Solid-state nuclear magnetic resonance study of relaxation processes in MEH-PPV

A. C. Bloise,[1] E. R. deAzevedo,[1] R. F. Cossiello,[2] R. F. Bianchi,[1] D. T. Balogh,[1] R. M. Faria,[1] T. D. Z. Atvars,[2] and T. J. Bonagamba[1,*]

[1]*Instituto de Física de São Carlos, Universidade de São Paulo, Caixa Postal 369, CEP: 13560-970, São Carlos - SP, Brazil*

[2]*Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, CEP: 13084-971, Campinas - SP, Brazil*

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Solid-state nuclear magnetic resonance methods were used to study molecular dynamics of MEH-PPV at different frequency ranges varying from 1 Hz to 100 MHz. The results showed that in the 213 to 323 K temperature range, the motion in the polymer backbone is predominantly slow (Hz–kHz) involving small angle librations, which occurs with a distribution of correlation times. In the side chain, two motional regimes were identified: Intermediate regime motion (1–50 kHz) for all chemical groups and, additionally, fast rotation (~100 MHz) for the terminal CH_3 group. A correlation between the motional parameters and the photoluminescent behaviors as a function of temperature was observed and is discussed.

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Despite the success of poly [2-methoxy,5-(2'-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) as an electroluminescent active polymer,[1,2] the knowledge of the molecular chain dynamics and its effects on the electroluminescent properties is still deficient. Recent studies have shown that polymer conformation and chain dynamics are especially important for the luminescent properties of conjugated polymers.[3,4] It is also known that thermal-induced morphological changes can affect the photophysics, mainly for processes which involve interchain species.[5,6] For instance, it is known that thermally induced torsional motion shortens the conjugation length, and consequently induces changes in the polymer photoluminescence (PL).[7] Moreover, it was also observed that a substantial narrowing of the photoluminescence band of MEH-PPV occurs below 220 K, although no further explanation was given.[8]

Modern solid-state nuclear magnetic resonance (NMR) methods achieved great success in studying dynamics and structural properties of organic materials.[9] Using different NMR methods, segmental dynamics and conformation can be studied at a molecular level and very specific information, such as correlation times, reorientation angles, and their respective distributions, can be obtained in a broad range of frequencies. Despite the great development of advanced NMR for studying molecular dynamics, there exist so far only few applications of such modern solid-state NMR techniques for investigating dynamics and structure of conjugate polymers.[10,11] In this work, a systematic study of the MEH-PPV chain dynamics using conventional and new advanced solid-state NMR methods is presented. Slow (1 Hz–1 kHz), intermediate (10 kHz–100 kHz), and fast dynamics (~100 MHz) were probed by different NMR techniques.

Molecular motions occurring with rates of the order of Larmor frequency (~100 MHz) can be probed using T_1-relaxation measurements.[12] Dynamic processes occurring with rates between 1 to 100 kHz are accessible by one-dimensional (1D)-DIPSHIFT experiments. Such experiments, performed under magic-angle spinning (MAS), provide a measurement of the ^{13}C–^{1}H magnetic dipolar coupling for each chemical group.[13] This is done by measuring the dependence of the signal amplitude with the evolution period (t_1), used for codifying the ^{13}C-^{1}H dipolar coupling,[13] which produces a typical curve that depends on the strength of the averaged dipolar coupling, $\langle \nu_{\mathrm{dip}} \rangle$. Since motions with correlation times shorter than ~10 μs average the dipolar coupling between ^{1}H and ^{13}C, from the measured $\langle \nu_{\mathrm{dip}} \rangle$ it is possible to distinguish rigid from mobile segments and estimate the amplitude of the molecular rotation. Molecular order parameters, S, for each chemical group can also be obtained as the ratio between this averaged dipolar coupling and its respective rigid-lattice value, $S = \langle \nu_{\mathrm{dip}} / \nu_{\mathrm{dip}}^{\mathrm{rigid}} \rangle$. Assuming wobbling in a cone model for CH carbons, these order parameters can be converted into the amplitude of motions of the CH bond vector given by the opening angle of the cone according to $S^2 = [\cos\theta(1+\cos\theta)/2]^2$, where θ is the cone semiangle.[14] Slow dynamics (1 to 1000 Hz) can be studied by the centerband-only detection of exchange (CODEX) method.[15,16] In summary, the experiment detects the signal reduction due to changes in the orientation-dependent chemical-shift frequencies, which results from segmental reorientations that take place during a long (~ms to s) mixing time (t_m). The t_m dependence of the ratio between each NMR line intensity, $S(t_m, Nt_r)$, and the respective line intensity obtained from a control experiment, $S_0(0, Nt_r)$, (that does not encode any molecular motion) provides the two-time correlation function of the slow molecular motions.[15,16] Other information that is taken from this experiment is the amplitude of the motion, which is determined from the dependence of the normalized line intensities, $E(t_m, Nt_r) = S(t_m, Nt_r)/S_0(0, Nt_r)$, with the period that the spin system has evolved under the chemical shift anisotropy (CSA), Nt_r.[15,16] These modern methods are particularly attractive, because model free information about the molecular dynamics can be obtained.

MEH-PPV with $\overline{M}_n = 86.000$ g/mol was purchased from Aldrich Chemical Company Inc. and studied as received. Films for photoluminescence (PL) experiments were cast from a toluene solution (thickness ~800 μm). Afterward, films were dried under a dynamic vacuum. NMR experi-

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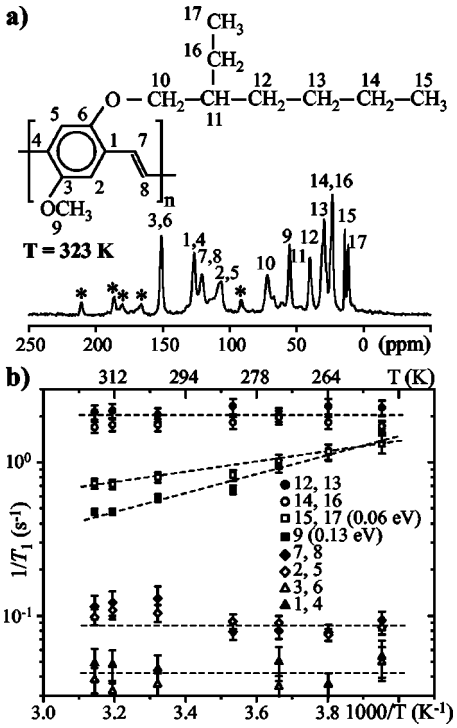

FIG. 1. (a) ^{13}C CP/MAS NMR spectra of MEH-PPV (* indicates the spinning side bands). (b) Temperature dependence of the ^{13}C spin-lattice relaxation rates (T_1^{-1}) for all the carbons of MEH-PPV.

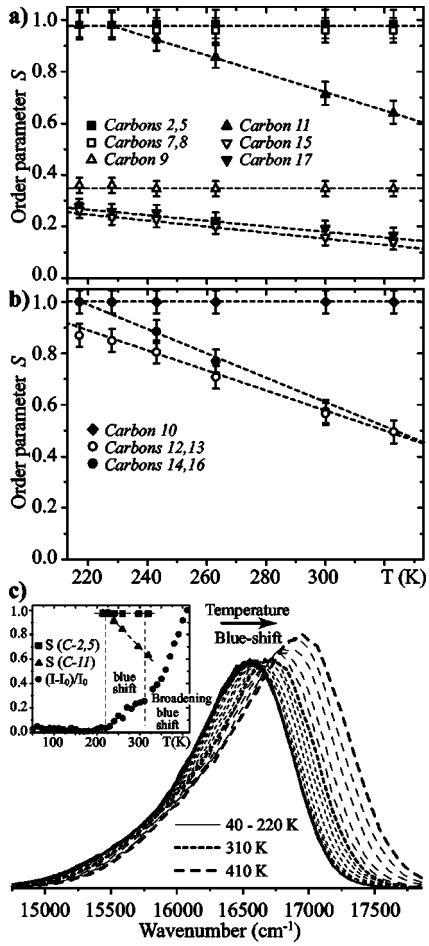

FIG. 2. (a) Plot of the molecular order parameters as a function of temperature for CH and CH_3 groups in MEH-PPV. (b) Same as in (a) for CH_2 groups. (c) MEH-PPV PL spectra at several temperatures (from 40 to 410 K). The inset shows the correlation between the differential normalized PL intensities and order parameters at several temperatures.

ments were performed using a 9.4 T VARIAN INOVA spectrometer in a 7 mm VT-MAS double-resonance probe head equipped with spinning speed control.

Figure 1(a) shows the repeat unit and the ^{13}C CP/MAS spectrum of MEH-PPV at 323 K with the corresponding line assignments. Figure 1(b) shows the corresponding ^{13}C spin-lattice relaxation rates (T_1^{-1}) as function of temperature. It can be observed that T_1^{-1} is temperature independent for all the carbons, except for the three methyl carbons (9, 15, and 17), where a slight decrease in temperature is observed. This indicates that the CH_3 groups execute molecular movements in the frequency scale of the order of Larmor frequency (100 MHz), and the estimated activation energies were about 0.1 eV, which is typical for CH_3 free rotations, as observed in Ref. 12, where the deuterated methyl groups in different molecules were studied using ^{2}H T_1 relaxation measurements and line shape analysis.

Figure 2(a) shows the temperature dependence of the molecular order parameters for CH and CH_3 groups in MEH-PPV measured using 1D-DIPSHIFT experiments. The main chain carbons have temperature-independent order parameters of approximately 1.0. The order parameter for methoxy carbons (9) is also temperature independent and the obtained S value is 0.33 ± 0.02, which shows that the CH_3 group motions correspond to axial rotations, occurring around its C3-axis.[13] For the CH carbon (11) in the side group, the order parameter remains equal to $\sim$1 below 230 K and decreases monotonically with temperature, indicating a gain of mobility. CH_3 carbons in the side group (15 and 17) also exhibit a S decay as a function of temperature and, in this case, it is smaller than 0.33. This is a consequence of the fact that these CH_3 groups located in the side chain follow the motion of the side groups in addition to the axial rotations. Another interesting issue is the temperature dependence of dipolar coupling for CH_2 groups along the side chain. Because the dipolar coupling for CH_2 carbon 10, $\nu_{\mathrm{dip}}^{\mathrm{C10}}$, was found to be temperature independent, the order parameters were calculated using the dipolar coupling of this group as a reference, $S=\langle \nu_{\mathrm{dip}}/\nu_{\mathrm{dip}}^{\mathrm{C10}}\rangle$. The temperature dependence of the order parameter for all side chain CH_2 groups is shown in Fig. 2(b). As it can be observed, overall the order parameters increase as a function of the proximity to the main chain. Additionally, the order parameters for side chain carbons (12, 13, 14, and 16) decrease as a function of temperature. For CH side group carbon (11), the average amplitude of the motions was estimated as $<\theta>=(14\pm5)°,(25\pm5)°$, $(37\pm3)°$, and $(42\pm3)°$ at $T=243$, 263, 300, and 323 K, respectively, indicating the progressive increase of motional amplitudes as a function of temperature.

Figure 3(a) shows the two-dimensional ^{13}C (2D) MAS-exchange spectrum of MEH-PPV. Cross peaks linking the

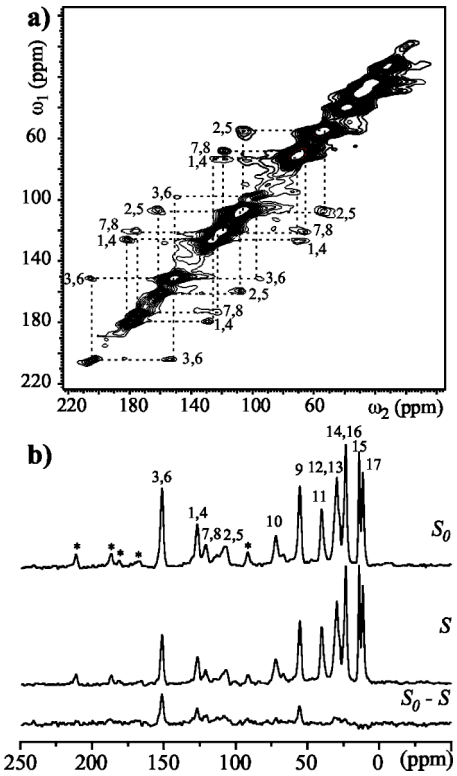

FIG. 3. (a) ^{13}C 2D-MAS exchange spectrum performed under 5.4 kHz. (b) Top: Reference CODEX spectrum; middle: CODEX spectrum; bottom: Pure-exchange CODEX spectrum. (* indicates the spinning side bands).

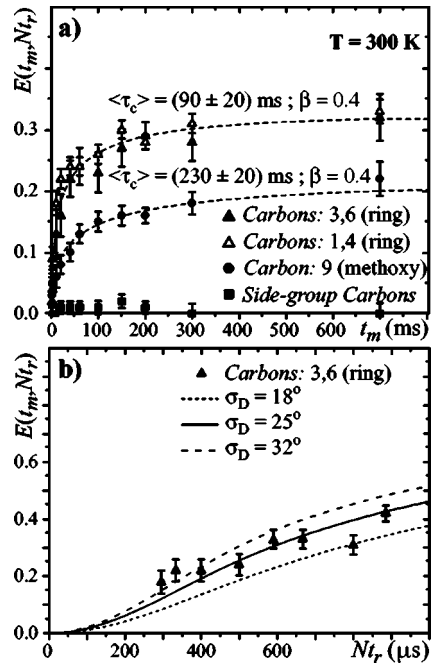

FIG. 4. (a) Mixing time dependence of the normalized CODEX intensities. (b) Evolution time, Nt_r, dependence of the normalized CODEX intensity.

sidebands of Carbons 1, 4, 3, 6, and 9 are clearly observed, showing that these groups experience dynamics in the slow motion regime.[17] This is confirmed by the series of ^{13}C CODEX spectra presented in Fig. 3(b), which were acquired at 300 K, with t_m=200 ms, Nt_r=667 μs. Exchange, $S(t_m,Nt_r)$, reference, $S_0(0,Nt_r)$, and pure-exchange, (S_0-S), CODEX spectra are shown. No (S_0-S) intensity is observed in the pure-exchange CODEX spectrum for the 0–50 ppm region, indicating the absence of slow motions of the side groups. In contrast, slow moving groups in the polymer backbone are directly detected as a significant (S_0-S) intensity for the phenylene and methoxy carbons. Together with the 1D-DIPSHIFT data, these results indicate that, while the main chain in MEH-PPV experiences slow dynamics ($\tau_c \sim 100$ ms) at room temperature, the side groups move faster ($\tau_c < 100$ μs).

Figure 4(a) shows the ^{13}C CODEX normalized intensities, $E(t_m,Nt_r)$, as a function of the mixing time $t_m(Nt_r=667\mu s)$ for backbone Carbons 1, 4, 3, 6, and 9, as well as for the sidegroups (the line intensity was obtained by integrating the spectrum in the 0–50 ppm range) at 300 K. The $E(t_m,Nt_r)$ intensity for the side group carbons remains approximately zero for all mixing times, confirming the absence of the slow motions in these molecular segments. In contrast, the backbone carbons have significant exchange intensity. The $E(t_m,Nt_r)$ versus t_m curves for the 1, 3, 4, and 6 phenylene carbons are identical, while OCH_3 carbon shows a different plateau value. This is attributed to differences in the CSA, which is smaller for OCH_3 as compared to phenyl ring carbons.[18] The $E(t_m,Nt_r)$ versus t_m curves were adjusted with the stretched exponential correlation function $E(t_m,Nt_r) = f_m[1-\exp(-(t_m/\tau_0)^{\beta})]$,[19] where f_m represents the fraction of molecular segments moving in the millisecond to second time scale and β is associated to the width of the correlation time distribution. The mean correlation time, $\langle\tau_c\rangle$, is calculated from τ_0 and β according to $\langle\tau_c\rangle = \beta^{-1}\tau_0\Gamma(1/\beta)$ and are shown in Fig. 4(a). The small β value ($\approx$0.4), accounts for a relatively large distribution of correlation times (about 3 decades) and suggests a significant dynamic heterogeneity for the polymer backbone at this temperature. The motional amplitudes involved in such processes were obtained by measuring the $E(t_m,Nt_r)$ versus Nt_r curves. Figure 4(b) shows such curves for the 3,6 phenylene carbons. The simulation was performed considering average motional amplitudes between 18° and 32°, Fig. 4(b) reproduces the experimental data. The observed slow backbone motions might be interpreted as small angle rotations, and their amplitudes reflect the width of the rotational barrier distribution around the planar configuration.[20,21] These slow torsional motions of the main chain may also play a role in the electroluminescence and PL of the polymers. Because the time scale of the electronic processes involved in the PL is at least six orders of magnitude faster than the time scale of the slow processes observed here, the average reorientation angle of $(25\pm7)^{\circ}$ measured in the CODEX experiments can be interpreted as the degree of chain disorder along the main chain. In Ref. 21, the backbone motion of PPV was investigated and a degree of motional heterogeneity that is substantially smaller than in the case of MEH-PPV was found (β for PPV main chain motion is $\sim$0.8 compared to $\sim$0.4 in the case of MEH-PPV). This might be related to the presence of the long side group

in MEH-PPV, which not only suppresses some motional modes (for example ring flips), but also introduces changes in the microenvironment that makes the system more heterogeneous.

Figure 2(c) shows MEH-PPV PL spectra at several temperatures, from 40 to 410 K. As can be seen, there are three regimes in this series of spectra. From 40 to ~220 K, the spectral characteristics remain unchanged; between ~220 and 320 K width and spectral intensity remain mostly constant and a spectral blueshift is observed; above 320 K, besides the blueshift, the width and spectral intensity increase continuously. Theoretical calculations and experimental results have shown that chain disorder is an important mechanism for blueshifting the PL spectrum of conjugated polymers.[3,20,22,23] Thus, the presence of small angle main chain motions at 300 K suggests that this blueshift of the PL bands is associated with the conformation disorder introduced by the small angle motion in the main chain as observed from CODEX experiments. The spectral changes starting at 220 K can be attributed to the onset of the β-relaxation processes[24] involving thermal activation of lateral segments of the polymer chain, increasing the conformational disorder. At temperatures above 320 K, the significant intensity increase and the blueshift in the PL spectra observed are associated with the onset of the glass transition process (measured by differential scanning calorimetry–not shown), which involves dissociation of interchain species. The dissociation of interchain producing intrachain excitons explains the simultaneous increase in emission intensity and spectral blueshift. In fact, an increase can be also observed of the plateau of the $E(t_m, Nt_r)$ versus t_m curves for temperatures higher than 300 K (not shown). This is an indication that there is an increase in the amplitude of the main chain motion as a function of temperature, characteristic of a glass transition process.

Analyzing the behavior of the order parameters for side chain carbons (11, 12, 13, 14, and 16) shown in Figs. 2(a) and 2(b), one can observe that it is about 1 at temperatures lower than ~230 K and decreases for higher temperatures. Because the decrease of the order parameter is strictly related to the increase of the amplitude of the polymer chain motion, the correlation between the PL changes and the onset of side group motion is apparent.[8,25] Therefore, the modifications in the PL spectra, which occur just above 220 K, might be correlated to the change in the microenvironment due to the onset of the side group motion, which produces regions where interchain interactions are less effective than in the frozen state. This shows that the secondary relaxation occurring in side chain is directly related with the processes that affect the photophysics of MEH-PPV.

*Author to whom correspondence should be addressed; E-mail: tito@if.sc.usp.br

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