

# Structures and Interactions in Polymer Systems Characterized by NMR Methods

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**Abstract:** The possibilities of liquid-state and solid-state NMR spectroscopies are illustrated on examples of several systems which are relevant to the field of polymer materials. Results on interactions in aqueous solutions of thermoresponsive polymers, on structural characterization of semicrystalline low – molecular weight poly(ethylene oxide)s and on phase structure in biodegradable starch/polycaprolactone blends are discussed.

**Keywords:** Thermoresponsive polymers, semicrystalline poly(ethylene oxide), biodegradable starch/polycaprolactone blends, NMR.

## INTRODUCTION

NMR spectroscopy is a powerful method in general and its significance for the structural characterization of polymers is well established. Here we shall discuss some results obtained recently in our laboratory on polymer systems which are relevant to the topic of polymer materials. The possibilities of both liquid-state and solid-state NMR spectroscopies will be illustrated on several examples. In the first example we will show some possibilities of liquid-state NMR spectroscopy in investigations of interactions in poly(vinyl methyl ether) (PVME) and poly(*N*-isopropylmethacrylamide) (PIPMAM) aqueous solutions during temperature-induced phase transition. Both these polymers fall in the category of thermoresponsive polymers which are now widely studied. The second example will be devoted to the structural characterization of another important polymer, semicrystalline low – molecular weight poly(ethylene oxide) (PEO), by combination of solid-state NMR and small-angle X-ray scattering (SAXS). Solid-state NMR spectroscopy was used also in investigations of the phase structure in the third polymer system, biodegradable starch/polycaprolactone (PCL) blends.

## POLYMER-SOLVENT INTERACTIONS IN SOLUTIONS OF THERMORESPONSIVE POLYMERS

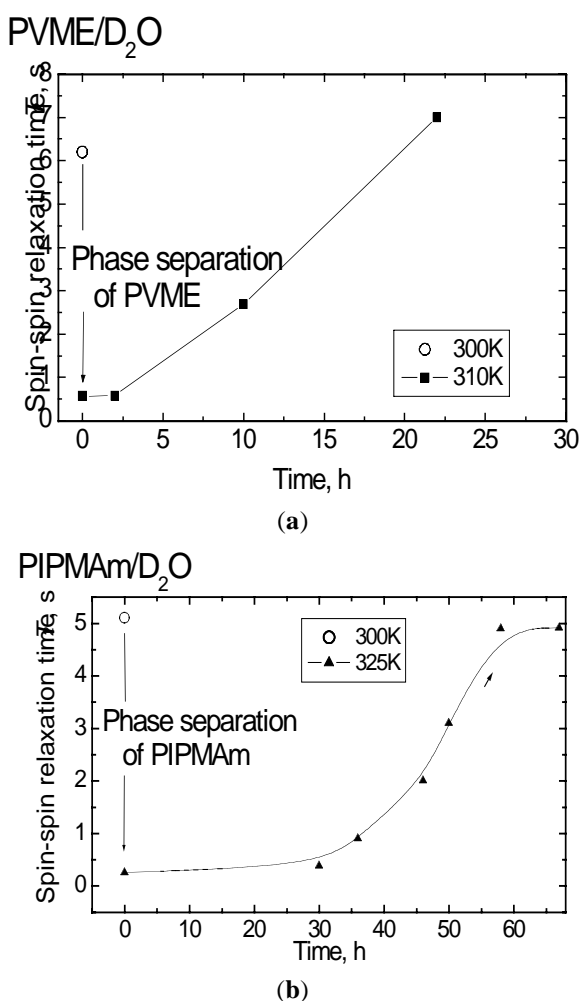
It is well known that some polymers with amphiphilic character, including PVME and PIPMAM, exhibit in aqueous solutions a lower critical solution temperature (LCST), i.e., they are soluble at lower temperatures, but their heating above the LCST results in phase separation. When these polymers are chemically crosslinked, then their hydrogels undergo a temperature-induced volume phase transition (collapse). On the molecular level, both phase separation in solutions and similar volume phase transition in crosslinked hydrogels are assumed to be a macroscopic manifestation of a coil-globule transition followed by aggregation and forma-

tion of so called mesoglobules [1]. Their thermosensitivity makes these systems interesting for possible biomedical and technological applications, especially if the systems are in the form of hydrogels which can be used in the creation of “smart” material systems (sensors, actuators, switching devices etc). The fact that LCST of these thermoresponsive polymers can be adjusted near to human body temperature (37 °C) makes them viable as drug release systems [2]. Among various methods, NMR spectroscopy was also applied in investigations of phase transition in aqueous polymer solutions and gels [3].

One possibility how to obtain information on polymer-solvent interactions (hydration) during temperature-induced phase transition in aqueous solutions of thermoresponsive polymers is an application of measurements of NMR relaxation times. Fig. (1) shows the results of the measurements of spin-spin relaxation times  $T_2$  of HDO in  $D_2O$  solutions ( $c = 5$  wt%) of PVME and PIPMAM. In both cases the  $T_2$  values at temperatures above the phase transition (310 and 325 K for PVME and PIPMAM solutions, respectively) were 1 order of magnitude shorter than those at 300 K, i.e., at temperatures below the transition. This shows that at temperatures above the transition there is a portion of HDO molecules that exhibit a lower, spatially restricted mobility. Evidently, this portion corresponds to HDO bound in globular-like structures [3]. Interestingly enough, from Fig. (1) it follows that with time  $T_2$  values increase showing that originally bound water is very slowly released from globular-like structures, in contrast to the fact that phase separation itself is rather fast.

In both cases shown in Fig. (1) there was a single line of HDO in  $^1H$  NMR spectrum and the  $T_2$  relaxation curves were exponential, indicating a fast exchange between bound and free sites. A contribution from the chemical exchange to the spin-spin relaxation rate  $(T_2)^{-1}$  is also important. The residence time of the bound HDO  $\sim 1$  ms was found both for PVME and PIPMAM solutions ( $c = 6$  and 20 wt%, respectively) from dependences of spin-spin relaxation rate on the time interval  $t_d$  in CPMG pulse sequence  $90^\circ_x - (t_d - 180^\circ_y - t_d)_n$ -acquisition [4]. For highly concentrated PVME/ $D_2O$  solu-

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**Fig. (1).** Time dependences of spin-spin relaxation times  $T_2$  of HDO in  $D_2O$  solutions ( $c = 5$  wt%) of PVME (a) and PIPMAm (b) measured at 500.1 MHz and 310 K (a) and 325 K (b) [4].

tions ( $c = 20$ -60 wt%) the existence of the separate signal of the bound HDO with  $\sim 0.74$  ppm smaller chemical shift in comparison with the main HDO signal shows a slow exchange process [5]. At the same time the fractions of bound water were unchanged even for 70 h; from their values it follows that the polymer concentration in mesoglobules is 89 wt%. To detect a slow exchange in highly concentrated PVME/ $D_2O$  solution ( $c = 50$  wt%) we applied an one-dimensional exchange  $^1H$  NMR experiment with selective excitation of the main HDO signal and for the residence time of the bound HDO we obtained the value 2.1 s. Taking into account that exchange between free and bound water is associated with diffusion process, a three orders of magnitude slower exchange in highly concentrated PVME solutions is in accord with our optical microscopy findings that mesoglobules are here approx. 20 times larger than in PVME solutions with  $c = 6$  wt%.

#### SEMICRYSTALLINE LOW – MOLECULAR WEIGHT PEO

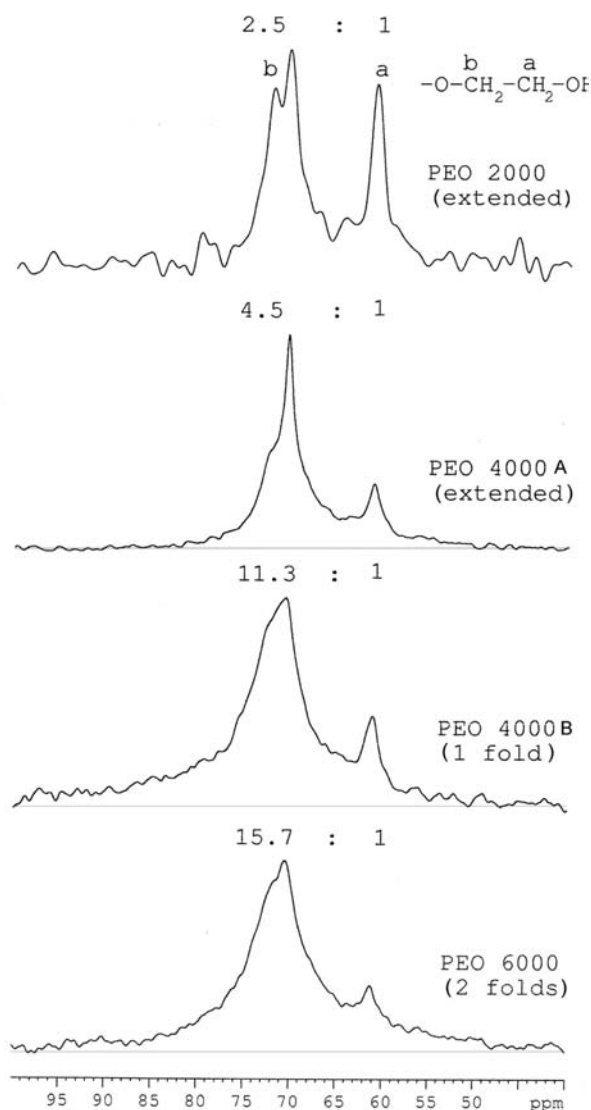
PEO is the most commercially important polyether. It has a low toxicity and therefore it is used in various pharmacological products, as a dispersant in toothpastes etc. PEO forms molecular complexes with alkali metal salts; they ex-

hibit high ionic conductivity and are known as solid polymer electrolytes [6]. An application of these systems in electrochemical devices like solid-state batteries has been suggested and the first commercial lithium-metal-polymer battery manufacturing plant by AVESTOR started production in 2002.

It is well known that at room temperature the  $^{13}C$  NMR spectrum of semicrystalline PEO consists of a broad (linewidth  $\sim 1$  kHz) and a narrow (linewidth  $\sim 200$  Hz) component with similar chemical shifts which in contrast to most other semicrystalline polymers were assigned to the crystalline and amorphous phase, respectively [7-9]. However, recently also a reverse assignment was published [10,11].

We applied the  $^{13}C$  NMR spectra, measured under conditions when only the narrow line component is detected, on a series of hydroxy-terminated (at both ends) low-molecular weight PEO samples. PEO samples with molecular weight 2000, 4000 and 6000 were used in this study. For PEO 4000 and 6000, samples crystallized isothermally at temperature 2 K below the melting point for  $\sim 24$  h (PEO 4000 A) or from the melt (PEO 4000 B and PEO 6000) were prepared. The degree of crystallinity of all investigated samples as determined by wide-angle X-ray scattering (WAXS) was  $\sim 80$  %. For PEO 4000 and 6000 the degree of crystallinity was also determined from wide-line  $^1H$  NMR spectra and by DSC; the values of the degree of crystallinity  $\sim 90$  %, i.e., higher by  $\sim 10$  % in comparison with values obtained by WAXS, were found. From SAXS measurements we have found that polymer chains in crystalline lamellae of PEO 2000 and PEO 4000 A are fully extended. For PEO 4000 B the chains are once folded while the twice folded chains predominate for PEO 6000 [12].

$^{13}C$  CP/MAS (cross polarization/magic angle spinning) solid-state NMR spectra of the studied PEO samples were measured with contact time 2 ms to detect only the signal from the narrow line component; these spectra are shown in Fig. (2). For PEO 4000 B the  $^{13}C$  MAS NMR spectrum without CP and with pulse repetition time 1 s (to suppress the signal from slowly relaxing crystalline component where  $T_1 \approx 10$  s) was also measured for comparison. This spectrum is virtually the same as the CP/MAS spectrum of this sample shown in Fig. (2), so confirming that CP/MAS NMR spectra shown in Fig. (2) as well as results derived from them are not affected by CP dynamics in a perceptible extent. For all samples the signal of chain-end  $CH_2OH$  carbons at 61.7 ppm was clearly resolved in the spectra. The ratios of integrated intensities of the main PEO signal at 70.6 ppm (together with a shoulder at  $\sim 72.5$  ppm corresponding to  $\underline{CH_2}CH_2OH$  carbons from chain ends) and the signal of chain-end  $CH_2OH$  carbons at 61.7 ppm were determined; these ratios are shown with the spectra in Fig. (2). For hydroxy-terminated low-molecular-weight PEO it was established by Skoulios *et al.* and Kovacs *et al.* that the chain ends are outside the crystalline phase [13,14]. Therefore the direct detection and integrated intensities of the signals from hydroxy-terminated chain-end units in spectra showing only the narrow line component (cf. Fig. 2) confirm that the narrow line component in solid state  $^{13}C$  NMR spectrum of PEO corresponds to the noncrystalline (amorphous) phase, in accord with former studies [7-9].



**Fig. (2).** Solid state  $^{13}\text{C}$  CP/MAS NMR spectra of the investigated PEO samples. Spectra were measured at 50.3 MHz and ambient temperature with the contact time 2 ms to detect only the signal from the narrow line component [12].

Taking into account that signal at 61.7 ppm corresponds to two  $\text{CH}_2\text{OH}$  carbons per chain, the mean total number of carbons per chain contributing to the amorphous phase (including chain ends) can be determined from the ratios of integrated intensities mentioned above [12]. This analysis does not require the knowledge of the degree of crystallinity which depends on the method of measurement; in our case the amount of the amorphous phase as determined by WAXS was twice larger than this amount determined by DSC or wide-line  $^1\text{H}$  NMR. Assuming two-phase model, in general both the chain ends (cilia) and folds usually contribute to the noncrystalline (amorphous) phase of the semicrystalline polymer. From the values of the mean number of carbons per chain contributing to the amorphous phase obtained from  $^{13}\text{C}$  NMR spectra for PEO 2000 and PEO 4000 A with fully extended chains it follows that cilia are 2-3 monomer units long. From the results obtained on PEO 4000 B with once folded chains and on PEO 6000 with twice folded chains it follows that the length of the fold is 6-7 monomer units.

## BIODEGRADABLE STARCH/PCL BLENDS

Research on biodegradable polymers has received increasing attention in recent years and PCL is one of the most often investigated systems. However, since this polymer is still expensive and does not match all the technical requirements for possible applications, its blends with starch, which is a cheap abundant resource, are also investigated (cf. references in [15]). The miscibility in these blends is one of the most relevant parameters related to blend properties. In this section, the results of the measurements of  $^1\text{H}$  spin-lattice relaxation times  $T_1(\text{H})$  and  $^1\text{H}$  spin-lattice relaxation times in the rotating frame  $T_{1\rho}(\text{H})$ , as obtained via  $^{13}\text{C}$  detection from  $^{13}\text{C}$  CP/MAS NMR spectra on starch/PCL and starch formate (starch modified by formylation)/PCL blends [15] are discussed from the point of view of the blend morphology (domain size). As the PCL component both the polymer of higher molecular weight ( $M_w = 80\,000$ ) and low-molecular-weight ester oligomers (1,6-hexane-diol adipate and phthalate; molecular weight  $M_w = 2\,700$ ) were used in these blends.

The approach used to characterize the molecular morphology (domain size) of investigated blend samples is based on the  $^1\text{H}$  spin-diffusion. The maximum diffusive path length  $L$  is approximately given as

$$L = (6DT_i)^{1/2} \quad (1)$$

where  $D$  is the spin-diffusion coefficient and  $T_i$  is either  $T_{1\rho}(\text{H})$  or  $T_1(\text{H})$  according to the relaxation experiment (for the  $T_{1\rho}(\text{H})$  experiment a scaling factor 1/3 should appear in parenthesis in eq. (1) [16]). For the spin-diffusion coefficient a value of  $8 \times 10^{-16} \text{ m}^2\text{s}^{-1}$  is expected for rigid (crystalline or glassy) organic systems. For the spin-diffusion coefficient in mobile amorphous PCL (in rubbery state at room temperature) a lower value can be expected. A value  $D = 0.5 \times 10^{-16} \text{ m}^2\text{s}^{-1}$  is probably a reasonable estimate.

$T_{1\rho}(\text{H})$  measurements on investigated blends have shown that  $T_{1\rho}(\text{H})$  values are markedly different when determined from analysis of signals of starch (or starch formate) carbons ( $T_{1\rho}(\text{H}) = 2.3 - 6.9 \text{ ms}$ ) in comparison with those determined from PCL (or ester oligomers) carbon signals ( $T_{1\rho}(\text{H}) = 24.5 - 46.5 \text{ ms}$ ). These results show that in all investigated blends both components are separated into domains of which the length scale exceeds the maximum diffusive path length  $L \approx 2\text{-}12 \text{ nm}$  (cf. eq. (1)).

To investigate the molecular miscibility on the larger scale, the spin-lattice relaxation times  $T_1(\text{H})$  were measured. The values  $T_1(\text{H})$  as determined from relaxation curves of various starch or starch formate carbons do not significantly differ; the same holds for  $T_1(\text{H})$  determined from signals of various PCL (or ester oligomers) carbons [15] showing that the spin-diffusion process is effective within domains formed by single components of the blends. Therefore only the mean  $T_1(\text{H})$  values as obtained for starch (starch formate) carbons and PCL (ester oligomers) carbons are shown in Table 1.

From Table 1 it follows that for the blends starch/PCL, starch/ester oligomers and starch formate/ester oligomers  $T_1(\text{H})$  of both components differ from one another. These results suggest that in these blends both components are phase separated even on the larger scale of 20-110 nm (cf.

Eq. (1)). A different behaviour was found from  $T_1(H)$  values for starch formate/PCL blend. From Table 1 it follows that in this blend the same  $T_1(H)$  values were determined for starch formate and PCL components. At the same time, the  $T_1(H)$  value found from signals of starch formate carbons is shorter in comparison with the neat starch formate and the value found from signals of PCL carbons is longer in comparison with the neat PCL, showing that the spin-diffusion process is sufficient to equilibrate  $T_1(H)$  values. Therefore it is possible to conclude that in starch formate/PCL blend both components are homogeneously mixed on the scale 20-90 nm and that formylation of starch significantly improves its miscibility with PCL.

**Table 1.**  $^1H$  Spin-Lattice Relaxation Times  $T_1(H)$  of Starch (or Starch Formate) and PCL (or Ester Oligomers) in Investigated Blends and Neat Components [16]

| Sample                                 | $T_1(H)^a$ (s) |     |
|--|----------------|-----|
|  | Starch         | PCL |
| starch                                 | 1.4            | -   |
| starch formate                         | 2.6            | -   |
| PCL                                    | -              | 1.1 |
| ester oligomers                        | -              | 1.5 |
| starch/PCL (40/60)                     | 1.6            | 1.1 |
| starch formate/PCL (40/60)             | 1.6            | 1.6 |
| starch/ester oligomers (40/60)         | 1.8            | 1.5 |
| starch formate/ester oligomers (40/60) | 2.5            | 1.6 |

<sup>a</sup>Estimated error  $\pm$  10%.

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