groups. The formation of carbonyl and amine groups as the end group was observed for PAA polymers in general throughout the study.

¹³C assignments with the help of ¹H ¹³C HMBC and ¹H ¹³C HSQC 2D NMR spectra of ODA-PMDA (Fig. 2b) and ODA-CPDA (Fig. 3b) revealed that different environments could give the same shifts. Such unlabeled ¹³C peaks in Figs. 2b, 3b are related to either differently sized polymers and cis-/trans-isomers of PAA polymers or for the same groups positioning in the edges or center of the same polymer.

Unlike the ODA-PMDA- and ODA-CPDA-based PAA polymers, DPS-PMDA PAA polymers gave an unexpected 1D and 2D NMR spectra. First of all, the amino group on PAA gave ¹H proton at 10.9 ppm (Fig. 4a) while it was obtained at 10.6 ppm for both ODA-PMDA- and ODA-CPDA-based PAA polymers. Another unexpected observation was that the amide carbon gave a peak further downfield than carboxyl carbon (Fig. 4b). In contrast to this, the ¹³C peak labeled as “4” in Fig. 4b moved downfield from 152 to 143 ppm as clearly shown by Fig. 4c. A similar shift was observed for EDA-PMDA-based PAA polymer as well. All these are most probably related to the differences in 3D orientation of the polymers as detailed in NOESY explanation part. The non-labeled peaks in Fig. 4b are most likely related to non-reacted PMDA and DPS, while the peaks at 167 ppm belong to the residual DMAC solvent. Therefore, it can be speculated that PMDA-DPS polymers synthesized under ambient conditions will contain starting materials, which might require the synthesized polymers to be purified for further usage.

Similar to DPS-PMDA, EDA-PMDA gave unexpected ¹H and ¹³C spectra. The carboxyl proton (Fig. 5) was not observed in the spectrum. This type of incidences was observed for ODA-PMDA-based PAA polymers in the case that the NMR run out of concentrated polymer solutions and crosslinked PAA polymers, which most likely was related to –COOH–NH– interactions and changes in 3D structure of PAA polymers in response to crosslinking [8]. It is possible that the loss/decrease in proton belonging to carboxyl group might be related to the effects of 3D conformation and concentration.

¹H ¹³C HMBC and ¹H ¹³C HSQC of DPS-PMDA shown in Fig. 4c reveal that there are four majorly different protons at aromatic region, which comes with cis-isomer. Unexpectedly nearly cis-isomer covers 100% of the synthesized PAA polymers. The bulky sulfur groups could be the reason behind these dramatic differences. In contrast to this, p-phenylenediamine-PMDA-based PAA polymers were shown to be overwhelmingly in the trans-form [12]. Based on ¹H integration, cis-/trans-isomerism for EDA-PMDA was obtained 50:50. It is possible that the ethylene group drove the EDA-PMDA polymer showing a unique elongation. Another interesting observation was that the EDA-PMDA polymer did only possess amino groups as the end group.

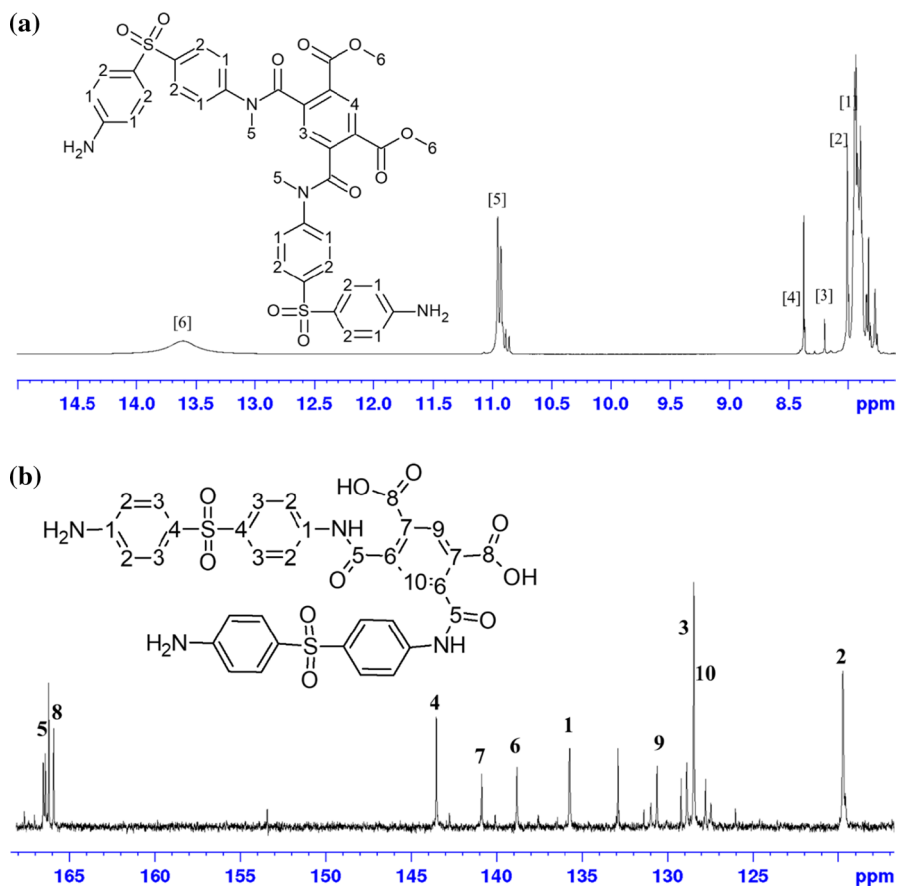


Fig. 4 **a** ^1H spectrum of DPS-PMDA-based PAA polymer synthesized in anhydrous DMAC. Numbers refer to corresponding proton atoms. **b** ^{13}C spectrum of DPS-PMDA-based PAA polymer synthesized in anhydrous DMAC. Numbers refer to corresponding carbon atoms. **c** Merged NMR spectra for ^1H ^{13}C HMBC and ^1H ^{13}C HSQC (circled) of DPS-PMDA-based PAA polymer synthesized in DMAC. **d** Merged NMR spectra for 2D NOESY and ^1H COSY of DPS-PMDA-based PAA polymer synthesized in DMAC. Only 2D NOESY interactions are depicted with arrows

2D NOESY NMR supported with ^1H COSY NMR was performed to evaluate any possible nuclear overhauser effect observed for the polymers in addition to the long-range coupling. 2D NOESY NMR revealed that amino groups on ODA-PMDA and CPDA-ODA PAA polymers showed interaction with both protons on the dianiline source and one proton on the dianhydride source, while for the PMDA-DPS PAA (Fig. 4c) polymer the interaction was only observed for one proton on the diamine source (labeled as 2 in Fig. 4a) and one proton on the dianhydride source (labeled as 4). In addition to these, a slight interaction between the amino group on ODA and the proton labeled as “5” in Fig. 3a, whereas the carboxyl proton and the proton labeled as “4” in Fig. 4a was observed for the NOESY spectrum but not observed for COSY peak. However, it should be stated

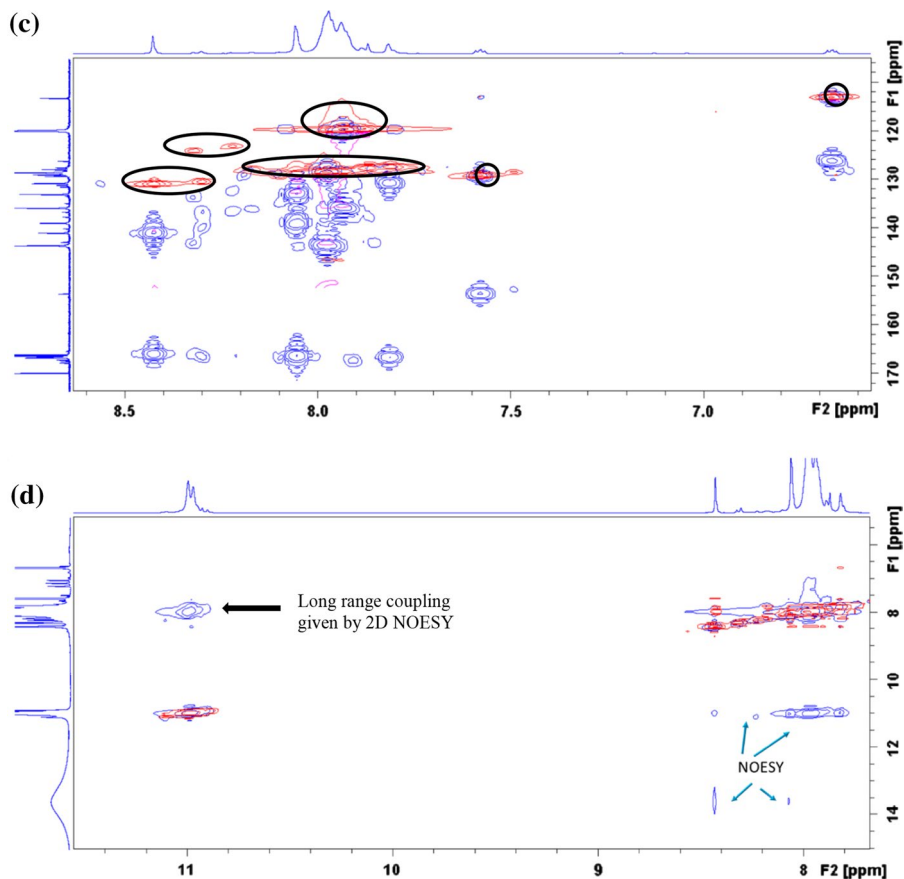


Fig. 4 (continued)

that 2D NOESY experimentation did not give an NOE peak for the carboxyl proton and the proton labeled as “4” in Fig. 4a, which could be related to the lower sensitivity of ROESY for the polymers. NOESY was observed between the aromatic protons and the amino group in EDA-PMDA. All these observations clearly indicate that the monomers presence of $-SOO-$ group greatly altered the 3D conformation of PMDA-DPS PAA polymer in comparison with ODA-PMDA-, EDA-PMDA- and CPDA-ODA-based PAA polymers. Previously, Kariuki et al. reported that p-phenylenediamine-PMDA-based PAA polymers can allow interaction between the proton of amino group and proton on PMDA despite the fact that the monomers were overwhelmingly binding to each other with trans-isomerism [12, 26]. Intramolecular interactions were observed at different intensities for all the synthesized PAA polymers. However, it should be stated that ratio of cis-/trans-isomerism alters the intensity of the intramolecular interactions [8].

2D DOSY NMR was used to find out the average molecular weight of the polymers, which is a common technique for polymers and whose results are

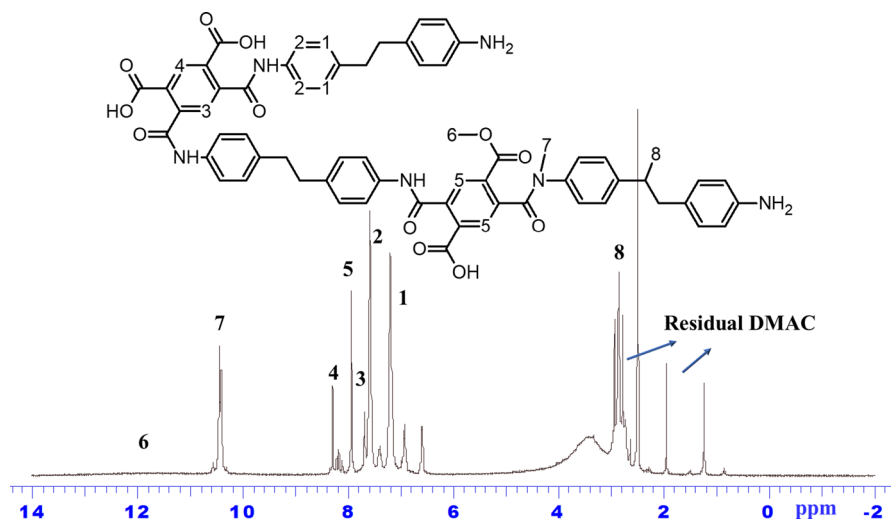


Fig. 5 ^1H spectrum of EDA-PMDA-based PAA polymer synthesized in anhydrous DMAC. Numbers refer to corresponding proton atoms

comparable with those obtained from gel-permeation chromatography [27]. The findings revealed that PMDA-ODA-based PAA polymers had the highest average molecular weight as 2.5×10^5 Da, while PMDA-DPS-based polymer showed the lowest at 6.6×10^4 Da. CPDA-ODA-based polymer gave 1.4×10^5 Da molecular weight, similar to ODA-PMDA PAA polymer. Literature shows that PMDA has higher electron negativity than the rest of the common aromatic dianhydride toward the dianilines, so it is expected to obtain a higher molecular weight for the PMDA-ODA-based PAA polymers. It was shown that solvent choice does not have much effect on molecular weight in the case of using DMAC as the main solvent such as 70:30, DMAC:ethanol and 70:20:10, DMAC:ethanol:water [8]. However, using tetrahydrofuran or acetone as the main solvent decreased the molecular weight dramatically (Fig. 6).

ATR-IR spectra of the PAA polymers for which PMDA was used as the dianhydride source were collected to compare particularly the amide and the carboxyl group peaks. The reason for using ODA-PMDA-based PAA polymer as the standard is because it is the only PAA polymer providing all the characteristic groups in ^1H and ^{13}C NMR. Despite of the minor alterations in IR spectra, ODA-PMDA, EDA-PMDA and DPS-PMDA gave similar spectra. The amide (peak at 3200 cm^{-1}) and carboxyl groups (broad peak at $3300\text{--}2700\text{ cm}^{-1}$) were matched in all cases, which proved the NMR spectra and the assumptions (e.g., absence of carboxyl proton).

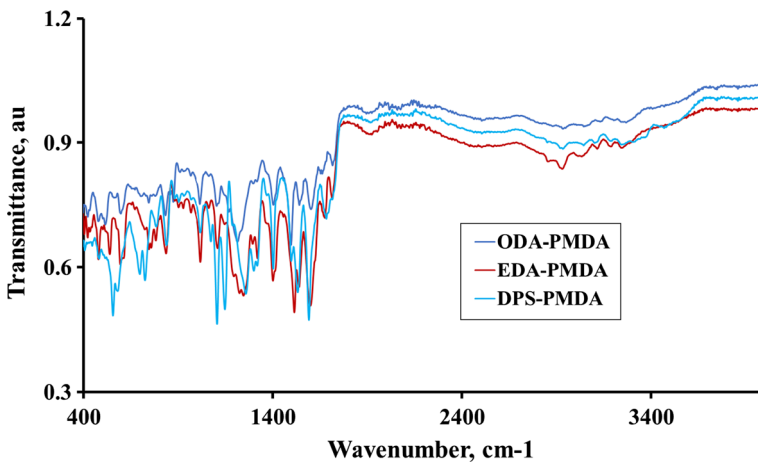


Fig. 6 ATR-IR spectra of some of the PAA polymers

Conclusions

Structural characterization of common polyamic acid polymers synthesized from aromatic monomers was successfully performed. *Cis*-/*trans*-isomers of the polymers, intramolecular interactions, end groups and the average molecular weight of the polymer depend on the monomers and the reaction solvent. The findings can provide a valuable source for the researchers working with polyamic acid and their further functionalized forms, where the chemistry and 3D conformation are important in applications such as drug delivery, sensor and material science applications.

Acknowledgements We acknowledge internal funds of Kastamonu University, the fund number is KÜ-BAP01/2018-33. Thanks to Dr. Abdurrahman Gümüş (İzmir Institute of Technology) for his help to perform NMR studies and Ersin Kanberli (Kastamonu University) for his help to perform ATR-FTIR studies.

Compliance with ethical standards

Conflict of interest The author declares no competing interests.

References

1. Padavan DT, Wan WK (2010) Synthesis and characterization of a novel versatile poly (amic acid) derived from ethylenediaminetetraacetic dianhydride. *Mater Chem Phys* 124:427–433. <https://doi.org/10.1016/j.matchemphys.2010.06.061>
2. Maıga M, Yazgan I, Kariuki VM et al (2018) Brilliant green sequestered poly(amic) acid film for dual-mode detection: fluorescence and electrochemical enzymatic biosensor. *Sens Actuators B Chem*. <https://doi.org/10.1016/j.snb.2017.10.002>
3. Patil YS, Salunkhe PH, Mahindrakar JN et al (2018) Synthesis and characterization of aromatic polyimides containing synthesis and characterization of aromatic polyimides containing tetrahydrofuran-thiazole moiety. *J Therm Anal Calorim*. <https://doi.org/10.1007/s10973-018-7567-2>

4. Terraza CA, Tagle LH, Santiago-garcía JL et al (2018) Synthesis and properties of new aromatic polyimides containing spirocyclic structures. *Polymer (Guildf)* 137:283–292. <https://doi.org/10.1016/j.polymer.2018.01.013>
5. Hsu SL, Wang U, King J, Jeng J (2003) Photosensitive poly (amic acid)/organoclay nanocomposites. *Polymer (Guildf)* 44:5533–5540. [https://doi.org/10.1016/S0032-3861\(03\)00626-8](https://doi.org/10.1016/S0032-3861(03)00626-8)
6. Yao J, Pantano MF, Pugno NM, Bastiaansen CWM (2015) High-performance electrospun co-polyimide nanofibers. *Polymer (Guildf)* 76:105–112. <https://doi.org/10.1016/j.polymer.2015.08.053>
7. Cao Z, Zhao X, Wang D et al (2017) Polymerization of poly- (amic acid) ammonium salt in aqueous solution and its use in flexible printed circuit boards. *Eur Polym J* 96:393–402. <https://doi.org/10.1016/j.eurpolymj.2017.09.023>
8. Yazgan I (2016) Novel poly(amic) acid membrane chemistries with experimentally-controlled pore size, transport, and disinfection properties. State University of New York at Binghamton
9. Noah NM, Omole M, Stern S et al (2012) Conducting polyamic acid membranes for sensing and site-directed immobilization of proteins. *Anal Biochem* 428:54–63. <https://doi.org/10.1016/j.ab.2012.06.008>
10. Yazgan I, Du N, Congdon R et al (2014) Biofunctionalized poly (amic) acid membranes for absolute disinfection of drinking water. *J Memb Sci* 472:261–271. <https://doi.org/10.1016/j.memsci.2014.07.048>
11. Zhang J, Yazgan I, Kariuki VM, Sadik OA (2017) Poly(amic) acid improves the efficiency and stability of PtCr nanoparticle catalyst during ethanol oxidation reaction. *J Electrochem Soc* 164:701–706. <https://doi.org/10.1149/2.0211712jes>
12. Kariuki VM, Hoffmeier JC, Yazgan I, Sadik OA (2017) Seedless synthesis and SERS characterization of multi-branched gold nanoflowers using water soluble polymers. *Nanoscale*. <https://doi.org/10.1039/c7nr01233k>
13. Metz S, Bertsch A, Bertrand D, Renaud P (2004) Flexible polyimide probes with microelectrodes and embedded microfluidic channels for simultaneous drug delivery and multi-channel monitoring of bioelectric activity. *Biosens Bioelectron* 19:1309–1318. <https://doi.org/10.1016/j.bios.2003.11.021>
14. Hsiao PF, Anbazhagan R, Hsiao-Ying C et al (2017) Thermoresponsive polyamic acid-conjugated gold nanocarrier for enhanced light-triggered 5-fluorouracil release. *RSC Adv* 7:8357–8365. <https://doi.org/10.1039/c6ra27563j>
15. Van Vlierbergh S, Sirova M, Rossmann P et al (2010) Surface modification of polyimide sheets for regenerative medicine applications. *Biomacromol* 11:2731–2739
16. Chao D, Wang S, Yang R et al (2013) Synthesis and properties of multifunctional poly (amic acid) with oligoaniline and fluorene groups. *Colloid Polym Sci* 291:2631–2637. <https://doi.org/10.1007/s00396-013-3012-z>
17. Padavan DT, Hamilton AM, Millon LE et al (2011) Synthesis, characterization and in vitro cell compatibility study of a poly(amic acid) graft/cross-linked poly (vinyl alcohol) hydrogel. *Acta Biomater* 7:258–267. <https://doi.org/10.1016/j.actbio.2010.07.038>
18. Yan Y, Jia X, Feng M et al (2017) Synthesis and electrochemical characterization of polyamic acid containing oligoaniline and triphenylamine. *J Polym Sci Part A Polym Chem* 55:1669–1673. <https://doi.org/10.1002/pola.28545>
19. Yang J, Lee M (2004) A water-soluble polyimide precursor: synthesis and characterization of poly (amic acid) Salt. *Macromol Res* 12:263–268
20. Cai D, Su J, Huang M et al (2011) Synthesis, characterization and hydrolytic stability of poly (amic acid) ammonium salt. *Polym Degrad Stab* 96:2174–2180. <https://doi.org/10.1016/j.polymdegradstab.2011.09.008>
21. Colonna M, Berti C, Binassi E et al (2011) Poly(1,4-cyclohexylenedimethylene-1, 4-cyclohexanedicarboxylate): analysis of parameters affecting polymerization and cis-trans isomerization. *Polym Int* 60:1607–1613. <https://doi.org/10.1002/pi.3128>
22. Laue A, Uhlig D, Fiedler B et al (2018) Mechanistic aspects on molecular structure formation of polymeric networks from diisocyanates with amidine compounds. *J Polym Sci Part A Polym Chem* 56:977–985. <https://doi.org/10.1002/pola.28975>
23. Morales-saavedra OG, Rivera E (2006) Linear and nonlinear optical properties of trans- and cis-poly (1-ethynylpyrene) based sonogel hybrid materials. *Polymer (Guildf)* 47:5330–5337. <https://doi.org/10.1016/j.polymer.2006.05.042>

24. Kumar A, Tateyama S, Yasaki K et al (2016) ^1H NMR and FT-IR dataset based structural investigation of poly (amic acid) s and polyimides. *Data Br* 7:123–128. <https://doi.org/10.1016/j.dib.2016.02.006>
25. Han M, Nikles DE (2001) Amine-quinone polyimides. *J Polym Sci Part A Polym Chem* 39:4044–4049. <https://doi.org/10.1002/pola.10027>
26. Kariuki VM, Panetier JA, Schulte J, Sadik OA (2016) Directional templating mechanisms of anisotropic nanoparticles using poly(pyromellitic dianhydride-p-phenylenediamine). *J Phys Chem C* 120:21027–21036. <https://doi.org/10.1021/acs.jpcc.6b03369>
27. Li W, Chung H, Daeffler C et al (2012) Application of ^1H DOSY for facile measurement of polymer molecular weights. *Macromolecules* 45:9595–9603. <https://doi.org/10.1021/ma301666x>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.