Raman analysis of polyethylene glycols and polyethylene oxides

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Abstract. We present Raman study of commercial liquids and powders of polyethylene glycols and polyethylene oxides with the average molecular weight from 400 Da to 10000 kDa. The most significant spectral changes were observed for the range of the molecular weights, where the liquid/semisolid transition has occurred. For the powders we revealed increase in the content of the molecules in the helical conformation and in the content of the monoclinic crystalline phase with growth of the molecular weight.

1. Introduction
Polyethylene glycols (PEGs, \(\text{OH}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{H}\)) and polyethylene oxides (PEOs, \(-(\text{CH}_2-\text{CH}_2-\text{O})_n\)–) are widely used in numerous areas of human activity, in particular, in chemical, food, pharmaceutical and cosmetic industries, in mechanical engineering, metal and oil processing, in agriculture. One of the rapidly growing state-of-the-art technologies is application of PEGs for creation of so-called PEGylated pharmaceuticals, which are used at treatment of various diseases, including some types of cancer and hepatitis, AIDS, and as drug delivery systems. Furthermore, PEGs/PEOs are extensively used in fundamental research, for example, as simple models of biomolecules.

Aggregate state of PEGs/PEOs (liquid, semisolid, or solid), conformational (helical \(\alpha_2\) or trans-conformation) and packing order (monoclinic or triclinic crystalline lattice, the degree of crystallinity), physical and chemical properties, toxicity and photo-thermal stability and, as consequence, possible areas of applications depend strongly on the molecular weight. For these substances the transition from liquid to semisolid state is observed at molecular weights from 700 to 1000 Da (depending on the purification that is the content of water and impurities/stabilizers). Using differential scanning calorimetry (DSC) and X-ray diffraction analysis Majumdar et al. [1] have found that the degree of crystallinity of PEG/PEO powders increases with growth of the molecular weight, reaches the maximum at the molecular weight of 8000-9000 Da, and then decreases slowly (the maximum investigated molecular weight was 23000 Da). Thus, because of numerous vital applications it is very...
important to be able to characterize the structure and state of PEG/PEO molecules and to identify the molecules of various molecular weights in both the neat forms, and in different compositions and blends, including PEGylated forms.

Furthermore, the PEG/PEO molecules form the homologous series, and these substances are commercially available in a wide range of molecular weights. Studying a homologous series is the way to investigate the supramolecular structure and properties of the series of molecular substances with sequential and stepwise changes in the molecule structure, realized by increase in the number of repeat units (so-called, the homological difference). This way, one can obtain extensive information about the structure - properties relations and to develop models, which allow predicting the supramolecular structure and the properties of uninvestigated homologs. This knowledge opens new ways for development of novel functional materials with desired properties by slight modification of the molecule structure.

There are two stereoregular conformations of PEG/PEO molecules: helical conformation \( \alpha \) (seven repeat units in the trans-gauche-trans (TGT) conformation of sequences \(-\text{O-CH}_2\text{-CH}_2\text{-O-}\) on two turns in an identity period) and trans-conformation. Based on data of X-ray diffraction analysis, the monoclinic crystalline lattice with four molecules in the unit cell was reported for PEG/PEO molecules in the distorted conformation of the helix \( \alpha \) [2] and the triclinic crystalline lattice with one molecule in the unit cell – for the molecules in the trans-conformation [3]. The triclinic modification is observed in stretched PEOs and is stable only under tension.

Raman spectroscopy is a highly informative, non-destructive and label-free technique of molecular spectroscopy, which can be effectively applied for both liquids and solids. In particular, using Raman spectra it is possible to evaluate the configurational order, the conformational composition (the contents of conformationally ordered monomer sequences of a certain length), the packing order (the degree of crystallinity, the type of the crystalline lattice(s), and the distribution of crystallite sizes), the chemical composition and the content of various chemical groups, the orientational order of molecules. However, Raman spectroscopy has been rarely used for systematic and detailed study of the homologous series of PEG/PEO molecules. Probably, it is connected with complex Raman spectra of these substances, where overlapping of numerous lines of various sequences of conformers is observed. This also makes the assignment of the PEG/PEO Raman lines not straightforward, and there are many contradictions between the assignments and peak positions of the Raman lines even in a few Raman studies of PEGs/PEOs, which were found in literature [4-12].

Based on experimental Raman study of PEG with the molecular weight of 6000 Da and the normal coordinate analysis on a large number of conformers of model molecules, Matsuura and Fukuhara [4,5] have suggested assignment of the Raman lines of PEGs/PEOs in the spectral region from 800 to 1500 cm\(^{-1}\) to the vibrations of various sequences of conformers. In particular, it was shown that the spectra of various conformer sequences are strongly overlapping, and it is a reason of difficulties in Raman analysis of conformational composition of PEG/PEO molecules. Temperature-dependent evolution of Raman spectra of PEG with the molecular weight of 2000 Da was studied in detail in the spectral range about 800 cm\(^{-1}\) [6].

Raman spectroscopy was applied to study the conformation order of PEG macromolecules of the molecular weight of 1500 Da [7,8]. The lines at 1227 and 1275 cm\(^{-1}\) were assigned to the CH\(_2\) wagging vibrations of trans- and gauche-conformers relative to C-C bond, respectively, while the lines at 1118 and 1136 cm\(^{-1}\) - to the CH\(_3\) twisting vibrations of trans- and gauche-conformers relative to C-O bond, respectively. Analyzing changes in integral intensities of these lines, Kozielski et al. [7,8] supposed that with decrease in PEG concentration in water solutions the ratio of contents of the PEG molecules in the helical and trans conformations increases. Using IR spectroscopy, similar results were obtained for a number of short-chain PEGs with various terminal groups in water solutions with varying PEG concentration [9]. Based on their proposed assignments of the Raman lines at 1118, 1136, 1227, and 1275 cm\(^{-1}\), Kozielski et al. [7] have stated that the conformational order of PEG/PEO molecules is practically independent on the molecular weight in the range from 1500 to 12000 Da.
Figure 1. Raman spectra of PEGs/PEOs in the region from 100 to 1800 cm\(^{-1}\). \(M_w\) is the average molecular weight in Daltons. PEGs with the molecular weight of 400 and 600 Da are liquids, while the other samples are semisolids and solids.
Figure 2. Raman spectra of PEGs/PEOs in the region from 2400 to 3400 cm\(^{-1}\). \(M_w\) is the average molecular weight in Daltons. PEGs with the molecular weight of 400 and 600 Da are liquids, while the other samples are semisolids and solids.
However, the assignment of Kozielski et al. [7,8] is not supported by results of Matsuura and Fukuhara [4,5]. On the other hand, the lines at 1124 and 1280 cm\(^{-1}\) were related to the vibrations of PEG/PEO molecules in the helical conformation TGT in the monoclinic crystalline phase [10].

Samuel and Umapathy [10] carried out temperature-dependent Raman study of PEG of the molecular weight of 1000 Da as well as the DFT calculations of the Raman spectrum of molecule \(\text{CH}_3\text{O-} (\text{CH}_2\text{-CH}_2\text{-O})_n\text{-CH}_3\), which was chosen as a model of one repeat unit of helix \(\tau_2\).

Yang et al. [11] studied Raman spectra of PEO with the molecular weight of 4600 Da in aqueous solution and in the melt. Using the normal coordinate calculations, Raman spectra of PEO were simulated by superposing the calculated spectra of an ensemble of various conformers.

Yang et al. [12] have investigated the effect of molecular weight on PEG/PEO molecular conformation (helix or \(\text{trans}\)-) by X-ray diffraction analysis, FTIR, and DSC. It was found that in the case of films, prepared by the solution-casting method, growth of the molecular weight leads to the decrease in the PEG/PEO crystallinity and the content of molecules in the helical conformation with simultaneous increase in the content of molecules in the \(\text{trans}\)-conformation.

Summing up, assignments of the Raman lines of PEGs/PEOs are still incomplete, and the qualitative and quantitative relationships between the Raman spectra and the molecular and supramolecular structure are not yet fully known. In this work we present Raman spectroscopic study of the series of commercial PEGs/PEOs with average molecular weight, varied in a wide range.

2. Experimental

PEG/PEO samples with the average molecular weight from 400 Da to 10000 kDa were purchased from BASF и FERAK Berlin companies. The samples with the molecular weights of 400 and 600 Da were liquids, while the other samples were in the forms of semisolids or powders. In this work the samples were analyzed as they were purchased, that is without any processing or treatment.

The Raman setup consisted of a Sapphire SF 532 laser (Coherent Inc., USA), a double monochromator U1000 (Jobin Yvon, France) and Peltier-element cooled photomultiplier detector, operating in the photon counting regime. The excitation wavelength was 532 nm. Non-polarized Raman spectra were recorded at room temperature at 90°-scattering with the spectral resolution of 5 cm\(^{-1}\). Diameter of the laser spot on a sample was about 2 mm.

Analysis of the experimental spectra was carried out using the homemade software. Shape of each line was described by the weighted sum of Lorentz and Gauss functions. Baseline was described as a second-order polynomial and fitted simultaneously with the Raman lines.

3. Results and Discussion

Figures 1 and 2 present the Raman spectra of PEGs/PEOs with the average molecular weights from 400 Da to 10000 kDa in the region from 100 to 1800 cm\(^{-1}\) and in the region from 2400 to 3400 cm\(^{-1}\), respectively. The spectra in the region from 100 to 1800 cm\(^{-1}\) are normalized to the maximum Raman intensity in the range 1450-1500 cm\(^{-1}\), where the lines, assigned to the CH\(_2\) bending vibrations [4], are manifested. This maximum intensity is observed at about 1470 cm\(^{-1}\) for the liquid PEGs and at about 1480 cm\(^{-1}\) for the semisolid and solid PEGs/PEOs. The spectra in the region from 2400 to 3400 cm\(^{-1}\) are normalized to the peak intensity of the most intense line in each spectrum. The Raman-active lines of PEGs/PEOs are absent in the region from 1800 to 2400 cm\(^{-1}\).

We found out that the peak positions and intensities of the PEG/PEO Raman lines are sensitive to the change in the molecular weight (Figures 1, 2, and 3). Most significant spectral changes with the increase in the molecular weight are observed for PEGs with the molecular weights of 600 and 1500 Da that is at the transition from liquid to semisolid state for our limited set of the samples. At the same time, the Raman spectra of two liquid PEGs (400 and 600 Da) are very similar as well as the Raman spectra of all the semisolid and solid PEGs/PEOs do not change dramatically with the increase in the molecular weight.
Figure 3. Raman spectra of PEGs/PEOs in the region from 100 to 1800 cm$^{-1}$. $M_w$ is the average molecular weight in Daltons.

Figure 4. Raman spectra of the semisolid/solid PEGs/PEOs in the region from 1090 to 1340 cm$^{-1}$. $M_w$ is the average molecular weight in Daltons. The spectra are normalized to the peak intensity of the line at about 1280 cm$^{-1}$.
Let’s first compare the spectra of two liquid PEGs under study. We found out three noticeable spectral distinctions, that are, first, presence of the weak line at about 1720 cm\(^{-1}\), second, higher intensity of the line at 880 cm\(^{-1}\), and, third, slightly higher intensity of the line at 2940 cm\(^{-1}\) in the spectrum of PEG with the molecular weight of 400 Da compared with the spectrum of PEG with the molecular weight of 6000 Da (Figures 1, 2, and 3).

The line at 1720 cm\(^{-1}\) most probably corresponds to the vibrations of C=O bonds in the formiates and other esters, which were formed due to PEG oxidation in air [13]. Matsuura and Fukuhara [4,5] have assigned the line at 880 cm\(^{-1}\) to the superposition of the C-O stretching vibration and the CH\(_2\) rocking vibration of sequences of conformers, distinct from the helical 7/2 structure. These authors [4,5] have observed the line at about 885 - 900 cm\(^{-1}\) in the Raman spectra of the melt and aqueous solutions of PEG with the molecular weight of 6000 Da, while this line was absent in the spectrum of the solid state of this PEG. This line is also absent in our spectra of all the semisolid and solid PEGs/PEOs under study (Figures 1 and 3). In principle, the line at 880 cm\(^{-1}\) can be also related [5] to the C-OH stretching vibration of terminal hydroxyl groups in low molecular weight PEGs.

Samuel and Umapathy [10] have noted that the intensities of the Raman lines at 884 and 2940 cm\(^{-1}\) of PEG with the molecular weight of 1000 Da increase with temperature growth. Kozielski et al. [6] have also observed appearance of the band at 880 cm\(^{-1}\) in Raman spectra of PEG with the molecular weight of 2000 Da with heating.

Summing up, we concluded that dumping of the lines at 884 and 2940 cm\(^{-1}\) is the evidence that conformational order of PEG molecules with the molecular weight of 600 Da is higher compared with that of PEG with the molecular weight of 400 Da.

The second step of our analysis is comparison of the spectra of semisolid and solid PEGs/PEOs with each other. In spite of the weak spectral variations for this series of the samples, we observed slight, but reliable increase in the intensities of the lines at 365, 536, 844, 859, and 1140 cm\(^{-1}\) with
growth of the molecular weight (Figures 1 and 3). In the region from 2400 to 3400 cm\(^{-1}\) the Raman spectra of the semisolid and solid PEGs are very similar (Figure 2).

Yang et al. have assigned [11] the line at 365 cm\(^{-1}\) to the C-O-C bending vibration of PEG/PEO molecules in the helical conformation. This band relates to the disordered longitudinal acoustic mode (D-LAM), corresponding to straight chain segments with a well defined specific chain conformation. This line is absent in the spectra of the liquid PEGs (Figures 1 and 3). The peak position of this line is the same for all the semisolid/solid PEGs/PEOs under study (within the limits of the spectral resolution used).

Samuel and Umapathy [10] have shown that heating of PEG of the molecular weight of 1000 Da leads to damping of the lines at 844 (the C-O stretching vibration + the CH\(_2\) rocking vibration), 863 (the C-C stretching vibration + the C-O stretching vibration + the CH\(_2\) rocking vibration), and 1140 cm\(^{-1}\) (the C-O stretching vibration + the CH\(_2\) rocking vibration) in its Raman spectrum. These authors [10] have assigned the line at 844 cm\(^{-1}\) to the vibrations of molecules in the helical conformation in the monoclinic crystalline phase. They showed that intensity of the line at 844 cm\(^{-1}\) decreases at heating and increases at cooling, and these variations are in very good agreement with DSC thermograms.

Based on experimental and calculated Raman spectra, Yang et al. [11] have assigned the band at 848 cm\(^{-1}\) to the C-O stretching vibrations of molecules in the helical conformation. Kozielsky et al. [6] have observed the decrease in intensity of the lines at 838 and 855 cm\(^{-1}\) in Raman spectra of PEG with the molecular weight of 2000 Da with temperature growth. Matsuura and Fukuhara [5] have found that the calculated PEG/PEO Raman spectra contain the lines in the range 825-870 cm\(^{-1}\), related to the sequences of conformers xGx-xGx (where x implies either T or G) in chain segments -O-CH\(_2\)-CH\(_2\)-O-CH\(_2\)-CH\(_2\)-O-.

Yang et al. [12] have related the IR line at 1140 cm\(^{-1}\) to the vibrations of molecules in the monoclinic crystalline phase.

Thus, we concluded that the increase in the intensities of the lines at 365, 844, and 1140 cm\(^{-1}\) with a growth of the PEG/PEO molecular weight (Figure 3) should be interpreted as increase in the content of molecules in the helical conformation and in the content of the monoclinic crystalline phase.

Figure 4 presents Raman spectra of the semisolid and solid PEGs/PEOs in the region from 1090 to 1340 cm\(^{-1}\). The spectra are normalized to the peak intensity of the line at about 1280 cm\(^{-1}\). In this region the lines at 1118, 1136, 1227, and 1275 cm\(^{-1}\) should be observed. As it was mentioned above, these lines were assigned to trans- and gauche-conformers of PEG/PEO molecules relative to C-O and C-C bonds [7,8]. It can be seen from Figure 4, that the distribution of the intensity of Raman scattering in this spectral range is not changed with growth of the molecular weight for all the semisolid and solid PEGs/PEOs under study.

Our deconvolution analysis (Figure 5) has shown that the structure of the PEG/PEO Raman spectra in this range is more complex, than it was proposed in [7,8]. In the spectra of the semisolid and solid PEGs/PEOs there are at least seven Raman-active lines with the peak positions at 1118, 1125, 1142, 1229, 1236, 1277, and 1283 cm\(^{-1}\). At the first stage of our deconvolution analysis we supposed presence of only five lines at 1125, 1142, 1229, 1236, and 1280 cm\(^{-1}\), which can be easily recognized in the PEG/PEO spectra. However, the spectra were poorly described by five lines, and, thus, two additional lines were introduced.

Matsuura and Fukuhara [4,5] have found six lines in this region in the spectra of solid PEG, that are the lines at 1112, 1127, 1143, 1233, 1239, and 1282 cm\(^{-1}\). However, these authors did not carry out the deconvolution analysis of the spectra, and, thus, two strongly overlapped lines at 1277 and 1283 cm\(^{-1}\) could not be resolved. The lines at 1233 and 1239 cm\(^{-1}\) were related to the TGT conformers in chain segments -O-CH\(_2\)-CH\(_2\)-O-, which form the helical conformation of PEG/PEO molecules [4,5].

Thus, we conclude that the assignment of the PEG/PEO Raman lines in the region from 1090 to 1340 cm\(^{-1}\), suggested by Kozielski et al. [7,8], requires additional justifications.
Finally, we proceed to the analysis of the spectral alterations at the liquid/semisolid transition, which in our limited set of the samples is observed at increase in the PEG molecular weight from 600 to 1500 Da. First, we observed the abrupt high-wavenumber shift (from 2874 to 2887 cm$^{-1}$) of the peak position of the symmetric C-H stretching vibration. Exactly the same effect was observed by Samuel and Umapathy [10] at heating of PEG with the molecular weight of 1000 Da, that is the shift of the line at 2887 cm$^{-1}$ to 2874 cm$^{-1}$.

The second feature at the transition from the liquid to semisolid PEG state is the sharp decrease in the intensity of the band at 810 cm$^{-1}$, which was assigned [10] to the vibrations of the sequences of conformers GGT, TGG, and GGG of chain segments -O-CH$_2$-CH$_2$-O-. However, Matsuura and Fukuhara [5] have calculated the lines in the region 810-825 cm$^{-1}$, arising due to conformer sequences xTx (x denotes either G or T) of chain segments -O-CH$_2$-CH$_2$-O-.

Samuel and Umapathy [10] showed that the line at 810 cm$^{-1}$ becomes more intense with temperature growth in Raman spectra of PEG with the molecular weight of 1000 Da. Thus, according to their assignment, the conformational order in the liquid PEGs (as well as in the melt of PEG with the molecular weight of 1000 Da [10]) differ from the conformational order of the semisolid/solid PEGs/PEOs in higher content of gauche-conformers about C-O bonds, while preference of gauche-conformation about C-C bonds is observed for both liquid and semisolid/solid states (as well as for the PEG melt [10]). In [6] appearance of the line at about 800 cm$^{-1}$ was observed at heating of PEG with the molecular weight of 2000 Da.

Samuel and Umapathy have stated [10] that the ratio of intensities of the lines at 810 and 844 cm$^{-1}$ is a measure of relative contents of gauche- and trans-conformers relative to C-O bonds. The reduction in intensity of the line at 844 cm$^{-1}$ with heating corresponded very well with the increase in intensity of the line at 810 cm$^{-1}$, indicating the transformation of one type of conformers to another [10]. However, it is not convenient and accurate to calculate the conformational composition of PEG/PEO molecules using these two lines due to strong overlapping of numerous lines in this spectral range. Samuel and Umapathy [10] have found at least 9 lines in this spectral region.

Third, a number of new Raman lines appear in the spectra of the semisolid/solid PEGs/PEOs compared with the liquids. Besides the line at 365 cm$^{-1}$, the most prominent new features are the lines at about 932, 1362, and 1391 cm$^{-1}$. Two lines at 930 and 934 cm$^{-1}$ were observed only in the spectra of solid PEG and were assigned to the superposition of the CH$_2$ rocking, the C-O stretching, and the C-C stretching vibrations of PEG/PEO molecules in the helical conformation [4]. This assignment was confirmed by calculation of the lines of the conformer sequences xGT-TGx of chain segments -O-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-O- in the region 940-950 cm$^{-1}$ [5]. The assignment of this feature to the vibrations of molecules in the amorphous domains of solid PEGs/PEOs [10] seems to be in error.

According to Matsuura and Fukuhara [4], the lines at 1364 and 1397 cm$^{-1}$ are related to the CH$_2$ wagging vibration for most of possible PEG/PEO conformations. However, the line at 1364 cm$^{-1}$ was not observed in Raman spectra of the melt and aqueous solutions of PEG with the molecular weight of 6000 Da [4]. Most probably this line corresponds to the calculated vibrations of the conformer sequences xGT-TGx of chain segments -O-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-O- in the region 1350-1360 cm$^{-1}$ [5].

At the same time, Matsuura and Fukuhara [4,5] have noted that the Raman bands at 997 and 1045 cm$^{-1}$ are characteristic of the PEG/PEO melts and aqueous solutions and can correspond to a number of possible conformations of PEG/PEO molecules. Line at 997 cm$^{-1}$ was related [5] to the vibrations of the conformer sequences, containing trans-conformers relative to C-C bond and gauche-conformer relative to C-O bond.

Indeed, the spectra of semisolid and solid PEGs/PEOs (Figures 1 and 3) do not contain Raman scattering at 997 and 1045 cm$^{-1}$, but the narrow and strong line at 1060 cm$^{-1}$ is evident. The spectra of the liquid PEGs under study contain broad band with complex structure and the peak position at about 1045 cm$^{-1}$.
4. Conclusions
We studied Raman spectra of the homological series of polyethylene glycols and polyethylene oxides, that are liquid, semisolid, and solid homologs for the range of the molecular weight from 400 Da to 10000 kDa. Most prominent spectral alterations were observed for the range of the molecular weight, where the liquid/semisolid transition has occurred. At the same time, the spectra of the liquids were very similar as well as the changes in the spectra of the semisolids/solids with growth of the molecular weight were weak. The Raman lines at 810, 880, 997, and 1045 cm\(^{-1}\) are characteristics of liquid polyethylene glycols and are absent (or very weak) in the spectra of semisolid/solid polyethylene glycols and polyethylene oxides. These lines were also observed by other authors only in the melts and aqueous solutions of polyethylene glycols and polyethylene oxides.

We found that the lines at 365, 932, 1362, and 1391 cm\(^{-1}\) are manifested only in the spectra of semisolids and solids. Based on the increase in the intensity of the lines at 365, 844, and 1140 cm\(^{-1}\), we concluded that the content of molecules of polyethylene glycols and polyethylene oxides in the helical conformation and the content of the monoclinic crystalline phase increase with growth of the molecular weight of these molecules.

The obtained results can be useful for development of new materials for various applications as well as for Raman characterization of molecular substances with similar chemical structure. However, additional investigations of polyethylene glycols and polyethylene oxides in liquid, semisolid, and solid states as well as in the melt and solutions are required for development of Raman methods of precise and reliable diagnostics of structure of these substances. In particular, the assignments of the most of the Raman lines of polyethylene glycols and polyethylene oxides as well as quantitative relationships between the Raman spectra and the molecular and supramolecular structure should be clarified in detail.

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