

## Solid-state characterization of poly(ethylene glycol) samples prepared by solvent cast technique

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The effect of solvents (H-donor; H-acceptor and both H-acceptor and H-donor solvents) casted on the poly(ethylene glycol) (PEG) samples with varying molecular weights (2000, 4600, 8000 and 10000) was performed solid-state characterization by Fourier Transform Infrared Spectroscopy (FTIR), Raman and X-ray Diffraction (XRD) in submitted study. In this study, spectral differences were classified with respect to stretching, bending, rocking, angle bending, internal rotation frequencies and low-frequency Raman region according to functional groups and thus crystallinity were evaluated as related with solvent character and polymer molecular weight. Crystalline and amorphous regions in the XRD diffractograms have been found by Polynomial Regression method through Microsoft Office Excel program and subsequently, crystallinity percentages were evaluated. From XRD spectra of PEG/solvent systems, the highest decrease in crystallinity percent has been detected in the sample cast from tetrahydrofuran. On the other hand, the largest frequency shifts of various stretching and bending vibrations of PEG have been observed for the samples cast from chloroform and especially tetrahydrofuran in FTIR and Raman spectra.

In the end of trio study, the parallelism of both computation and thermodynamic and spectroscopic data about solubility profiles of PEG/solvent systems has been determined. The results indicated that association power of solvents in PEG samples prepared by solvent cast technique was decreased below order:

tetrahydrofuran > chloroform > dimethyl sulfoxide > methanol > water.

**Key words:** Poly(ethylene glycol); solvent cast technique; fourier transform infrared spectroscopy; raman; x-ray diffraction.

### INTRODUCTION

Insecticides are essential tools for preventing or m Poly(ethylene glycol)s (PEG)s comprehend a series of water soluble, no irritating, linear chain polymers of oxyethylene units, with low toxicity. These properties enable their use for commercial and technological applications such as purification of biological materials, pharmaceutical drugs, edible films for food coating and water treatment [1-6]. Chen et al. [7] remarked that PEG aqueous solutions can profoundly affect water structure, reducing cohesivity and some aspects of H-bonding and thereby increasing the solubility of relatively less polar species. Dinc et al. [8] have calculated solubility parameters with group contribution methods among indirect methods for PEG and different solvents. They have been determined as the best solvent is THF and weakest solvent is water with algorithmic calculations. In addition, have been investigated solution thermodynamics of PEG/solvent systems with viscometric studies [9]. The unperturbed molecular dimensions of PEG samples have been evaluated. The thermodynamic aspects of PEG in dilute solutions have been

explained. The investigation of spectral evidences for algorithmic calculations and thermodynamic magnitudes presents purpose of offered study. In the submitted spectroscopy study, PEG samples prepared by solvent casting technique and pristine PEG samples (no solvent interaction) were compared and characterized in solid-state by FTIR, Raman and XRD imagines.

### MATERIALS AND METHODS

#### *Reagents*

PEG samples used in this study were supplied from Aldrich. The molecular weight distribution and densities of polymer samples were determined by the manufacturer and are given in Table 1.

Different solvents (H-donor solvent: chloroform; H-acceptor solvents: THF and DMSO; both H-acceptor and H-donor solvents: methanol and water) were used without further purification to prepare sample by casting technique. All other reagents were of analytical grade and used without further purification. The water used in the study was of ultrapure grade.

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**Table 1.** The molecular weight characteristics and densities of pristine PEG samples.

polymer	density at 25 °C (g/ml)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	polydispersity index
PEG 2000	1.127	1880	2030	2666	1.080
PEG 4600	1.127	3940	4040	4099	1.025
PEG 8000	1.270	7330	7550	7659	1.030
PEG 10000	1.070	10850	10950	11069	1.009

\*GPC-RALS study conditions:

Solvent: NaH<sub>2</sub>PO<sub>4</sub>, NaCl, Column set: 2xG2500PWXL aqueous column. Triple detector: refractive index, right angle light scattering, viscometer. Detector temperature: 35 °C.

*Preparation of samples by solvent casting technique*

Twenty different solutions were prepared by adding of the appropriate amount of the each solvent (water, chloroform, DMSO, THF and methanol) on PEG samples with different molecular weights (2000, 4600, 8000 and 10000). The concentrations of PEG solutions were changed between 1.0-0.2 g/dL according to molecular weight of polymer. And then, these solutions were magnetically mixed for 2h until completely homogenized at room temperature and dried at 25°C under vacuum.

#### *XRD measurements*

Casting technique for XRD samples was done by using best solvent (THF), and weakest solvent (water) determined for PEG from algorithmic calculations [8]. XRD patterns were taken at Hacettepe University, in Physics Engineering Department by using a Rigaku DMAX 2200 X-ray Powder Diffractometer in the  $2\theta = 5^\circ - 60^\circ$  range with CuK<sub>α</sub> radiation. This diffractometer consists of a RINT2000 wide angle goniometer with a 1/2° dispersion slit, a 0.73 mm scatter slit and a 0.3 mm receiving slit. The Cu anode X-ray tube was operated at 40kV and 36mA in combination with a Ni filter to give monochromatic CuK<sub>α</sub> X-rays. Measurements were taken from 5° to 60° in the Bragg's angle  $2\theta$  scale at a step size of 4° per min for qualitative analysis. Diffractograms were taken at room temperature consecutively. Crystalline and amorphous regions were found by polynomial regression method subsequently, crystallinity percentages were evaluated.

#### *FTIR measurements*

Samples (0.01 g) were finely ground and analyzed by dispersing them in 0.09 g of dried spectroscopic grade KBr (Merck) by pressed-disc technique. The FTIR spectra were recorded on an ATI UNICAM Mattson 1000 FTIR spectrometer at room temperature. The spectra were collected over the range 4000-400 cm<sup>-1</sup> by averaging 40 scan at a maximum resolution of 2 cm<sup>-1</sup>.

#### *Raman Measurements*

Casting technique for Raman samples was done by using best solvent (THF), mediate solvent (chloroform) and weakest solvent (water) determined for PEG from algorithmic calculations [8]. Raman spectra of samples were recorded using Labram HR800 Raman spectrometer (Jobin Yvon) with a He-Ne laser source emitting at 633 nm, 600-1200 grooves/mm holographic grating and a charge coupled device (CCD) detector. Raman spectra were obtained in 250 s integrations with an average of three scans. Spectra were recorded with reproducibility within 1 cm<sup>-1</sup>, hole: 400 μm, slit: 150 μm, resolution: 0.1 μm.

## RESULTS AND DISCUSSION

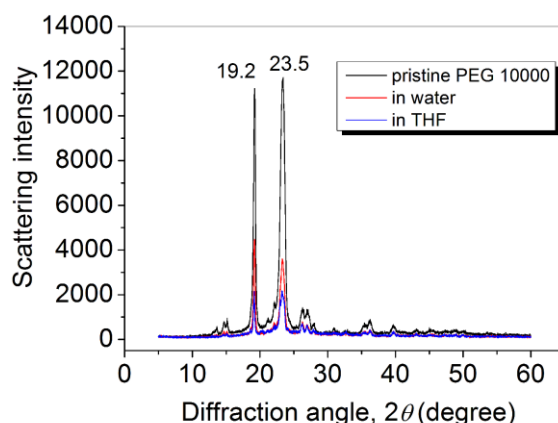
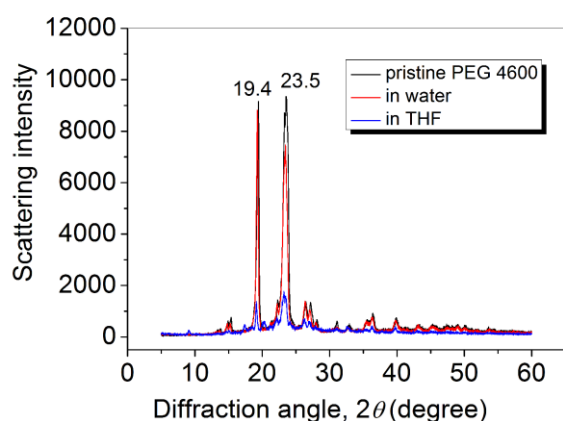
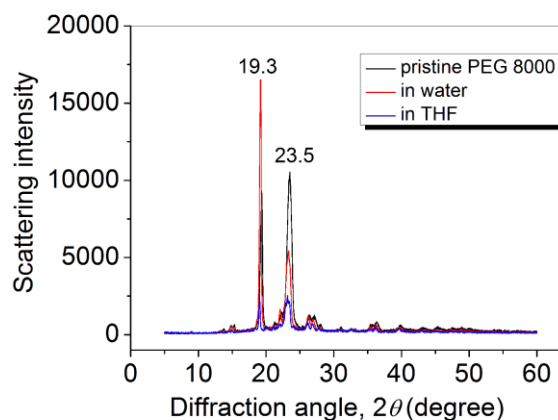
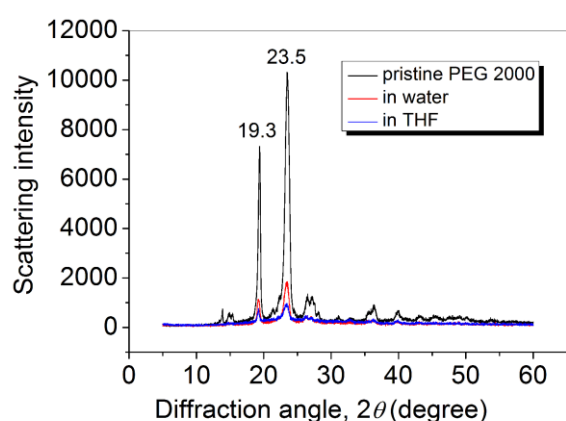
#### *XRD analysis*

X-ray powder diffractograms of PEG samples are shown in Figs. 1-2 which show diffuse areas with sharp band, suggesting uniform crystallization.

In Figs. 1 and 2, diffractions were mainly observed at two angles ( $2\theta = 19.3^\circ$  and  $23.5^\circ$ ). It was found that these two angles are in quite good agreement with those in literature and it is a semi-crystalline polymer [10-15].

The crystallinity results of PEG samples were given in Table 2.

In pristine polymer samples, percentage of crystallinity for PEG 2000 and 4600 was yielded 62-63% whereas for PEG 8000 and 10000, this value is dropped to 56%. As the molecular weight of the PEG increases, concentration of the OH groups is reduced, and, in this way, the number of H-bonds and crystallinity is decreased. From Table 2, it was observed crystallinity was decreased as the solvents penetrate into the structure of pristine PEG. The crystallinity results revealed that THF being more effective than water was led to a greater change in polymer conformation with introducing to PEG structure. This behavior, in turn, was ended up with the conclusion that crystallinity of samples prepared by casting THF is drop more than those in water. While Petrova et al. [11] find the crystallinity as 65% through X-ray studies for PEG 2000.



**Figure 1.** XRD patterns of the pristine and solvent-treated PEG (2000 and 4600).

**Figure 2.** XRD patterns of the pristine and solvent-treated PEG (8000 and 10000).

**Table 2.** The percent crystallinity of pristine and solvent-treated PEG samples.

	$X_c$ (%)		
	pristine PEG	PEG prepared by casting water	PEG prepared by casting THF
PEG 2000	62	44	33
PEG 4600	63	44	33
PEG 8000	56	46	33
PEG 10000	56	46	32

#### FTIR and Raman spectroscopy

In this part, spectral differences have been grouped with respect to characteristic fields and thus changes related with solvent character and molecular weight was evaluated.

#### O-H stretching

When investigated on the basic of molecular weight among pristine PEG samples, whilst the OH stretching frequency of the pristine PEG 2000 was observed at  $3426\text{ cm}^{-1}$ , the OH stretching frequency of pristine PEG 10000 was shifted towards  $3504\text{ cm}^{-1}$ . This shift is around  $\sim 80\text{ cm}^{-1}$ . It can be clearly stated that much higher OH stretching frequency is attributed to the presence of intra- and

intermolecular H-bonding interactions [ $\text{O}-\text{H}\cdots\text{O}-\text{H}$  as well as  $\text{O}-\text{H}\cdots\text{O}$  (ether oxygen)] in PEG [16]. PEG 2000, as a consequence of the abundance of OH end-groups and H-bond formation of these groups among themselves, the OH stretching frequency is weakened and the spectrum shifted towards lower wavenumbers. As the molecular weight increases, peak areas were decreased relatively because the number of end groups fall by increasing molecular weight. The shift of free OH vibrations to higher wavenumbers displayed in pristine PEG samples with increasing molecular weight was also observed in the samples prepared by casting solvent (Table 3).

**Table 3.** FTIR bands of OH end-group stretching for different molecular weight PEG/solvent systems.

Polymer	$\nu_{\text{OH}} \text{ (cm}^{-1}\text{)}$					
	pristine PEG	PEG casting from				
		water	methanol	DMSO	chloroform	THF
PEG 2000	3426(m)	3494(m)	3424 (m)	3475(m)	3444(m)	3289(m)
		3421(m)				
PEG 4600	3478(m)	3490(m)	3490 (m)	3475(m)	3482(m)	3270(m)
		3428(m)	3424 (m)			
PEG 8000	3484(m)	3498(m)	3486 (m)	3490(m)	3478(m)	3289(m)
		3421(m)				
PEG 10000	3504(m)	3579(m)	3552 (m)	3594(m)	3583(m)	3278(m)
		3509(m)				
		3421(m)				

\*) m: medium, w: weak

*C-H stretching*

C-H stretching vibrations display a broad and multishouldered spectral behavior in a wide frequency range of 2800-2950  $\text{cm}^{-1}$  [17-19]. In FTIR spectra of pristine (PEG)s, antisymmetrical  $\text{CH}_2$  stretching vibration is determined as a shoulder between 2942 and 2952  $\text{cm}^{-1}$ . On the other hand, this frequency was shifted to lower fields and occurred  $\sim 10 \text{ cm}^{-1}$  in samples prepared by casting solvent. This is clear evidence that implies that the hydrophobic interactions between the  $\text{CH}_2$  groups of polymer were being destructed in the presence of solvent. The frequency values were not vary much for the samples prepared by casting the other solvents whilst this shift was occurred at much lower frequency values in the sample prepared by casting THF. This behavior implies that symmetrical stretching was weakened as a consequence of the hydrophobic interactions of  $\text{CH}_2$  groups.

*CH<sub>2</sub> Bending*

Scissoring vibrations of  $\text{CH}_2$  groups (in-plane bending) displayed in the range 1468-1473  $\text{cm}^{-1}$  for pristine PEG samples were observed to weaken and shifted towards lower frequencies for samples prepared by casting of different solvents from FTIR spectra. The highest  $\text{CH}_2$  bending shift was observed on the sample prepared by casting THF. It was considered that scissoring motion is more flexible within the measure of disruption of hydrophobic interactions of  $\text{CH}_2$  groups.  $\text{CH}_2$  in-plane bending vibrations almost impossible to detect in FTIR were also mostly observed as doublet peaks at around 1480  $\text{cm}^{-1}$  at Raman spectra of submitted study.

*C-O stretching*

In FTIR evaluations of all PEG samples, bands observed at 1000-1200  $\text{cm}^{-1}$  are extremely broad and highly shouldered. After treatments with the solvents, the three specific bands (two shoulders and a weak band) were become more prominent. The first one among these is the band appearing at the wavenumber range 1145-1153  $\text{cm}^{-1}$ . This region may be described as the region of C-O-C asymmetrical stretching vibrations [20] and these vibrations may be observed as two distinct bands [21]. The band appearing at a higher frequency value was the one participating in intramolecular H-bond while the latter occurring at a lower wavenumber was characterized the C-O stretchings vibrations participating in intermolecular H-bond.

The bands occurring at 1145-1153  $\text{cm}^{-1}$  in pristine PEG samples were considered as C-O stretchings which do not participate in H-bonding. The shift towards lower frequency (about 5  $\text{cm}^{-1}$ ) of these bands in samples prepared by casting other solvents apart from THF is quite significant. However, more important than this, in THF which is considered as the best solvent, this band surprisingly was vanished. Polymer coil extends in good solvents thus leading to H-bond formation between etheric oxygen and OH groups, consequently weakening C-O stretching vibration, shifting of spectrum towards a down-field and even with the complete extinction of that band.

The quite significant band observed at 1103-1106  $\text{cm}^{-1}$  in all samples was showed somewhat spectral variations although very slight. This band may be considered as the C-O stretching incorporated in intermolecular H-bond formation together with the OH group.

### *CH<sub>2</sub> rocking*

In FTIR studies, spectral distinctions in this region were observed at two specific wavenumbers (842 and 962 cm<sup>-1</sup>). These frequency values were shifted towards lower wavenumber for samples prepared by casting the different solvents. The behavior supporting previous implications were existed here as well. As a consequence of the disruption of CH<sub>2</sub> groups through hydrophobic interactions, it was considered that bending vibrations of these groups certainly was disrupted and the spectrum was shifted towards lower frequency values.

### *C-C-O and C-O-C bending*

C-C-O and C-O-C bending vibrations were observed as three prominent peaks at 363-365 cm<sup>-1</sup>, 536-538 cm<sup>-1</sup> and 582-585 cm<sup>-1</sup> in Raman spectra of this study. As a consequence of the H-bonding between the etheric oxygen and OH end groups in PEG, both two bending vibrations were violated and subsequently, the spectrum was shifted towards lower frequency values.

### *C-O-C angle bending and C-O internal rotation*

The Raman bands characterizing two vibrations within the range of 215-230 cm<sup>-1</sup> were observed in submitted study. The spectral behavior of PEG samples prepared by casting solvent was exhibited discriminates significantly from that of the pristine (PEG)s. As the solubility power of the employed solvent rises, a shift towards higher wavenumbers was unavoidable. In the samples prepared by casting chloroform and THF (qualified as good solvents), shifts were observed towards highest wavenumbers.

### *Low-frequency Raman region (<400 cm<sup>-1</sup>)*

Bending (**O – H ... O bending**, C-O rotation, C-C-O angle bending and C-O-C) vibrations have been investigated in detail within the range of 48-88 cm<sup>-1</sup> at the Raman analyses. The spectral evaluations were highly illustrated the spectral distinctions in the behavior of pristine (PEG)s and those prepared by casting different solvents. It was shifted towards higher frequency values for the samples prepared by casting solvent when compared with pristine PEG samples. The highest frequency shift values were displayed for the samples prepared by casting chloroform and THF. It was considered that **O – H ... O** in-plane deformation, C-O rotation and C-C-O angle bending vibrations were shifted towards higher wavenumbers. This observation is a strong evidence illustrating the achieve role of H-bond for the samples prepared by casting THF and chloroform.

The shifts towards higher frequency values were observed within the measure of H-bond achieved by H-acceptor oxygen atom and OH end groups at the Raman analyses. This behaviour implies that the mentioned vibrations were occurred less favorably as long as the degree of H-bond formations increases. The greatest frequency shifts were observed in the samples prepared by casting chloroform and THF samples. Consequently, it is noteworthy to say that, in the end of trio study, the parallelism of both computation [8] and thermodynamic [9] and spectroscopic data about solubility profiles of PEG/solvent systems were determined.

## CONCLUSIONS

In this study, it was investigated association of solvents to the pristine PEG by FTIR, Raman and XRD spectroscopic analyses. The solubility profile of PEG/solvent systems was evaluated as connected with solvent character and molecular weight.

When the XRD charts of PEG samples were compared, it was observed that THF is more effective than water in decreasing the crystallinity of the polymer. On the other hand, it was perceived that frequency shifts of various stretching and bending vibrations was risen to maximum for PEG samples prepared by casting chloroform and especially THF as a consequence of both FTIR and Raman interpretations' evaluation.

Solid-state characterization revealed that THF being more effective than water with introduction to PEG structure. The results were indicated that the shift was occurred towards higher frequency values with increased interaction because number of OH end groups and H-bonds for low molecular weight PEG 2000 was increased.

As a consequence of the interaction of end groups with etheric oxygen resulting from the unfolding of the polymer coil in a good solvent it can be clearly stated association power of solvents in PEG samples prepared by solvent cast technique decreased below order: THF > chloroform > DMSO > methanol > water.

PEG chains could easily be attached to several molecules due to of the reactive OH end groups, constituted copolymer or blend. In recent years, it have been found applications in a variety of purposes as conservation material, cellular material, binding agent, anti-foaming agent in food ingredient of e-liquid used in electronic cigarettes, electrolyte solvent in lithium polymer cells, preservative objects salvaged from underwater, lubricating coating for various surfaces, skin creams or toothpastes. As revealed that solvent factor is very important for PEG.

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