SOLUTION NMR CHARACTERIZATION OF POLYIMIDES BASED ON 4,4'-DIAMINOTRIPHENYLMETHANE

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Introduction

Aromatic Polyimides find widespread technological applications due to their unique combination of low dielectric constant, chemical resistance and high thermal and thermooxidative stability. [1-4] Polyimides (PIs) can be conveniently prepared by the condensation polymerization of dianhydrides with diamines. In general, polyimides are synthesized by a multistep method through a polyamic acid or a polyamic ester intermediate. Direct one-step high temperature polycondensation is an alternative route to the preparation of PI when they are soluble in organic solvents.

We have previously reported that polyimides obtained by one-step high-temperature polycondensation of diaminotriphenylmethane (DA-TPM) and aromatic dianhydrides yield flexible and tough films with good mechanical properties. [5-7] Properties of these polyimides, named PI-TPMs, are mainly due to the homogeneity of the repeating units in the polymer backbone, which was demonstrated by UV-visible spectroscopy, CP-MAS ^{13}C-NMR and WAXD analysis. [7,8].

PI-TPMs are soluble in DMF, so they are amenable to be studied by solution NMR in that solvent. In this paper we report a study of the solution NMR spectra of PI-TPMs, obtained by the one-step route, in DMF-d_7. The structure of the model compound and the polymers are shown in Figure 1. Molecular characteristics of the model compound and polymers were obtained by a geometry optimization, following by conformational analysis and PM3 molecular orbital semiempirical calculations. The correlation between the calculated net atomic charges localized at ring carbons and their ^{13}C NMR chemical shifts are also discussed.
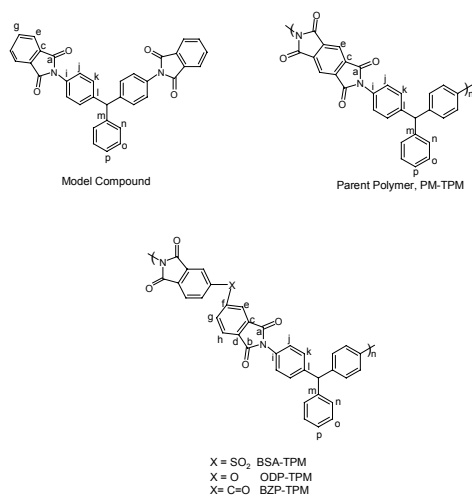

Figure 1. Structures of the Model compound, Parent Polymer (PM-TPM) and the other PI-TPMs studied in this work.

Experimental.

Synthesis of Model Compound. Model compound were obtained by condensation of phthalic anhydrides with DA-TPM, as described elsewhere.[7]

Synthesis of Polyimides. The polyimide films of PI-TPMs were prepared via polycondensation of DA-TPM with the aromatic dianhydrides by one step high temperature procedure in nitrobenzene. [5-7] Structures of PI-TPM are shown in Figure 1, and the used nomenclature is based on the dianhydride moiety as PM-TPM, BSA-TPM, ODP-TPM and BZP-TPM.

NMR Measurements. All the solution NMR measurements were performed at ambient probe temperature using 5 mm o.d. sample tubes. Solution ^{1}H and ^{13}C NMR spectra in DMF-d_7, and CDCl$_3$ were recorded using Varian Gemini 200 and Varian Unity *Plus* 300 spectrometers. Oxygen was removed from samples by freeze-pump thaw cycles. The chemical shifts are reported taking as a reference the chemical shift positions of the solvent with respect to TMS.

For APT, COSY and ^{13}C/ [1]H HETCOR experiments, standard pulses sequence were used. [9-11] For the long-range HETCOR experiment, J(C,C,H) was assumed to be 8 Hz. NOE Difference spectra (homonuclear [1]H{[1]H} decoupling experiments) were recorded using the *cyclenoe* sequence. 1024 scans were recorded for each spectrum.

Theoretical calculations. Energy minimization, conformational searching and semi-empirical calculations were performed using Alchemy 2000 program system from Tripos. Net atomic charges were obtained for the minimum-energy conformer by a PM3 single point semiempirical calculation. The molecular structure for the lowest energy conformer of the BZP-TPM repeating unit obtained by this method is depicted in Figure 2. The torsion angles defining the chain conformation are also shown.
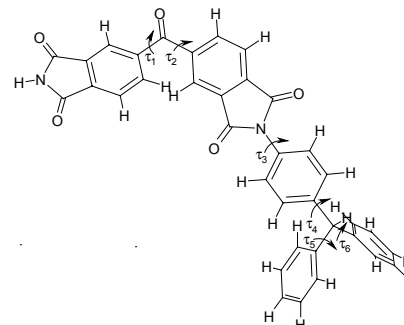

Figure 2. Molecular structure of the minimum-energy conformer for the BZP-TPM repeating unit.

Results and Discussion

^{1}H and ^{13}C NMR spectroscopy. To assign ^{1}H and ^{13}C spectra of model compound and PI´s, tentative chemical shifts were determined using substituent additivity rules**.** The APT spectrum allows to determine the number of protons attached to each carbon. [13]C/^{1}H chemical shift correlation experiment permits the assignment of the protonated carbons, while the non-protonated carbons connectivity is obtained from the long-range HETCOR diagram.

The ^{1}H NMR spectrum for BZP-TPM is presented in Figure 3. A discussion on the main features of this spectrum is given elsewhere. [12] This spectrum is the base for NOE measurements described below.
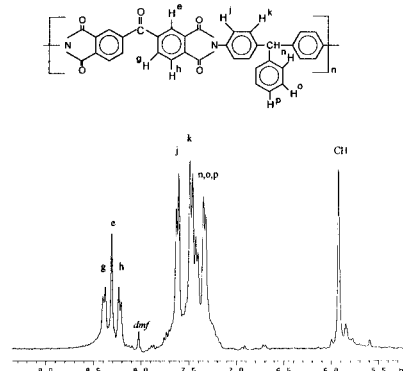

Figure 3. 300.1 MHz high-resolution 1H NMR spectrum (5.1-9.4 ppm region) of BZP-TPM in *dmf-d_7*

NOE Difference Spectrum of BZP-TPM. Nuclear Overhauser Enhancements (NOEs) are useful to understand the conformation and steric configuration of substituents along the polymer backbone. [13,14] NOEs depend in a complex way upon the distances from the observed nucleus to the nearest neighbor protons.

In Figure 4, NOE Difference spectra for BZP-TPM upon irradiation of the different protons are shown. As expected, NOE between neighbors atoms are present, but negative peaks near irradiated protons are due to partial saturation by the used irradiation. Spectra obtained upon irradiation of protons *e*, *g* and *h* show

a positive NOE with protons *j* and *k*. There is a very small NOE interaction between protons *e*, *g* and *h* and proton *n*. When CH is irradiated, a positive NOE can be distinguished for protons *j, k* and a small negative NOE with proton *n*. According to Figure 1, interatomic distances are the following (two values are reported due to inequivalence of protons in the conformer): d_{en} = 8.9, 11.1 Å, d_{ej} = 5.0, 6.8 Å, d_{ek} = 7.5, 8.8 Å, d_{gn} = 11.3, 13.4 Å, d_{hn} = 9.8, 11.7 Å d_{gj} = 7.2, 7.9 Å, d_{gk} = 9.6, 10.2 Å, d_{gh} = 5.0, 6.8 Å, d_{hk} = 7.4, 8.8 Å, d_{CH-j} = 4.8, 5.3 Å, d_{CH-k} = 2.7, 3.5 Å and d_{CH-n} = 2.6,3.6 Å. Distances from protons *e*, *g* and *h* to proton *n* indicates that these atoms are very far from each other, so peaks are not expected in the NOE difference spectra [15] Because theoretical calculations are obtained for one repeating unit in the gas phase, solvent interactions and effects of the other monomeric units are not considered. This probably means that the real conformation of the overall polymer in *dmf* place these protons in a closer position.
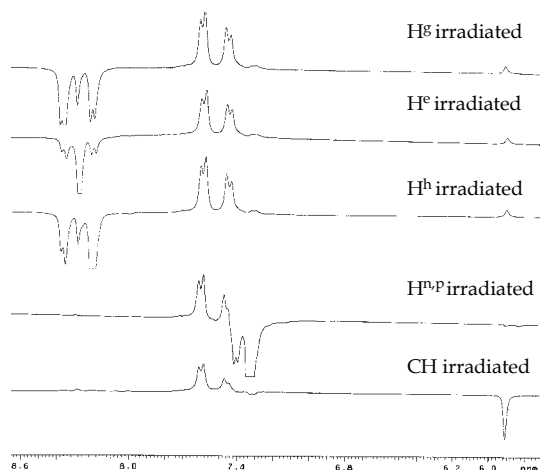

Figure 4. NOE difference spectra of BZP-TPM.

Semiempirical calculations. An optimization of the electronic structure by PM3 semiempirical molecular orbital calculations was carried out. Molecular characteristics correspond to the minimum-energy conformer using the optimization routines of the program. Calculated net atomic charges are shown in Table 1.
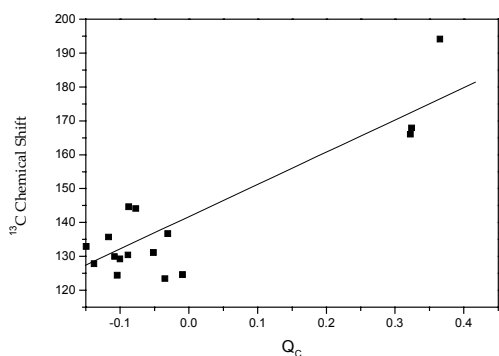

Figure 5. Plot of ^{13}C Chemical shifts against the net atomic charge of the ring carbons for BZP-TPM.

^{13}C chemical shifts depends on several effects such as the hybridization state of carbon, inductive effects of substituents, electric fields, hyperconjugation and mesomeric interactions among other factors. For aromatic systems, delocalization of charges across the π electron systems produce large shielding changes due to the dependence of the paramagnetic shielding term upon the effective nuclear charge. In figure 5, a plot of the ^{13}C NMR chemical against net atomic charges for BZP-TPM is shown. Similar plots were obtained for the other molecules. Fitting to a straight line show a poor correlation (r = 0.89). This means that other effects aside from the mesomeric (neighbor group anisotropy, steric and solvent

interactions, redistribution of π electron densities, etc.) have an important contribution to the shielding of aromatic carbons of the polyimide system. [16]

Table 1. Net atomic charges on carbons, Q_C, of model compound and PI-TPMs obtained by PM3 semiempirical calculations.

Atom	Model compound	Parent Polymer	X = O	X = SO$_2$	X = CO
a	.3280	.3113	.3222	.2942	.3224
b			.3280	.2751	.3244
c	-.1392	-.1232	-.1075	-.2090	-.1493
d			-.1661	-.0542	-.1168
e	-.0254	.0403	-.1084	.1415	-.0093
f			.0900	-.8166	-.1511
g	-.0882		-.1080	.0823	-.0306
h			.0058	-.0828	-.0348
i	-.0440	-.0647	-.0491	-.0988	-.0516
j	-.1380	-.1290	-.1391	-.1175	-.1379
k	-.0835	-.0864	-.0827	-.0837	-.0885
l	-.0925	-.0781	-.0895	-.0810	-.0875
m	-.0774	-.0725	-.0765	-.0861	-.0772
n	-.0980	-.1035	-.1032	-.1034	-.1080
o	-.1017	-.1028	-.1010	-.1000	-.1002
p	-.1032	-.1035	-.1038	-.1033	-.1042
CH	.0728	.0897	.0697	.0792	.0720
C=O					.3654

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