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NMR AND VIBRATIONAL SPECTROSCOPIC STUDY OF THE ORDER AND MOBILITY IN POLYCARBONATE AND POLYCARBONATE – POLY(ETHYLENE OXIDE) BLENDS

Jiří Dybal*, Jiří Brus, Pavel Schmidt

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic

SUMMARY: Time dependence of the gel formation in toluene solutions of polycarbonate (PC) was investigated by two-dimensional Fourier-transform infrared (2D FT-IR) correlation spectroscopy. The 2D correlation approach reveals that there are at least three bands in the C=O stretching region. The intensity increase of the band at 1771 cm^{-1} occurs later compared with the onset of the intensity changes of the bands at 1778 and 1765 cm^{-1} corresponding to amorphous and crystalline-like domains, respectively. The band at 1771 cm^{-1} is assigned to the chain conformations occurring in the partial-order regions accompanying crystalline-like domains. Splitting of the signals of aromatic carbons in the solid-state ^{13}C CP/MAS NMR spectra of semicrystalline PC and PC-PEO blends indicates restricted mobility resulting from the fixed ordering due to partial crystallinity of PC itself and from blending of PC with PEO. The decreasing mobility of PC with the increasing content of highly mobile PEO in the blends was proved by the dipolar dephasing rates obtained in the ^1H-^1H CRAMPS (combined rotation and multi-pulse spectroscopy) NMR experiments.

INTRODUCTION

In some solvents (e.g., in toluene and benzene), aggregation of PC occurs, which is characterized by the formation of ordered molecular structures analogous to those observed in the crystalline phase of semicrystalline PC[1)]. The chain arrangement is preserved in solid samples obtained by the room temperature evaporation of the solvent from the gel. Studies of several samples of semicrystalline PC obtained by varying thermal and solvent treatment showed that the values of crystallinity determined by WAXS are considerably higher compared with those obtained with DSC. The observed differences were related to the degrees of ordering as determined by characteristic Raman bands at 735 and 1235 cm^{-1}, predominantly sensitive to the intrachain and interchain ordering, respectively. It was suggested that observed the effects are associated with the partial ordering in the interfacial region between the crystalline and amorphous phases[1)]. The main aim of the present work was to characterize the structure and dynamics of PC as well as in the PC-PEO blends using generalized 2D FT-IR correlation spectroscopy[2)] and solid state ^1H and ^{13}C NMR spectroscopy.

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EXPERIMENTAL PART

Samples were prepared from commercial-grade Bisphenol A polycarbonate SINVET 251 (ENI, Italy) with a weight-average molecular weight M_w = 24 000 and from PEO ($M_w = 6\times10^5$) produced by BDH Chemicals, Ltd. (UK). The samples of PC and PEO homopolymers and PC-PEO blends were obtained by dropwise precipitation from a chloroform solution (2 % w/w) into pentane, slow evaporation of the solvents at room temperature and subsequent heating at 80 °C for 64 h. Time dependence of the FT-IR spectra during aggregation of PC and PC-PEO in toluene was measured on a Bruker FT-IR spectrometer IFS-55. Prior to filling a KBr cell, the solutions were homogenized in a sealed glass tube at 130 °C for 1 h.

NMR spectra were measured using NMR spectrometer Bruker DSX 200 in 4 mm ZrO_2 rotors at the frequencies 50.33 MHz and 200.14 MHz (^{13}C and ^1H, respectively). The number of data point was 6 K, magic angle spinning (MAS) frequency 3.2 kHz, B_1 field (^1H and ^{13}C) strength 62.5 kHz. The number of scans for accumulation of ^{13}C cross-polarization (CP) MAS NMR spectra was 3600, the repetition delay 4 s and the spin lock pulse length 0.7 ms. The ^{13}C scale was calibrated by an external standard, glycine (176.03 ppm – low-field carbonyl signal). In the ^1H CRAMPS experiments, the BR-24 pulse sequence$^{3)}$ was used, with a 90° pulse length of 1.8 μs and large and short delays 3.8 μs and 1.0 μs. The MAS frequency was 2.5 kHz, the data size 2 K points and the repetition delay 4 s. The scaling and ^1H chemical shifts were calibrated using aspartic acid (the lowest-field and the second-high-field signals 15.6 ppm and 3.41 ppm, respectively). For a dipolar dephasing CRAMPS experiment, $\pi/2$ and π pulses spaced by τ delays were added before the BR-24 pulse train ($\pi/2 - \tau - \pi - \tau$ – BR-24)$^{4)}$. The 2τ delay was incremented from 3 to 1000 μs.

AGGREGATION OF POLYCARBONATE

PC is hardly soluble in solvents such as toluene and transparent homogeneous solutions can be prepared only by 1-h heating the samples in sealed glass tubes at a high temperature (~ 130 °C). After cooling the sample to room temperature, a gradual aggregation of the polymer is observed and, finally, an opaque homogeneous gel is formed. In the infrared spectra, the increasing intensity of the characteristic bands at 1765 (Fig. 1a) and 1250 cm^{-1} shows the gel formation of PC in solution and analogous spectroscopic effects are characteristic of the crystalline form of PC$^{1)}$. We have applied generalized 2D FT-IR correlation spectroscopy$^{2)}$ to explore the aggregation behavior of PC in toluene in more detail. The synchronous and asynchronous correlation spectra of a toluene solution of PC (2 % w/w) in the carbonyl stretching region are shown in Fig. 2. By following the standard convention,

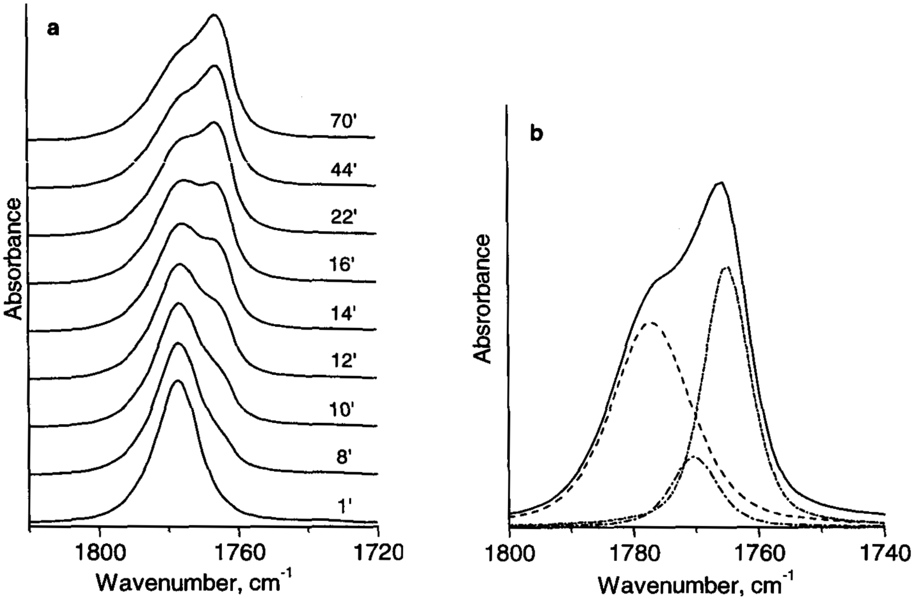

Fig. 1: (a) Time dependence of infrared spectra of a toluene solution of PC (2 % w/w) measured at room temperature after homogenizing at 130 °C. The solvent spectrum was subtracted. (b) Infrared spectrum of aggregated PC in a toluene solution together with three components obtained by the least-squares curve-fitting method.

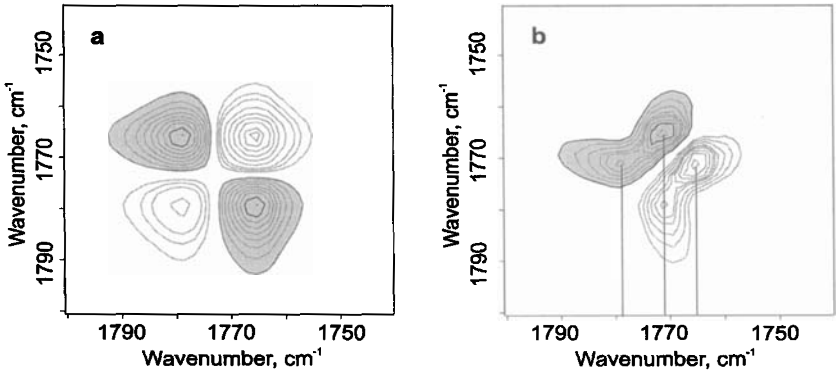

Fig. 2: Synchronous (a) and asynchronous (b) 2D FT-IR correlation spectrum of a toluene solution of PC (2% w/w). The negative peaks are shaded.

the negative-peak-intensity regions are indicated with shading. In the synchronous spectrum (Fig. 2a), a negative cross peak indicates that the intensity changes observed at the two wavenumbers are in the opposite direction. While only one peak corresponding to aggregated

(~ 1766 cm^{-1}) and non-aggregated (~ 1778 cm^{-1}) PC is observed in the synchronous spectrum, the appearance of the cross peak pair near the diagonal line in the asynchronous spectrum (Fig. 2b) reveals interesting development. It indicates that the aggregation of PC is manifested by two close but separate carbonyl bands at 1765 and 1771 cm^{-1}. The signs of the asynchronous correlation peaks suggest2) that the intensity variations of the PC band at 1771 cm^{-1} occur later compared with the onset of the intensity increase of the crystalline-like band at 1765 cm^{-1}. Analogous behavior is observed in the region of the C-O stretching vibrations at 1220–1260 cm^{-1}.

Figure 1b shows the results of the band separation obtained by the least-squares methods. The curve fitting was carried out using the routine in the OPUS software (Bruker). The band profile was approximated by the sum of Gaussian and Lorentzian functions (1:1). First, the fitting routine with no fixed parameters was run for all the spectra shown in Fig. 1a. In the final fitting run presented in Fig. 1b, only the peak position and halfwidth of the band at 1778 cm^{-1} were fixed at values obtained from the spectrum of non-aggregated PC (1′). It is seen that all three highly overlapped bands differentiated by 2D correlation analysis are detected in the spectrum. The fact that the total integrated absorbance of the carbonyl stretching region is changed only by a few percents during aggregation suggests that integrated absorptivities of the carbonyl stretching vibrations in the aggregated and non-aggregated forms of PC are approximately the same and thus the integrated intensities of bands correspond to the relative content of the respective PC structures. The band at 1778 cm^{-1} (52%) in the final spectrum (120’) corresponds to non-aggregated PC, the band at 1765 cm^{-1} (38%) corresponds to the crystalline-like structures, the shift is caused by the transition dipole coupling in the ordered carbonate groups. We suggest that the band at 1771 cm^{-1} (10 %) reflects the presence of partly ordered chains in the neighborhood of the crystalline-like structures, analogous to partly ordered interfacial regions in semicrystalline PC1).

POLYCARBONATE – POLY(ETHYLENE OXIDE) BLENDS

^{13}C CP/MAS NMR spectra of amorphous and semicrystalline PC as well as two PC-PEO blends are shown in Figs. 3a-d. The signal assignment of PC in ^{13}C CP/MAS NMR spectra was made on the basis of the results published in the literature5-7). The small signals in spectra labeled with stars are spinning side bands (SSB). An interesting feature of the spectra is a significant splitting of “low-field” signals corresponding to carbon positions 3-7 of PC in semicrystalline PC and PC-PEO blends. Recently published NMR experiments showed that the glassy PC consists on average of densely packed chains and the local orientation order is not completely random6,8,9). However, also such packed materials expose extensive mobility

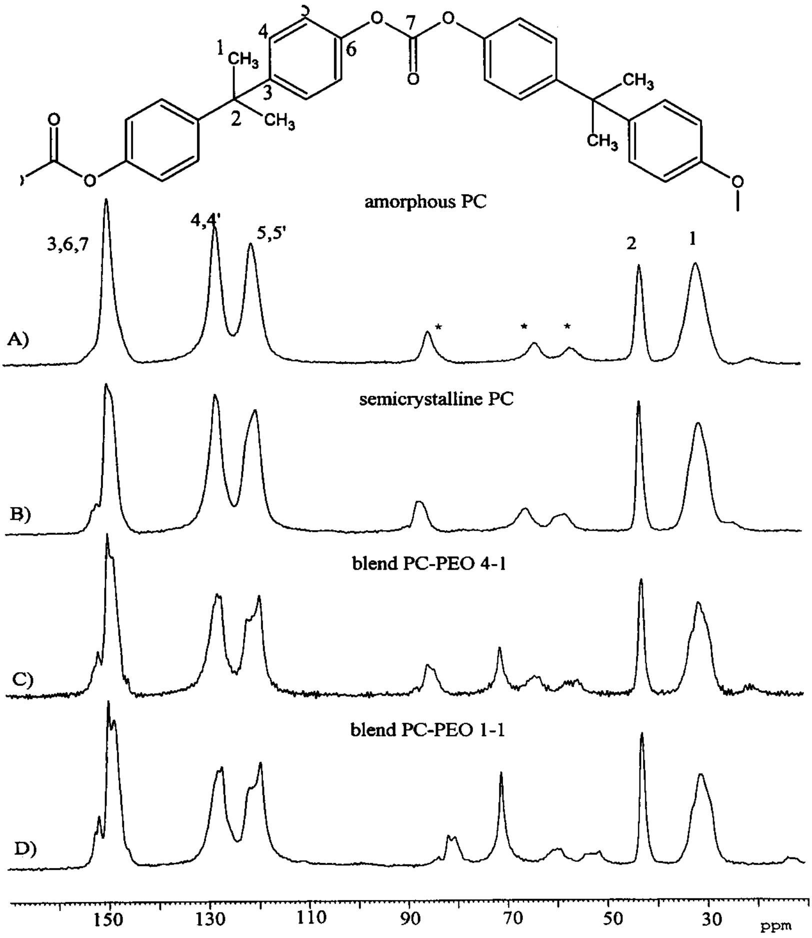

Fig. 3: ^{13}C CP/MAS NMR spectra: (A) amorphous PC, (B) semicrystalline PC, (C) blend PC-PEO 4-1, (D) blend PC-PEO 1-1.

involving 180° flips at frequency 300 kHz accompanied by small angle fluctuations about the same C2 axes in cooperative motions involving at least two rings down the chain and four or five other rings on another chain[10,11]. Such fast molecular motion easily averages out possible chemical shift dispersion due to magnetic nonequivalence of ^{13}C nuclei following from different orientation, packing and conformation. That is why in pure completely amorphous PC no splitting of protonated aromatic signals is observed. In general, however, aromatic rings in PC chains are twisted with respect to the isopropylidene group and 5, 5′ and 4, 4′ protonated aromatic carbons in PC chains have nonequivalent local environment interacting differently with methyls and adjacent aromatic rings[5]. We suggest that splittings observed in ^{13}C CP/MAS NMR spectra of semicrystalline PC (Fig. 3b) indicate restricted mobility and hindered cooperative motions resulting from fixed ordering due to partial crystallinity. As the crystallinity of PC is relatively low$^{1)}$, molecular mobility is probably restricted not only in crystallites themselves but the presence of crystallites retards cooperative motions in the neighboring amorphous phase (interface). It is seen in Figs. 3c and 3d that additional blending of PC with PEO causes the increase in the splitting of the signals. As the degree of crystallinity of PC and dynamic behavior of PC chains in crystallites are unchanged by blending$^{12)}$, the presence of PEO causes slowing down of the molecular motions of amorphous PC in mixed domains in spite of the fact that the mobility of amorphous PEO is much higher compared with that of amorphous PC. This indicates intimate mixing of PC with PEO in mixed domains where the presence of PEO hinders cooperative motions of neighboring PC chains. The signals of 5 and 5′ carbons are also sensitive to the conformations of the carbonate groups because they reflect two nonequivalent carbon sites in trans-trans as well as three or four nonequivalent sites in trans-cis conformation. Therefore, multiple splitting of the signal at ca. 120 ppm indicates comparable amounts of both conformational structures, as it was proposed on the basis of quantum mechanical DFT calculations and Raman spectroscopy$^{1)}$.

In order to prove the decreasing mobility of PC molecules by blending with PEO, the ^{1}H-^{1}H dipolar dephasing experiment was performed. We used very promising sensitive and time-saving technique based on the combination of a simple Hahn-echo experiment with multipulse averaging of dipolar interaction during the data acquisition. High-resolution ^{1}H NMR spectra of blends were obtained using the CRAMPS NMR technique. These spectra (Fig. 4a) are well resolved giving three signals corresponding to aromatic (6.1 ppm) and methyl (1.7 ppm) protons of PC, and methylene protons (4.3 ppm) of PEO.

The dipolar dephasing rate is an important probe of the effective strength of dipolar interactions. The standard pulse sequence$^{4)}$ under slow MAS monitors dipolar dephasing caused by both coherent and incoherent relaxation processes. Generally, the dephasing rate forabundant nuclei increases with decreasing molecular dynamics because the intensity of static homonuclear dipolar interaction increases. The magnetization decay measured at low spinning speed reflects the strength of both static and fluctuating local magnetic fields. By this method we compared dipolar dephasing rates of the 4-1 and 1-1 PC-PEO blends and significant differences in the dipolar dephasing rates between the two blends are shown in Figs. 4b-d. It is clear that the magnetization decay of the signals is much faster in the blend PC-PEO 1-1, which reflects decreasing molecular mobility of PC with increasing content of PEO. Slower magnetization decay of the PEO signal in PC-PEO 4-1 (Fig. 4b) corresponds with a lower crystallinity of PEO in this blend$^{12)}$.

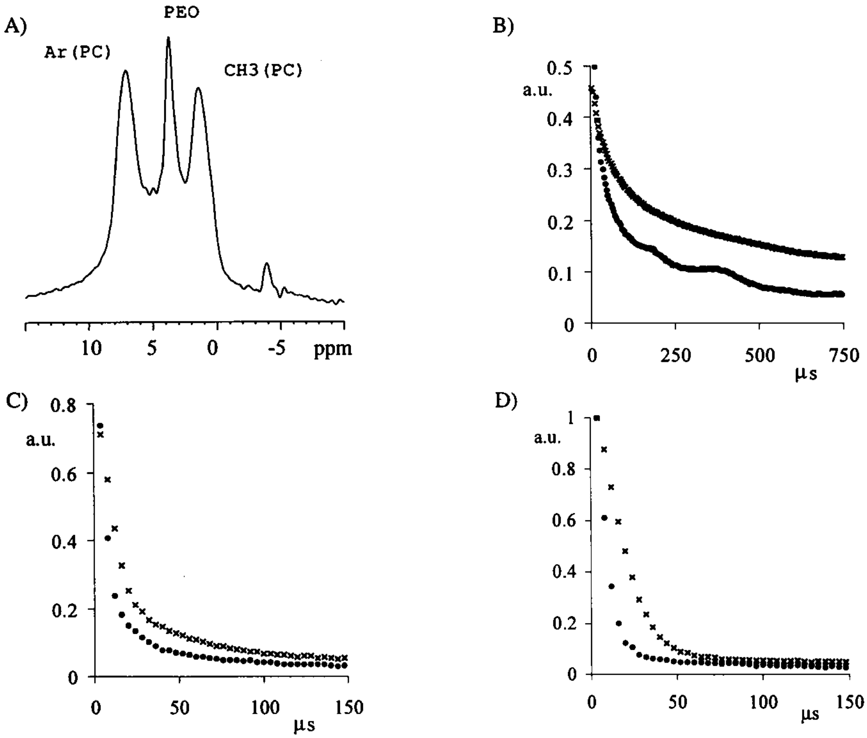

Fig. 4: High-resolution ^{1}H NMR spectrum of the blend PC-PEO 1-1 obtained by CRAMPS NMR technique (A); dipolar dephasing rates for the methylene protons of PEO (B) and aromatic (C) and methyl (D) protons of PC: (×) blend PC-PEO 4-1, (•) blend PC-PEO 1-1.

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