

High-Resolution ^{13}C -Nuclear Magnetic Resonance Study of Heterogeneous Amorphous Polymers

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ABSTRACT: The combination of solid-state nuclear magnetic resonance (NMR) techniques is very helpful for examining the behavior of heterogeneous amorphous polymers. With the magic-angle spinning (MAS) technique, employing special conditions, only the mobile fraction of the molecule can be assigned. Cross-polarization magic-angle spinning (CPMAS) permits the evaluation of changes in the NMR line shapes and chemical shifts. The employment of proton spin-lattice relaxation times (T_1 and $T_{1\rho}$) gives useful information on the molecular dynamic in heterogeneous polymers. From

these parameters the response of the molecular mobility behavior of the polymer chains can be obtained. The results of the present work are discussed in this article in terms of molecular mobility and domain formations of heterogeneous amorphous polymers in order to understand the relations in the structure–mobility property. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 473–476, 2003

Key words: relaxation process; solid-state NMR; amorphous polymers

INTRODUCTION

Amorphous polymers have been the subjects of several investigations to elucidate the solid morphology and its influence on the physical properties of polymeric materials. Solid-state nuclear magnetic resonance spectroscopy without a doubt has a fundamental value for the study of the solids morphology of amorphous and heterogeneous materials. The ^{13}C solid-state spectra have discriminating pulse sequences that provide the components present in different domains because they present distinct mobilities.

It is very well known that solution NMR provides narrow lines comparing with the solid state. Because of this, useful information on the microstructures of amorphous polymers can be fully investigated. Therefore, the basic MAS ^{13}C technique permits the evaluation of a part of or the whole sample. Using the acquisition conditions necessary to detect mobile carbons, information on sample mobility and heterogeneity can be obtained. The CPMAS ^{13}C technique allows information to be obtained on changes in the sample environment, as it depends on the extent of the interaction and the molecular motions because the CP rates depends on the exchange of protons directly attached or of neighboring protons. It is known that mobile carbons atoms take longer to cross polarize and are then less mobile. Solid-state NMR spectroscopy also offers a great variety of relaxation times, which are very important and informative on molec-

ular mobility studies in different time scales.^{1–12} As the spin-lattice relaxation process is generally dominant in the solid state, the proton spin-lattice parameter can provide direct information on molecular motion. Proton spin-lattice relaxation can be measured in the laboratory frame with a constant designated as T_1 and, in the rotating frame, with a constant characterized by $T_{1\rho}$. The proton $T_{1\rho}$ relaxation time is highly important and used to study the segmental dynamic of samples because it is sensitive both to molecular motion in the tens of kilohertz frequency and to spin diffusion.^{6–12}

The main purpose of this work was to establish the dependence of chemical structures and microstructures with molecular mobility to understand the relations in the structure–mobility property of heterogeneous amorphous polymers such as poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), poly(vinyl alcohol) (PVA), and polystyrene (PS).

EXPERIMENTAL

Samples

The commercial PVC, PMMA, PVA and PS were analyzed by differential scanning calorimetry (DSC) to obtain their glass transition temperatures (T_g), and their values are listed in Table I.

NMR measurements

The solution ^{13}C -NMR spectra were carried out on a Varian Mercury 300 spectrometer operating at 75.4 MHz for ^{13}C . A 90° pulse and a delay of 20 s were used

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TABLE I
 T_g Measurements by DSC

Polymer	T_g (°C)
PVC-A	81
PVC-B	85
PMMA	102
PVA	73
PS	110

to acquire the quantitative spectra. The ^{13}C -NMR spectra were obtained on an INOVA 300 spectrometer operating at 75.4 MHz for ^{13}C . All experiments were performed at probe ambient temperature using high-power proton decoupling. A 7-mm diameter zirconium oxide rotor was used to acquire the NMR spectra at rates of 5.5 kHz. ^{13}C -NMR spectra were referenced to the chemical shift of the methyl carbons of hexamethyl benzene (17.3 ppm). The MAS ^{13}C spectra were acquired with a short delay between the 90° pulses to observe the mobile region in this time scale. The ^{13}C -NMR experiments were also carried out in the cross-polarization mode with magic angle spinning (CPMAS) with a 90° pulse and a delay of 2 s. The CPMAS with variation of contact time was recorded employing the same CPMAS conditions, and the range of contact time was established as 50–10,000 μs . The values of the proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}^{\text{H}}$) were determined from the intensity decays of the ^{13}C peaks with increasing contact times. The $T_{1\rho}^{\text{H}}$ parameter also was evaluated by delayed contact time, and a range of spin locking, τ , was established, from 200 to 8,000 μs .

RESULTS AND DISCUSSION

In this work the heterogeneous amorphous polymers such as poly(vinyl chloride), poly(methyl methacrylate), poly(vinyl alcohol), and polystyrene were investigated by solution and solid-state NMR techniques to obtain information on chemical structure, microstructure, and molecular dynamics.

Solution results

The ^{13}C -NMR solution analyses were carried out to obtain information on the microstructure of the poly-

TABLE II
Triad Sequence of Monomer Distribution for Heterogeneous Amorphous Polymer

Polymer	Triad sequence (% heterotactic)		
	Isotactic	(% heterotactic)	syndiotactic
PVC - A	21	38	39
PVC - B	20	51	29
PMMA	15	45	40
PVA	25	50	25
PS	23	36	42

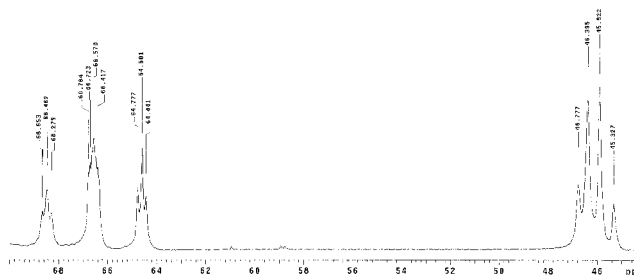


Figure 1 ^{13}C solution NMR spectrum of PVA at 75.4 MHz in quantitative conditions.

mers in the study, given that they present different types of chain packing and ordinations of monomer sequence distribution along the chains. From the ^{13}C solution NMR spectra of those polymers, the percentage of triad sequences distribution were measured, and their values are listed in Table II.

From the data shown in Table II, it is clear that these polymers are heterogeneous because they are amorphous. PVC-B and PVA are not the predominant syndiotactic configuration. PVA, in particular, presents the same amount of isotactic and syndiotactic triads configuration.

From the ^{13}C solution NMR spectrum of PVA, the pentads sequence of the monomer distribution along the polymer macromolecular chains also was characterized. Figure 1 shows the ^{13}C solution NMR spectrum, and Table III shows the assignments of the pentads configuration.

Solid-state measurement results

Solid-state measurements were carried out to understand the molecular dynamic behavior of these polymers in order to obtain information on microstructure and properties.

The basic MAS ^{13}C -NMR spectrum of PVC-A and -B showed that this polymer comprised at least two domains with different molecular mobilities, as two wide NMR signals were detected in low frequencies for both types of PVC. The PMMA MAS ^{13}C -NMR re-

TABLE III
Assignments of Pentad Sequences of Monomer Distribution in PVA Chains

Pentad sequence type	Chemical shift (ppm)
rrrr	64.43
mrrr	64.60
mrrm	64.78
rmrr	66.42
rmmr	66.52
mmrr	66.72
mrrm	66.78
rmmr	68.28
mmmr	68.46
mmmm	68.65

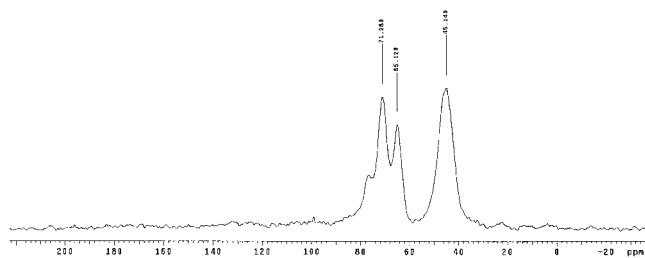


Figure 2 much smaller amount CPMAS ¹³C-NMR spectrum of PVA at 75.4 MHz.

sponse showed the presence of signals from the carbonyl group (176 ppm), CH—O (76 ppm), and the methyl group (17 ppm), which are the most mobile groups in the chains. MAS ¹³C-NMR of PVA showed two signals, one at 45.3 ppm, because of the CH_{2β}, and another one 71.2 ppm, because of the CH—OH, which derives from an uniaxial reorientation of this group. The MAS ¹³C-NMR of the PS showed only two signals, one from aromatic carbons, at 128 ppm, and the other one very broad, at 40–42 ppm, which was attributed to the CH₂ and CH groups. Broadening of the signals is compatible with the rigidity and heterogeneity of the polymer.

Routine CPMAS ¹³C-NMR spectra of all the polymers in the study were done to evaluate the resonance line shapes in order to determine the chemical-shift assignments. It is known that solid-state NMR spectra present useful information on polymer mobility behavior because solid morphology is present. The PVC-B exhibited two wide NMR resonance lines, compared with the PVC-A; the signals were assigned as CHCl at 57.2 ppm and CH₂ at 47.4 ppm. PMMA showed five NMR peaks—at 176.2 ppm (C=O), 76.2 ppm (C—O), 52.2 ppm (CH₂), 45.2 ppm (C_{quaternary}), and 17.8 ppm (CH₃). The PVA showed two signals, one at 45.3 ppm, because of the CH_{2β} and another one split into three peaks, at 65.2, 71.1, and 78.4 ppm, because of the microstructure of CH—OH (rr, mr, and mm; Fig. 2). For the PS four wide lines were detected, at 145.2 ppm (C₁), 128.4 ppm (C_{aromatic}), 42.0 ppm (CH₂), and 40.0 ppm (CH). The shape of the lines reflects the heterogeneity and amorphousness of these polymers.

It is known that the variation in the contact time experiment^{6–8} can inform the optimum contact time for CPMAS ¹³C, which permits measuring of the value of the proton T₁ρ for all resolved ¹³C peaks. Analyzing the distribution forms of the decay of the ¹³C peaks, obtained from the VCT experiment, showed a typical distribution form for the amorphous polymers. The optimum contact time for each type of carbon depended on the polarization transfer rate, which changed with changes in the chemical environment as well as with molecular mobility. Therefore, in general, the optimum contact time for PVC-A was 600 μs; for PVC-B, 400 μs; for PMMA, 1 ms; for PVA, 200 μs; and for PS, 1 ms. The values of proton T₁ρ relaxation,

TABLE IV
T₁^H ρ Values for Amorphous Polymers, Obtained by VCT, as a function of Chemical Shift

Polymer	T ₁ ^H ρ (ms)				
	178.2	145.2	57.7	47.7	45.2
PVC-A			2.6	6.7	
PVC-B			3.5	11.5	
PMMA	2.5				4.6
PS		1.8			4.5

obtained for VCT, for all carbon-resolved carbons, showed exponential decays. Their values were measured from those decays and are listed in Table IV.

The values of T₁^Hρ indicate that these polymers have different relaxation rates, which comes from the difference in chain molecular motions and structural arrangements and ordination. Additional information learned from T₁^Hρ data is that all polymers presented at least two domains with different mobilities, which can be derived from the monomer sequence distribution along the chains, because of the polymerization process promoting a monomer insertion position in the macromolecular chains. PVC-B seems to be more mobile than the PVC-A as a consequence of polymerization process as well as domain size formations, indicating heterogeneity and showing that there are more ordered and less ordered domains in these polymers. PMMA and PS for coincidence show similar proton T₁ρ values, which can be interpreted in terms of the relaxation process. They are similar because of the dipolar coupling. Therefore, the values of this parameter are lower than that measured for PVC, because PMMA and PS are more rigid than the PVC and their glass transitions higher than the value determined for PVC. The microstructure did not show a difference for this parameter, which is a consequence of having the same relaxation time and a homogeneous distribution of domain size because the domain size is around 100 nm.

The values of proton T₁ρ relaxation, obtained for VCT, for all carbon resolved carbons, and for the PVA sample were measured from those decays and are listed in Table V.

From the data shown in Table V, the values are similar, even the signals at 65.2 and 71.1 belonging to the CH—OH detected for different configurational sequence, which can be attributed to all types of configuration sequences having the same efficiency for po-

TABLE V
T₁^H ρ Values for PVA, Obtained for VCT, as a Function of Chemical Shift

PVA δ (ppm)	T ₁ ^H ρ (ms)
71.1	2.6
65.2	2.4
45.3	3.0

TABLE VI
 $T_1^H \rho$ Values for All Polymers, obtained by DCT,
 as a Function of Chemical Shift

Polymer	$T_1^H \rho$ (ms)				
	178.2	145.2	57.7	47.7	45.2
PVC-A	—	—	4.1	4.2	—
PVC-B	—	—	4.0	4.1	—
PMMA	2.3	—	—	—	—
PS	—	2.3	—	—	—

larization transfer because they probably have the same relaxation rate. From analyzing the values of this parameter for all resolved carbons, it can be seen that PVA presents a homogeneous domain distributions along the chains.

Table VI shows the values of the $T_1^H \rho$ parameter, obtained from delayed contact time, for all polymers excepted PVA, as a function of chemical shift.

The values of proton $T_1 \rho$ relaxation, obtained for DCT for all carbon-resolved carbons of the PVA sample, were measured from ^{13}C decays and are listed in Table VII.

The values of $T_1^H \rho$ indicate that each polymer presented a different proton $T_1 \rho$ relaxation process, which is dependent on the lattice that derives from the chains' ordination focusing the monomer insertion distribution and molecular packing.

Another important point in this study was the characterization of a relationship between configuration sequence and molecular mobility for distinct polymers. Taking into consideration the changes in the chemical shifts in the solid-state spectra with the evolution of contact times, the assignment of the microstructure obtained by solution NMR of PVC, PMMA, and PS showed three distinct values for chemical shifts of the asymmetric carbons. In accordance with the assignment of the triad sequences, associations between configurational sequence and molecular mobility were obtained and are listed in Table VIII.

From Table VIII it is clear that the association between configurational sequence and molecular mobility is only dependent on polymerization process, which is responsible for the distribution of monomer

TABLE VII
 Proton $T_1 \rho$ Values, Obtained for DCT, for PVA Sample,
 as a Function of Chemical Shift

PVA δ (ppm)	$T_1^H \rho$ (ms)
71.1	2.2
65.2	2.1
45.3	3.0

TABLE VIII
 Relationship Between Configurational Sequence and
 Molecular Mobility of Chains

Polymer	Configurational sequence	Molecular mobility
PVC	isotactic	mobile
	syndiotactic	rigid
PMMA	isotactic	rigid
	syndiotactic	mobile
PVA	isotactic	rigid
	syndiotactic	mobile
PS	isotactic	rigid
	syndiotactic	mobile

sequence ordinations along the macromolecular chains.

CONCLUSION

Through the ^{13}C -NMR spectra and the proton spin-lattice relaxation time in the rotating frame together with the ^{13}C solution assignments, it was possible to correlate the configurational sequence distribution with the molecular mobility of chains.

The $T_1^H \rho$ results revealed that those polymers presented different local motions, which seems to be uniaxial reorientation of mobile groups. Indeed carbon-13 solid-state NMR has proved to be a very useful source in determining the configuration and molecular mobility of chains in heterogeneous amorphous polymers.

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