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Solid State NMR and Fluorescence Studies of Conjugated Polymer Nanocomposties

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Abstract: ^{13}C spin-lattice relaxation times (T_1) of a conjugated polymer MEH-PPV in polymer/layered silicate nanocomposites together with the steady state fluorescence emission and transient fluorescence decay measurements have been investigated. The T_1 values of the conjugated carbons decrease dramatically according to the reduction of polymer concentration in the nano composites, while the fluorescence life times (τ) show a linear prolonging tendency. The results are explained from the point of view of molecular dynamics.

Keywords: Conjugated polymer, nanocomposites, fluorescence, solid state ^{13}C NMR.

Semiconducting polymer materials have inspired considerable researches since Burroughes *et al.* had demonstrated that these materials could be used as light-emitting diodes [1, 2]. These conjugated polymers can be exploited in various novel end-use devices, OLEDs [3-5], photovoltaic cells [6, 7] and thin film transistors [8-10]. Currently, a great deal of attention is being paid to the polymer-nanoparticle hybrid materials since the nanoscale mutiphase materials can display some novel properties that are not present in the individual phases[11]. Park *et al.*[12] reported that poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) /clay nanocomposites exhibit better luminescent behaviors than the bulk polymer material. However, the underlying mechanism of the luminescence enhancement of MEH-PPV in this kind of layered silicate nanocomposites has not been fully understood. In this work, we investigated the ^{13}C spin-lattice relaxation time of the conjugated polymer MEH-PPV, along with the steady state fluorescence spectra and transient fluorescence decay measurements, as a function of its concentrations in a series of polymer/organic-montmorillonite (OMMT) nanocomposites. The confinement effect produced by the nano-dispersed clay is supposed to play an important role in the improvement of the luminescence properties.

Experimental

MEH-PPV was synthesized according the literature [13, 14]. The organophilic nano-clay

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was provided by Key Laboratory of Engineering Plastics, CAS[15]. The nanocomposites of MEH-PPV and OMMT were prepared through solution mixing method in chloroform at room temperature. The weight ratio of MEH-PPV to OMMT was 100:0, 70:30, 50: 50, 30:70, and 10:90, respectively. The morphologies of the intercalated composites were detected and confirmed by a Rigaku D/Max-2500 X-ray diffractometer.

Steady state fluorescence emission spectra of the spin-coated films were observed on a Hitachi F-4500 fluorescence spectrophotometer with an angle of incidence 30^o to the surface normal of the films, λ_{ex}480 nm. Fluorescence decay measurements were carried out on a time-resolved picosecond photon-counting type streak camera (Hamamatsu C2909) with an instrumental response function of 30 ps in half-width. The excitation light pulses were 120 fs in pulse width, 480 nm in wavelength and 1 KHz in repetition rate. The decay profile of the conjugated polymeric samples was fitted as single exponential characteristics. Solid-state ^{13}C NMR spectra and spin-lattice relaxation time T_1 data on the individual carbons of MEH-PPV in the nanocomposites were measured on a Bruker DMX-300 instrument by Cpirt1 pulse sequence. The relaxation curves of the individual carbon atoms of the polymer/OMMT samples show typical single-exponential characteristics. The values of relaxation time T_1 obtained from ^{13}C spin-lattice relaxation curves are listed in **Table 1**.

Results and Discussion

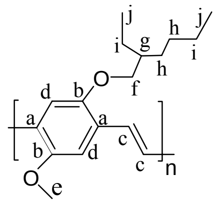
Table 1 shows that the spin-lattice relaxation times T_1 of MEH-PPV for the conjugated carbons in main chains shortened with increasing the percentage of OMMT in the nanocomposites, while the aliphatic carbons in side chains kept steady approximately.

The value of T_1 is primarily related to the local molecule environment and sensitive to the local free volume and its distribution, a shorter spin-lattice relaxation time indicates a higher mobility for the conjugated segments in a higher OMMT content sample. It is speculated that during the preparation process, the presence of layered

Table 1 Spin-lattice relaxation time T_1 of individual carbons of MEH-PPV in different samples

Carbon code*	T_1 (s)				
	100% PPV	70%PPV	50% PPV	30%PPV	10%PPV
C-a	4.1817	2.2625	1.0802	0.6868	0.6007
C-b	7.9420	5.7480	3.5590	4.1820	1.3150
C-c	7.8268	3.4375	1.5859	1.0834	0.0065
C-g	0.5839	0.6461	0.2386	0.3173	0.2326
C-h	0.2525	0.2462	0.2752	0.2066	0.1414
C-j	1.2529	1.4105	1.7510	1.5267	1.6215

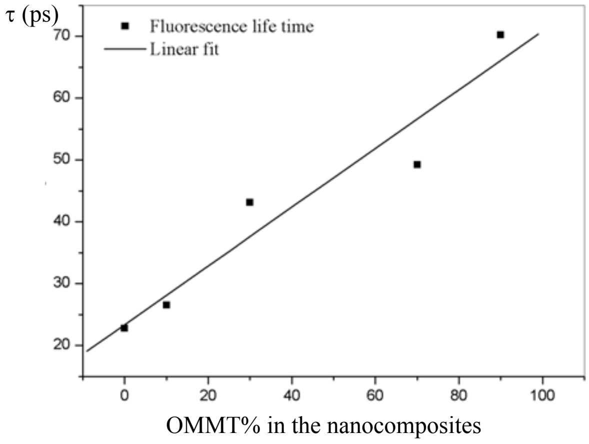
* MEH-PPV molecular structure:



OMMT would separate the polymer chains, decrease their self-aggregation and then force the polymer chains turning to the constrained conformations. After evaporation of the solvent, superfluous energy would be reserved in the polymer segments in form of entropy, which can increase the molecular mobility. This state would be kept in the solid samples without suffering any heat treatment. More OMMT contents would produce more confinement effect, so the T_1 values become shorter corresponding to the increase of OMMT content in the nanocomposites. This conclusion was also consistent with the steady state fluorescence spectra and fluorescence life- time results.

The excited state life times (τ) of MEH-PPV showed a linear prolonging tendency with increasing OMMT content in PPV/OMMT nanocomposites, as demonstrated in **Figure 1**. Since the fluorescence life time of the conjugated polymer samples are very short within the range of picoseconds and related to the $\pi-\pi*$ transition process, the prolongation of fluorescence life times indicated the decrease of the interchain $\pi-\pi*$ transition in the conjugated segments. Besides, MEH-PPV/OMMT nano composites with higher OMMT contents displayed larger Stokes shifts on the emission spectra. The longer fluorescence life times and enlarged Stokes shifts occurred in the nanocomposites could be attributed to the fact that the conjugated polymer chains were separated by the layered silicates and the segments with fluorophore are confined on the surface and interface of the nanoclay, and then, both the self-aggregates of polymer chains and self-quenching of fluorescence emission were reduced.

Figure 1 Fluorescence life times (τ) of MEH-PPV /OMMT nanocomposties.



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