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Polymer 45 (2004) 1111–1117

polymer

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Structural determination of Torlon® 4000T polyamide–imide by NMR spectroscopy☆

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Received 15 October 2003; received in revised form 8 December 2003; accepted 9 December 2003

Abstract

High field ^{1}H and ^{13}C NMR spectroscopy and published information in the scientific literature were combined in the determination of the chemical structure of the commercially available Torlon® 4000T, a polyamide–imide which is widely used in applications where good mechanical, thermal and oxidative properties are required. It was found from qualitative and quantitative NMR analysis that the three monomers used to synthesize Torlon are as follows: 1.0 trimellitic anhydride chloride, 0.7 4,4′-oxydianiline, 0.3 *m*-phenylenediamine. It was also shown that the sequence of appearance of the polymer's amide and imide functional groups follows a certain distribution of Amide–Imide, Amide–Amide and Imide–Imide repeat units due to the dual reactive sites, acid chloride and anhydride, of the monomer trimellitic anhydride chloride.

Keywords: Torlon® 4000T; Polyamide–imide; Chemical structure

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1. Introduction

Polyamide–imides (PAI) have been commercially available for several decades. Their synthesis, properties and applications have been extensively described along with those of polyamides and polyimides. Their superior mechanical, thermal and oxidative properties have made them suitable for various applications in industrial processes, transportation, electrical equipment and so on. We are currently studying molecularly imprinted films derived from Torlon® 4000T PAI, which show promising results. The lack of published information on the exact structure of Torlon PAI precipitated this investigation, since it was necessary to determine the molar ratio of imprint molecules to the amide structural groups within the polymer repeat unit (RU). In addition, we are also testing Torlon as a membrane material for vapor permeation and pervaporation. Solvay Advanced Polymer is the producer of the Torlon 4000 series, where Torlon 4000T is the unfilled PAI powder for adhesive applications according to the Polymer Data Handbook [1]. A literature survey on the chemical structure of Torlon 4000T revealed only partial information about the composition of the commercial polymer. In fact, there appears to be only a few articles and patents about the structure and chemistry of Torlon 4000T. In one article [2], Torlon 4203L (4203L is the pure 4000T PAI with the following fillers: 0.5% wt% PTFE and 3.0 wt% TiO_2 [1]) is explicitly named and the composition of its RUs disclosed, but no mention is made as to the source of that information. According to the article, the monomers used in the preparation of commercial Torlon 4000T polymer are trimellitic anhydride chloride (TMAC), *m*-phenylenediamine (*m*-PDA) and 4,4′-oxydianiline (ODA), as illustrated in Scheme 1(B). In the same article, the ratio of the monomers is not disclosed. A literature search using the CAS registry number[1] of Torlon 4000T (CAS# 42955-03-3) and the monomer *m*-PDA (CAS# 108-45-2) retrieved patents [3,4] in which the thermal properties of other synthetic PAIs were compared to those of Torlon without giving structural information on the commercial polymer. According to the CAS Registry File entry for Torlon 4000T, the three components (trimellitic anhydride acid (TMAA),

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☆ NRCC No. 46457.

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[1] Chemical Abstract database, date of search: 7th August 2003.

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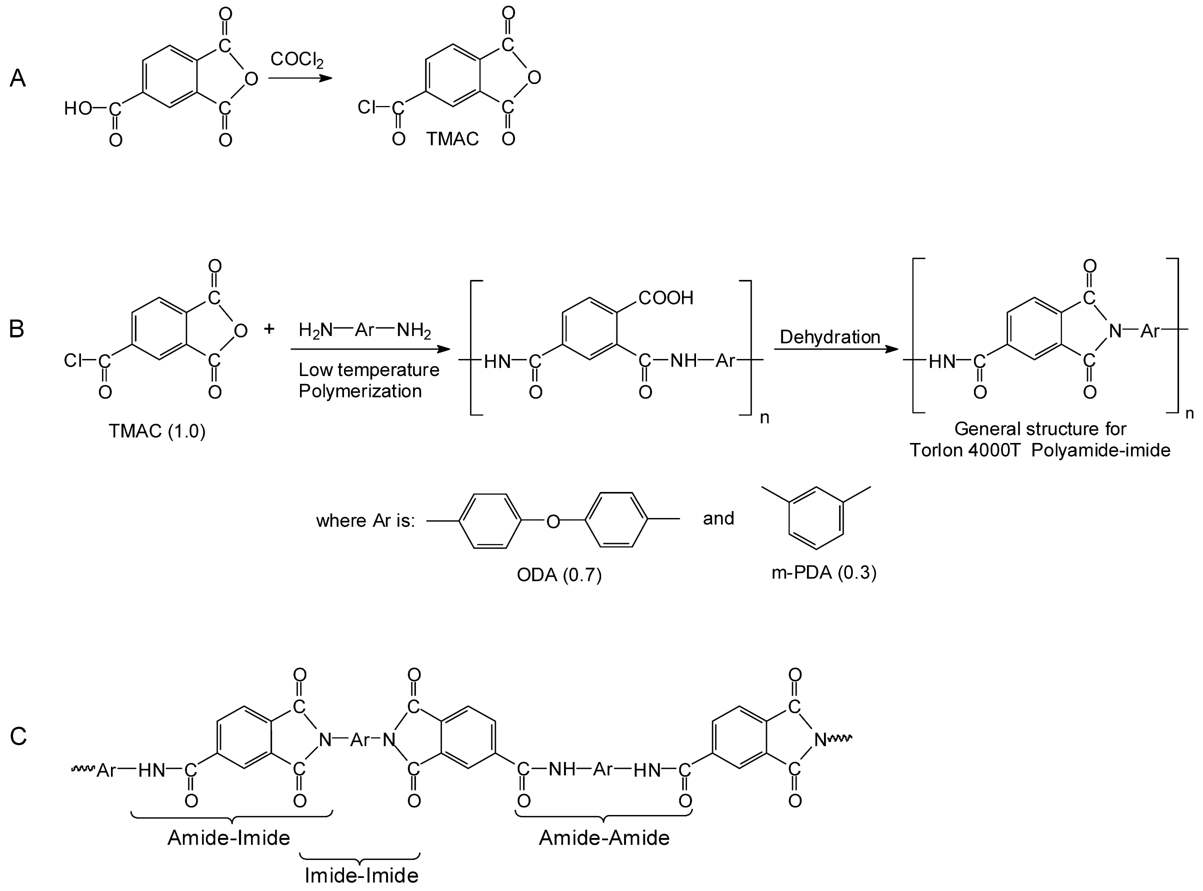
doi:10.1016/j.polymer.2003.12.029



Scheme 1. (A) TMAC by phosgenation of trimellitic anhydride; (B) polyamide–imide Torlon 4000T by low-temperature solution polymerization method followed by dehydration; (C) microstructure of the polymer chain showing the distribution of A–I, I–I and A–A repeat units.

m-PDA, ODA) of the polymer are essentially the same as what was reported in Ref. [2]. Consequently, we decided to exploit the published information about the polymer and fully characterize and determine its structure using high field nuclear magnetic resonance (NMR) spectroscopy. Torlon 4000T PAI polymer is prepared by reacting the monomer TMAC, obtained from the phosgenation of trimellitic acid anhydride (Scheme 1(A)) [5,6], with the diamines mentioned earlier (*m*-PDA and ODA) using a low-temperature solution polymerization method, [7] followed by dehydration as illustrated in Scheme 1(B). Also illustrated, in Scheme 1(C), is the microstructure of the polymer showing all possible RU resulting from the polymerization process. This can be explained by the presence of two reactive sites on the TMAC monomer. Both the acid chloride and the anhydride groups of TMAC are reactive towards aromatic amines, and the diamine monomers can react at either of these two sites by condensation with the acyl chloride or by addition and ring-opening of the anhydride group. The occurrence of the two simultaneous reactions results in a polymer microstructure consisting of head to tail Amide–Imide (A–I) but also as head to head Amide–Amide (A–A) and tail to tail Imide–Imide (I–I) [6,7]. The polyamide intermediate is further converted into polyamide–imide, usually by thermal treatment, resulting in dehydration ring closure to form the imide groups. De La Campa et al. [8] measured the ratio of A–I, A–A and I–I RU for their synthetic PAI polymers prepared from TMAC and 4,4′-diaminodiphenylmethane using a similar low temperature polymerization reaction process. A comparison of the intensities of the distinct methylene signals for the various RU revealed a unit distribution of 40% A–I, 30% A–A, 30% I–I (for a synthetic polymer prepared from similar reaction methods). The proposed general structure of Torlon 4000T is represented in Scheme 1(B), but it really consists of a mixture of RU as illustrated in Scheme 1(C) and as observed and discussed later in Section 3. Our objective, based on published information, was to confirm the presence of each monomer and establish their ratios for Torlon 4000T. The presence of three different monomers used in different proportions as well as the three possible unit distributions inevitably renders the NMR spectral analysis a difficult challenge.

2. Experimental section

Torlon® 4000T polymer was obtained from BP Amoco Polymers Inc. (now Solvay Advanced Polymers) and the NMR solvent DMF-d$_7$ was obtained from Cambridge

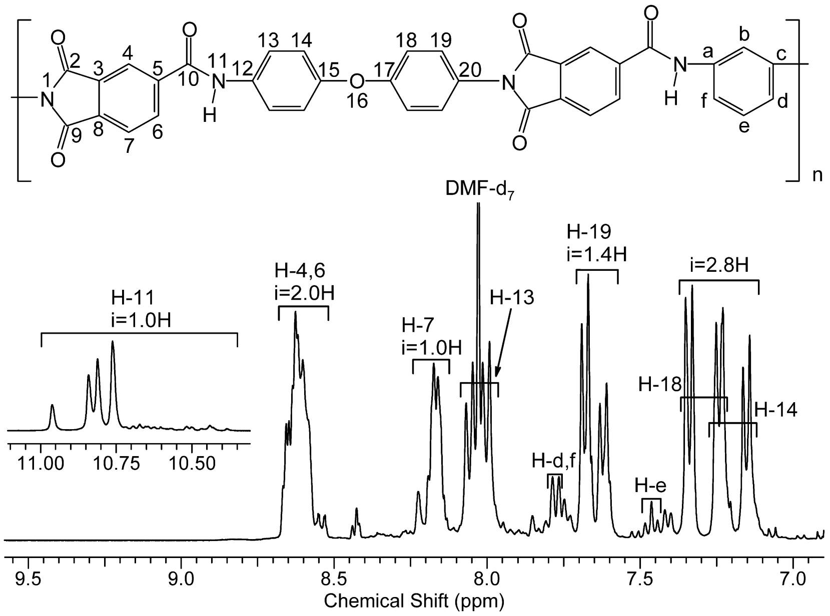


Fig. 1. ^{1}H NMR spectrum of Torlon 4000T PAI dissolved in DMF-d_7. (i = intensity).

Isotope Laboratories Inc. NMR analyses were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz for ^{1}H and 100.579 MHz for ^{13}C. ^{1}H NMR spectra (1D, homonuclear decoupling and 2D-COSY) were obtained from a Torlon polymer sample dissolved in DMF-d_7 (8 wt%) using a 5 mm indirect detection probe. A 10 mm broadband probe was used for acquiring a 1D ^{13}C NMR spectrum with quantitative carbon nuclei intensities. The ^{1}H noise decoupled carbon spectrum was acquired using a 45 degree pulse angle, 5 s acquisition time and 30 s relaxation delay for 4096 scans on a concentrated polymer sample in DMF-d_7 (17 wt%). Decoupling of the hydrogen frequencies was done only during the acquisition time in order to obtain quantitative carbon intensities. 2D carbon–hydrogen correlation (HETCOR) spectra were recorded for one-bond ^{1}J C–H (140 Hz) and three-bond ^{3}J C–H (7.5 Hz) spin correlations. For each analysis, the deuterated DMF aldehyde signals were used as the reference (^{1}H C$\underline{H}$O 8.03 ppm, ^{13}C $\underline{C}$HO 163.15 ppm).

3. NMR analysis

3.1. ^{1}H NMR predominant intensity signals assignment

An initial assessment of the NMR spectra obtained for Torlon indicated that the polymer was not composed of a single repetitive unit. Additional smaller signals as well as peak integration values from both ^{1}H and ^{13}C NMR suggested that trimellitic anhydride and oxydianiline were not the only monomers used in the preparation of Torlon 4000T as suggested in the Polymer Data Handbook [1]. After having assigned most of the predominant ^{1}H signals, it was evident that another diamine was present as a co-monomer in a smaller proportion. Fig. 1 shows the aromatic region along with signal assignments for the ^{1}H NMR spectrum of Torlon 4000T PAI dissolved in DMF-d_7. Most signals were assigned based on well-known proton NMR chemical shift displacements resulting from electron shielding/deshielding of the hydrogen nuclei by the inductive effects or from the diamagnetic anisotropy of various neighboring functional groups. For example, the inductive effect of the electron-rich ether linkage of the ODA segment has a shielding effect on the phenyl rings' *ortho*-oxygen protons, thus their shifts to lower frequency (H-14, 18; 7.10–7.38 ppm). On the other hand, the induced magnetic field resulting from circulating π electrons found in the carbonyl of the amide groups has a deshielding effect on the neighboring aromatic hydrogen atoms of the trimellitic group, consequently shifting them to higher frequency (H-4, 6; 8.50–8.70 ppm). ^{1}H homonuclear decoupling experiments and ^{1}H–^{1}H correlation (COSY) shown in Fig. 2, revealed the position of H-7 (8.11–8.25 ppm) through a 3-bond coupling with H-6. Assignment of H-13 (7.95–8.10 ppm) and H-19 (7.57–7.71 ppm) was determined by COSY, which showed 3-bond coupling from these signals with the already assigned ODA *ortho*-ether H-14 and H-18. It is the presence of a 3-bond ^{13}C–^{1}H coupling between C-13 and the amide H-11 found in a 2D ^{13}C–^{1}H correlation spectrum that allowed unambiguous assignment of the numerous ^{1}H aromatic signals arising from the ODA segment (H-13, 14, 18, 19). This C-13–H-11 correlation made it possible to distinguish the *ortho*-amide proton H-13 from the *ortho*-imide H-19. The presence of these multiple signals originating from atoms in the same positions is due to the distribution of diamine units as explained earlier and shown in Scheme 1(C). The general structure shown in Fig. 1 is not truly representative of the actual RU

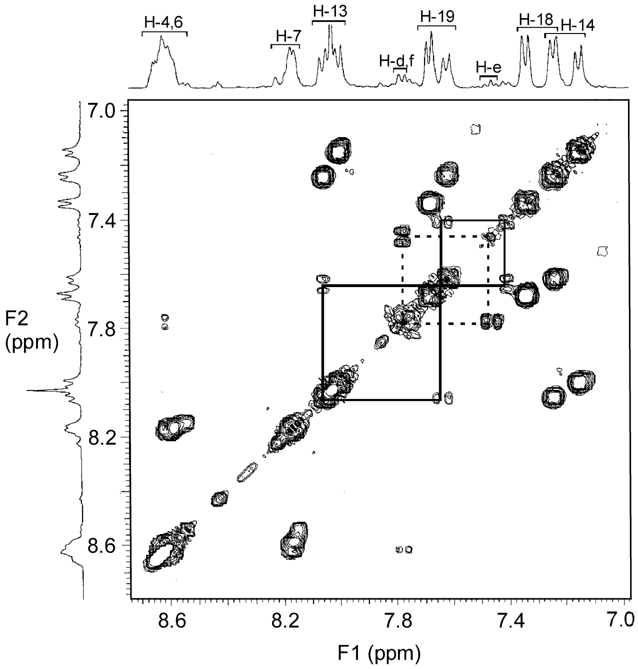


Fig. 2. COSY spectrum of Torlon 4000T PAI in DMF-d_7.

distribution, in which ODA groups can be bordered in the manner A–I, A–A or I–I. Consequently, phenylene protons near an amide linkage (H-13 or 14) appear as two distinct signals because the other extremity of the ODA monomer consists of either an amide or an imide. The same principle is applicable to phenylene protons near the imide linkage (H-18 or 19) being influenced by either an amide or imide group at the other end of the ODA monomer. As a result of this, all ODA proton nuclei appear as two distinct signals. Furthermore, they are all doublets due to 3-bond aromatic spin–spin coupling of about 8 Hz. The labile amide NH proton chemical shifts (10.35–11.00 ppm) were validated by proton–deuterium exchange using D_2O. Assignment of the remaining smaller signals believed to arise from a second diamine monomer will be discussed later.

3.2. ^{13}C NMR predominant intensity signals assignment

Fig. 3 shows the aromatic region with partial signal assignments for a ^{13}C NMR spectrum (^{1}H noise decoupled during acquisition) of Torlon PAI dissolved in DMF-d_7. The carbon signals were assigned using well-known carbon chemical shifts displacement as well as $^{13}C-^{1}H$ correlation spectroscopy of ^{1}J C–H (140 Hz) and ^{3}J C–H (7.5 Hz). The carbon atoms attached to heteroatoms, mainly those attached to oxygen atoms, were valuable in the determination of the presence of two diamine monomers and supported the evidence observed in ^{1}H NMR. Amide carbon C-10 at high frequency (164.2–165.4 ppm) was found to exhibit coupling with the NH proton. Consequently the other signals at higher frequency were assigned to the imide carbonyl C-2, 9 (167.0–168.5 ppm). The two carbon atoms C-15, 17 constituting the ODA ether segment also appeared at high frequency (153–159 ppm) due to their direct connection with the electronegative oxygen atom. On the other hand, carbon atoms C-14, 18 located at the *ortho* position of the same ether linkage are subject to electron shielding from the oxygen atom due to delocalization through aromatic π bonds; hence their shift to lower frequency (118.5–121.5 ppm). Additional carbon signals

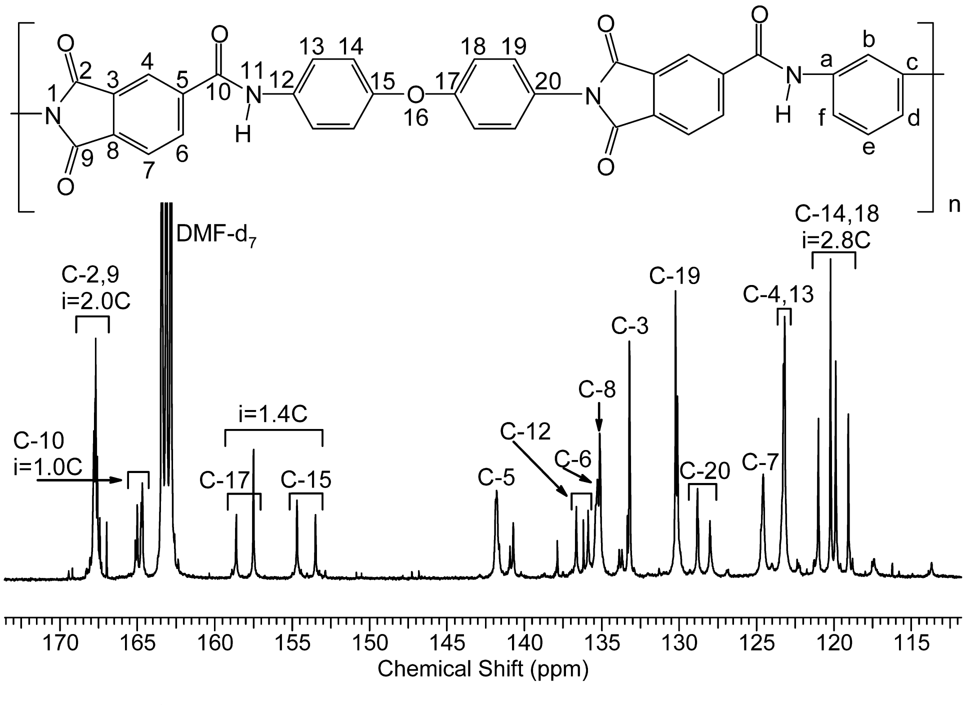


Fig. 3. ^{13}C NMR spectrum (^{1}H noise decoupled during acquisition time) of Torlon 4000T PAI dissolved in DMF-d_7. (i = intensity).

were assigned based on 1 or 3-bond CH coupling. Once again, as seen in ^{1}H NMR, groups of signals arising from carbon atoms in the same position were observed due to the distribution of A–I, A–A and I–I RU. For example, the ether linkage carbon atoms C-15 and C-17 appear as four signals (153–159 ppm) of which two are of equal intensity. This is readily explained by examining each RU displayed in the microstructure of Scheme 1(C). For an A–I RU, C-15 and C-17 are chemically non-equivalent atoms due to the different amide or imide linkage on the oxyphenylene segment. The intensities of their respective signals are expected to be identical as there is one C-15 for every C-17 of an A–I RU. On the other hand, A–A or I–I RU have C-15 and C-17 equivalent; hence there is one signal for both carbon atom of an A–A RU and one signal with a different chemical shift for an I–I RU. As expected, we also observed the same pattern for low frequency carbon atoms C-14, 18 and C-12, 20 (C–N) which are also affected in an identical way by the RU distribution. Using the intensity values from all of these signals, one can estimate the ratio of A–I, A–A and I–I RU in Torlon in a similar way to that of De La Campa et al. [8] for his synthetic PAI polymers. The Advanced Chemistry Development (ACD) HNMR prediction software [9] suggests that the chemical shift of an aromatic ether linkage carbon atom of an I–I RU is 6.5 ppm less than the same carbon atom of an A–A RU. Based on ACD predictions, we suggest that the highest intensity C–O signal at 157.5 ppm is of A–A RU, the smaller C–O signal at 154.8 ppm is of I–I RU and the two other signals of equal intensity (153.5 and 158.6 ppm) are C–O–C carbon atoms from A–I RU. Assuming the prediction is correct, the distribution ratio for the ODA segment in Torlon 4000T is in the order of: 38% A–I: 35% A–A: 27% I–I. The remaining smaller carbon signals from the *m*-PDA segments were not assigned due to the complexity of the spectrum and also because their assignment was not essential for the structural determination. On the other hand, the integral values of regions of the spectrum were utilized as it will be described later.

3.3. Determination of monomer ratios used in the preparation of Torlon

As mentioned before, Torlon is made from TMAC and two diamines of which one is ODA. As for the other diamine, we made the initial presumption that it is unknown, in order to validate by NMR what was reported in Ref. [2]. Considering the nature of the polymerization process, every RU must be comprised of one imide and one amide functional group independently of the ratio of each of the diamine monomers. Thereupon, it was decided to set the integration of the amide hydrogen signals H-11 (10.35–11.00 ppm) to 1.00. The integration values of the previously assigned major aromatic signals revealed the presence of 1.0 trimellitic group for 0.7 oxydianiline group. That ratio was obtained by comparing the integration values from signals arising exclusively from the trimellitic group, H-4, 6, 7 (3.0H), with signals from the oxydianiline group, H-13, 14, 18, 19 (5.6H). From this ratio we can conclude that another diamine, in addition to the monomer ODA, was used in the preparation of Torlon 4000T. The ^{13}C NMR spectrum is consistent with the previous conclusions drawn from the ^{1}H NMR spectrum. Using the same logic as before, two imide and one amide carbon atoms must be present for each polymer RU. Therefore, the carbonyl signals C-2, 9 (167.0–168.5 ppm) were set to a total integration value of 2.00. As a result, the integration values of the distinct ODA aromatic carbon C-15, 17 (1.37C) and C-14, 18 (2.90C) matched the expected number of carbon atoms for a ratio of 0.7 oxydianiline group per 1.0 trimellitic group supporting in this way what was uncovered in ^{1}H NMR. Based on these NMR results, the ratio of monomers used in production of the commercial polyamide–imide is believed to be: 1.0 TMAC, 0.7 ODA and 0.3 other diamine.

3.4. Elucidation of the structure of the second diamine monomer used in the preparation of Torlon PAI

As previously mentioned in the introduction and found in the literature [2], the third component in Torlon 4000T was found to be *m*-phenylenediamine (*m*-PDA). It was previously established in the preceding NMR discussion that for each average RU of Torlon, there are 1.0 trimellitic group, 0.7 oxydianiline groups and therefore 0.3 unknown diamine groups. From that ratio, one can use the integration values in both ^{1}H and ^{13}C NMR to find the C and H composition of the unknown diamine. In ^{1}H NMR, two regions were integrated: region 1 from 10.35–11.00 ppm (1.00H) attributed to the amide H-11 protons, region 2, defined as I total in the equation below, is from 7.0–8.8 ppm (9.84H) and includes all aromatic protons. Note: the intensity value of the aldehyde signal from the solvent DMF-d_7 (8.04 ppm) was removed from the integration of aromatic region 2. Subtracting the known number of aromatic protons originating from the trimellitic and oxydianiline groups from an average polymer RU leaves the number of protons found on the unknown diamine monomer group:

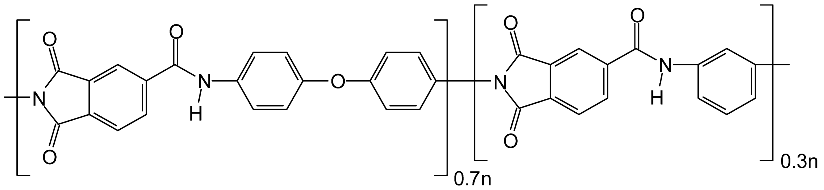
$$\text{I total} = [1.00 \times \text{trimellitic H}] + [0.70 \times \text{oxydianiline H}] + [0.30 \times \text{unknown diamine H}]$$

$$\text{I total} = [1.00 \times (\text{H-4, 6, 7})] + [0.70 \times (\text{H-13, 14, 18, 19})] + [0.30 \times (x\text{H})]$$

$$9.84\text{H} = [3\text{H}] + [5.6\text{H}] + [0.30 \times x\text{H}]$$

$\therefore x = 4.1$ H atoms in unknown diamine group of one averaged RU of Torlon.

The chemical shift of the signals from these 4Hs implies they are aromatic protons. With this information, one could



Scheme 2. The proposed general structure for Torlon 4000T polyamide–imide.

already suspect the unknown monomer to be phenylenediamine. A similar type of calculation was applied to the quantitative ^{13}C NMR spectrum. As before, the imide signals from C-2, 9 (167.0–168.5 ppm) arising from the trimellitic group were used to set the integration value to 2.00C. It is difficult to obtain accurate integration data for ^{13}C NMR spectrum due to several factors such as long relaxation delays for some carbon atoms, poor baseline because of low nucleus sensitivity (high noise) and large spectral window (over 5000 Hz). Therefore the same FID was independently processed five times and the integration numbers were computed in the following equation to yield an average number of carbon atoms equal to 5.5 ± 0.5 for the unknown diamine.

$$\text{I total} = [1.00 \times \text{trimellitic C}] + [0.70 \times \text{oxydianiline C}] + [0.30 \times \text{unknown diamine C}]$$

$$\text{I total} = [1.00 \times (\text{C-2-10})] + [0.70 \times (C\text{-12-15, 17-20})] + [0.30 \times (x\text{C})]$$

$$16.05\text{C} = [9\text{C}] + [8.4\text{C}] + [0.30 \times x\text{C}]$$

$\therefore x = 5.5$ C atoms in unknown diamine group of one averaged RU of Torlon.

Similarly to what was observed before in ^{1}H NMR, the chemical shift of the signals from these 6 Cs indicates they are aromatic. The number of hydrogen (4H) and carbon (6C) atoms derived from the previous calculations and the chemical shift displacements of the minor signals seen in both observed nuclei suggests that the unknown diamine used in the preparation of Torlon 4000T PAI is phenylenediamine, with both amine groups at either *ortho*, *meta* or *para* positions of the phenyl ring. Close examination of the small aromatic signals on the ^{1}H NMR spectrum (Fig. 1) and their connectivity through the COSY spectrum (Fig. 2) strongly supports the *meta* substituted phenylenediamine structure, as suggested in the literature. As explained before, the distribution of many different RUs multiplies the number of signals from the hydrogen atoms in the same position and therefore more than one signal is expected from each atom of the same phenylenediamine group. The 2D COSY spectrum shows coupling taking place between the triplet at 7.47 ppm (1H) and the doublet at 7.78 ppm (2H) (Fig. 2, dotted line). In the same COSY spectrum, an overlapped signal at 7.64 ppm is 3-bond coupled with a doublet signal at 7.41 ppm and another overlapped signal at 8.06 ppm (Fig. 2, full line). Of the three possible phenyl substitution sites, only the *ortho* or *meta* substitution could show spin-coupled systems such as the ones observed in the COSY spectrum. *Ortho* dianiline is a possible but unlikely choice due to excessive steric hindrance. We also could not find any reports in the literature of polyamide–imides synthesized with the *ortho* substituted monomer and therefore, *meta* dianiline is believed to be the second diamine monomer used in the preparation of commercial polyamide–imide Torlon 4000T. Based on the NMR analysis, the proposed general structure for an average RU of the polymer is displayed in Scheme 2.

4. Conclusions

Published information on Torlon engineering plastics and ^{1}H and ^{13}C NMR spectroscopy were combined in the determination of the chemical structure of Torlon 4000T polyamide–imide, which we are currently utilizing for the preparation of molecularly imprinting membranes. Evidence was found that the three following monomers, trimellitic anhydride chloride, oxydianiline and *m*-phenylenedianiline are present in the polymer in the following ratio 1.0:0.7:0.3. It was also shown that the sequence of appearance of the polymer's amide and imide functional groups follows a certain distribution due to the dual reactive sites, acid chloride and anhydride, of the monomer trimellitic anhydride chloride. The presence of Amide–Imide, Amide–Amide and Imide–Imide RUs were detected by NMR.

Acknowledgements

The authors gratefully acknowledge support from Dr. Katherine Cook from the Canada Institute for Scientific and Technical Information (CISTI) for conducting the scientific literature searches.

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