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Poly(ϵ-caprolactone)-poly(fluoroalkylene oxide)-poly(ϵ-caprolactone) block copolymers. 2. Thermal and surface properties

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Abstract

The thermal and the surface properties of PCL–PFPE–PCL block copolymers having different PCL and PFPE block lengths were investigated by DSC, contact angles and XPS measurements. DSC analysis reveals for all the copolymers the presence of different amorphous phases; the phase located at low temperature was attributed to the fluorinated moiety. T_m values also demonstrated that PCL crystallizes from a pure phase. XPS measurements showed a strong surface enrichment in PFPE with respect to the bulk. Contact angle values showed a hydrophobic character of the film surface even if the trend was found not depending on the fluorine concentration as detected by XPS: this behavior may be explained by the presence of very flexible blocks, providing a highly dynamic surface. These structures can be potentially used as additives for the formation of polymers having 'smart surfaces' with selective adhesive properties.

Keywords: Block copolymers; Perfluoropolyethers; Poly(caprolactone)

1. Introduction

Poly(fluoroalkylene oxide)s (also named perfluoropolyethers, PFPEs) [1] represent a class of fluorinated materials extremely interesting for their unusual properties which are not shown by other common polymers. These properties include very low glass transition temperatures (about −120°C), chemical inertia, solvent and high temperature resistance, barrier properties, low coefficient of friction, hydrophobicity (water repellency), lipophobicity and in particular low surface energy.

In fact, some of the most interesting features of PFPEs derive from their surface properties which distinguish them from all other polymers, with the exception of poly(siloxane)s [2]. Surface tension of linear PFPEs varies in the range of 20–22 $\mathrm{mN\,m^{-1}}$, at least 10 $\mathrm{mN\,m^{-1}}$ lower than other conventional polymers such as poly(vinyl chloride), poly(styrene), poly(methyl methacrylate), poly(urethane)s and poly(ethylene terephthalate). Furthermore, PFPEs are extremely non-polar substances and their very low solubility parameters lead to a marked thermodynamic incompatibility with most of the common organic polymeric systems.

The improvement of the surface characteristics of the polymeric materials represents an industrial goal of always increasing importance. In this context, fluorinated polymers are particularly suitable and different strategies can be exploited to modify the surface properties of conventional polymers. First of all, surface fluorination of previously molded items, even though this represents a highly expensive technology [3].

Alternatively, surface properties can be modified by the addition of fluorine-containing monomers during the polymerization. Usually the copolymerization of traditional fluorinated monomers, such as perfluorinated alkenes with non-fluorinated olefins, leads to random copolymers with properties intermediate between those of the parent homopolymers [4]. In these systems a significant modification of the surface properties requires a high molar ratio of the fluorinated comonomers which could frequently be accompanied by a modification of the bulk properties (especially mechanical properties). In addition, the high cost of fluorinated monomers leads to very expensive polymeric materials.

Other fluorinated products such as acrylic and methacrylic esters copolymerize with their hydrogenated homologues and give rise to copolymers having peculiar surface properties, even when the ratio between the fluorinated and the hydrogenated monomers is very low. In these

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systems the bulk properties are those of the corresponding hydrogenated homopolymers [5].

The recent availability of telechelic PFPEs with reactive terminal groups [6] makes the preparation of segmented copolymers containing fluorinated blocks by using PFPEs as macromers during the polymerization possible [7–10]. It was shown that the PFPE segments contained in polyester–PFPE multiblock copolymers are able to migrate toward the surface (because of their low surface energy) leading to a fluorine-rich surface even when the amount of PFPE in the bulk is very low [11–13]. The main drawback of this last approach is that the chemical modification has to be carried out during the polymerization and that a fraction of PFPE could remain unreacted at the end of the polymerization [14]. This may not be economically convenient and can be exploited for a limited number of polymers, as it requires that the terminal groups of the telechelic macromers are able to react with the monomers.

In a different approach, fluorine surface modification can be achieved by blending fluorinated polymers with other polymers, taking into account that the air–polymer surface of blends is dominated by the low surface energy fluorinated polymer as a result of its surface activity and incompatibility, previously discussed. Unfortunately, pure PFPEs are not easily usable because of their extreme incompatibility with other organic polymers combined with a very low viscosity, which lead to an exudation from the system over a short period of time. An effective way to produce a true and permanent surface modification in such blends is represented by the employment of PFPE-based multiphase block, segmented or graft copolymers. Of course, the chemical nature of the non-fluorinated block is of primary importance in order to obtain compatibilization with the host polymer. In this respect, poly(ϵ-caprolactone) (PCL) is a polymer which offers some interesting features because it gives miscible blends with a wide variety of organic polymers [15], such as PVC, ABS, SAN, and PC. In these systems the hydrogenated chain can provide the miscibility with respect to the non-fluorinated polymer when the fluorinated chains migrate onto the surface: both miscibility and diffusion may be controlled by an appropriated choice of the type and length of both the fluorinated and non-fluorinated blocks.

In this paper we investigate the thermal and surface properties of ABA block copolymers containing PCL blocks (A) together with PFPE blocks (B), whose synthesis and molecular characterization have been reported in a previous work [16]; moreover the relationship existing between morphology and surface composition is discussed.

2. Experimental

2.1. Materials

Table 1
Molecular characteristics of PCL–R_H–PFPE–R_H–PCL block copolymers

Code	Molecular weight of blocks in PCL–R_H–PFPE–R_H–PCL[a]	PFPE (wt%)	PCL (wt%)[a]
TX1CL5	550–100–900–100–550	41	50
TX1CL10	1150–100–900–100–1150	27	67
TX1CL20	2300–100–900–100–2300	17	79
TX1CL40	4600–100–900–100–4600	9	89
TX2CL5	550–100–2000–100–550	60	34
TX2CL10	1150–100–2000–100–1150	45	51
TX2CL20	2300–100–2000–100–2300	30	67
TX2CL40	4600–100–2000–100–4600	18	80
TX3CL5	550–100–3200–100–550	71	25
TX3CL10	1150–100–3200–100–1150	56	41
TX3CL20	2300–100–3200–100–2300	40	57
TX3CL40	4600–100–3200–100–4600	25	73

[a] Nominal, from initial reactants ratio, in good agreement with composition data obtained from ^{1}H NMR analysis.

The fluorinated macromers were supplied by Ausimont (registered name Fomblin Z-DOL TX); they are liquids with the following formula:

$$\mathrm{H{-}(OC_2H_4)_{\mathit{n}}{-}OCH_2CF_2O{-}(C_2F_4O)_{\mathit{p}}}$$

$$\times\mathrm{(CF_2O)_{\mathit{q}}{-}CF_2CH_2O{-}(C_2H_4O)_{\mathit{n}}{-}H}$$

which can be schematized as: HO–R_H–PFPE–R_H–OH, and in which the constitutional units –C_2F_4O– and –CF_2O–, randomly distributed along the macromolecular chains, constitute the internal body (PFPE) where $p/q \approx 0.9$. The poly(ethylene oxide) chain (schematically R_H) is the end-capping segment containing the functional hydroxyl group, with an average n value close to 1.5. The molar mass of the three studied fluorinated macromers is 1100, 2200 and 3400 g mol^{-1} (in the following they are named TX1, TX2 and TX3, respectively). Poly(ϵ-caprolactone)-poly(fluoroalkylene oxide)-poly(ϵ-caprolactone) block copolymers were prepared by ring opening polymerization of ϵ-caprolactone (CL) using telechelic hydroxyalkyl terminated PFPE oligomers as transfer agent in the presence of titanium tetrabutoxide initiator [16]. As reported in Table 1, the copolymers are indicated with the code TXxCLy in which x (1, 2 or 3) and y (in the range from 2 to 40) identifies the fluorinated macromer and the average number of repeating units contained in each PCL block, respectively.

The structure

$$\mathrm{H[O{-}(CH_2)_5{-}CO]_{\mathit{y}}{-}(OC_2H_4)_{\mathit{n}}{-}OCH_2CF_2O{-}(C_2F_4O)_{\mathit{p}}}$$

$$\times\mathrm{(CF_2O)_{\mathit{q}}{-}CF_2CH_2O{-}(C_2H_4O)_{\mathit{n}}{-}[CO{-}(CH_2)_5{-}O]_{\mathit{y}}H}$$

can be schematized as PCL–R_H–PFPE–R_H–PCL.

Different PCL diols (purchased from Aldrich) having an average number molecular weight of 530, 1250 and 2000 g mol^{-1} (approximately corresponding to 5, 11 and 18 CL units, respectively), were used as-received. They will be named hereafter as PCL5, PCL11 and PCL18.

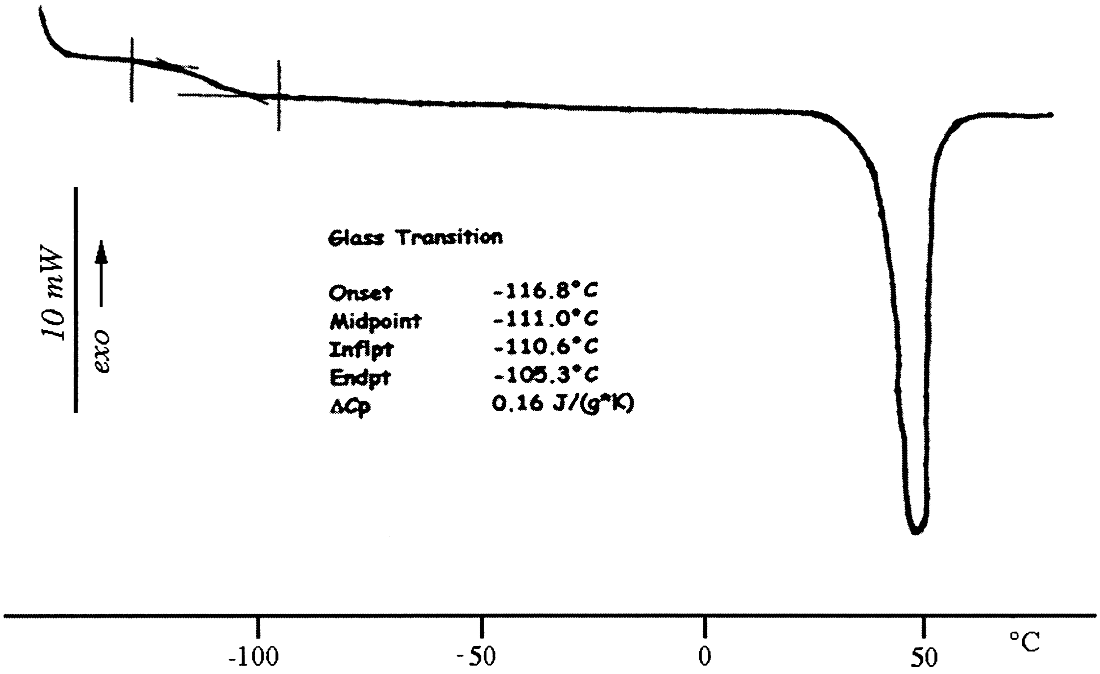


Fig. 1. DSC thermogram of TX3CL10 copolymer.

2.2. Film preparation

The films for contact angle measurements were obtained by casting from dichloromethane solution (5%, w/v) onto a glass slide. After the solvent was evaporated, the thermoplastic films were put into an oven at about 60°C for 10 min, in order to minimize the presence of air bubbles and surface defects, and then solidified at room temperature. Films were also obtained by placing the sample directly onto a glass slide followed by the same thermal treatment above described, in order to verify the absence of any solvent effect in the surface formation. No differences in contact angle values were found for films of the same sample prepared in the two different ways. The thickness of the obtained films was about 150 μm.

The specimens for XPS measurements were obtained by solvent-casting as films in clean aluminum weighing pans from chloroform solution (0.5%, w/v). The samples were allowed to air-dry at room temperature for over 60 h. The thickness of the resultant films was approximately 50 μm.

2.3. Film characterization

DSC analyses were performed by means of a Mettler DSC 30 instrument in the range from −150 to +100°C with a heating rate of 10°C min^{-1}. In order to minimize the effect of recrystallization from the dichloromethane solution, for each sample two thermal scans were collected in the aforementioned temperature range. The evaluation of the crystallinity content was performed on the second thermal scan immediately after a recrystallization from the melt at a cooling rate of 60°C min^{-1}. The T_g values were assumed as the mean value of the energy jump of the thermogram (average value between the onset and the endpoint of the glass transition range). Contact angle measurements were performed with a Kruss G1 instrument. The measurements were made in air at room temperature by the sessile drop technique; advancing and receding angles were obtained by increasing or decreasing the drop volume until the three-phase boundary moved over the surface. The microsyringe needle was kept immersed inside the drop during the measurements. On every samples at least nine measurements were performed, placing the liquid drops in different parts of the sample surface; their difference with the average value was no more than 2°. Because of the strong film adhesion on glass, wettability measurements of films were carried out only on the air-side and not on the glass-side.

XPS measurements were carried out on the air-side surface with a Perkin–Elmer Physical Electronics 5300 electron spectrometer using a hemispherical analyzer and a single-channel detector. Mg $K\alpha_{1,2}$ X-rays were used as the source, operated at 150 W (15 kV and 10 mA). High-resolution spectra of carbon 1s (C_{1s}) core level for each sample were acquired with a pass energy of 35.75 eV, a binding energy window of 20 eV and a rate of 0.2 eV per step. A maximum of 5 min at 150 W of X-ray exposition for each specimen was used. Under this analysis conditions the effects of X-ray damage were determined to be minimal [17]. Data were collected at 30° takeoff angle (TOA) between the sample and the analyzer and lead to sampling depths of approximately 50 Å [18,19]. Binding energies were referenced to the C–H level at 285.0 eV. Overlapping peaks were resolved into their individual components by using a curve-fitting program. The deconvolutions were based on the knowledge of the line widths determined from studies of the homopolymers and were in agreement with the literature data [13,20].

3. Results and discussion

3.1. Thermal properties

A typical DSC thermogram for the TX3CL10 sample is reported in Fig. 1; two thermal transitions at about −110 and +50°C are clearly evident. The first one is attributable to the glass transition of the perfluoropolyether phase [1], whereas the second one is attributable to the melting of the crystalline PCL phase. Similar results were found for the other triblock copolymers.

In Table 2 the T_g and T_m values obtained through DSC measurements on the block copolymers and also on some PCL diols with different molecular weight are shown.

3.2. Crystalline phase

The melting transition (T_m) observed for all the block copolymers is due to the PCL blocks; in fact by comparing the T_ms of the block copolymers to those of the PCL homopolymers having the same number of CL units, a good agreement can be found. The T_m values increase by increasing the number of the CL units and a value close to 64°C, i.e. the literature value of the PCL homopolymer [21], was observed for the longest PCL blocks. These results suggest that in the molten state PCL crystallizes from an almost pure PCL phase indicating the presence of a biphasic system in the molten state.

For all the block copolymers the crystallinity degree was determined considering a melting enthalpy of the PCL homopolymer of 142 J g^{-1} [21]. Its variation as a function of the CL units in the PCL diols and in the block copolymers is reported in Fig. 2. For the PCL diols the degree of crystallinity increases by increasing the number of CL units probably due to the progressive decrease of the relative weight of terminal groups which behave like defects. Also the fluorinated copolymers show the same trend, with an increase of the crystallinity percentage by increasing the number of the CL units and with the number of CL units being constant, the crystallinity of the PCL segments decreases by increasing the molecular weight of the PFPE macromer.

Table 2
T_g and T_m of PCL diols and block copolymers (values obtained from DSC; (a) not evident)

Code	T_g (°C)	T_m (°C)
PCL5	−76.8	+39.0
PCL11	−70.5	+50.0
PCL18	−64.2	+56.0
TX1	−89.5	–
TX1CL5	−76.7	+39.0
TX1CL10	−77.5	+49.0
TX1CL20	−68.5	+55.8
TX1CL40	−64.9	+59.5
TX2	−102.7	–
TX2CL5	−102.8	+39.8
TX2CL10	(a)	+54.3
TX2CL20	(a)	+53.1
TX2CL40	(a)	+59.8
TX3	−113.4	–
TX3CL5	−115.6	+37.6
TX3CL10	−111.0	+48.4
TX3CL25	−118.0	+59.1
TX3CL40	−114.3	+57.4

These data which were obtained after a fast cooling from the melt suggest that the mobility of the PCL blocks decreases with increasing the lengths of the PFPE midblock. The reduction of the mobility can be attributed to the presence of entanglements caused by PFPE segments whose number depends on both the amount and the length of the PFPE blocks.

Alternatively one can hypothesize that the crystallization occurs from a mixed liquid phase including a significant amount of PFPE blocks together with PCL segments. This hypothesis does not agree with the T_m values reported in Table 2. In fact they are clearly independent of the type of PFPE blocks and demonstrate that PCL crystallizes from a pure phase.

3.2.1. Amorphous phase

In the case of TX2CL and TX3CL type copolymers, the glass transitions can be attributed to domains containing almost pure PFPE chains. In fact these glass transition temperatures correspond to those of the homologous TX macromers. In the case of TX3CL samples the T_g observed for the fluorinated phase is slightly lower than that observed for the pure TX3 macromer and is similar to that observed for the PFPE without terminal hydrogenated segments [22]. Probably this is due to the fact that the hydrogenated segments (R_H) are miscible with the PFPE segments in the TX3 macromer; on the contrary, in the TX3CL copolymers, they are segregated and form hydrogenated domains.

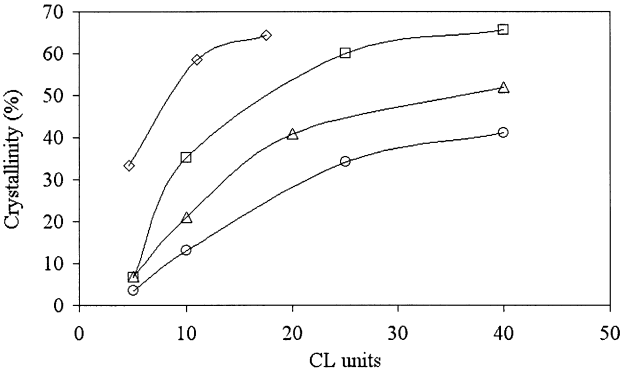


Fig. 2. Percentage of crystallinity vs. CL units in PCL diols and block copolymers (values obtained from DSC: ◇, PCL diols; □, TX1CLs; △, TX2CLs; ○, TX3CLs).

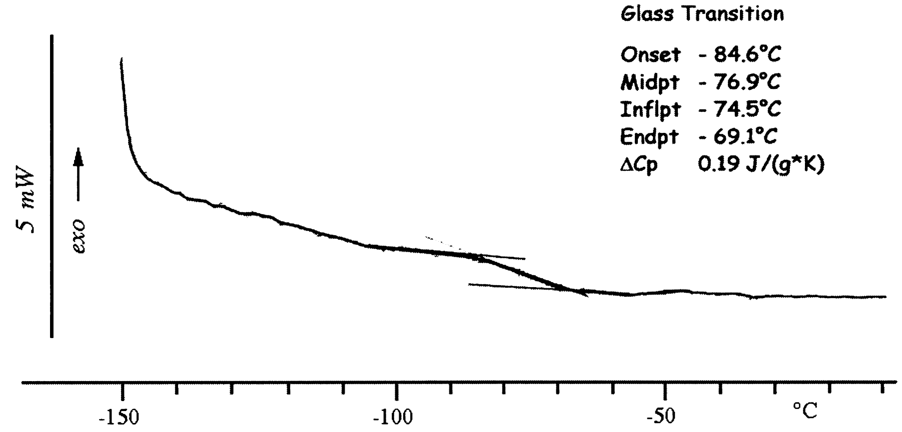


Fig. 3. DSC thermogram related to the TX1CL10 copolymer.

For the TX1CL type copolymers, a glass transition region was detected at temperatures higher than those of the TX1 macromer and the shift was found to increase by increasing the CL units content. A typical DSC thermogram which evidences the T_g shift toward higher temperatures is reported in Fig. 3. All the T_g data are reported in Table 3.

In the case of the TX1 type copolymers with very long PCL blocks, the T_g approximates the typical values of PCL homopolymers. Considering the T_g of the pure homopolymer equal to −89.5°C for TX1 and −60°C for PCL [23], a good correlation can be achieved by applying the Gordon–Taylor equation [24] to the amorphous phase of TX1CL copolymers. These results suggest that for TX1CL samples there is a mixed amorphous phase containing both fluorinated and hydrogenated segments. This conclusion does not exclude the presence of PFPE aggregates: in fact

- a single T_g is not a direct indication of miscibility of the system (from a thermodynamic point of view) but it depends also on the state of dispersion of two immiscible phases [25];
- the T_m values demonstrated that a heterogeneous system is also present in the molten state.

Therefore we think that in TX1CL samples the PFPE segments are actually separated in microdomains of such a small dimension that cannot be evidenced by DSC measurements. However, a phase separation (LCST), of the PFPE and PCL segments occurring at high temperatures cannot be excluded.

Table 3
Comparison between experimental data and T_g values obtained by applying Gordon–Taylor equation for the investigated copolymers

Copolymer	T_g (°C)	
	Experimental	Calculated
TX1CL5	−76.7	−73.7
TX1CL10	−77.5	−71.8
TX1CL20	−68.5	−69.5
TX1CL40	−64.9	−67.4

As far as the TX2CL and TX3CL type copolymers are concerned, since the PCL segments contained in crystalline domains are only a fraction of the overall PCL segments, an amorphous phase (probably containing the R_H hydrogenated segments also) should be present as a distinct phase. Actually this phase was detectable neither with DSC nor with DMTA. This fact could be explained considering the existence of amorphous domains with a composition gradient from the PFPE domains to the PCL ones, which spread their transitions in a wide temperature range.

The consequence is that the expected glass transition temperatures related to the hydrogenated segments are not detectable by conventional calorimetric analysis. For the same reasons, and probably also for constrains exerted by the hydrogenated segments [26], the glass transition of the PFPE segments is not evident for most TX2 type copolymers. It becomes evident again for TX3 type copolymers (see Table 2) which contain longer PFPE chains: a certain amount of these ones (80–40%) are able to form a separate phase of pure PFPE as it appears from a semiquantitative analysis of the ΔC_p related to the PFPE phase which shows that the experimental values are 20–60% lower than the theoretical ones. This confirms the existence of a mixed phase made of PFPE and PCL segments.

3.2.2. Surface composition

The PFPE surface composition was evaluated from information in the C_{1s} regions of the spectra.

Peaks from hydrogenated segments (PCL and R_H, between 284 and 290 eV) and fluorinated segments (PFPE, between 292 and 296 eV) were found. In particular, the curve-fitting analysis (Fig. 4) evidenced the presence of seven peaks centered at 285.0 eV (C–CH$_2$–C), 286.6 eV (–O–CH$_2$–C), 287.4 eV (CF$_2$–CH$_2$–O), 288.9 eV (O–CO–CH$_2$), 292.4 eV (O–CF$_2$–CH$_2$), 293.5 eV (O–C_2F$_4$–O), 294.9 eV (O–CF$_2$–O), respectively.

A deconvolution program was used to separate the

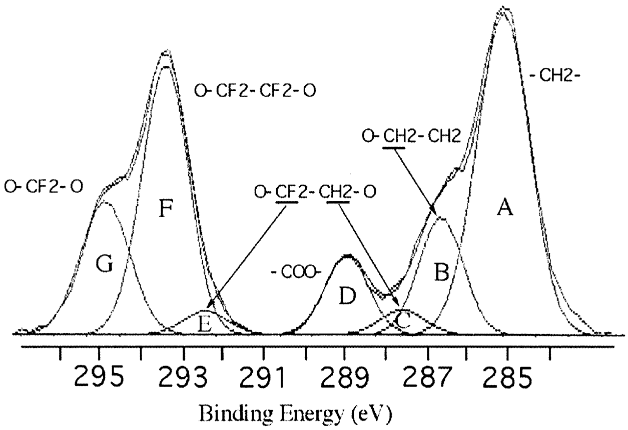


Fig. 4. Raw and curve-fit data of the C1s region of TX2CL40 collected at 30° TOA.

different contributions, as reported in Fig. 4; from the area of these peaks it was possible to calculate the surface weight percent of PFPE, PCL and R_H segments using the following equation:

$$\mathrm{PFPE(wt\%)} = \frac{\dfrac{(A_E + A_F + A_G)}{n^C_{PFPE}} M_{PFPE}}{\dfrac{(A_E + A_F + A_G)}{n^C_{PFPE}} M_{PFPE} + \dfrac{6\cdot(A_D)}{n^C_{PCL}} M_{PCL} + \dfrac{(A_B + A_C - A_D)}{n^C_{RH}} M_{RH}}$$

$$\mathrm{PCL(wt\%)} = \frac{\dfrac{6\cdot(A_D)}{n^C_{PCL}} M_{PCL}}{\dfrac{(A_E + A_F + A_G)}{n^C_{PFPE}} M_{PFPE} + \dfrac{6\cdot(A_D)}{n^C_{PCL}} M_{PCL} + \dfrac{(A_B + A_C - A_D)}{n^C_{RH}} M_{RH}}$$

$$\mathrm{R_H(wt\%)} = \frac{\dfrac{(A_B + A_C - A_D)}{n^C_{RH}} M_{RH}}{\dfrac{(A_E + A_F + A_G)}{n^C_{PFPE}} M_{PFPE} + \dfrac{6\cdot(A_D)}{n^C_{PCL}} M_{PCL} + \dfrac{(A_B + A_C - A_D)}{n^C_{RH}} M_{RH}}$$

M_{PFPE}, M_{PCL}, and M_{RH} are the molecular weight of the representative monomeric units of the different segments (88.5, 114 and 96, respectively); where the value corresponding to PFPE was calculated accounting for the relative weight of CF_2O and C_2F_4O units. n^C_{PFPE} n^C_{PCL} and n^C_{RH} are the number (or the average number) of carbon atoms present in the same representative monomeric units (1.45, 6 and 4, respectively). The details of the method for the determination of PFPE surface composition have been discussed and reported elsewhere [17].

In Table 4 some data related to the surface composition from XPS measurements are reported. In any case a dramatic surface enrichment of the fluorinated blocks with respected to the bulk, as determined from the block copolymers composition, is evident (e.g. in the case of TX1CL40 an increase of 588% is measured). On the contrary the amount of PCL is lower than the theoretical value of the bulk. The surface enrichment of fluorine was found in other copolymeric systems containing the PFPE chains [11–13,27,28], even when their concentration in the bulk was very low. The fluorinated groups, whose surface tension is very different from the hydrogenated part of the copolymers, behave as surfactants and concentrate at the air interface, lowering the surface energy.

Being equal the length of the fluorinated block, as expected, the PFPE percentage detected onto the surface decreases by increasing the length of the PCL segments, i.e. by decreasing the PFPE content in the bulk. Moreover, being equal the length of the PCL block, when the average length of the PFPE increases, the fluorine concentration at the surface increases.

Finally from the comparison of sample TX1CL10 with samples TX2CL40 and TX3CL40 we can see that these last two have a higher PFPE concentration at the surface notwithstanding at lower PFPE content in the bulk. This fact evidences that the surface modification depends not only on the available fluorine concentration, but also on the different surface activity of the fluorinated chains having different length. Similar results were obtained in a previous work concerning the surface modification of hydrogenated resins with acrylic esters of alcohols having fluorinated chains in the range from C_4F_9 to $C_{10}F_{21}$ [29]: the effect of the modification of the surface induced by adding a small quantity of $C_{10}F_{21}$ into the hydrogenated resin was found always stronger than that obtained by introducing higher amounts of C_4F_9 derived ester.

In Table 5 the advancing contact angle values measured with respect to water and *n*-hexadecane are reported. The results with water show that almost all the copolymers have a high hydrophobicity ($\vartheta > 90°$). Quite surprisingly, the wettability of the films containing PFPE with the same molecular weight decreases by increasing the PCL block length, i.e. by decreasing the PFPE content, referred to the bulk.

On the contrary, when the measurement liquid is apolar (*n*-hexadecane), the behavior is reversed: the values of ϑ_{adv}

Table 4
Comparison between bulk and surface composition

	Bulk composition (wt%)[a]			Surface composition (wt%)[b]		
	PFPE	PCL	R_H	PFPE	PCL	R_H
TX1CL5	41	50	9	78	17	5
TX1CL10	27	67	6	70	25	5
TX1CL40	9	89	2	61	35	4
TX2CL5	60	34	6	88	10	2
TX2CL10	45	51	4	80	17	3
TX2CL40	18	80	2	72	26	2
TX3CL5	71	25	4	92	5	3
TX3CL40	25	73	2	73	24	3

[a] From the chemical composition of the copolymer.

[b] From XPS analysis, 30° TOA.

are quite constant for all the TX1 type copolymers, while a limited change of the wettability can be evidenced for TX2 and TX3 copolymers. Furthermore it is worth to note that, for the same CL units value in PCL block, the best lipophobic characteristics were obtained for the block copolymers having PFPE molecular weight of 2200 (TX2CL samples) even though the percent PFPE content is higher for the TX3CL copolymers.

These results obtained with water seem to be in contrast with the XPS results (Table 4): in the three different TX*x*CL*y* series the contact angle values increase while the PFPE content on the surface decreases. In other words the wettability cannot be directly correlated to the surface composition. This behavior can be explained considering that the composition of the outermost layer of the film is measured in high vacuum atmosphere by XPS analysis, whereas contact angle evaluations are related to the characteristics of the interface between the polymer and the measuring liquid (water). The composition of such an interface can vary very much during the measurements due to possible interactions between the two phases [30]. These interactions can depend on both the hydroxy end groups concentration and the mobility of the block which the hydroxyls belong to.

Table 5
Advancing contact angle and hysteresis values for the investigated block copolymers (measurement liquids: water and *n*-hexadecane)

Code	Liquid: water		Liquid: *n*-hexadecane
	ϑ_{adv} (°)	Hysteresis (°)	ϑ_{adv} (°)
TX1CL5	70.6	24	64.6
TX1CL10	90.6	43	62.8
TX1CL20	94.6	41	62.6
TX2CL40	93.0	38	61.6
TX2CL5	87.0	56	73.0
TX2CL10	82.4	51	67.2
TX2CL20	97.2	53	64.0
TX2CL40	93.0	35	60.2
TX3CL5	83.8	47	69.8
TX3CL10	91.4	39	60.4
TX3CL20	92.2	46	59.0
TX3CL25	95.4	44	60.8
TX3CL40	96.0	59	57.2

In order to verify the effect of the hydroxy end groups concentration on the water wettability, contact angle measurements were performed on PCL diols having different molecular weights (and therefore different hydroxyl concentration). The results are reported in Fig. 5 where a strong decrease of wettability is shown when the MW of PCL diols increases, i.e. when both the hydroxy terminal groups concentration and the chain mobility (see melting temperatures reported in Table 2 and crystallinity values of Fig. 2) decreases. On the other hand, when the measurement liquid is non-polar (*n*-hexadecane), the contact angle values of the PCL diols (Fig. 5) are quite constant, within the experimental error as reported for the TX*x*CL*y* copolymers. Furthermore, it can be noted that the contact angle values of the PCL diols are in the range of 17–19° and are much lower than the TX*x*CL*y* copolymers (in the range of 57–73°): this fact indicates that the high contact angle values showed in this case are due to the presence of the fluorinated blocks.

On the basis of these data, a surface rearrangement depending on the type of substrate interfaced to polymer surface can be supposed, according to Scheme 1 which shows the representation of surface rearrangement depending on the type of environment interfaced to the polymer surface.

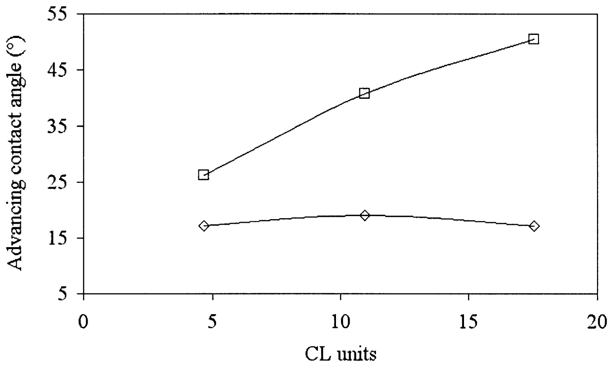
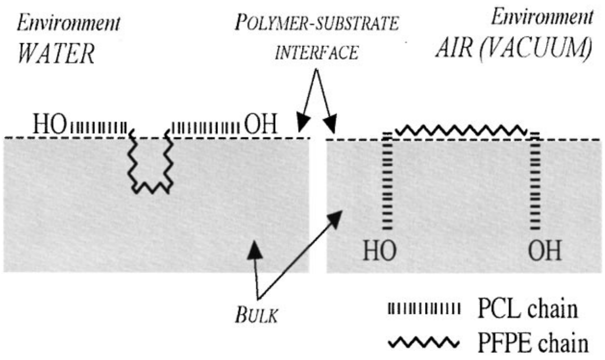


Fig. 5. Advancing contact angle values for PCL5, PCL11 and PCL18 (◇, *n*-hexadecane as measurement liquid; □, water as measurement liquid).



Scheme 1.

In the case of polar substrate (contact angle measured in water), the polar hydroxy and ester groups of the polymeric system tend to migrate to the interface water–polymer increasing the wettability (it has to be noted that the glass transitions of the amorphous phase, where the hydroxyl groups are contained, is far below the temperature of measurement). On the contrary, in the case of non-polar substrate (contact angle measured in *n*-hexadecane and XPS analysis in vacuum), there is no affinity with the hydroxyl and ester groups of the hydrogenated polymer: therefore the fluorinated blocks tend to migrate to the polymeric surface decreasing the wettability. In any case, the driving force, which determines the surface composition, is the minimization of the interfacial tension between polymer and environment.

The increasing of contact angle values (in water) by increasing the PCL block content, for the same PFPE block length (see Table 1) can be explained by considering that there is a decrease of chain mobility due to the higher crystallinity percentages (see Fig. 2). According to the proposed mechanism, the crystalline domains act as 'physical crosslinks' and tend to hinder the migration of hydrophilic hydroxyl and ester groups of the copolymers onto the surface. In other words, the presence of crystalline regions of PCL decreases the chain mobility and minimizes the surface rearrangement due to the presence of a polar substrate at the polymer surface.

The hysteresis values, i.e. the difference between the advancing and receding angles are also reported in Table 5. The hysteresis is quite high; this is expected when both hydrophylic and hydrophobic groups are present as in the copolymers under investigation. The reasons for this phenomenon are many: the surface roughness, the surface heterogeneity, the reorientation of the surface structure under the measuring liquid [31,32], and finally the possibility that the droplet molecules penetrate into the material. None of these effects can be excluded in our systems moreover the different contributions cannot be separated in details.

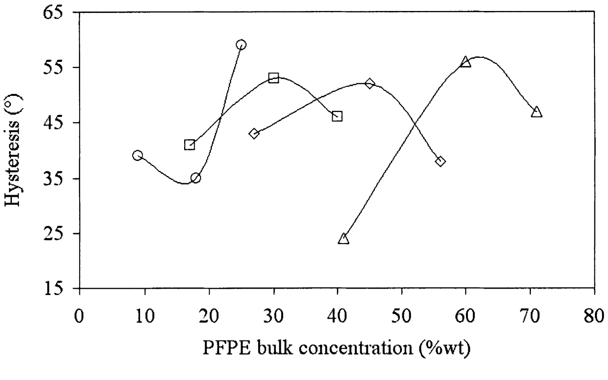


Fig. 6. Hysteresis values vs. PFPE bulk concentration (△, TX*n*CL5; ◇, TX*n*CL10; □, TX*n*CL20; ○, TX*n*CL40).

In fact the film surfaces are visibly rough due to the procedure of preparation taking into account the block copolymer nature of the products, the very different chemical nature of the segments (with a perfluorinated central unit endcapped by hydrogenated groups) and the presence of crystalline domains of PCL. The reorientation of the surface structure has been discussed before.

Water penetration cannot be forgotten. Diffusion of liquid water in the fluorinated phase of the films is negligible; in the hydrogenated domains made by PCL units, water diffusion should preferentially occur in the amorphous phase. Considering the α, values reported in Fig. 2, one could expect that water penetrates more easily in the TX3CLy systems than in the others. In agreement with these results hysteresis is always lower in the TX1CLy films.

If the hysteresis data are plotted as a function of the bulk PFPE weight percentage (Fig. 6), being equal the length of the PCL chain, a maximum is observed with the only exception of the TX*n*CL40 copolymers. Probably this behavior can be ascribed to a morphological transition from a fluorinated dispersed phase to a fluorinated continuous phase; at this composition the maximum of heterogeneity (i.e. hysteresis) is expected [33].

4. Conclusions

In this work poly(ϵ-caprolactone-*b*-perfluoropolyether-*b*-ϵ-caprolactone) (PCL–R_H–PFPE–R_H–PCL) block copolymers having different PCL and PFPE block lengths were prepared in form of films and subjected to DSC and surface investigation.

As far as the thermal characterization is concerned, the obtained films reveal, for all the copolymers, the presence of two different phases. For the copolymers having the longest PFPE blocks (TX2 and TX3 type), the phase located at low temperature was attributed to the fluorinated moiety; the T_m values, related to the PCL blocks, were found to increase by increasing the PCL block length reaching the homopolymer PCL melting temperature. In the case of copolymers having the PFPE block with lower molecular weight (TX1 type), the T_g values are intermediate between those of the pure PFPE macromer and pure amorphous PCL. This does not exclude the presence of two phases, which can have such a small dimension that cannot be detected by DSC or DMTA analyses. In all cases, T_m values demonstrated that PCL crystallizes from a pure phase.

Considering the surface properties, XPS measurements showed a strong increase of the amount of fluorinated phase of the films at the air-side surface with respect to the bulk; moreover the longer the PCL block, the lower the fluorine content.

In agreement with these results, contact angle values (both in water and *n*-hexadecane) revealed a hydrophobic character for almost all the investigated copolymers in spite of the presence of many polar hydroxy terminal groups, especially when the longest PCL blocks were considered.

The trend of the contact angle was found not depending on the fluorine concentration detected by XPS: this behavior was attributed to the different measuring conditions adopted for the two analytical techniques (high vacuum ambient for XPS measurements, water for contact angle evaluations) and may be explained by the presence of very flexible blocks, providing a highly dynamic surface.

Since the wettability of a film depends on the characteristics of the nature of the substrate interfaced to the polymer, the chemical composition of the surface can be modified during the contact angle evaluation. Wettability measurements performed both on films of PCL diols having different molecular weight evidenced an increase of the contact angle values with water by increasing the molecular weight of the copolymers, i.e. by decreasing the concentration of the hydroxy groups, the higher hydrophobicity was reached.

Taking into account the obtained results, these structures can be potentially used as additives for the formation of polymers having smart surfaces with selective adhesive properties [34]. In fact, the functional end groups (hydroxy or other) can be chosen to interact selectively with a complementary receptor located on a target substrate. When the modified polymer surface and a substrate are placed in contact, adhesion is enhanced only if the functional end group senses an appropriate receptor on that substrate with which it can form the specific interaction. If a receptor is not present, the modified surface exhibits release properties.

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