

NANOSTRUCTURED POLYMERIC THIN FILMS: PREPARATION, ESR AND ATR-FTIR INVESTIGATIONS

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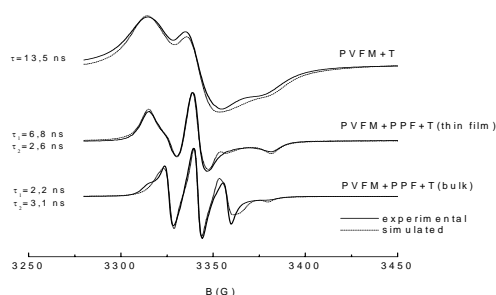
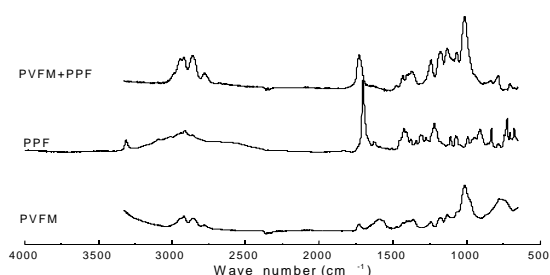
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Introduction/Background

Understanding of a complex correlation between polymer structure and its properties is the key to the polymer-specific morphology design ready to meet new technological requirements such as "smart" polymers, electro-optical materials, artificial organs, antireflection surface coatings, permselective membranes and drug delivery devices. At the basis of such systems are the nanostructured thin layers of polymers, co-polymers or polymeric composites, following the application purpose. The paper describes the results of Electron Spin Resonance (ESR) and Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) investigations of some polymeric films made by combining in equal proportions polyvinylformaldehyde resin with protoporphyrin and tempo as nitroxidic compound for investigating the microstructure of the prepared copolymeric films.



Besides the similarities, the ATR-FTIR spectra show considerable differences in the region of 1000-1800 cm⁻¹, suggesting the existence of strong interactions between the two components in the complex. The broadening and shifting of the characteristic peaks in the ATR-FT-IR spectrum of polyvinylformaldehyde resin with protoporphyrin, as compared to the counterparts in their simple mixture, indicate the presence of certain intermolecular interactions between polyvinylformaldehyde resin with protoporphyrin in the nanostructured complex. Simulation of the composite ESR spectra with a set of particular components was used to determine a fraction of slow/fast components in spectra of nitroxyl radicals (in this case T = tempo) correlated with nonuniformity in the nanostructured polymers. Due to increased spatial restrictions of protein structure in the vicinity of nitroxyl radicals, by polymerization, the mobility of spin probe is slow on the ESR time scale (~5·10⁶ s⁻¹), leading to a broadening of the ESR lines, with the peak-to-peak distance between the external peaks of the spectrum () depending on the magnitude of the rotational correlation time of the probe molecules.

Rotational correlation time:

$$\tau = a(1 - A_{zz}/A_{zz}^R)^b$$

$$a = 8,52 \cdot 10^{-10}$$

$$b = -1,16$$

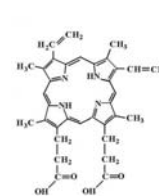
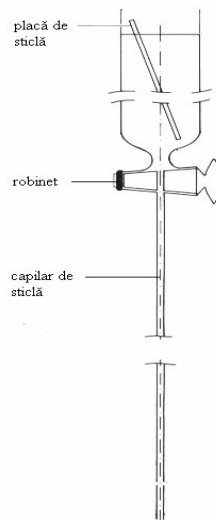
Conclusions

The ATR-FTIR spectra show considerable differences in the region of 1000-1800 cm⁻¹, suggesting the existence of strong interactions between the two components in the complex.

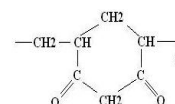
Simulation of the composite ESR spectra with a set of particular components was used to determine a fraction of slow/fast components in spectra of nitroxyl radicals (in this case T = tempo) correlated with nonuniformity in the nanostructured polymers.

Experimental

Such thin films are routinely prepared in laboratories [2] by controlled allowance of the polymeric solution from a separation funnel, by adjusting the valve. A clean piece of thin glass is mounted on the reservoir, and the evaporation of the solvent leave a thin polymeric layer of high homogeneity which sticks to the surface. Polyvinylformaldehyde was used as skeleton resin in surface and bulk nanostructured materials because of the good physico-chemical properties for multifunctional nanostructured systems [3]. Nitroxyl radicals, which are dispersed (spin probe) in polymer matrix or covalently bonded to polymer chains (spin label), are sensitive to the environment [1]. Therefore, molecular motion and microstructure of polymer systems can be identified from the ESR spectra.



PPF = protoporphyrine



PVFM = polyvinylformaldehyde

USEFUL REFERENCES:

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3. Simina Dreve, E. Indrea, I. Bratu, Margareta Bako, Gh. Mihailescu, Liliana Olenic, Stela, Pruncanu, V. Znamirovski, L. Barbu-Tudoran, *Studia Universitatis 'Babes-Bolyai', Physica*, Special Issue, 1 (2003) 381-384.