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Interactions between PVC and solvents by longitudinal nuclear relaxation times

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ABSTRACT

PVC/aliphatic ketone systems were investigated by NMR relaxation times such as proton and carbon-13 spin-lattice relaxation time (T_1) and proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}$). The proton T_1 results showed that these systems are homogeneous, while proton $T_{1\rho}$ indicates the existence of more than one domain.

INTRODUCTION

The analyses of interactions in polymer compositions have been studied by many researchers employing different methods. High-resolution nuclear magnetic resonance techniques applied to solids have to solve such problems (1-3).

The NMR longitudinal relaxation parameters of proton and carbon-13 can provide information over molecular motions. Proton T_1 is a parameter associated to high frequencies while proton $T_{1\rho}$ is attributed to low frequencies; as a consequence, the response obtained from T_1 and $T_{1\rho}$ for protons is related to distinct regions of molecular mobility, so that, an analysis of macroscopic and microscopic domains can be done (1-5). In addition to this there is a controversy in the literature about the interpretation of $T_{1\rho}$ data of PVC and their compositions that suggests several studies involving these kind of systems (3-4). Carbon-13 T_1 gives specific information about the local environment of the nuclei that may be associated with the process of interaction present in the sample investigated (5).

The great majority of PVC/solvent studies on specific interaction are not well understood yet. This fact is related to the complex nature of PVC, due to the presence of quadrupole nuclei (3-5).

According to the nature of PVC the main purpose of this work is to study PVC systems using films cast from solution with residual solvent as samples. The systems studied were composed by PVC and aliphatic ketones such as methyl ethyl ketone(MEK), diethyl ketone (DEK) and methyl propyl ketone (MPK). Tetrahydrofuran (THF) was chosen as a standard solvent for the polymer.

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EXPERIMENTAL

The samples were prepared from commercial PVC with a weight-average molecular weight of 90,000. Thick cast films were prepared by dissolving PVC with MEK, DEK and MPK with different content of PVC (5-20% w/w). The solutions were cast onto glass plates kept in a dessicator at room temperature for one week. The films were removed from the support by immersion into distilled water, dried and stored at room temperature.

The relaxation times T_1 for proton decays were determined directly from inversion recovery pulse sequence on a NMR spectrometer constructed in the laboratory operating at 60 MHz. The T_1 carbon-13 measurements were carried out using Bruker CXP 200 MHz instrument and the T_1 carbon-13 values were calculated by the null method (6). $T_{1\rho}$ for protons was measured by using variable contact time experiment on a Varian VXR 300 MHz spectrometer and using a $T_{1\rho}$ program on an equipment operating at 60 MHz. This experiment was based on about four spin locking measurements of intensity, with an accuracy of 5% and a precision of 2%. All measurements were carried out at room temperature with at least duplicate samples.

RESULTS AND DISCUSSION

NMR relaxation times for protons measured by inversion-recovery pulse sequence showed that PVC/solvent films have a typical behaviour related to this parameter. All samples with residual solvent present one value for T_1 that was closer to the result obtained for pure PVC (1.5 sec). These values did not change for three months of aging and can be considered the same for all systems investigated. They also are independent of the ketone. As expected these results indicate that the solvent is eliminated rapidly and the films become rigid and brittle. These results may be due to the specific interactions between PVC and ketones as the interaction does not change with time (12).

The T_1 carbon-13 was measured for CH_2 and CH groups of PVC chains. The values of T_1 carbon-13 for PVC carbons were 0.06 sec for CH_2 and 0.12 sec for CH. According to the literature (6, 13), the measurement of this parameter shows the free motion of interacting groups. T_1 ^{13}C data showed that the molecular motion of PVC/aliphatic ketone systems are the same, while for PVC/THF the carbons from PVC present values of T_1 ^{13}C which are longer than PVC/aliphatic ketone. In this case, it can be suggested that the type of the interaction between PVC and aliphatic ketone is different from PVC/THF system. Figure 1 exhibits T_1 ^{13}C measurements for PVC/DEK films with residual solvent, measured at 50.32 MHz.

The spin-lattice relaxation time in the rotating frame for protons was investigated for the same systems and using the same range of aging time.

Proton $T_{1\rho}$ measurements of pure PVC showed two values_ a long value (11.5 msec) and a short value (3.5 msec). However, the pure solvents exhibited only one component of this parameter.

A particular behaviour was found for PVC/THF film obtained from a 5% solution of PVC. Just one value for $T_{1\rho}$ was detected. It was also observed that this value increases during six months of aging. After this time two distinct values were found. Table 1 shows the proton $T_{1\rho}$ values.

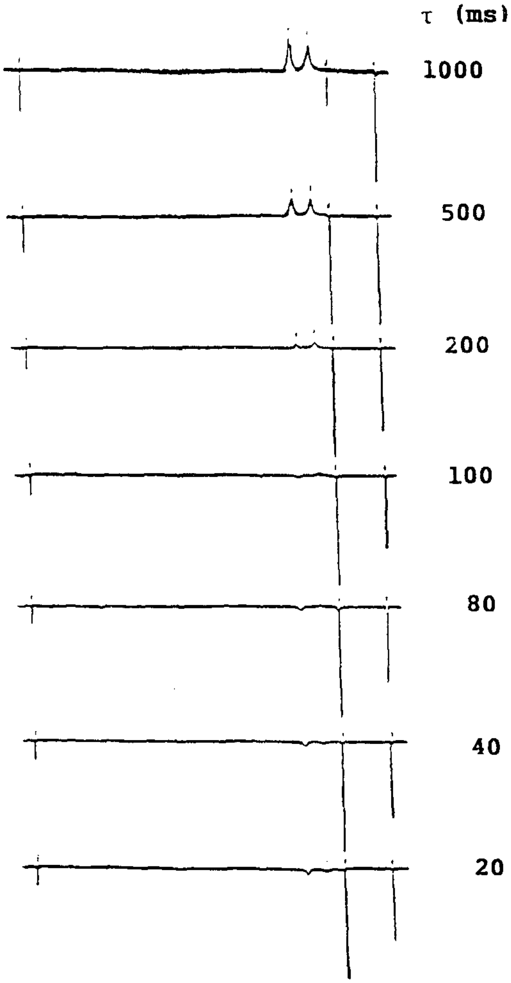

Figure 1 - T_1 ^{13}C experiment for PVC/DEK film with residual solvent, measured at 50.32 MHz.

AGING TIME (months)	PROTON $T_{1\rho}$			
	PROPORTION (%)		VALUE (msec)	
0	100		4.3	
3	100		6.5	
4	100		9.7	
5	100		11.6	
6	42.65	57.35	15.6	5.5

Table 1 - Proton $T_{1\rho}$ values for PVC/THF films obtained from 5% PVC solution.

The results in Table 1 suggest that this sample is a homogeneous film. However, with aging distinct domains were detected as a consequence of solvent elimination that occurs after a period of 6 months.

The cast films presented two components for proton $T_{1\rho}$ (Table 2), when the PVC/THF solutions where more concentrated. These results suggest the presence of at least two domains with different mobilities, which become more rigid with time (10 and 20%).

SOLUTION CONC. (%)	AGING TIME (months)	PROTON $T_{1\rho}$ PROPORTION (%)		PROTON $T_{1\rho}$ VALUE (msec)	
7	3	51.77	48.23	12.0	3.0
	12	26.83	73.17	10.8	2.0
10	3	38.80	61.20	8.0	1.0
	6	30.12	69.88	15.3	6.3
	12	41.08	58.92	16.0	3.1
20	3	23.82	76.37	7.8	0.6
	6	56.44	43.56	13.0	5.2
	12	32.05	67.95	16.0	5.3

Table 2 - Proton $T_{1\rho}$ for PVC/THF systems as a function of PVC solution concentration and aging time.

The same behaviour of $T_{1\rho}$ observed for pure PVC and for PVC/THF systems was also verified for PVC/MEK and PVC/MPK systems. These two components are an indication of microheterogeneity due to the presence of regions with characteristic mobilities.

PVC/DEK solutions revealed a lower degree of heterogeneity _ all films presented one value of proton $T_{1\rho}$ during six months of aging (Table 3) which suggests that PVC/DEK systems may be more stable and consequently take longer time to lose the residual solvent.

A comparison of all systems can be seen in Table 4 for films prepared from 10% PVC solutions after three months of aging.

From $T_{1\rho}$ results for all systems it can be seen that this parameter confirms the existence of at least two regions having distinct mobilities. Solvent elimination is completely random and is independent of time and PVC concentration, except for PVC/DEK.

SOLUTION CONC. (%)	AGING TIME (months)	PROTON $T_{1\rho}$			
		PROPORTION (%)		VALUE (sec)	
7	3	100.0		0.13	
10	3	100.0		0.0035	
	6	67.20	33.0	0.001	0.003
20	1	100.0		0.16	
	2	100.0		0.20	

Table 3 - Proton $T_{1\rho}$ data for PVC/DEK systems as a function of PVC concentration and aging time.

SYSTEM	PROTON $T_{1\rho}$			
	PROPORTION (%)		VALUE (msec)	
PVC/THF	38.80	61.20	8.0	1.0
PVC/MEK	25.70	74.30	6.9	0.4
PVC/MPK	9.80	90.20	3.8	0.4
PVC/DEK	-----	100.0	----	3.5

Table 4 - Proton $T_{1\rho}$ measurements for all PVC systems, with three months of aging (10% PVC solution).

$T_{1\rho}$ for protons was also measured by the variable contact time experiment to confirm the existence of more than one domain. At the end of this experiment the peaks of PVC nuclei were still observed as can be seen in Figure 2, and Figure 3 shows the decay of $T_{1\rho}$ and T_{C-H} by variable contact time experiment.

$T_{1\rho}$ for protons and $T_{C\text{-}H}$ for the systems under investigation compared with pure PVC are shown at Table 5.

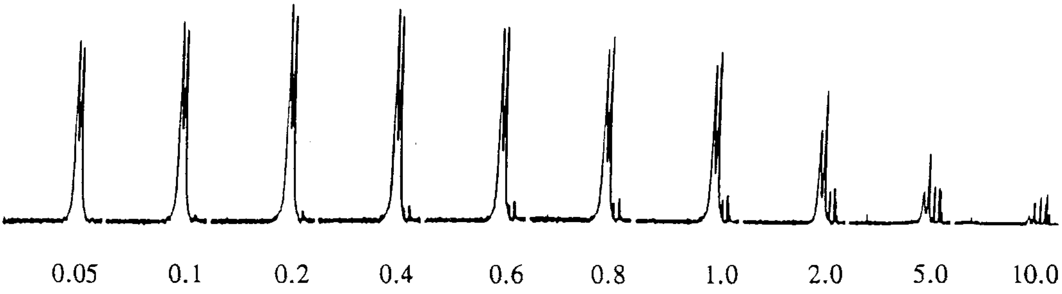

Figure 2 - Variable contact time experiment for PVC/MPK system carried out at 75.34 MHz.

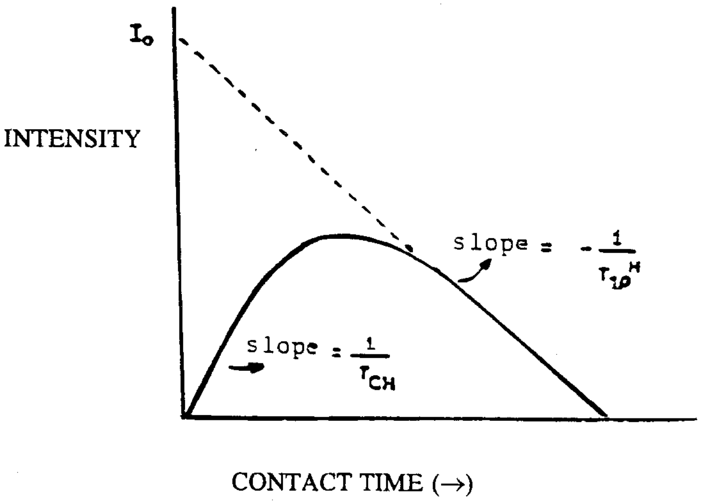

Figure 3 - $T_{1\rho}$ and $T_{C\text{-}H}$ measurements for protons obtained from variable contact time experiments for all systems.

From the results it can be seen that there is no difference among the values of $T_{1\rho}$ for the two types of PVC carbons for PVC/MEK and PVC/THF systems. This can indicate the same mobility. For PVC/MPK systems the CH group in PVC has a higher mobility than the CH_2 group, which may be due to interaction process.

SYSTEM	$T_{1\rho}$ - PVC (msec)		$T_{C\text{-}H}$ PVC (msec)	
	CH_2	CH	CH_2	CH
PVC	4.8	4.7	0.05	0.07
PVC/MEK	5.5	5.1	0.04	0.06
PVC/MPK	4.3	2.4	0.04	0.04
PVC/THF	3.7	3.8	0.04	0.04

Table 5 - PVC CH_2 and CH groups proton $T_{1\rho}$ and $T_{C\text{-}H}$ measurements by variable contact time experiments (75 MHz).

CONCLUSIONS

Spin-lattice relaxation time measurements for PVC/ketone and PVC/THF systems showed one value for T_1 because of the homogeneity of these systems. The values are independent of aging time, concentration, and the solvent. T_1 carbon-13 data suggest that the type of interaction in PVC/ketone is not the same as in PVC/THF systems.

From spin-lattice relaxation time in the rotating frame measurements it is clear that the domains observed in pure PVC are still present in all systems. As the pure polymer is heterogeneous the blends present the same behaviour.

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