Mobility study of amorphous polymers by high-resolution NMR at solid-state

Naira M. da Silva, Maria Inês B. Tavares *

Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro,
P.O. Box 68525, 21945-970 Rio de Janeiro, RJ, Brazil

Summary
Mobility of amorphous polymers such as poly(vinyl chloride) (PVC), atactic polypropylene (PPA) and ethylene-propylene-diene terpolymer (EPDM) were studied by proton spin-lattice relaxation time (T_1 H), proton spin-lattice relaxation time in the rotating frame ($T_1{}^H\rho$), and dipolar dephasing pulse sequence. The data are discussed in terms of mobility and by the distribution of configurational sequences.

Introduction
NMR relaxation measurements can be used to elucidate certain aspects of polymer microstructure and the properties that are affected by molecular mobility. The spin-lattice relaxation time measures the time in which the nuclear spin system comes to thermal equilibrium with the lattice. T_1 is used to have the response of global homogeneity[1-4]. The proton spin-lattice in the rotating frame is analogous to T_1, except the difference in the frequency range detection, because of this $T_1\rho$ determines the local molecular mobility[5,6]. Thus T_1 and $T_1\rho$ have been used as experimental sources of information on internal molecular motion in polymers, as a consequence of domain microstructure[7,8].
Dipolar dephasing is normally used to observe non-protonated carbons[5]. Therefore, carbons that present high mobility are also detected. Thus, using this technique it is possible to get useful information from the spectrum.
The present work focus on the evaluation of the difference on molecular mobility in amorphous polymers.

Experimental
Poly(vinyl chloride) (PVC): PVC Norvic, comercial, was received from Camaçari (Bahia). This polymer was characterized as to molecular weight, thermal stability and structure. The viscometric molecular weight was found to be 77.800, in tetrahydrofuran as a solvent at 30°C. The number average and weigth average molecular weights were found to be 30.000 and 90.0000, respectively by use of a Toyo Soda HLC 803A chromatograph, operating with G2000 HXL and G4000 HXL columns of type TKS gel, at 24°C, and tetrahydrofuran as solvent (0.05% solution). The glass transition temperature (Tg) was 85°C by differential scanning calorimetry (DSC). PVC was also characterized by infrared spectroscopy (FT-IR, Perkin-Elmer 1720x) and by nuclear magnetic resonance spectroscopy (NMR Varian 400 MHz).

---

* Corresponding author

Polypropylene (PPA): This polymer was characterized as to molecular weight, thermal stability and structure. The number average molecular weight was found to be 4000 and the weight average molecular weight was 25900, respectively, by the use of a Waters 600 E, at 24° C, and toluene as solvent (0,05% solution). The glass transition temperature was found to be -16°C, measured by differential sacnning calorimetry (DSC Dupont 9900).

Ethylene-Propylene-Diene Terpolymer (EPDM): The molecular weight distribution (M_w/M_n) of the samples was determined by GPC (2.82 for EPDM A, 11.80 for EPDM B and 3.65 for PPA). The grades are listed in Table 1.

Table 1 - EPDM Grades.

Physical properties	EPDM A	EPDM B
Mooney viscosity ML $_{1+4}$ (100°C)	47	38
Iodine index	19	6
Volatiles (%)	0.5	0.4

- NMR Measurements:
All samples were analysed on a Varian VXR 300 Spectrometer at 75.4MHz for carbon-13 nuclei. All measurements were made at ambient probe temperature, performed using gated high power decoupling. Zirconium oxide rotors of 7 mm diameter with Kel-F caps were used to acquire the NMR spectra. The chemical shift was scaled using hexamethyl benzene, and magic angle spinning was employed to all the samples to reduce the chemical shift anisotropy. Proton spin-lattice relaxation time $(T_1 H)$ were obtained by inversion-recovery method [180° -τ -90°] and values of $T_1{}^H\rho$ from the signal following a spin-locking period at r.f. power equivalent to 40KHz. Typically four transients were used for each point and 64 points were used for each measurements. These measurements were carried out in a custom-built relaxation spectrometer[9] operating at 60MHz for protons. The dipolar dephasing technique was done in the cross-polarization mode with magic angle spinning and the gated used for selecting nuclei was 40µs.

Results and discussion
Table 2 shows the values of proton spin-lattice relaxation time for the polymers, measured by inversion-recovery technique.

Table 2 - T_1 H values of polymers in study.

Sample	T_1 H (s)
PVC	1.5
PPA	0.25
EPDM	0.08

From the data of proton T_1 listed on the aforementioned Table, it is clear that PVC is more rigid than PPA and also EPDM, as expected. EPDM presents high mobility relative to the others as it is an elastomer. The spin-diffusion is averaged and T_1 H will only give information on global mobility. So, just one microdomain was detected for all polymers.

Proton T_1 ρ was obtained from the spin-locking method and the results are listed on the Table 3.

Table 3 - Proton T_1 ρ data of the polymers.

Sample	T_1 ρ (ms)	
	short values	long values
PVC	3.5	11.5
PPA	0.8	9.1
EPDM	4.2	21.0

Direct measurements of proton spin-lattice relaxation time in the rotating frame show an exponential decay and those were analysed into two components. The values of T_1 ^{H}ρ are normally associated with domain mobiltity. So, as expected EPDM is more flexible than the others. PPA has two domains with distinct less mobilities when compared with PVC. In our opinion the reason for that can be attributed to the configurational sequence distribution, maybe, due to different relaxation mechanism.

The analyses of configurational sequence distribution for both polymers are illustrated at Table 4.

Table 4 - Distribution of configurational sequence of PVC and PPA.

Sample	Isotatic (%)	Syndiotatic (%)	Heterotatic (%)
PVC	22.0	40.0	38.0
PPA	20.5	11.7	67.7

PVC is an amorphous polymer, but it has a great contribution of syndiotactic sequences, that seem to be more flexible than the isotactic sequences. PPA is much more atactic and the major contribution comes from isotactic sequences, for this specific sample it was found that the isotactic form is more rigid than the others.

The dipolar-dephasing spectra were also recorded to confirm the mobile region present in all polymers. By analysing the PVC spectrum both peaks were detected at different chemical shift observed for a normal carbon-13 NMR analysis. The EPDM spectrum was found to be the same by using carbon-13 NMR CP/MAS. As for PPA a shoulder was encoutered in the methyl region, the chemical shifts correspond to heterotactic and syndiotactic sequences, which confirms that these sequences belong to the mobile region (See Figure 1). In a previous work it was found that the isotactic sequence is part of the rigid domain[10].
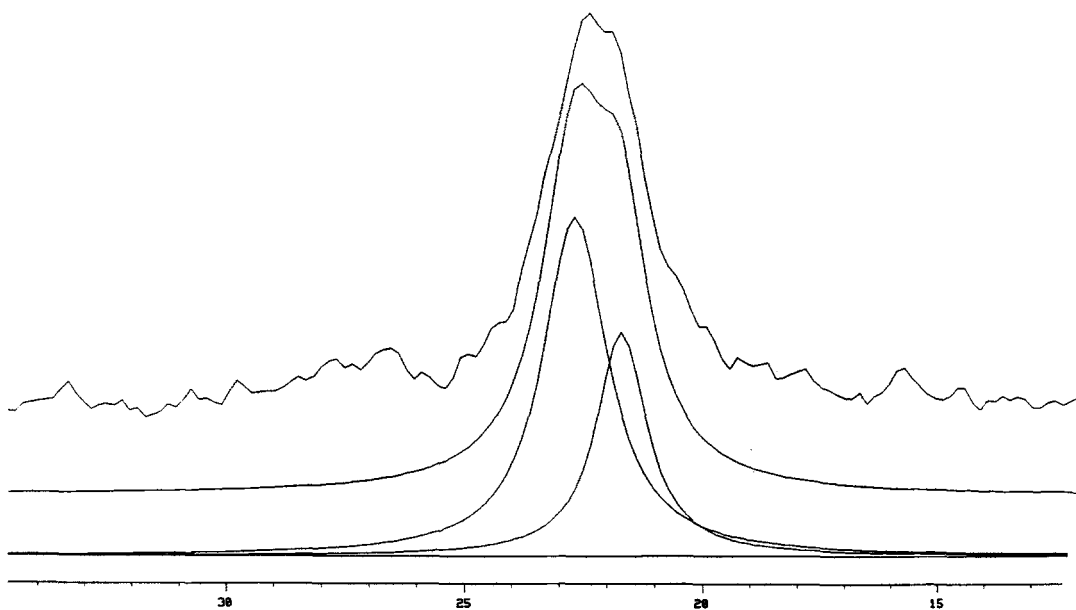
Figure 1 - Carbon-13 NMR CP/MAS with dipolar dephasing of methyl region of PPA.

References
1) Axelson D E, Russell K E (1985) Polym Sci **11**: 221
2) Schaefer J, Stejskal E O in Levy C G ed., "Topics in Carbon-13 NMR Spectroscopy", 3, John Wiley & Sons, New York, 1979.
3) Simmons A, Natanshon A (1991) Macromolecules **24**: 3651
4) Feng H, Feng Z, Shen L (1993) Polymer **34:** 2516
5) Stejskal, E O & Memory J D "High Resolution NMR in the Solid State", Oxford University Press, New York, 1994.
6) Tavares M I B, Monteiro E E C, Harris R K, Kenwright A M (1994) Eur Polym J **30:**1089
7) Sankar S S, Stejskal E O, Fornes R E, Fleming W W, Russel T P, Wade CG (1992) Polym Fiber Sci, Recent Adv **11**: 133
8) Fyfe CA, "Solid-State NMR for Chemists", CFC Press, Guelph, 1983
9) Harris R K, Kenwright A M, Royston A, Say B S (1990) Meas Sci Technol **1:** 1304
10) Silva N M, Tavares M I B (1995) Polymer Testing **14:**329