Polymer Bulletin 47, 291–296 (2001)

Polymer Bulletin

Studies on the crystalline intercalate formed by poly(ethylene oxide) and two different kinds of guest molecules

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Received: 9 August 2001/Revised version: 13 September 2001/ Accepted: 17 September 2001

Summary

The intercalate with poly(ethylene oxide) as the host compound and dichlorobenzene/dibromobenzene as the guest compounds (PEO-PDCL/PDBB) was studied by the aid of DSC, WAXD, and ^{13}C CP/MAS NMR. No selectivity was observed during the intercalating process of poly(ethylene oxide) (PEO) with p-dichlorobenzene (PDCL) and p-dibromobenzene (PDBB). The orientated PDCL and PDBB molecules are randomly distributed in the benzenic layers between PEO sheets. With increasing PDBB molar fraction, the melting point of the intercalate rises up. WAXD results indicate that the size of orthorhombic crystal cells of PEO-PDCL/PDBB intercalates enlarges as PDBB molar fraction increases. Thereby, It is possible to control the size of crystal cell via adjusting PDBB content in the PEO-PDCL/PDBB intercalates. The ^{13}C CP/MAS NMR experiments imply that the carbons of PEO chains in the PEO-PDCL/PDBB intercalate are in the same chemical environment. This again supports that neither PDCL nor PDBB has priority in interacting with PEO.

Introduction

Poly(ethylene oxide) (PEO) can form various molecular complexes with some organic molecules such as urea, resorcinol, p-nitrophenol, hydroquinone, etc.[1-6], in which strong hydrogen bonds exist. Another interesting type of complexes is PEO-p-dihalogenobenzene intercalates [7-10]. In these complexes, only weak Van Der Waals interactions are involved. The size and shape of small guest molecules determine whether they can be accommodated by sheetlike PEO or not [7,11]. Both PEO-p-dichlorobenzene (PEO-PDCL) intercalate and PEO-p-dibromobenzene (PEO-PDBB) intercalate were reported by Point and coworkers [7, 8], and the stoichiometry was determined to be 0.23 (i.e., three guest molecules for ten ethylene oxide units) [7]. It is interesting to investigate the intercalation behavior of two sorts of guest molecules (PDCL and PDBB) between PEO sheets, and to check if the host preferentially selects one out of the two guest molecules to form the intercalates, which is the aim of the present paper.

Experimental

Poly(ethylene oxide) (PEO) of low molecular weight (M_w=6000) was obtained from Shanghai Medicine and Chemical Reagent Corp.. P-dichlorobenzene (PDCL) and p-dibromobenzene (PDBB) were analytical pure reagents and used as received. The intercalates, noted as I0, I1, I2, I3, I4, I5, and I6, were prepared by four successive meltings and recrystallizations of PEO/PDCL/PDBB mixtures whose compositions were listed in Table 1. The molar ratio of PDCL/PDBB molecules to ethylene oxide units (EO) was kept to be 3:10 to make sure that the obtained intercalates were in stoichiometry. In order to prevent volatilizing of small molecules, the preparation of intercalates is carried out in sealed tubes.

Thermal analysis was made on a Pyris-1 series differential scanning calorimeter in a flowing nitrogen atmosphere. Sealed aluminum caps for volatile samples containing about 3 mg sample were used and the scanning rate was 5 °C/min. Benzoic and Indium were used for calibration of temperature and power scales.

The powder wide-angle X-ray diffraction patterns were recorded on a Riguku Geiger Flex D-Max IIIa using Ni-filtered CuKα radiation (40KV, 25mA). A scanning rate of 2 °/min was employed.

Solid-state ^{13}C CP/MAS (cross polarization, magic angle spinning) NMR measurement was performed on a Bruker DSX-300 spectrometer at 75.47MHz and 27 °C. The typical measurement conditions were as follows: spinning rate, 6000Hz; pulse repetition time, 5s; spectral width, 20 kHz; number of points, 8K; number of scans, 256-512; contact time: 1 ms.

Table 1 Composition of the prepared intercalates

Intercalate	PDCL molar fraction	PDBB molar fraction	molar fraction of EO units
I0	0.231	0	0.769
I1	0.192	0.039	0.769
I2	0.165	0.066	0.769
I3	0.116	0.115	0.769
I4	0.092	0.139	0.769
I5	0.077	0.154	0.769
I6	0	0.231	0.769

Results and discussion

The DSC curves of the prepared intercalates with various compositions are given in Figure 1. Each one of the melting curves reveals only one sharp fusion peak and no eutectic endotherm is observed. It suggests that these intercalates were prepared stoichiometrically. The melting points of PEO-PDCL (I0) and PEO-PDBB (I6) intercalates are 83.5 °C and 95.7 °C respectively, which are in agreement with those reported by Point [7, 11]. In the series of I1, I2, I3, I4, and I5 intercalates, PDCL and PDBB coexist as guest molecules. The fusion peak of every sample is so sharp that it is impossible to separate the fusion peak into those of PEO-PDCL intercalate and PEO-PDBB intercalate. Therefore, the three-component intercalates composed of PEO, PDCL and PDBB are not the mixtures of PEO-PDCL crystals and PEO-PDBB crystals. As it is known, the PEO-p-dihalogenobenzene intercalate is made of benzenic layers sandwiched between PEO sheets [9]. Based on the DSC data, it is believed that PDCL and PDBB array statistically in the benzenic layers. This means PDCL and PDBB molecules are embedded into PEO sheets without selectivity. Furthermore, it can be seen that the melting points of the three-component intercalates elevate with increasing PDBB molar fraction. Figure 2 is the plot of the melting point of PEO-PDCL/PDBB intercalates versus the PDBB molar fraction in the PDCL/PDBB. The dash line in Figure 2 represents the expected variation of the melting points if PDCL interacts weakly with PDBB and the deposition of the two guest molecules in the benzenic layers is random and homogenous. The deviation of measured melting points from the dash line is very small, which further supports that PDCL and PDBB molecules are almost unselectively accommodated between PEO sheets. It is therefore concluded that PEO-PDCL/PDBB intercalate is not the blend of pure PEO-PDCL and PEO-PDBB crystals.

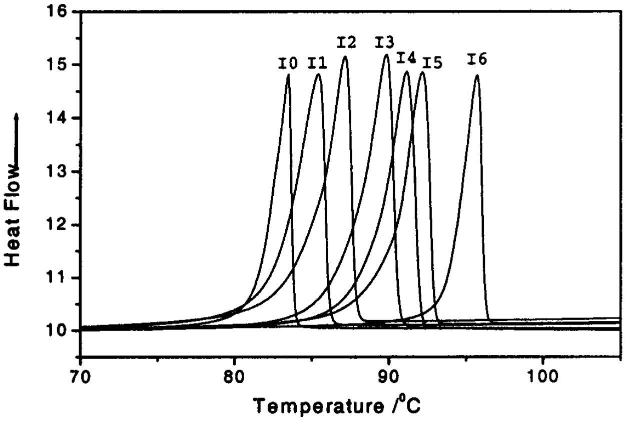

Figure 1. DSC traces of I0, I1, I2, I3, I4, I5, and I6 intercalates.

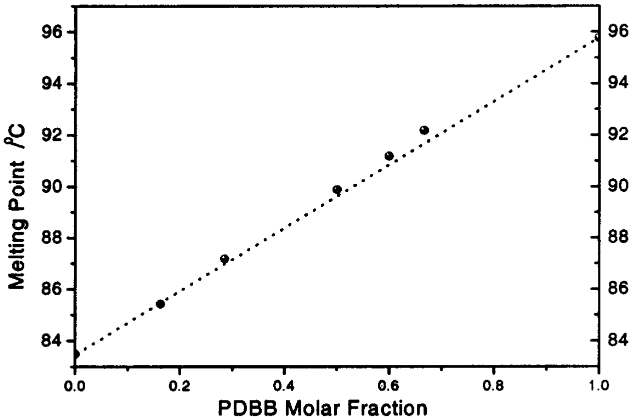

Figure 2. Melting points of PEO-PDCL/PDBB intercalates (●) plotted versus PDBB molar fraction in the PDCL/PDBB guest molecules. The straight dash line represents the expected variation of melting points if PDCL interacts weakly with PDBB and the deposition of the two guest molecules in the benzenic layers is at random.

An orthorhombic crystalline model was proposed for the category of PEO-p-dihalogenobenzene intercalates[10], which was different from the monoclinic crystal structure of pure PEO[12, 13]. Figure 3 shows the wide-angle X-ray diffraction patterns obtained for I0, I2, I4, and I6 intercalates at different 2θ ranges. On the basis of ref.10 and our calculation, the diffraction peaks of interest are indexed as noted in Figure 3. It can be seen from Figure 3b that the reflection at 23.0° characteristic of pure PEO crystal structure is absent in the WAXD patterns of these four intercalates, indicating difference of crystal structures between pure PEO and the investigated intercalates. At different 2θ ranges (Figure 3a, 3b, 3c and 3d), the diffractograms of I2 and I4 intercalates are very close to those of PEO-PDCL intercalate (I0) and PEO-PDBB intercalate (I6), which implies that the PEO-PDCL/PDBB intercalates belong to the same orthorhombic crystalline system with PEO-PDCL and PEO-PDBB intercalates. Moreover, the d spacings of (2, 2, 0), (2, 2, 3), (2, 2, 5), (2, 2, 6), (1, 1, 3), (3, 1, 3) (5, 1, 3), and (4, 2, 6) crystalline planes enlarge with the increasing PDBB molar fraction in these intercalates. Taking the group of (2, 2, 3) reflections as an example, the diffraction peaks of I2 and I4 intercalates are relatively sharp, so they can never come from the overlapping of the diffraction peaks of PEO-PDCL (I0) and PEO-PDBB (I6) intercalates. It suggests that PDCL and PDBB molecules are arranged in benzenic layers statistically and the PEO-PDCL/PDBB intercalate is not the mixture of pure PEO-PDCL crystals and PEO-PDBB crystals. Additionally, the size of crystal cell for the three-component intercalates get large with the increasing PDBB content. So it is possible to control the parameters of orthorhombic unit cell for the intercalates via adjusting PDBB molar fraction.

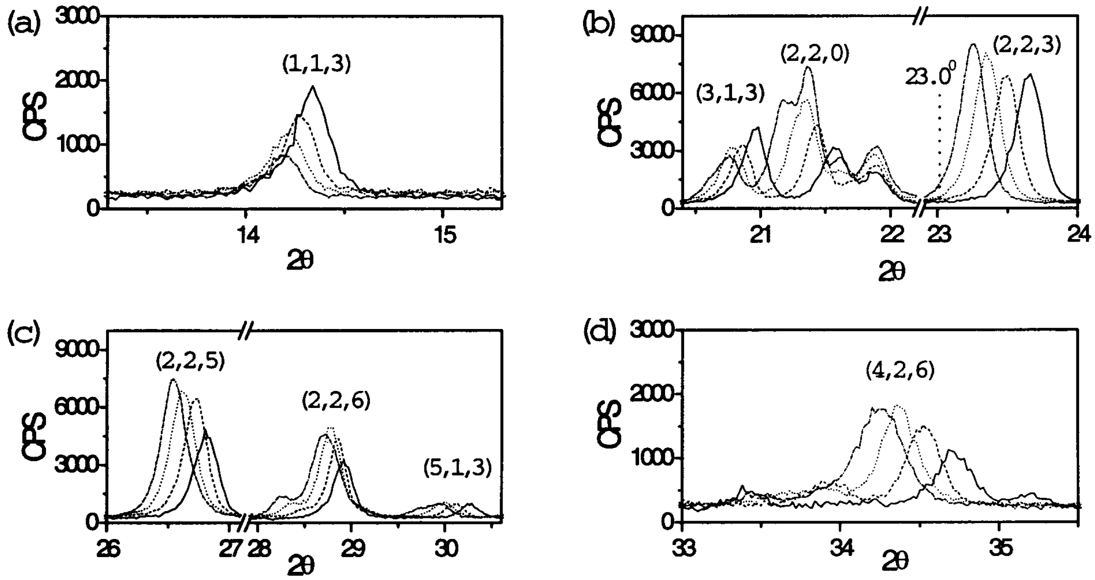

Figure 3. WAXD patterns obtained for I0 (solid line), I2 (dash line), I4 (dot line), and I6 (dash dot line) intercalates at different 2θ ranges: 13.5—15.5^0 (a), 20.5—24^0 (b), 26—30.5^0 (c), 33—35.5^0 (d).

Several authors have reported that the ^{13}C NMR line attributed to the crystalline phase in pure PEO is very broad (line width > 1KHz) and centered at 72 ppm[14-16]. The unusual broadness of this line was considered to originate from the competition between molecular motion and decoupling[14, 17, 18]. The ^{13}C CP/MAS NMR spectra of I0, I2, I4, I5, and I6 intercalates were given in Figure 4. The dotted line presents the position of the resonance signal in the crystalline phase of pure PEO. All of the PEO lines in ^{13}C NMR spectra of the studied intercalates are much narrower than that of pure crystalline PEO. For PEO-PDCL (I0) and PEO-PDBB (I6) intercalates, the PEO lines are detected at 71.2 and 71.6 ppm, respectively. In I2, I4, and I5 intercalates, PDCL and PDBB coexist as the guest molecule. The PEO resonance signal lies in the range of 71.2 to 71.6 ppm and gradually shifts to “lowfield” with the increasing PDBB molar fraction. Compared with pure crystalline PEO (72 ppm), the PEO resonance for all the intercalates is shifted about 0.4-0.8 ppm “upfield”. This small “upfield” shift could be due to the ring current shielding by benzenic molecules [19]. Furthermore, in the ^{13}C NMR spectra of I2, I4, and I5 intercalates, the PEO resonance signal is a single peak with high symmetry, which does not come from the overlapping of the resonance signals of PEO-PDCL and PEO-PDBB intercalates. This means that the carbons of PEO chains in PEO-PDCL/PDBB intercalate are in the same chemical environment. It further supports that PEO does interact with PDCL and PDBB without selectivity, in the meantime, PDCL and PDBB deposit into benzenic layers statistically.

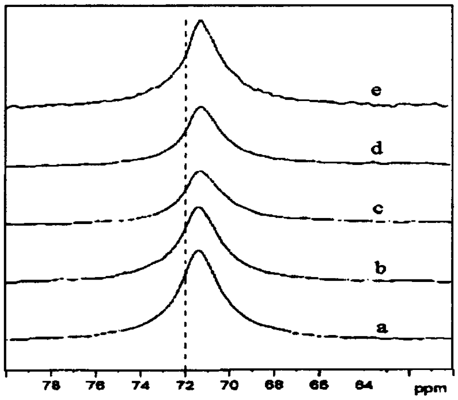

Figure 4. The solid-state ^{13}C CP/MAS NMR spectra measured at 75.47MHz and 27 ^{0}C for I0 (a), I2 (b), I4 (c), I5 (d), and I6 (e) intercalates in the range of 62-78 ppm. The dash line represents the position of the resonance in pure crystalline PEO.

Conclusion

The PEO-PDCL/PDBB intercalates, in which PDCL and PDBB coexist as guest molecule, was investigated by DSC, WAXD, and ^{13}C CP/MAS NMR. DSC results show that the melting points of these three-component intercalates elevate with increasing PDBB molar fraction. Moreover, the melting peak of the PEO-PDCL/PDBB intercalate is quite narrow, which can never result from the combination of melting peaks of PEO-PDCL and PEO-PDBB intercalates. This implies there is no crystals of pure PEO-PDCL intercalate and pure PEO-PDBB intercalate in the PEO-PDCL/PDBB intercalate. It is therefore believed that PEO interacts unselectively with PDCL and PDBB. And the two kinds of guest molecules are statistically arranged in benzenic layers. In the ^{13}C CP/MAS NMR spectra, it is found that PEO lines of PEO-PDCL/PDBB intercalates range from 71.2 to 71.6 ppm, and shift to "lowfield" with increasing PDBB content. Each of PEO resonance signals is a single narrow peak with symmetry. It suggests that carbon atoms of PEO chains in three-component intercalates are in the same chemical environment. This result further corroborates the aforementioned assumption that PDCL and PDBB molecules are statistically distributed in benzenic layers. The WAXD patterns of PEO-PDCL/PDBB intercalates show that d spacings of some crystalline planes such as (2, 2, 0), (2, 2, 3), (2, 2, 5), (2, 2, 6), (1, 1, 3), (3, 1, 3) (5, 1, 3), and (4, 2, 6) get large with increasing PDBB molar fraction, which implies that the size of crystal cells of the PEO-PDCL/PDBB intercalates augments with increasing PDBB molar fraction. It provides an approach to control the size of orthorhombic unit cell for PEO-p-dihalogenobenze intercalates.

Acknowledgements. This work is subsidized by the Special Funds for Major State Basic Research Projects (G1999064800).

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