ELSEVIER

Polymer 43 (2002) 7003–7006

polymer

www.elsevier.com/locate/polymer

Morphological study of a poly(3,4-ethylenedioxythiophene)/polystyrenesulfonic acid mixture by solid state ^{13}C-CP/MAS NMR relaxometry

P. Adriaensens, R. Carleer, L. Storme, D. Vanderzande, J. Gelan*

Department of SBG, Institute for Material Research (IMO), Limburg University, Universitaire Campus, Building D, 3590 Diepenbeek, Belgium

Abstract

The nanometer morphology of a mixture of the electrically conductive polymer poly(3,4-ethylenedioxythiophene) and polystyrenesulfonic acid is studied by means of solid state ^{13}C-CP/MAS NMR relaxation experiments. Based on the T_1H and $T_{1\rho}$H NMR relaxation decay times, determined via the chemical shift selective carbon resonances, it can be concluded that the mixture is homogeneous on the nanometer scale. Consequently, charge transport (hopping) between PEDT chains is hindered, resulting in antistatic properties. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(3,4-ethylenedioxythiophene; Polystyrenesulfonic acid; ^{13}C-CP/MAS NMR relaxometry

1. Introduction

Among the numerous electrically conductive polymers that have been studied and developed over the past three decades, poly(3,4-ethylenedioxythiophene), also known as PEDT or PEDOT, has appeared to be one of the most successful materials [1]. It possesses several advantageous properties as compared to unsubstituted polythiophene and other polythiophene derivatives: it combines a low oxidation potential and moderate bandgap with good stability in the oxidized state [2–5]. Also, by blocking the β positions of the ring, the formation of α–β linkages during polymerization is prevented, resulting in a more regiochemically defined material. In addition to a high conductivity (ca. 600 S/cm) [6], PEDT was found to be highly transparent in thin, oxidized films [2–5]. Unfortunately, PEDT itself is an insoluble polymer. This drawback can, however, be circumvented by polymerising EDT in combination with a water-dispersible polyelectrolyte such as polystyrenesulfonic acid (PSS). The resulting PEDT/PSS (Scheme 1) is a dark blue, aqueous polymer that can easily be processed. Upon spincoating or casting, one can obtain highly transparent films with conductivities between 0.1 and 1 s/cm. Due to these properties, PEDT/PSS has found its way into industrial applications such as anti-static material for photographic film.

Despite its commercial success, there are still numerous questions about PEDT/PSS that need to be answered. One of the most striking questions is: how does this material, consisting of two polymers, look like on the molecular level? In order to give an answer to this fundamentally as well as practically important question, we studied the PEDT/PSS mixture by high resolution ^{13}C-CP/MAS solid-state proton NMR relaxometry. Although microscopic techniques as SEM, TEM and AFM are useful to study the morphology at the surface, solid state NMR spectroscopy and specially relaxometry are unique to investigate the nanometer aspects (structure, chain dynamics and miscibility) in the bulk in a non-invasive and non-destructive way [7,8].

2. Experimental

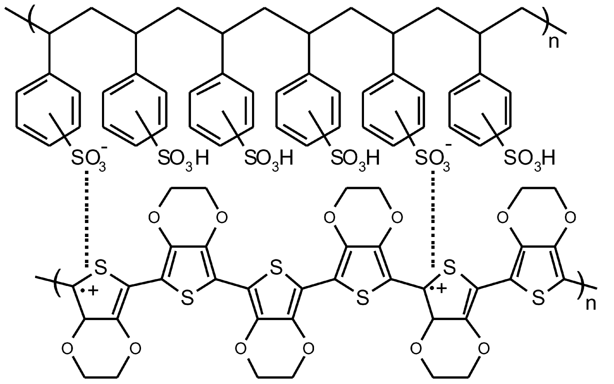
2.1. Materials

PEDT/PSS was prepared by mixing 3,4-ethylenedioxythiophene (10.65 g, 75 mmol), 439 g of 5.99 wt% PSSA solution and $Na_2S_2O_8$ (21.4 g, 104 mmol) in water (2062 ml). After initial stirring at RT for 10 min, $Fe_2(SO_4)_3$ (187 mg) was added and the mixture was stirred vigorously for 24 h. After this period the dark, aqueous PEDT/PSS mixture was purified by ion exchanging with

---

* Corresponding author. Tel.: +32-11-26-8388; fax: +32-11-26-8301.
E-mail address: jan.gelan@luc.ac.be (J. Gelan).

PII: S0032-3861(02)00322-1



Scheme 1. Poly(3,4-ethylenedioxythiophene)/polystyrenesulfonic acid (PEDT/PSS).

acidic and basic resin (LEWATIT products from Bayer AG) resulting in dark blue, aqueous PEDT/PSS.

A nice, transparent film of PEDT/PSS (thickness ca. 200 nm) was obtained by casting the above mentioned, aqueous PEDT/PSS (100 ml), mixed with Zonyl® FSO100 (few milligrams), onto a PET substrate after which it was dried for several minutes at 45 °C.

2.2. Instruments

High resolution solid-state ^{13}C-CP/MAS NMR spectra were recorded at room temperature on an Inova 400 Varian spectrometer operating at a static magnetic field of 9.4 T. Magic angle spinning was performed at 4550 Hz, making use of ceramic Si_3N_4 rotors. KBr was used to adjust the magic angle. The aromatic signal of hexamethylbenzene was used to determine the Hartmann–Hahn condition ($\omega_{1H} = \gamma_H \ \beta_{1H} = \gamma_C \ \beta_{1C} = \omega_{1C}$) for cross-polarization and to calibrate the carbon chemical shift scale (132.1 ppm). Other spectral parameters used were a $\pi/2$ pulse length of 5.0 μs, a spectral width of 50 kHz, an acquisition time of 25 ms, a preparation delay of 3 s and 1000 accumulations. The strength of the spin lock B_1 field was 50 kHz while the strength of the high power decoupling B_2 field was set to 65 kHz during the acquisition time. The proton spin–lattice (T_1H) and spin–lattice relaxation time in the rotating frame ($T_{1\rho}$H) were measured via the chemical shift selectives carbon nuclei by means of a multipurpose pulse sequence [9] in which a fixed contact time of 1 ms was used for cross-polarization. In the T_1H experiment, an inversion recovery filter was placed in front of the standard cross-polarization pulse sequence. In the $T_{1\rho}$H experiment, the proton magnetization is kept in spin lock for a variable period of time before it is cross-polarized to the carbon nuclei. A preparation delay of five times the longest T_1H value has been respected for the determination of the $T_{1\rho}$H decay times. The T_1H and $T_{1\rho}$H decay times were obtained by fitting the carbon signal intensity versus the evolution time t according to Eqs. (1) and (2), respectively

$$M(t) = M_0\big(1 - 2\exp(-t/T_1\mathrm{H})\big) \tag{1}$$

$$M(t) = M_0 \exp\Big(-(t + \mathrm{CT})/T_{1\rho}\mathrm{H}\Big) \tag{2}$$

In these equations, $M(t)$ is the magnetization as a function of the variable evolution time t and CT the fixed contact time of 1 ms. Based on Eq. (1), the equilibrium magnetization M_0 can easily be determined by means of a classical exponential analysis. Further adaptation of this equation to an exponential function of the type $M'(t) = 2M_0\exp(-t/T_1H)$ than allows a visual comparison of the T_1H time constants, obtained via the different resonances in the carbon spectrum, by means of the slopes in a logarithmic plot of $M'(t)$ versus the evolution time t.

All non-linear least-square analyses of relaxation data have been performed on a Macintosh computer using the program Kaleidagraph 3.0.

3. Results and discussion

For rigid polymer systems, i.e. below the glass transition temperatures (T_g), the proton relaxation times T_1H and $T_{1\rho}$H provide information about the level of heterogeneity (nano-structured morphology) on the nanometer scale due to the process of proton spin diffusion [8]. Under the condition of efficient spin diffusion, both proton relaxation times can be directly related to the sizes of molecular domains. The proton $T_{1\rho}$H decay time, in the order of milliseconds, will be averaged out over a short distance of about 1–2 nm. Since the $T_{1\rho}$H relaxation time is sensitive to frequency motions of several tens of kilohertz, it reflects the motions of short segments in the polymer chain. The T_1H decay time on the other hand, in the order of seconds, is sensitive to the spectral density of Larmor frequency motions (several hundred MHz) and is averaged out over a larger distance (in the order of tens of nanometers), making it a more large-scale molecular property. The maximum path length L, over which proton–proton spin diffusion can occur, is approximately given by $L \approx (6DT_i)^{1/2}$ where D is the spin diffusion coefficient ($\sim 10^{-16}$ m^2/s for rigid solids) and T_i the relaxation time T_1H or $T_{1\rho}$H [10]. If the intrinsic relaxation times of the molecular domains are different, multiple

Table 1
T_1H and $T_{1\rho}$H relaxation times of PSS and the PEDT/PSS mixture

Species	PSS aliphatic signals		PEDT ether signal		Aromatic signals	
	T_1H (s)	$T_{1\rho}$H (ms)	T_1H (s)	$T_{1\rho}$H (ms)	T_1H (s)	$T_{1\rho}$H (ms)
PSS	0.10	3.6			0.10	3.7
PEDT/PSS mixture	0.51	4.8	0.51	4.8	0.50	4.8

The averaged 95% confidence limit for T_1H and $T_{1\rho}$H is $<5\%$.

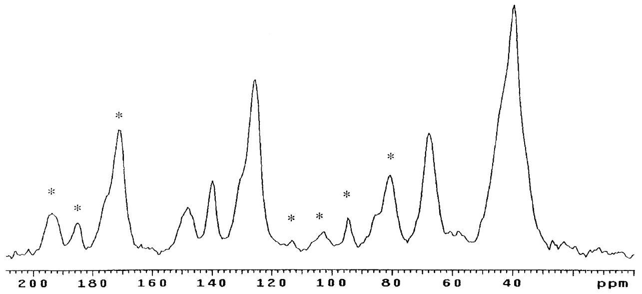


Fig. 1. 100 MHz solid-state ^{13}C CP/MAS spectrum of the PEDT/PSS mixture acquired with a contact time of 1 ms. Peaks marked with an asterisk are spinning side bands. The ether carbon resonance of PEDT at 68 ppm is clearly separated from the aliphatic carbon resonances of PSS around 42 ppm. The aromatic carbon resonances can be assigned to PEDT (128 and 140 ppm) and PSS (127 and 148 ppm).

(domain specific) relaxation times will only be observed if the domain sizes are larger than *L*.

Fig. 1 shows a typical ^{13}C solid-state NMR spectrum of the PEDT/PSS mixture. Since the ether carbon resonance of PEDT (68 ppm) is completely separated from the aliphatic carbon resonances of PSS (around 42 ppm), the proton relaxation behavior of both polymers can be investigated separately. The aromatic carbon resonances of both PEDT (128 and 140 ppm) and PSS (127 and 148 ppm) are situated between 120 and 160 ppm.

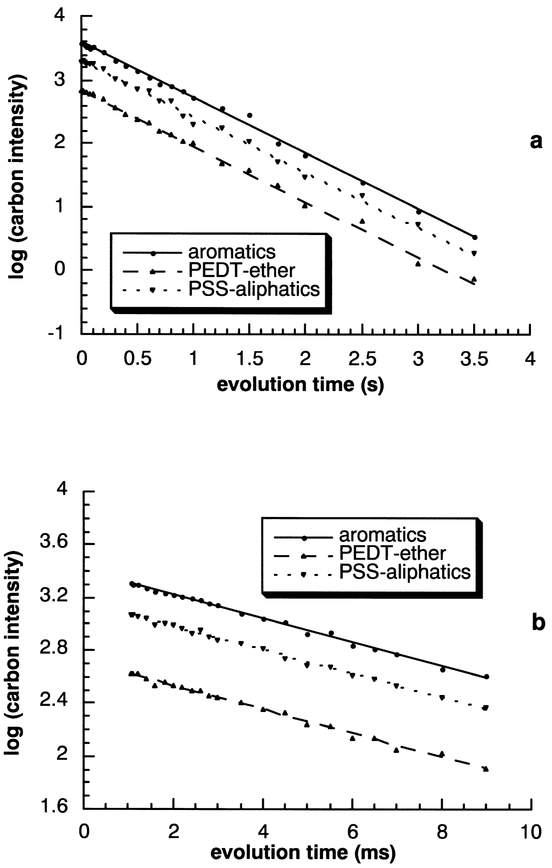


Fig. 2. Plots of the logarithm of the carbon intensity of the PEDT ether resonance (▲), the PSS aliphatic resonances (▼) and the aromatic carbon resonances (•) versus the variable evolution time of the T_1H (a) and $T_{1\rho}$H (b) experiment.

Table 1 shows the T_1H and $T_{1\rho}$H decay times obtained for the PEDT/PSS mixture under investigation and for pure PSS. Fig. 2a presents the plot of the logarithm of the carbon intensity versus the variable evolution (inversion) time for the PEDT ether signal, the PSS aliphatic signals and the aromatic signals of the PEDT/PSS mixture of the T_1H experiment. Straight lines are obtained, being indicative for a mono-exponential relaxation behavior. Furthermore, the lines are nicely parallel, which means that the slopes, and so T_1H decay times, are quasi-identical for all carbon resonances of the mixture. For pure PSS, the T_1H decay times determined via the aliphatic and aromatic carbon resonances are identical, but clearly different from those obtained for the PEDT/PSS mixture.

As expected, spin diffusion causes all carbon resonances of pure PSS to show the same T_1H decay time of 0.1 s. For the PEDT/PSS mixture, a similar T_1H decay time of about 0.5 s is observed via the ether carbon resonance of PEDT as well as via the aliphatic PSS carbon resonances and the aromatic resonances. Moreover, from the observation that the T_1H decay time obtained via the aliphatic PSS resonances of the mixture is different from that obtained via the aliphatic resonances of pure PSS, it can be concluded that spin diffusion of proton magnetization takes place efficiently throughout the PEDT/PSS mixture. Due to efficient spin diffusion, a single T_1H decay time is observed via all carbon resonances of the mixture, which is the molar fraction weighed average of the T_1H decay times of pure PSS and PEDT. It allows to conclude that PEDT and PSS have to be intimately mixed on a length scale of about 20 nm: if the mixed polymers are phase separated, the molecular domains have to be smaller than 20 nm. Based on the molar ratio of the mixture (PEDT/PSS ~ 1/2) and the T_1H decay times of the mixture and pure PSS, a T_1H decay time of about 1.5 s can be estimated for pure PEDT. This less efficient T_1H relaxation, caused by a low spectral density of fast MHz molecular motions, is in agreement with the rigid, stiff structure of PEDT.

Table 1 further presents the $T_{1\rho}$H decay times obtained for the PEDT/PSS mixture and for pure PSS. A linear relation between the logarithm of the carbon intensity and the variable spin lock evolution time, being indicative for a mono-exponential relaxation decay, is observed for all carbon resonances of the PEDT/PSS mixture in the $T_{1\rho}$H experiment (Fig. 2b). Furthermore, the resulting straight lines are nicely parallel: the slopes, and so $T_{1\rho}$H decay times, are identical for all carbon resonances. For pure PSS, the $T_{1\rho}$H decay times determined via the aliphatic and aromatic carbon resonances are identical as expected, but clearly different from those obtained for the PEDT/PSS mixture. This means that due to efficient spin diffusion, a single $T_{1\rho}$H decay time of 4.8 ms is observed via all carbon resonances of the mixture. This decay time represents the molar fraction weighed average of the $T_{1\rho}$H decay times of pure PSS and PEDT. This clearly means that the PEDT/PSS mixture has to be fully homogeneous on the nanometer scale (intimately mixed on a length scale <2 nm).

As mentioned in the introduction, the material described here has an electrical conductivity in the order of 0.1–1 S/cm, a typical value for an antistatic material. When one compares this value with that of chemically (in-situ) [11] or electrochemically prepared PEDT [6] carrying low molecular weight counter ions such as perchlorate or tosylate (i.e. 300–600 S/cm), one observes a distinct difference, although their degrees of doping (i.e. number of charge carriers on the PEDT chains) are identical (ca. 30%). Apparently, the homogeneous mixing between PEDT and PSS on the nanometer scale results in the isolation of PEDT chains between PSS chains. Therefore, the transport (hopping) of charge carriers from one PEDT chain to another is hindered, which explains the low conductivity of PEDT/PSS.

4. Conclusions

High resolution ^{13}C solid state proton NMR relaxometry shows no indications for a phase separated nano-structured morphology for the PEDT/PSS mixture: both the T_1H and $T_{1\rho}$H relaxation behavior are indicative for a homogeneous mixture on the nanometer length scale. As a result, the PEDT chains are isolated by PSS chains, which hinders the transport (hopping) of charge carriers within the material, explaining the lower conductivity of PEDT/PSS compared to other (electro)chemically prepared PEDT systems.

References

[1] Groenendaal L, Jonas F, Freitag D, Pielarzik H, Reynolds JR. Adv Mater 2000;12:481.

[2] Jonas F, Schrader L. Synth Met 1991;41–43:831.

[3] Heywang G, Jonas F. Adv Mater 1992;4:116.

[4] Winter I, Reece C, Hormes J, Heywang G, Jonas F. Chem Phys 1995; 194:207.

[5] Dietrich M, Heinze J, Heywang G, Jonas F. J Electroanal Chem 1994; 369:87.

[6] Groenendaal L, Zotti G, Jonas F. Synth Met 2001;118:105.

[7] Schmidt-Rohr K, Spiess HW. Multidimensional solid-state NMR and polymers. London: Academic Press; 1996.

[8] Fedotov VD, Schneider H. Structure and dynamics of bulk polymers by NMR-methods. Berlin: Springer; 1989.

[9] Hoogmartens I, Adriaensens P, Vanderzande D, Gelan J. J Anal Chim Acta 1993;283:1025.

[10] Douglas DC, Jones GP. J Chem Phys 1966;45:956.

[11] de Leeuw DM, Kraakman PA, Bongaerts PFG, Mutsaer CMJ, Klaassen DBM. Synth Met 1994;66:263.