Interactions and Temperature Transitions of Ethylene Oxide – Propylene Oxide – Ethylene Oxide *tri*-block Copolymers in Water Media

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Summary: ATR FTIR spectra of two ethylene oxide – propylene oxide – ethylene oxide $(EO)_n$-$(PO)_m$-$(EO)_n$ *tri*-block copolymers (Pluronics) with different lengths of the EO blocks were investigated in water media at various temperatures. The observed wavenumber shifts and intensity changes of the bands of different chemical groups of polymers and of water molecules served as a basis for the estimation of structural changes and interactions of polymers with the surrounding water molecules. Two types of such interactions, i.e. hydrophilic (ether group – water) and a hydrophobic (methyl group – water) are detected. In the copolymer with shorter length of the EO blocks, an interchain H_2O bridge in a liquid crystalline phase was discovered and confirmed by *ab initio* calculations. A model for the structural changes during the temperature transitions is specified.

Keywords: FTIR; polyethers; structure; transition; water-soluble polymers

Introduction

Ethylene oxide – propylene oxide – ethylene oxide $(EO)_n$-$(PO)_m$-$(EO)_n$ *tri*-block copolymers (Pluronics) are widely applied in medicine, biochemistry, pharmacy and have many other industrial, agricultural and technological uses. A good survey of their application can be found in [1]. These copolymers are characterised in water media by typical transition temperatures T_t; below that points they tend to form water solutions, above T_t they aggregate. These effects are phenomenogically well described and there exist also publications trying to use vibration spectroscopy for the explication of the phase changes of copolymers with temperature[2–11]; nevertheless, the structural origin of such behaviour is not yet sufficiently explained.

In this article the structural changes and interactions of two copolymers having different length of EO blocks in water media will be compared and some newly found effects in the spectra will be clarified.

Experimental Part

Materials

Two Pluronic materials, PE6200 (producer BASF, a liquid of nominal average formula $(EO)_5(PO)_{31}(EO)_5$) and F68 (producer FLUKA, a solid of nominal average formula $(EO)_{81}(PO)_{31}(EO)_{82}$) were used. Their EO molar fractions obtained from ^{1}H NMR were 0.373 and 0.837, respectively. Copolymers were measured in water media (their weight fraction of prepared solution $W_P = 0.1$) and as pure compounds. Water of the type LC-MS CHROMASOLV was a product of Riedel-de-Haen.

Measurements and Processing of Spectra

For the measurement of spectra, a FTIR spectrometer Nexus Nicolet 870 purged with dry air and equipped with a cooled MCT detector was used. Samples were measured on a horizontal micro-ATR

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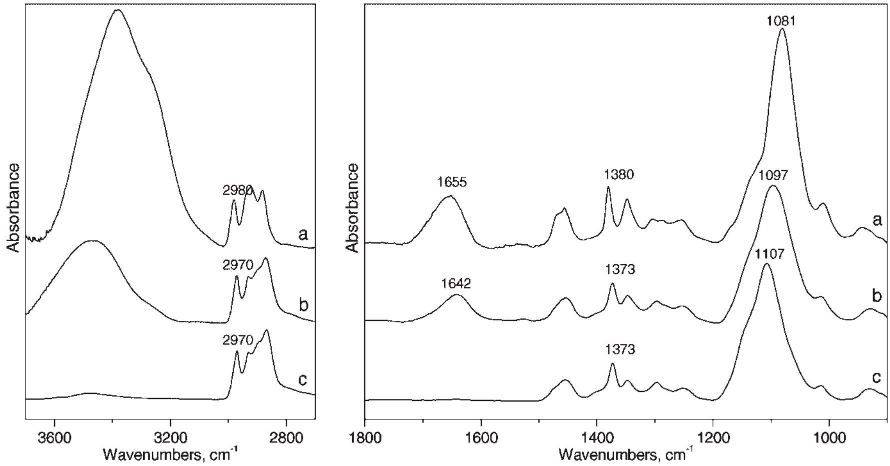

Figure 1.
ATR FTIR spectra of copolymer PE6200. $W_p = 0.1$, at 10 °C (a), at 70 °C (b), spectra of bulk water subtracted. (c) Pure copolymer at 24 °C.

Golden Gate unit (SPECAC), having a control-heated top plate with a diamond window. Spectral resolution was 4 cm^{-1}. The samples were gradually heated and subsequently cooled in the temperature range 5–80 °C in the steps of 2 °C. From the spectra of copolymers in water media, the spectra of bulk water measured at the corresponding temperature were subtracted. For this, the highest reasonable subtraction coefficients k were chosen. Their values were estimated by the criterion that no counter peaks of bulk water intersect the baseline in the region of 3100-3000 cm^{-1} (see Figure 1 and 2, curves a, b). All the spectra were processed by ATR correction and by introducing proper baselines. Integration of intensities of C–H stretching bands was carried out in the range 3020–2800 cm^{-1}, integration of H_2O bending in the range 1760–1560 cm^{-1}. For proper location of the baselines under the bands

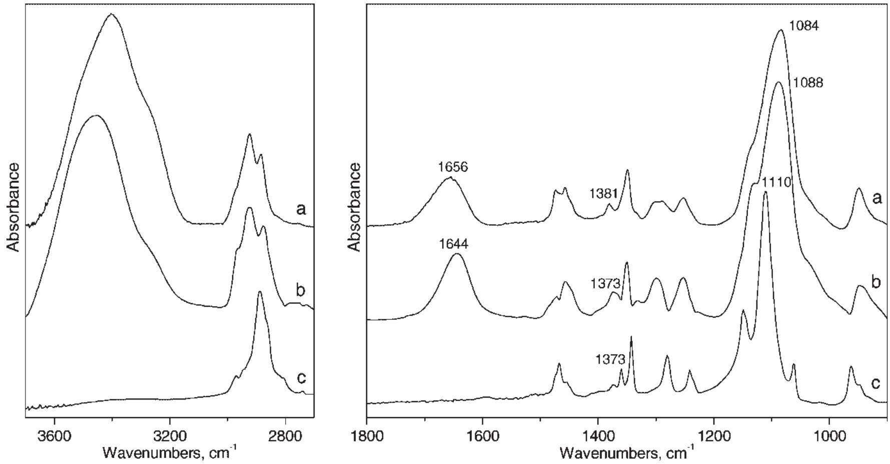

Figure 2.
ATR FTIR spectra of copolymer F68. $W_p = 0.1$, at 10 °C (a), at 70 °C (b), spectra of bulk water subtracted. (c) Pure copolymer at 24 °C.

and for suppressing the rest of water vapour some spectra were smoothed.

Local Concentration Changes during ATR Measurement in Water Media

ATR method appeared to be useful for the measurement of spectra in water media, facilitating infrared measurements of strongly absorbing water solutions and preventing rather unnatural conditions and water evaporation which would appear during a transmission measurement in a thin layer. On the other hand it must have been taken into consideration that by that method spectral information is obtained only from a layer of the material touching closely the surface of the ATR diamond prism. Above the transition temperature and sometimes also below it the copolymer material in the water layer had a tendency to settle down on the prism increasing its local concentration there. Local concentrations of the measured copolymers in water media near the ATR diamond prism are reflected both in values of subtraction coefficients of bulk water and in values of area under the C–H stretching bands (see in Figure 3). They will be discussed later.

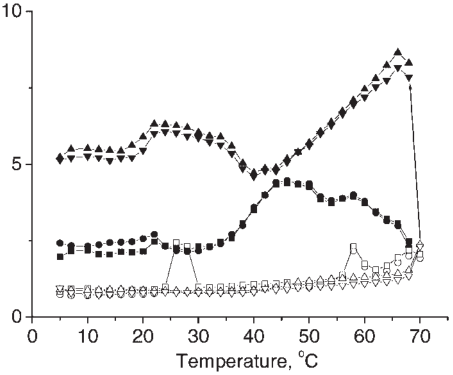

Figure 3.
Local concentration changes of copolymers in the water media near the diamond ATR prism, expressed by the integral intensity of C–H stretching ***A*** under curve 3020–2800 cm^{-1} and by the coefficient ***k*** found for a proper subtraction of bulk water. PE6200: ***A*** heating (○), ***A*** cooling (●); ***(1-k)*** × ***10*** heating (□), ***(1-k)*** × ***10*** cooling (■) F68: ***A*** heating (△), ***A*** cooling (▲); ***(1-k)*** × ***10*** heating (▽), ***(1-k)*** × ***10*** cooling (▼).

Results and Discussion

Typical spectra of $(EO)_n$-$(PO)_m$-$(EO)_n$ *tri*-block copolymers can be found in Figure 1 and 2. Comparing difference spectra of copolymers in water media, it is obvious that wavenumbers of bands and their relative intensities change with temperature. For the polymer solutions below T_t, the C–O stretching vibrations near 1090 cm^{-1} lie at lower, the CH_3 deformation vibration near 1380 cm^{-1} at higher wavenumbers comparing with the situation in water media above T_t, where the wavenumbers of these vibrations approach to those of the pure compounds.

After subtraction of spectra of bulk water, also some residual absorption remains in the spectra with the maxima near 3400 and 1650 cm^{-1} corresponding to water molecules directly interacting with copolymers.

From the Figure 3 it can be concluded that the integral intensity of the C–H stretching bands and the values *(1-k)* derived from the subtraction coefficient of bulk water sufficiently correlate together, both expressing the local concentration of copolymers near the diamond prism. Beginning at the low temperature, the concentrations increase with heating only slightly for PE6200 and F68 copolymers. It appears that both the solutes below T_t and the aggregated materials till the temperature ~60 °C are in the whole liquid layer on the diamond prism mostly homogenously dispersed. At the temperature ~70 °C and/or during the further course of cooling the aggregated materials begin to sediment. The amount of the sediment on the ATR prism is temperature dependent. The maximum local copolymer concentration near prism approaches for PE6200 to a quadruple and for F68 to an octuple compared with the originally prepared homogeneous solutions.

Wavenumber Shifts of CH_3 Bending and C–O Stretching Vibrations

Changes in the structure and interactions of $(EO)_n$-$(PO)_m$-$(EO)_n$ *tri*-block copolymers in water media with temperature can be

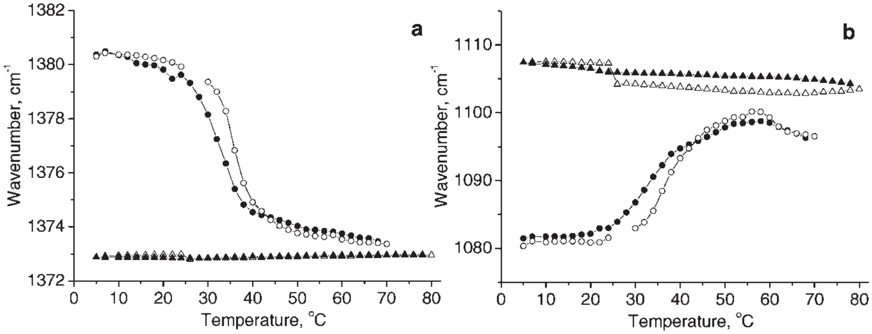

Figure 4.
Wavenumber shifts of methyl deformation (a) and C–O stretching (b) vibration in copolymer PE6200 with temperature. Water medium, heating (○), Pure, heating (△); Water medium, cooling (●), Pure, cooling (▲)

well characterised using the wavenumber shifts of maxima of the appropriate infrared bands. The important vibration bands are the CH_3 stretching and bending bands, lying near 2980 and 1370 cm^{-1} respectively, and a C–O stretching band lying near 1100 cm^{-1}. Detailed wavenumber shifts of two most important bands during heating and reverse cooling of samples can be found in Figure 4 and 5.

Hydrophobic interaction of methyl groups with water exhibits a blueshift, hydrophilic interaction of ether groups with water a redshift of the appropriate infrared bands comparing with the pure compounds. For the copolymer **PE6200** in water, maximum of the CH_3 bending near 1370 cm^{-1} (Figure 4a) and C–O stretching vibration near 1100 cm^{-1} (Figure 4b) shifts for both vibrations on heating to lower and to higher wavenumbers respectively. For the both vibrations, the shift is steepest for the temperature ~35 °C, which corresponds to T_t of this copolymer. At 70 °C, the wavenumber of CH_3 bending vibration decreases almost to the value of respective vibration of the pure copolymer (see Figure 4a). This effect is related with almost complete removing of water from the vicinity of methyl groups. The values of maxima of the C–O stretching band first strongly increase till ~55 °C and then slightly decrease again showing still significant level of C–O groups H-bonded to the vicinal water (see Figure 4b). The slight wavenumber decrease of the C–O stretching band above 55 °C can be explained by some redistribution of water, by its stronger binding to ether group.

For the copolymer **F68** in water, the CH_3 bending vibration behaves on heating analogously as for the copolymer PE6200, with the steepest wavenumber shift appearing

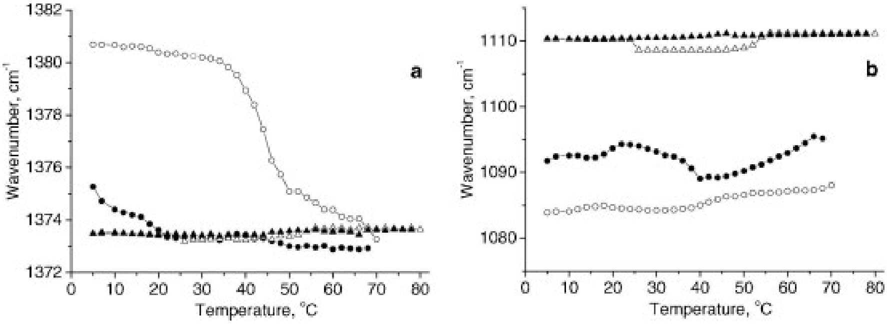

Figure 5.
Wavenumber shifts of methyl deformation (a) and C–O stretching (b) vibration in copolymer F68 with temperature. Water medium, heating (○), Pure, heating (△); Water medium, cooling (●), Pure, cooling (▲).

at the temperature ~45 °C (Figure 5a). The wavenumber of the C–O slightly increases with the increase of temperature; nevertheless its values remain much lower than those for the pure copolymer (see Figure 5b). This can be explained by the fact that the investigated band near 1100 cm^{-1} reflects the C–O vibrations both in PO and EO units. It is apparent that in comparatively long EO blocks of the copolymer F68 the water molecules remain bound even at temperatures between 45 and 70 °C, whereas they were forced out only from the PO blocks at this temperature region.

It is interesting to monitor the wavenumber shifts of the band maxima on **reverse cooling** of the samples. Whereas for PE6200 on cooling only a slight hysteresis appears at increased temperature in the temperature – wavenumber curves for CH_3 bending and C–O stretching vibrations compared with preceding heating (Figure 4a, b), for F68 the previous values of wavenumbers were never reached (Figure 5a, b). This holds especially for the CH_3 bending vibration. Apparently the water molecules, having been expelled from the vicinity of methyl groups in the central PO blocks, could not in this sample penetrate again into the PO parts of the chains. Further, taking into account the results of Figure 3 it follows that the whole sample is not reversibly homogenized on cooling, the local concentration near the diamond crystal remains very large.

Vibrations of Water in Copolymer Neighbourhood

Besides of the vibration bands of copolymers, in Figure 1 and 2 can be also found the bands belonging to the stretching and bending vibrations of water in the vicinity of the polymer material, lying near 3400 and 1650 cm^{-1} respectively. As the origin of the stretching vibrations and the shape of its spectral envelope are rather complicated, only the H–O–H bending vibration in the region 1800–1500 cm^{-1} is used for the further discussion.

A course of the wavenumber in the maxima of the water bands remaining in the difference spectra after subtraction of the curve of bulk water can be found in Figure 6. It can be seen that the wavenumber of the bending bands of water in the vicinity of both copolymers and also of bulk water generally decrease with increasing temperature. This is not surprising, as it reflects a weakening of the hydrogen bonds with temperature. As the maxima of remaining water bands lay for both copolymers at higher wavenumbers than those of bulk

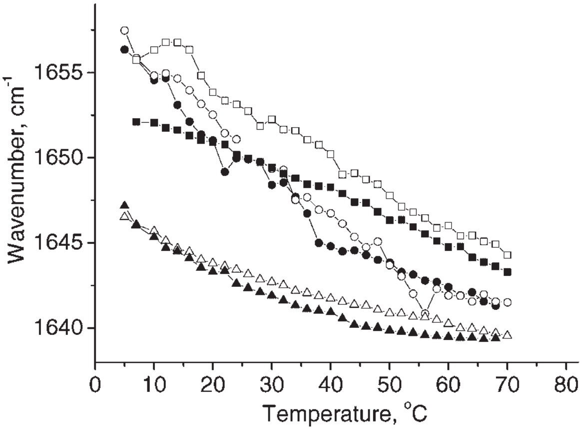

Figure 6.

Wavenumber shifts of H_2O deformation bands with temperature. Water near copolymer PE6200, heating (○), cooling (●); water near copolymer F68, heating (□) cooling (■); bulk water, heating (△), cooling (▲).

water, it can be derived that the average strength of hydrogen bonds in a water envelope around the polymer chains is higher than in bulk water. From this follows that the effect of hydrophilic bonding of vicinal water molecules to ether oxygen apparently predominates over the hydrophobic influence of methyl and methylene groups.

The integral intensities of the H_2O bending bands remaining in difference spectra of both copolymers after subtraction of bulk water were divided by the integral intensities of C–H stretching vibration, so that the concentration effects of sedimentation and other inhomogeneities appearing in the measured layer were partly suppressed. The results are plotted in Figure 7. Supposing the absorption coefficient of bending vibration of water is roughly constant for the measured temperature range, it can be concluded for the sample PE6200 with shorter EO blocks that the relative amount of water in the vicinity of chains diminishes with increasing temperature – water vicinal to copolymer being forced out from the material. During the backward cooling the amount of water near the polymer chains increases again, but below 30 °C the increase is stopped and a decrease begins (see thick line between points in Figure 7). For the sample F68, a copolymer material with a strongly suppressed content of remaining water appeared near the diamond prism at the beginning of backward cooling at 70 °C. This is in accordance with the Figure 3, from which a steep concentration increase of this copolymer near the diamond prism at the beginning of backward cooling can be derived. It is apparent that the vicinal water was expelled from the sedimenting material (compare the arrows in Figure 3 and 7).

A new interesting effect was observed for the copolymer PE6200 in water medium. After heating above transition temperature followed by reverse cooling below 28 °C, a new distinct band with the maximum ~1740 cm^{-1} appeared. Together with its appearance, the bands in the range 3000–2800 cm^{-1} were sharpened and their relative intensities were exchanged (see Figure 8). We assign the new band near 1740 cm^{-1} to a deformation vibration of H_2O molecules forming water bridges connecting EO blocks of two neighbouring copolymer chains. Examples of two PEO segments hydrogen bonded with water molecules are seen in Figure 9. Calculations suggest that the appearance of the band at

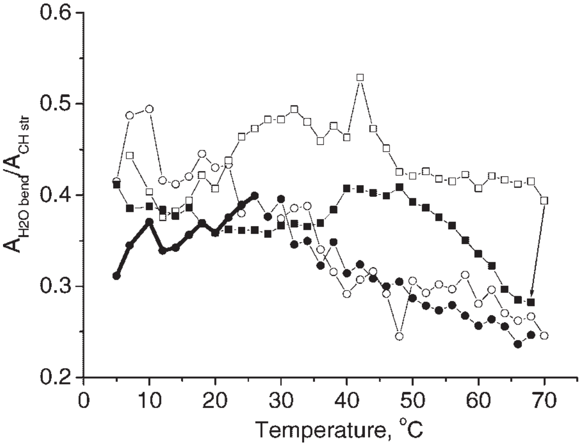

Figure 7.

Changes of relative integrated intensities of deformation band of water near polymer chains ($A_{H2O\ bend}/A_{CH\ str}$). Water near copolymer PE6200, heating (○), cooling (●); thicker line reflects a formation of a new liquid crystalline phase. Water near copolymer F68, heating (□), cooling (■).

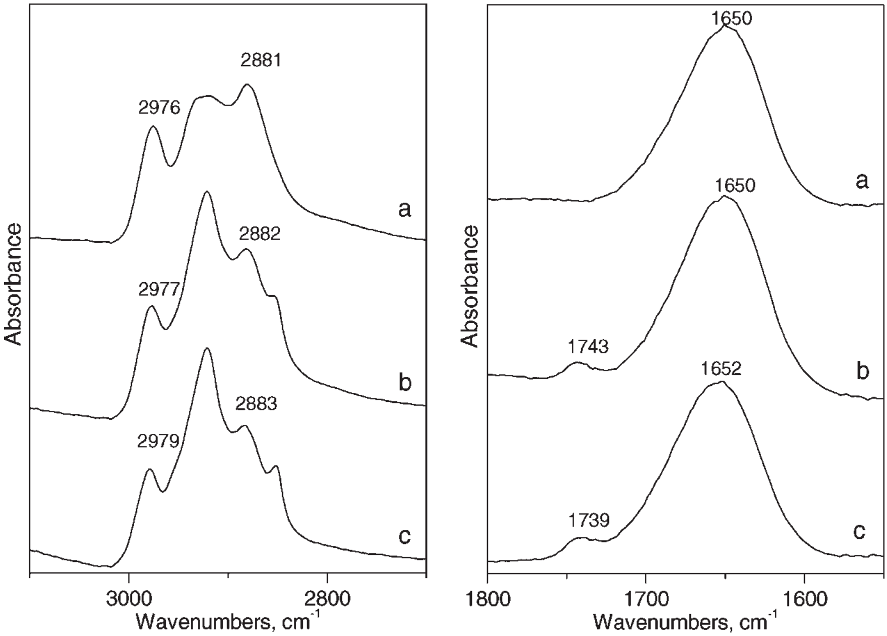

Figure 8.
Changes in infrared spectra during backward cooling of the copolymer PE6200 in water. Solution heated above T_t and cooled to (a) 28, (b) 20, (c) 10 °C.

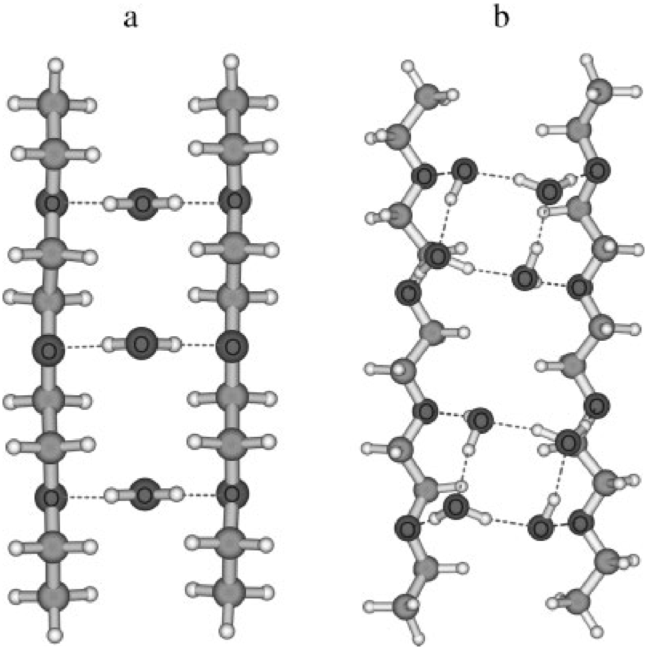

Figure 9.
Optimized geometries of model PEO segments hydrogen bonded through water molecules calculated with the B3LYP/6-31G(d) method.

1740 cm^{-1} can be explained by formation of structures like that shown in Figure 9b. It is supposed that new water bridges between the vicinal EO chains of a micelle with a rigid PO nucleus were formed during heating above the transition temperature, where water redistribution was found (see above the discussion to Figure 4b about redistribution of water). Nevertheless the presence of interchain water bridges in copolymer is visualised by a new band only on backward cooling (below 28 °C) together with a sharpening of the bands in the C–H stretching region. It might be also reflected by a thick line in Figure 7 showing that water ceased to penetrate back among the polymer chains during the end of the reverse cooling. These effects can be explained by the formation of a new liquid crystalline phase. Taking into account that the local weight concentration of the copolymer PE6200 near the ATR prism during the backward cooling reaches ~25% (as can be derived from Figure 3), it is supposed that the phase is identical with that-one shown for this copolymer in.[12] We suppose that the regular water bridges between the vicinal EO blocks are formed only near PO nucleus of the micelles holding the distance between the threads of the EO fringes sufficiently small. This can be the reason why the liquid crystalline phase was detected only in PE6200 having comparatively short EO blocks. As in F68 the EO blocks are roughly 10-times longer, the distance between their outer ends is much larger and the regular water bridges between them can be formed and detected with much lesser probability.

Conclusion

- At low temperatures, unimer chains of copolymers in water are surrounded by water envelopes. Copolymer – water interactions cause the shifts of infrared bands. On increasing the temperature above the appropriate transitions, water molecules are gradually removed from the vicinity of the polymer chains and infrared wavenumbers approach values found for pure copolymers.
- Hydrophobic interaction $H_2O\ldots H_3C$– is weaker than hydrophilic interaction $OH_2\ldots OC$–. At higher temperatures, water molecules are removed from the central part of the tri-block containing methyl groups and micelles with PO nuclei are formed.
- The transition temperatures increase with the EO molar fraction.
- Above the transition temperature of PE6200, a redistribution of the bound water molecules appears. The polymolecular water clusters between the EO chains are destroyed and water molecules bound by hydrogen bonds form bridges between the ether groups of the vicinal EO chains of the copolymer. During further backward cooling a new liquid crystalline structure is formed.

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