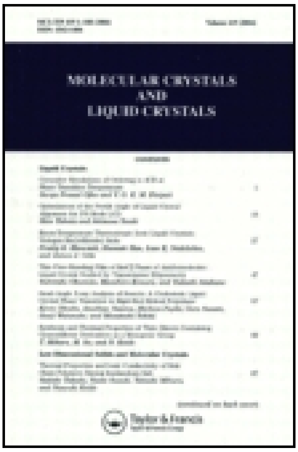

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Block Copolymers of Methoxypoly(Ethylene Oxide) and Poly(ϵ-Caprolactone): Synthesis, Structure, Micellization, and Interaction with Prednisolon

Sofia Partsevskaya [a] , Tatyana Zheltonozhskaya [a] , Vitaliy Khutoryanskiy [b] , Nataliya Permyakova [a] & Alexey Kolendo [a]

[a] Department of Macromolecular Chemistry, Faculty of Chemistry, Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

[b] Reading School of Pharmacy, University of Reading, Reading Berkshire, United Kingdom

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Block Copolymers of Methoxypoly-(Ethylene Oxide) and Poly(ε-Caprolactone): Synthesis, Structure, Micellization, and Interaction with Prednisolon

SOFIA PARTSEVSKAYA,[1] TATYANA ZHELTONOZHSKAYA,[1]
VITALIY KHUTORYANSKIY,[2] NATALIYA PERMYAKOVA,[1] AND ALEXEY KOLENDO[1]

[1]Department of Macromolecular Chemistry, Faculty of Chemistry,
Taras Shevchenko National University of Kyiv, Kyiv, Ukraine
[2]Reading School of Pharmacy, University of Reading, Reading
Berkshire, United Kingdom

A series of MOPEO-b-*PCL diblock copolymers (DBCs) with* $M_{nMOPEO} = 2.5 \cdot 10^3$ *and* $M_{nPCL} = (0.28 \div 2.43) \cdot 10^4$ *was synthesized using the anionic ring-opening block copolymerization. A bulk structure of the copolymers was studied with DSC. One glass transition and three melting peaks for MOPEO*-b-*PCL were found, thus implying the existence of separate crystalline domains of both blocks in a copolymer structure. The intense micellization of DBCs in dioxane/aqueous solutions was found with a spectrophotometry, a static light scattering, and photography. A reduction in* CMC *and an increase in* $-\Delta G^\circ$ *values with growth of the PCL length and at the addition of prednisolon (PS) were established. The hydrogen bonding of PS with DBCs was confirmed with FTIR spectroscopy.*

Keywords Diblock copolymer; drug; micellization; nanocontainer; structure

Introduction

Amphiphilic block copolymers with biocompatible and biodegradable polymer components, in particular polyethers and polyesters, have been of great interest during the last years in the context of their applications as nanocontainers for different drugs [1,2]. Such copolymers form micelles of a variable morphology: spherical, rod-like, and vesicular structures in dependence on the relative length of polymer blocks and the solvent quality [3]. Many studies are devoted to the block copolymers containing hydrophilic methoxypoly(ethylene oxide) (MOPEO) and hydrophobic poly(ε-caprolactone) (PCL) [4–6]. It was shown that small spherical micelles of the

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Address correspondence to Sofia Partsevskaya, Department of Macromolecular Chemistry, Faculty of Chemistry, Taras Shevchenko National University of Kyiv, 64, Volodymyrska Str., Kyiv, Ukraine. E-mail: partsevskaya@ukr.net

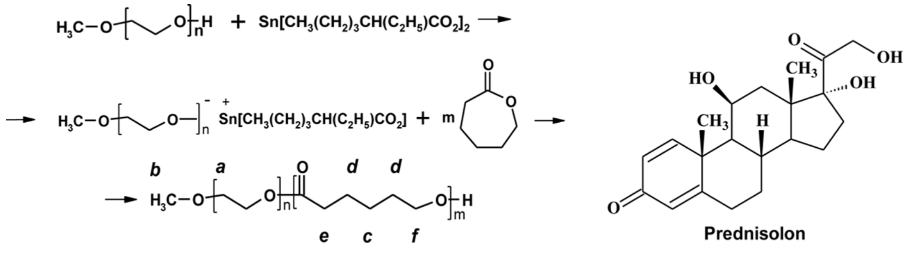
copolymers with a size of some tens of nanometers, which include the drug molecules solubilized, can internalize into living cells by means of an endocytotic pathway and release a drug there as a result of the biodegradation [7,8]. In spite of a large scientific interest in these block copolymers, many aspects of their bulk structure, micellization, and interaction with different drugs were studied not enough. In the given work, we have synthesized and characterized the physicochemical properties of a series of MOPEO-*b*-PCL diblock copolymers (DBCs) with a fixed length of the MOPEO block and a variable length of the PCL block. We also studied their interaction with a model drug prednisolon (PS).

Experimental

Synthesis of MOPEO-*b*-PCL copolymers was carried out using the anionic ring-opening block copolymerization with stannous octoat as an initiator (Fig. 1a).

The samples of MOPEG with $M_v = 2 \cdot 10^3$ from "Fluka" (USA), ε-caprolactone (CL) from "Sigma-Aldrich" (USA) and stannous octoat [$Sn(Oct)_2$] from "Acros Organics" (USA) were used in the block copolymerization. To 10 g of MOPEG in an inert atmosphere, a necessary quantity of CL (depending on a desirable length of the PCL block) and $Sn(Oct)_2$ was added, and the reaction of block copolymerization was carried out at 135°C for 24 h. The molar ratio $[Sn(Oct)_2]/[MOPEG] = 1$ was used in all the cases. A hard product was dissolved in dioxane, precipitated by ethanol, and dried in an evacuated case at 40°C. NMR spectroscopy was used to confirm a chemical structure of the copolymers and to determine their molecular weights. ^1H NMR spectra of DBCs and MOPEG in CCl_4 ($C = 10\,\mathrm{kg \cdot m^{-3}}$) were recorded at 20°C with a 400-MHz "Mercury-400" spectrometer from "Varian" (USA). The PS sample (Fig. 1b) from "Sigma Aldrich" (USA) was used as a model drug.

A bulk structure of MOPEG and DBCs was studied with DSC using a differential microcalorimeter DSC-210 and a thermoanalyzer 1090 "Du Pont" (USA). The sample (~10 mg) was introduced in an open capsule, cooled with liquid nitrogen, and heated up to 150°C with a rate of $16\,°\mathrm{C \cdot min^{-1}}$ (the 1st scan). Then it was sharply cooled with liquid nitrogen up to the initial temperature and heated again with the same rate (the 2nd scan). The instrument was calibrated with indium and zinc. A sapphire crystal with $m = 61.66$ mg was heated with the (co)polymer samples to obtain dependences of the specific heat capacity (C_p) on the temperature.



(a) (b)

Figure 1. Schematic representation of (a) the anionic ring-opening block copolymerization of PCL with MOPEG and (b) a molecular architecture of PS.

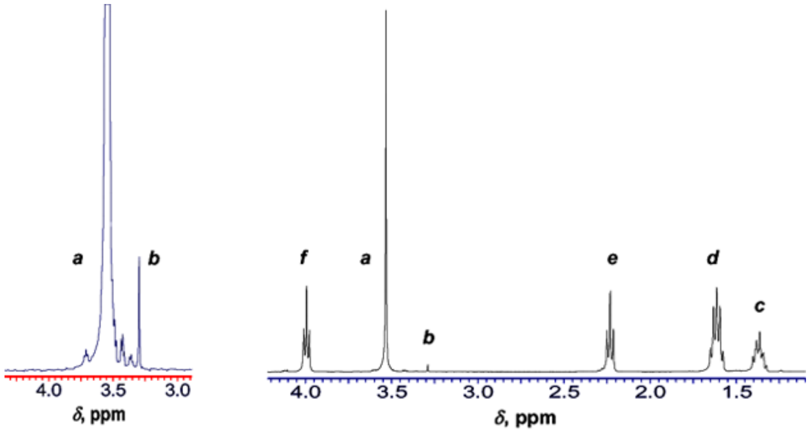
Spectrophotometry, static light scattering, and photography were applied to study the micelle formation of DBCs and those in the presence of the drug in dioxane/aqueous solutions. The optical density (turbidity) of all the solutions was measured with a UV/VIS spectrometer "Perkin Elmer Lambda 20" (Sweden) at $\lambda = 500$ nm. The scattering intensity of the vertically polarized light with $\lambda = 520$ nm was determined at the scattering angle $\theta = 90°$ with the use of a modernized instrument FPS-3 (Russia) containing a light-emitting diode WP7113VGC/A from "Kingbright", the controller ADC-CPU^{TM} from "Insoftus" (Ukraine), and the computer program "WINRECORDER".

FTIR spectra for one of DBC sample, PS and DBC+PS blend in the KBr medium and/or in the form of a thin film cast on CaF_2 glasses were recorded by 32 scans with an instrument "Nexus-470 Nicolet" (USA) which had a resolution of 4 cm^{-1}.

Results and Discussion

The examples of ^{1}H NMR spectra for MOPEG and one of DBC samples are shown in Figure 2.

Their interpretation was carried out in accordance with the data in [9] and [10]. There were two resonance signals in the spectrum of MOPEG with the chemical shifts $\delta = 3.54$ and 3.30 ppm (Fig. 2a) which can be attributed to the protons of (***a***) methylene and (***b***) terminal methoxy groups. In the spectrum of DBC2 (Fig. 2b), additionally 4 groups of signals with $\delta = 1.37$, 1.62, 2.24, and 4.00 ppm appeared. They correspond to the protons of: (***c***) a central methylene group in the PCL unit (Fig. 1a), (***d***) two methylene groups near the central one, (***e***) a methylene group near carbonyl and (**f**) a methylene group disposed near the oxygen atom of an ester group [10]. The following relations based on the integral intensities (A) of corresponding signals were used to calculate the average molecular weights of



(a) (b)

Figure 2. The examples of ^{1}H NMR spectra for: (a) initial MOPEG and (b) DBC2 in CCl_4. $T = 20°C$.

Table 1. The main molecular parameters of MOPEO-*b*-PCL diblock copolymers

Copolymer	$M_{n\text{MOPEO}} \cdot 10^{-3}$	$M_{n\text{PCL}} \cdot 10^{-4}$	$M_{n\text{DBC}} \cdot 10^{-4}$	w_{MOPEO}[1], %	n[2]
DBC1	2.50	0.28	0.53	47.3	0.42
DBC2	2.50	0.80	1.05	23.7	1.25
DBC3	2.50	2.39	2.64	9.5	3.68
DBC4	2.50	2.43	2.68	9.3	3.74

[1] The weight fraction of MOPEO in the diblock copolymer.
[2] The ratio between units in PCL and MOPEO blocks, base-mol$_{\text{PCL}}$/base-mol$_{\text{MOPEO}}$.

MOPEG, PCL, and then DBCs:

$$M_{nMOPEG} = \frac{3 \cdot M_{0MOPEG} \cdot A_a}{4 \cdot A_b}; \quad M_{nPCL} = \frac{M_{0PCL} \cdot M_{nMOPEG} \cdot A_d}{M_{0MOPEG} \cdot A_a} \quad \text{or}$$

$$M_{nPCL} = \frac{2 \cdot M_{0PCL} \cdot M_{nMOPEG} \cdot A_{c,e,f}}{M_{0MOPEG} \cdot A_a}$$

Here, $M_{0\ \text{MOPEG}}$ and $M_{0\ \text{PCL}}$ are the molecular weights of MOPEG and PCL units. All the results are represented in Table 1.

In DBC1, the length of a hydrophobic PCL block turned out to be by 2.4 times less than that of a hydrophilic MOPEO block. The second DBC2 sample was composed of blocks with approximately equal length, while the DBC3 and DBC4 copolymers contained PCL chains, whose lengths were more than by 3 times higher than those of the MOPEO block.

Structural studies of the copolymers are of special interest because of crystalline properties of PCL and PEO. Moreover, the temperatures of their glass and melting transitions are close [11]. Therefore, many works were devoted to the crystallization of bound PCL and (MO)PEO chains in diblock and triblock copolymers [12,13]. Some examples of our MOPEG and DBC bulk structure investigations with DSC are represented in Figure 3.

The only melting peak at 53°C (without glass transition) was displayed on the DSC thermogram of MOPEG (they are not shown) because of its high crystallinity (Table 2). DSC thermograms of all the copolymers (examples in Fig. 3a,b) showed 3 melting peaks and one glass transition. Due to the appreciable overlapping of some

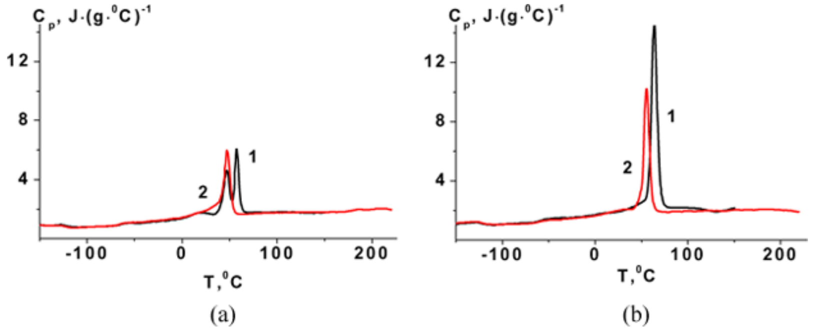


Figure 3. The examples of DSC thermograms (the 1-st –1 and 2-nd –2 scans) for: (a) DBC1 and (b) DBC3. The heating rate was 16 degree · min^{-1}.

Table 2. Parameters of thermal transitions in the structure of MOPEG and the diblock copolymers

Polymer	Scan	T_g[1], °C	ΔT_g[2], °C	ΔC_p[3], $J \cdot (g \cdot °C)^{-1}$	Melting peaks	T_m[4], °C	ΔT_m[2], °C	ΔH_m[5], $J \cdot g^{-1}$	X_c[6], %
MOPEG	1-st	–	–	–	–	53.0	39	194.8	99.0
	2-nd	–	–	–	–	50.6	85	167.2	85.0
DBC1	1-st	−63.5	13	0.20	1	19.5	34	4.8	–
					2	47.0	19	22.7	24.4
					3	57.4	21	23.3	32.2
	2-nd	−64.0	12	0.21	1	~19	~32	20.5	–
					2	~35	~12		–
					3	47.1	34	29.2	40.3
DBC2	1-st	−58.5	13	0.28	1	14.0	40	2.4	–
					2	51.0	23	6.4	13.7
					3	62.5	22	80.7	76.9
	2-nd	−62.0	12	0.24	1	19.6	45	5.7	–
					2	53.5	33	70.5	67.2[7]
					3				
DBC3	1-st	−57.0	18	0.30	1	14.2	27	0.7	–
					2	~51	~25	~2.9	~15.5
					3	64.0	27	103.8	83.4
	2-nd	−60.0	16	0.25	1	~20	~29	7.7	–
					2	33.4	~17		–
					3	55.2	33	66.3	53.3
DBC4	1-st	−58.0	12	0.29	1	19.4	25	0.6	–
					2	~51	~23	~2.5	~13.7
					3	64.5	31	94.8	76.0
	2-nd	−64.5	17	0.26	1	25.3	~29	13.5	–
					2	35.6	~20		–
					3	54.5	33	63.4	50.8

[1] The glass transition temperature.

[2] The temperature region for a certain thermal transition.

[3] The specific capacity jump.

[4] The melting temperature.

[5] The melting enthalpy.

[6] The crystallinity degree: for pure MOPEG $X_c = \Delta H_m / \Delta H_m^{\circ}$, where ΔH_m° is the melting enthalpy for 100% crystalline PEO ($196.8\,J \cdot g^{-1}$) [14], but for MOPEO and PCL blocks in the copolymer $X_c = \Delta H_m / (\Delta H_m^{\circ} \cdot w)$ [14], where w is the mass fraction of corresponding block in DBC; the value of $\Delta H_m^{\circ} = 137.5\,J \cdot g^{-1}$ for 100% crystalline PCL was taken of the study [12].

[7] The crystallinity degree, calculated under condition of a participation of only PCL blocks in this melting process.

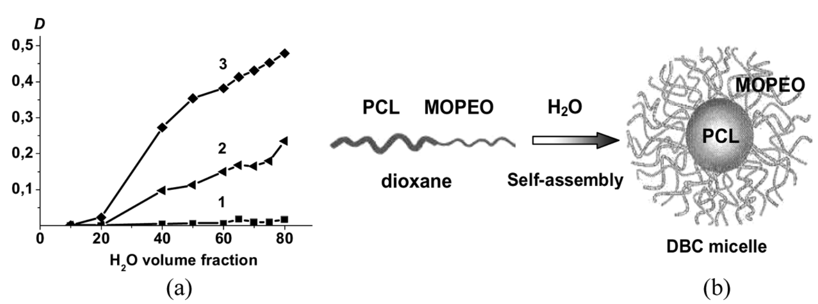
melting peaks, their parameters cannot be exactly determined with an ordinary computer program of the instrument. For these cases, only approximate values of the corresponding parameters are represented in Table 2.

According to the literature data [11] and changes in the relative intensity (ΔH_m values in Table 2) of all the melting peaks with the DBC content (Table 1), one can conclude that the second melting peak with $T_m \sim 47$–51°C at the 1st scan would be attributed to the melting transition in PEO microcrystalline domains. Further, the highest and most intense melting peak with T_m from 57.4 to 64.5°C (at the 1st scan) reflects the melting process in separate microcrystalline regions of PCL. The appearance of the lowest melting peak in the interval of $T_m = 14.0–19.5°C$ (according to the 1st scan) is not clear yet. In order to highlight this question, additional researches are necessary.

It is seen that T_m values for PCL microcrystalline regions grow up to the constant value with increase in the PCL length (and the weight fraction). It is accompanied by an essential rising in the crystallinity degree, X_c, of the blocks. The parameter achieves the maximum value of 83.4% in the case of DBC3, and then (for DBC4) it somewhat reduces. Simultaneously, the crystallinity of MOPEO blocks decreases (Table 2). Interestingly, that X_c value for MOPEO blocks turns out to be less than that for PCL even in the case of DBC1, whose MOPEO block is significantly longer than the PCL block. In view of a higher crystallization rate of PCL as compared with that of PEO [11], this result means that the more quick PCL crystallization depresses the crystallization of MOPEO blocks.

A change in the glass transition parameters in dependence on the PCL block length is in full accordance with the above data. Note that T_g for a pure PCL (near −59°C [15]) is somewhat higher than that for pure PEO (−57°C [16]). Therefore, when the relative length (or the weight part) and X_c of PCL blocks in DBC grew, the fraction of their segments in amorphous regions decreased, and T_g (found from the 1st scan) reduced up to a characteristic value for pure PEO (Table 2). In addition, T_g values increase for all DBCs at the repeated scanning due to a decrease in X_c for PCL blocks.

The micellization of most DBC samples, excluding DBC1 with the shortest PCL block is developed at the addition of water to dioxane solutions (Fig. 4a). Dioxane is a good solvent for whole copolymer chains, while water was a selective solvent only for MOPEO blocks. Due to this, an increase in the water content in dioxane/aqueous solutions of DBCs stimulated a hydrophobic self-assembly of their macromolecules in micellar structures, as it is schematically shown in Figure 4(b). The process was essentially intensified (Fig. 4a, curves 2 and 3) at the lengthening of PCL blocks. These blocks formed a micellar "core," but hydrophilic MOPEO chains remained in the "corona". It is clear that the spherical micellar structures of DBCs



(a) (b)

Figure 4. Increasing in (a) the optical density (turbidity) of DBC1 −1, DBC2 −2 and DBC3 −3 dioxane solutions ($C_{DBC} = 0.8\,kg \cdot m^{-3}$) due to (b) micellization of DBC macromolecules at H_2O addition. $T = 20°C$.

Table 3. The micellization thermodynamic characteristics, found with (A) a spectrophotometry and (B) a static light scattering

		$CMC \cdot 10^5$, $mol \cdot dm^{-3}$		$-\Delta G°$, $kJ \cdot mol^{-1}$	
System	Solvent (dioxane/H_2O)	A	B	A	B
DBC2		8.78	0.48	22.91	27.80
DBC3	30/70	3.69	0.08	25.04	31.87
DBC4		3.04	0.15	25.57	30.44
DBC2 + PS[1]		6.93	–	23.56	–
DBC3 + PS	30/70	2.80	–	25.79	–
DBC4 + PS		1.87	–	26.79	–

[1] The molar ratio between PS and DBC $\varphi = 0.25\,mol_{PS}/base\text{-}mol_{DBC}$ was constant in all the blends.

will differ one from another by the "core" size (and, possibly, by the aggregation number Z), the dimension of the "corona" being constant.

Using spectrophotometry and static light scattering, we established the critical micellization concentrations (*CMC*s) for DBC2–DBC4 (Table 3). Note that the second method provides more exact and lower *CMC* values. In DBC series, the longer the hydrophobic block, the less the *CMC* value. The Gibbs free micellization energies were determined from *CMC* values according to the following relation: $\Delta G° \approx RT \cdot \ln CMC$ [3]. The results (Table 3) indicate an increase in the stability of DBC micellar structures with the PCL block lengthening.

The introduction of the drug in DBC solutions (dioxane/H_2O = 30/70 vol. %) at the constant ratio $\varphi = [PS]/[DBC] = 0.25\,mol_{PS}/base\text{-}mol_{DBC}$ intensified the micellization process, as it is shown in Figure 5. The corresponding reduction in *CMC* numbers and an increase in $-\Delta G°$ values in DBC +PS blends were revealed with spectrophotometry (Table 3). Thus, the effect of an additional stabilization of DBC micelles by the drug due to its possible interaction with micellar structures was established.

The analysis of a chemical structure of the drug (Fig. 1b) shows that only 3 hydroxyl groups can interact through hydrogen bonds with MOPEO and/or PCL

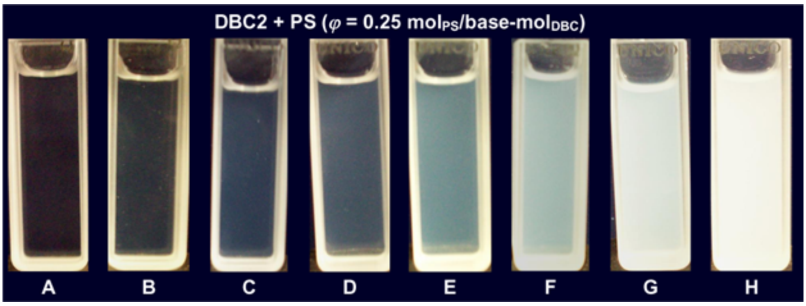


Figure 5. Photos of DBC2 + PS dioxane/aqueous (30/70 vol %) solutions at DBC2 concentrations: (A) 0.1, (B) 0.2, (C) 0.3, (D) 0.4, (E) 0.5, (F) 1.0, (G) 1.5, and (H) 2.0 $kg \cdot m^{-3}$. $T = 20°C$.

blocks of DBC. Therefore, FTIR spectroscopy was chosen to confirm such a hypothesis. FTIR spectra for commercial PS, one of DBC samples, and their blend with $\varphi = 0.25\,\mathrm{mol_{PS}/base\text{-}mol_{DBC}}$ in two most important regions are demonstrated in Figure 6. The spectrum of crystalline PS in KBr contained the bands of $\nu_{C=O}$ vibrations at $1707\,\mathrm{cm^{-1}}$ and $1657\,\mathrm{cm^{-1}}$ for free and H-bonded carbonyl groups, $\nu_{C=Cas}$ and $\nu_{C=Cs}$ vibrations at $1616\,\mathrm{cm^{-1}}$ and $1602\,\mathrm{cm^{-1}}$ for two unsaturated bonds (Fig. 6a), as well as the bands of $\nu_{O\text{-}H}$ vibrations at $3575\,\mathrm{cm^{-1}}$, $3464\,\mathrm{cm^{-1}}$, and $3388\,\mathrm{cm^{-1}}$ for H-bonded hydroxyl groups (Fig. 6b). In the spectrum of DBC (KBr medium), there are two overlapping bands of $\nu_{C=O}$ vibrations at $\sim 1735\,\mathrm{cm^{-1}}$ and $1726\,\mathrm{cm^{-1}}$ for PCL ester groups which are placed in amorphous and crystalline regions, consequently (Fig. 6c, curve 1), and a wide band of $\nu_{O\text{-}H}$ vibrations at $3437\,\mathrm{cm^{-1}}$ for probably H-bonded terminal hydroxyl groups of PCL and/or some

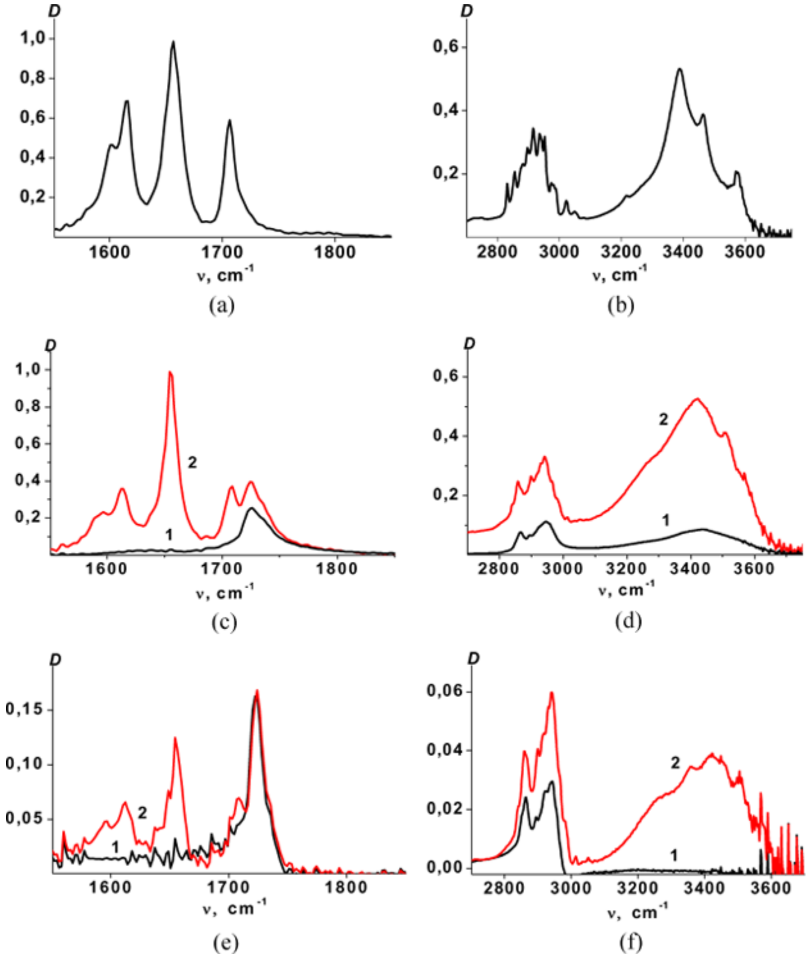


Figure 6. FTIR spectra for: (a,b) commercial PS in KBr medium, (c,d) DBC2 –1 and DBC2 + PS –2 in KBr, and also (e,f) DBC2 –1 and DBC2 + PS –2 thin films ($l \sim 4$–$5\,\mu\mathrm{m}$), which were cast on CaF_2 glasses. Two best important regions of (a,c,e) $\nu_{C=C}$, $\nu_{C=0}$ and (b,d,f) $\nu_{C\text{-}H}$, $\nu_{O\text{-}H}$ vibrations are shown. $\varphi = 0.25\,\mathrm{mol_{PS}/base\text{-}mol_{DBC}}$.

water molecules (Fig. 6d, curve 1). The FTIR spectrum of DBC+PS blend in KBr (Fig. 6c, d, curves 2) is not a very informative to confirm the existence of H-bonds between PS and DBC. Only the appearance of an intense band at $\sim 3290\,\text{cm}^{-1}$ points out a reality of these bonds. At the same time, the FTIR spectra of very thin (~4–5 μm) films which were cast on CaF_2 glasses of DBC and DBC+PS solutions (Fig. 6e, f, curves 1 and 2), allow proving the hydrogen bonding between DBC and the drug. This conclusion is based on the appearance of two new bands at $3284\,\text{cm}^{-1}$ and $3358\,\text{cm}^{-1}$ which had an enough resolution in the DBC+PS spectrum.

Conclusion

Thus, the anionic ring-opening block copolymerization of PCL with MOPEG is an available method to obtain MOPEO-*b*-PCL diblock copolymers with regulated length of a hydrophobic block. A bulk structure of the copolymers contains amorphous regions and microcrystalline domains formed by MOPEO and PCL separately. When the relative length of PCL block grows, its crystallinity degree sharply increases, while the crystalline properties of MOPEO practically disappear. DBC macromolecules form stable micellar structures in dioxane/aqueous solutions with a "core" of PCL blocks and a "corona" of MOPEO blocks. These micelles can actively bind prednisolon due to hydrogen bonds and hydrophobic interactions, thus playing a role of nanocontainers.

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