

Low adherence coating containing polymers with low surface energy

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(54) Title: LOW ADHERENCE COATING

(57) Abstract: The invention relates to a coating having a low adherence towards different types of contaminants. Such a coating comprises a crosslinked polymeric network provided with an end-functionalized dangling chain, as a result of which the surface maintains its low surface energy.



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LOW ADHERENCE COATING

The present invention relates to a coating of which the surface has a low adherence towards various contaminants. It also relates to the preparation of such a coating.

Regular maintenance of various outdoor coatings is time and labor consuming. Lowering the surface energy of a coating will be helpful in reducing the adherence between the coating surface and various contaminants, rendering the coating easily cleanable and even self-cleanable. In *Macromolecules* (2000), 33, pages 6886 – 6891, crosslinked low surface energy (10-20 mN/m) films have been developed via surface segregation of fluorinated species during film formation. However, the very thin fluorine-rich layer has shown to be vulnerable to sustain various mechanical forces (scratch, rubbing, etc.), leading to the loss of the low adherence character of the film in time. The objective of the present invention is to present coatings that will sustain low adherence even upon surface damage, via a self-replenishing strategy.

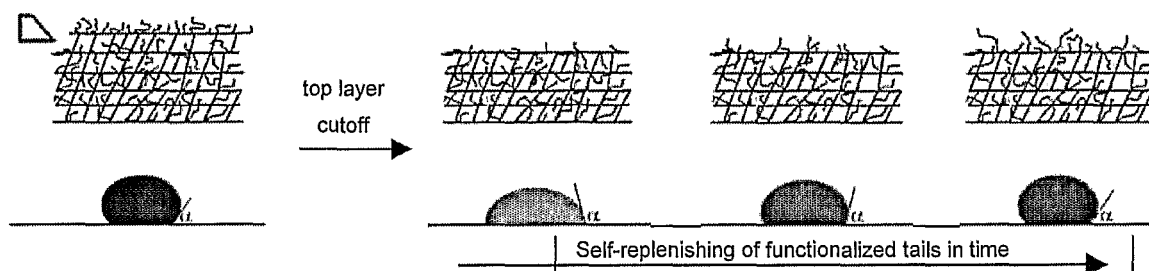
This is achieved according to the present invention by a coating comprising:

- a) a crosslinked polymeric network (N), based on a first polymer (P),
- b) a low-surface-energy group (E), coupled to the network N via
- c) a polymeric spacer (S),

having the following relationship between the native surface energies of P, E, and S (resp. σ_p , σ_e , and σ_s , in mN/m):

$$\sigma_e \leq \sigma_s \leq \sigma_p$$

In a coating according to the invention the network N is provided with a so-called dangling chain (the polymeric spacer S), at the end of the chain being provided with a functional group, the low surface energy group E. As a result, the self-replenishing low-adherence coatings have long functionalized dangling chains relatively homogeneously distributed (a gradient functional group concentration may still well exist) in a coating network. In case of surface damage that leads to loss of the functionalized tails originally sitting at the surface, due to the mobility of the functionalized tails and the flexibility of the network, the functionalized tails from sub-layers will be able to reorient themselves to minimize the air/film interfacial energy (Scheme 1).



Scheme 1. Self-replenishing low adherence-coatings.

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The approach is to control the diffusion of the functionalized species during film formation by, for instance, tuning the spacer length in the functionalized species, and adjusting the miscibility of P, E and S. The synthesis of the network precursors is therefore of great importance, since the length, mobility, and miscibility of these chains have to be well controlled.

10

The term "native surface energy" of the respective groups in the coating refers to the surface energy of each individual group (P, E and S) in its separate form, i.e. before they are coupled to each other to form the coating. This native energy is measured according to the geometric mean method of Owens and Wendt (J. Appl. Polymer. Sci. (1969), 13, 1741).

15

Regarding the first polymer P, each polymer is suitable, when it is crosslinkable into a polymeric network, as a result of which the dangling chains coupled thereon are restricted in their mobility. With preference, P is selected from the group comprising polyurethane, polyester, polyether, polyetherester, and polyesterether.

20

As the skilled man is aware, each polymer P has the need of its own crosslinker, in order to become a crosslinked polymeric network N. In preference, N is obtained via crosslinking of the polymer P with a crosslinker selected from the group comprising a polyisocyanate, a blocked polyisocyanate, a polycarbodiimide, a polyepoxide, or an alkylated melamine resin.

25

In preference, N is a polyurethane network based on a polylactone P, made of a lactone and a polyfunctional alcohol, and a polyisocyanate crosslinker. In more preference the lactone for such a polyurethane based coating is caprolactone or an alkylsubstituted caprolactone (examples being 4-methylcaprolactone or 4-t-butylcaprolactone); and the polyfunctional alcohol is a trimethylol alkane, more preferred a trimethylol propane.

30

The functional group (E) at the end of the dangling chain (S) has to have a low native surface energy (σ_s). Preferably this σ_s has a value between 5 and 25 mN/m. This can be achieved by different low-surface-energy groups E, as such known in the art. Preference is given to E being selected from the group comprising a perfluoroalkyl, a perfluoropolyether, and a polysiloxane. The native surface energy of E (σ_e) preferably has a value between 5 and 25 mN/m. In case E is a perfluoroalkyl group, there is a preference for the perfluoroalkyl group to be a perfluoro hexyl ethyl, or a perfluoro octyl ethyl group. In case E is a polysiloxane group, it is preferred that this group is a polydimethylsiloxane group.

In order to achieve the results of the present invention the polymeric spacer (S) has to have a certain length (or molecular weight). In general, S is a hydrocarbon based polymer having at least 10 C-atoms in the backbone. More preferred, S has a number-averaged molecular weight $M_{n,s}$ of between 200 and 10,000; preferably between 500 and 5,000. The molecular weights referred to are determined by gel permeation chromatography (GPC).

One of the other criteria for a proper selection of S is its glass transition temperature, which in general should not be below $-150\text{ }^\circ\text{C}$, and not above $75\text{ }^\circ\text{C}$. Preferably, S has a glass transition temperature $T_{g,s}$ (in $^\circ\text{C}$) according to the following relation:

$$-100 \leq T_{g,s} \leq 50; \text{ preferably } -60 \leq T_{g,s} \leq 20.$$

In general, S can be any polymer obeying the above referenced criteria. More preferred, S is selected from the group comprising polyurethane, polyester, polyether, polyetherester, and polyesterether. Preferably S is a polylactone; in its most preferred form a polycaprolactone. The number-averaged molecular weight of S ($M_{n,s}$) is preferably between 200 and 10,000; the glass transition temperature of S ($T_{g,s}$) is preferably between -100 and $50\text{ }^\circ\text{C}$.

The coating of the present invention in general has a glass transition temperature ($T_{g,c}$, in $^\circ\text{C}$) of at least $-40\text{ }^\circ\text{C}$; more preferred $T_{g,c}$ has the following relation:

$$-20 \leq T_{g,c} \leq 50, \text{ even more preferred } -10 \leq T_{g,c} \leq 40.$$

The coating has a relationship between the respective surface energies of: $\sigma_e \leq \sigma_s \leq \sigma_p$. In preference the relation is $\sigma_e < \sigma_s \leq \sigma_p$. In another preference the coating has the following parameters:

$$200 \leq M_{n,s} \leq 10,000$$

$$-100 \leq T_{g,s} \leq 50$$

$$\sigma_e < \sigma_s \leq \sigma_p$$

The coating according to the present invention can, as described above, be based on different polymeric constituents. In the following the preparation of a fluorine containing polyurethane coating will be described, as one of the embodiments of the present invention. Such a process comprises the following steps:

- ring-opening polymerization of a first lactone with a perfluorinated alcohol,
- ring-opening polymerization of a second lactone with a di-, tri- or tetra hydroxyfunctional hydrocarbon, or its ether-derivative,
- crosslinking a mixture of the products obtained in step a) and step b) with a polyisocyanate crosslinker.

Ring-opening polymerization of lactones has been chosen to synthesize the precursors with well-defined structures (e.g. controlled molecular weight with a low molecular weight distribution index (PDI), functionality per polymer) in a controlled manner.

Different lactones can be polymerized via ring-opening polymerization with different alcohols as initiators, with an example shown in Figure 1; a perfluoroalkyl-end-capped mono-hydroxyl-functional polycaprolactone (PCL) and a 3-armed tri-hydroxyl-functional PCL can be obtained.

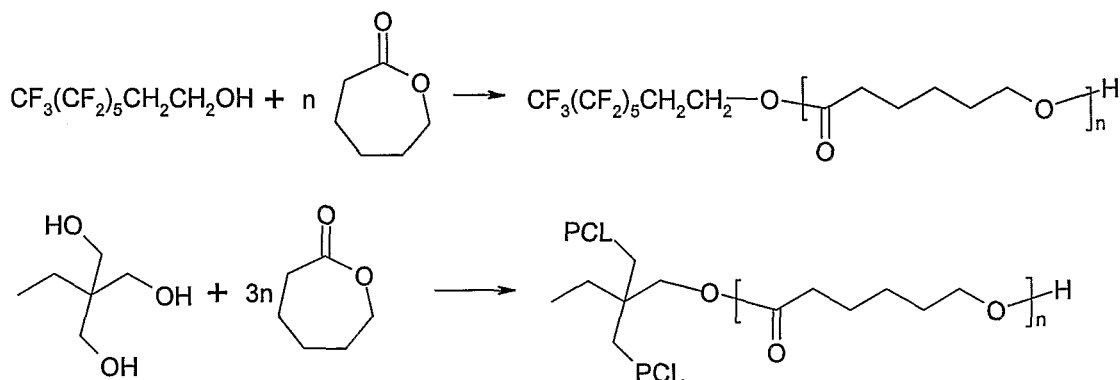


Figure 1. Ring-opening polymerization of ϵ -caprolactone, initiated with reps. perfluorohexylethanol and trimethylolpropane.

Furthermore, copolymerization of different lactones will reduce crystallization of the precursors and, hence, the mobility of the chains will increase. A certain degree of miscibility between the fluorinated precursors and other components renders a relatively homogeneous distribution of the fluorinated dangling chains in the network. This miscibility is enhanced by using the same building blocks for the fluorinated and the non-fluorinated precursors; i.e. the lactones used in step a) and b) are the same.

The lactones can be any known in the art; preferably at least one of the lactones is ϵ -caprolactone.

The dangling chain, based on a perfluorinated alcohol, preferably has, in its backbone, 6 – 20 C-atoms; more preferably said alcohol is selected from the group comprising perfluorohexyl ethanol, perfluorooctyl ethanol, or a mixture thereof.

As a result of step a) the above mentioned polymeric spacer S with the low-surface-energy group E is formed; the product of this step a) should preferably have a number-averaged molecular weight ($M_{n,a}$) of between 1,000 and 4,000.

As a result of step b) the first polymer P is formed, which, after the crosslinking with a polyisocyanate based crosslinker, results in the crosslinked polymeric network N.

In order to have controlled formation of the coating from the constituting ingredients, the products from the process steps a) and b) generally should have a PDI of at most 4.0; more preferred at most 2.5; and even more preferred at most 1.5.

For obtaining an effective coating, in which the network is sufficiently crosslinked, the molar ratio of the isocyanate and hydroxyl groups in the mixture of step c) is at least 1.0.

The present invention also relates to a coating comprising a fluorine containing crosslinked polyurethane. Said fluorine containing crosslinked polyurethane can contain every desirable amount of fluorine. During the underlying research it was found that above a so-called plateau-level of fluorine in the coating, no additional improvement of the contact angle was noted. Said plateau-level appeared to be at a value of about 2.5 wt%. As a result, the fluorine containing crosslinked polyurethane of the present invention comprises preferably up to 2.5 wt% of chemically bound fluorine.

The present invention also relates to a fluorinated polylactone, obtainable from a reaction between a lactone and a perfluorinated alcohol. Preferably

the lactone is ϵ -caprolactone. In another preference the perfluorinated alcohol has 6-12 C-atoms; more preferred the perfluorinated alcohol is either perfluorohexyl ethanol, perfluorooctyl ethanol, or a mixture thereof. Said fluorinated poly lactone is, as will be clear from the above, suitable as the building block for the combination of the spacer (S) with the terminal low-surface-energy group (E) in the coating of the invention. The preferences for the precursors of the fluorinated poly lactone (i.e. the perfluorinated alcohol, and the lactone) are already given above.

In the preparation of such a fluorinated poly lactone, - a process comprising a ring-opening polymerization of a lactone with a perfluorinated alcohol -, use is made of the influence of a weak acid as a catalyst. Preferably, such a weak acid is fumaric acid. The temperature for such a preparation lies in general between room temperature and 150 °C. Generally atmospheric pressure is applied, but, depending on the nature of the precursors, higher pressures can be applied.

The coating of the present invention can be applied to any type of substrate (metal, glass, etc.). It will generally be present in a thickness of 10-100 μm . More preferably, said thickness is between 20-75 μm . The coating of the present invention is very suitable as a so-called top-coat, in a system of a multilayer coating. This belongs to the general knowledge of the skilled man.

The invention will hereafter be elucidated by Examples. These Examples relate to a (process for the preparation of a) fluorinated coating. It is to be understood that variations in the three essential elements of the coating (i.e. the first polymer P, the low-surface-energy group E, and the polymeric spacer S) can be performed by the skilled man, following the teachings presented herein.

25 Materials and methods

Two perfluoroalkyl alcohols, perfluorohexyl ethanol (R_6) and perfluorooctyl ethanol (R_8), were supplied by Clariant GmbH (with trademarks of EA 600 and EA 800, respectively). ϵ -Caprolactone (ϵ -CL) was purchased from Acros Organics, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) from Merck, and fumaric acid from Sigma-Aldrich. A polyisocyanate crosslinker, Desmodur N3600, containing primarily the trimer of hexamethylenediisocyanate, was obtained from Bayer. ϵ -Caprolactone was dried with anhydrous MgSO_4 for 24 h and then vacuum distilled to remove water. Fumaric acid and the alcohols were dried in a vacuum oven at 40 °C for 3 h before use. Solvents were used as received without further purification.

¹H NMR spectra were recorded on a Varian 400 spectrometer operating at 400.162 MHz at 25 °C. CDCl₃ (with TMS as an internal standard) was used as a solvent. Melting and glass transition temperatures were determined on a Perkin Elmer Pyris 1 differential scanning calorimeter (DSC), with a heating/cooling rate of 10 °C/min. The onset temperature during the second heating run was taken as the melting point. MALDI-TOF MS measurements were performed on a Voyager-DE Pro instrument (Perspective Biosystems, Framingham, MA). Polymers were dissolved in THF, and NaTFA or KTFA (Na- or K-trifluoroacetic acid) were used as the ionizing agent. Isotopic distribution calculations were performed using DataExplorer Advanced Biosystems. Contact angle measurements were performed on a Dataphysics OCA 30 Instruments, using deionized water and hexadecane (>99%, Merck) as probe liquids. Dynamic advancing contact angles were collected. SEC was carried out on a Waters SEC instrument equipped with a Waters Model 510 pump and a Model 410 refractive index detector (at 40 °C). The column used was PL2mixC, and THF (Biosolve, stabilised with BHT) was used as the eluent at a flow rate of 1.0 mL/min. Samples were filtered over a 13 mm × 0.2 µm PTFE filter (Alltech). Calibration was made using a universal calibration curve.

Microtoming was performed using Cryostat HM 550 from Microm Systems. To ensure parallel-slicing, a special home-made sample holder was used. Each time a slice of about 30 µm thick was collected, and its top surface was examined by XPS. XPS measurements were performed with a VG-Escalab 200 spectrometer using an aluminum anode (Al Kα = 1486.3 eV) operating at 510 W with a background pressure of 2 × 10⁻⁹ mbar. Spectra were recorded using the VGX900 data system. All C1s peaks corresponding to hydrocarbon were calibrated at a binding energy of 285 eV to correct for the energy shift caused by charging. All spectra were acquired at two different take-off angles (between the surface normal and the axis of the analyzer lens): 0° and 60°, corresponding to the probe depths of ~8 and ~4 nm, respectively. The fluorine-to-carbon (F/C) molar ratio was determined by curve fitting of the C1s signal to match the corresponding carbon environment (C-C / C-H; C-O / C-N; C=O; C-F₂; C-F₃).

Synthesis of PCLs initiated by different alcohols and film preparation

To tune the molecular weight of the PCL precursors, ε-CL and alcohol were added to the flask in different molar ratios. The molar ratio between ε-CL and fumaric acid was kept at 10. The synthesis was performed under dry nitrogen

atmosphere. A typical procedure is as follows: a mixture of TMP and fumaric acid was heated to 90 °C and then ϵ -CL was added to the flask. The reaction mixture was stirred with a magnetic stirrer. After 24 h, it was diluted with THF, and the polymer was precipitated in n-heptane. The formed precipitate was filtered off and washed with
5 methanol (in the case of low MW PCL initiated by TMP, a mixture of water and methanol (1:2) was used). White, sticky powder was, after washing, dried in vacuum at 40 °C for 4 h.

Polyurethane coatings were prepared from a mixture of PCL precursors and a polyisocyanate crosslinker with either THF or N-methyl pyrrolidone
10 (NMP) as a solvent. The molar ratio of NCO/OH was kept at 1.1. Films were applied on aluminum panels using a doctor blade driven by a 509 MC Coatmaster automatic film applicator. The films were then cured at 40 and 90 °C when THF was used as the solvent, and at 125 °C with NMP as the solvent.

15 Characterization of PCL precursors

During the ring-opening polymerization of ϵ -CL, fumaric acid has been chosen as a catalyst. Fumaric acid is a weak acid and activates monomer at rather high temperature for ring-opening polymerization; a long reaction time (e.g. 24 h) is usually needed for a complete polymerization, given that the primary polymerization
20 pathway is through the activated monomer mechanism. For this reason, polymerization has a living character (shown later). On the other hand, fumaric acid is insoluble in the monomer, and it acts as a heterogeneous catalyst. Good mixing of the reaction mixture is therefore important, especially if a high molecular mass is aimed in the experiment.

The proton NMR spectra of the synthesized precursors are shown in
25 Figure 2. The signals at $\delta = 4.05$ (d, H atoms next to the ester bond) and at $\delta = 2.3$ (b, H atoms next to the carbonyl group) can be assigned to the CL monomer unit.

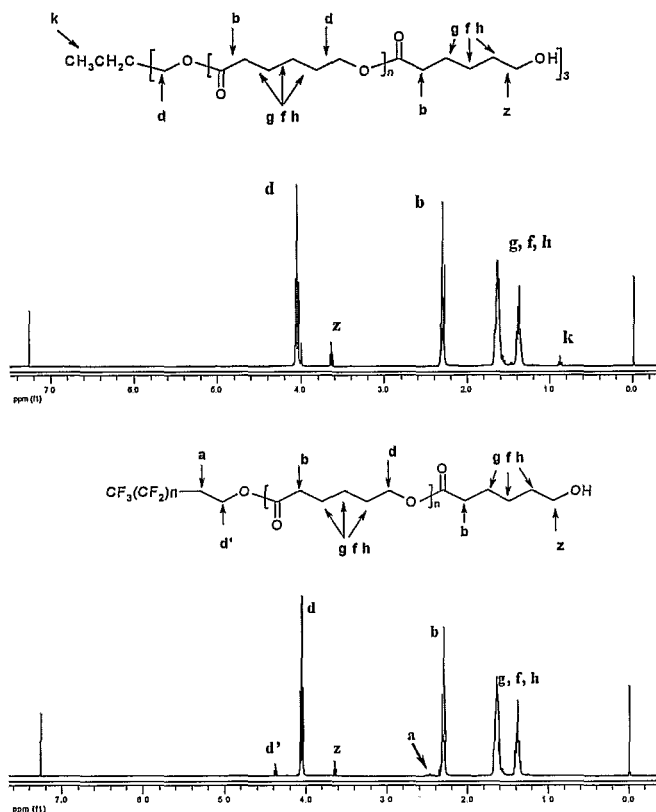


Figure 2. ¹H NMR spectra of PCL initiated by TMP (upper) and R_f6 (below).

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For the PCL initiated by TMP (TMP-PCL), the area ratio of the signals z and k, $A(H_z)/A(H_k)$ is 2, which corresponds well to the molecular structure of TMP-PCL. The degree of polymerization (d_p) can be estimated by:

$$d_p = A(H_d) / A(H_z)$$

10 And the number-average molecular weight of TMP-PCL is:

$$M_n = d_p \cdot M(\epsilon - CL) + M_{TMP}$$

The perfluoroalkyl-end-capped PCLs initiated by R_f6 (R_f6-PCL) and R_f8 (R_f8-PCL) appeared to have the same ¹H-NMR spectra. There is noticeable difference in the spectra between R_f6-PCL and TMP-PCL (Figure 2): the peak d' can be assigned to the CH₂ group next to the ester group connected to the perfluoroalkyl group. Another signal (a) emerges at $\delta = 2.5$, corresponding to the CH₂ group neighboring the C₆F₁₃- group. The area ratio of the signals d' and z, $A(H_{d'})/A(H_z)$ is 1, indicating that R_f6-PCL has a well defined structure with a perfluoroalkyl group at the one end of the chain and a hydroxyl group at the other end (further evidence is provided by MALDI TOF MS analysis below). The degree of polymerization (d_p) can be

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estimated by:

$$d_p = [A(H_d) + A(H_d')] / A(H_z)$$

The number-averaged molecular weights (M_n) for fluorinated PCL and TMP-PCLs are shown in Table 1. By adjusting the molar ratio between ϵ -CL and the alcohol initiator, the molecular weight for all the precursors can be tuned.

	Targeted	¹ H-NMR	GPC	MALDI TOF MS		
	M_n	M_n	M_n	PDI	M_n	PDI
R ₁₈ -PCL samples	1000	1420	2880	1.12	1663	1.16
	2000	2370	3780	1.11	2313	1.06
	3000	2400	5140	1.18	2525	1.16
	4000	2480	5510	1.16	3373	1.10
R ₁₆ -PCL samples	1000	1490	2990	1.13	1449	1.15
	2000	1860	3100	1.11	2286	1.06
	3000	2450	4300	1.13	2155	1.11
	5000	3120	/	/	3071	1.11
TMP-PCL samples	2000	2450	/	/	2816	1.11
	3000	2870	6390	1.12	4852	1.04
	4000	3500	/	/	3412	1.14

Table 1. Molecular weights of synthesized PCLs determined by different methods.

The evolution of M_n for R_f8-PCL was monitored during the course of the polymerization, and its dependence on the ϵ -CL conversion is shown in Figure 3. There is a good agreement between the experimental and the predicted values, confirming the living character of the ring-opening polymerization of ϵ -CL catalyzed by
5 fumaric acid. This living character allows the precise control on both the molecular weights and polymer architecture of the PCL precursors.

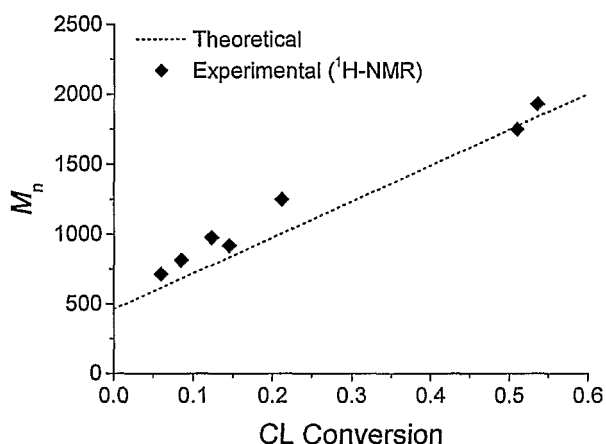
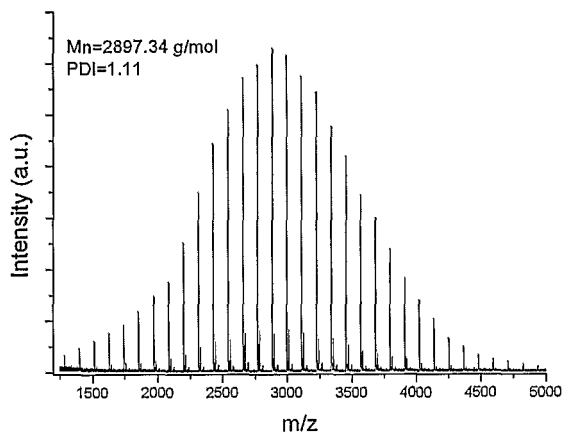


Figure 3. The M_n for R_f8-PCL as a function of monomer (ϵ -CL) conversion during the
10 polymerization.

Although $^1\text{H-NMR}$ results indicate that the structure of PCLs is as expected, this technique cannot be used to detect the possible existence of cyclic PCL or PCL initiated by water, especially if these species are present in a very small
15 amount. MALDI TOF MS proved to be a very effective technique for the end-group analysis, and was therefore employed to further examine the PCLs synthesized.



(a)

(b)

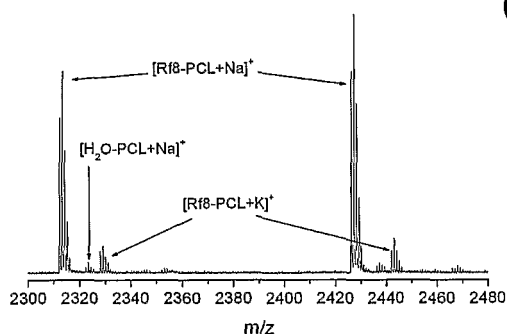


Figure 4. (a) The MALDI mass spectrum of R_f8-PCL, and (b) an expanded spectrum in the m/z range of 2300-2480.

A typical full MALDI mass spectrum for R_f8-PCL is given in Figure 4. The sets of signals are separated by 114 Da (Figure 4a), characteristic of the caprolactone repeating unit. The molecular weights of individual main peaks correspond to the expected structure: $\{C_8F_{17}CH_2CH_2O-[C(O)-C_5H_{10}O]_n-H + Na\}^+$. With a closer look at the mass spectrum (Figure 4b), two more sets of signals are noticed: one set corresponding to the potassium adduct of R_f8-PCL, while the other, though much lower in the intensity, attributing to the water-initiated PCL, $HO-[C(O)-C_5H_{10}O]_n-H + Na\}^+$. Water is likely present in fumaric acid. Cyclic structures are not observed, indicating the ring-opening polymerization proceeds in a controlled manner.

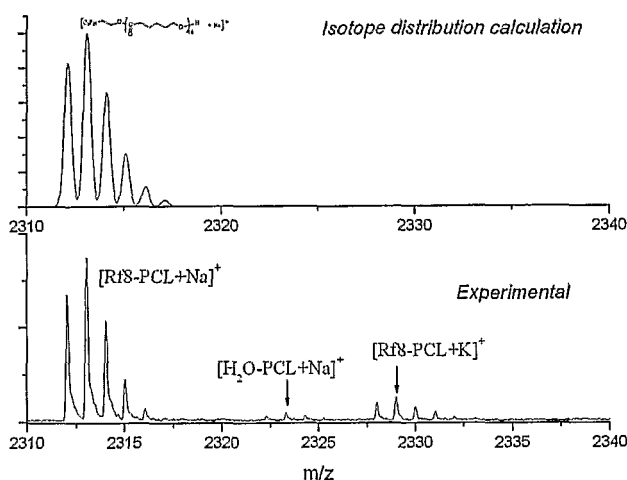


Figure 5. The isotopic distribution of the mass spectrum for R_f8-PCL from experiments as compared with a simulated one.

- 5 The isotopic distribution of the mass spectrum of R_f8-PCL has also been examined. The perfect match between the experiment and the simulation (Figure 5) confirmed unambiguously the expected well-defined structure of R_f8-PCL: a perfluoroalkyl group at the one end of the polymer chain and a hydroxyl group at the other end.
- 10 Since the PDI of these polymers (determined with SEC) is below 1.2, MALDI TOF MS can be used as the quantitative technique for determining the average molecular weight of precursors. Average molecular weights determined by ¹H NMR, SEC and MALDI TOF MS for a number of samples are given in Table 1. As expected, PDI for all the samples (according to SEC below 1.2 and according to MALDI MS
- 15 around 1.1) is low, which also indicates that PCLs initiated by TMP have similar numbers of monomer units per arm. Average molecular weights determined by MALDI MS and ¹H-NMR are in agreement. SEC measurement gave values that were significantly higher compared to the other two techniques. It has been shown from MALDI TOF MS and SEC that the targeted PCLs (controlled MW, low PDI, and
- 20 controlled functionality) have been successfully synthesized, with the presence of only a minimal amount of water-initiated species.

Melting points of the precursors (measured by DSC) were below 60 °C. Some examples are shown in Table 2. For the polymers with similar molar masses, melting temperatures differ in a range of 10 °C. One has to note that

fluorinated PCLs are linear molecules, while TMP-PCLs have three branches that influence the crystallinity of these polymers.

	M_n (MALDI TOF)	T_m [°C]
TMP-PCL	2873	32
R _f 6-PCL	2450	45
R _f 8-PCL	2561	52

5 Table 2. Melting points (T_m) for some PCLs of similar average molecular weights.

Wettability of films based on fluorinated PCLs

Fluorinated PCLs of different molar masses were spin-cast from THF solutions (100 mg/1 mL of THF) on aluminum panels and then annealed in a vacuum oven at 60 °C for 2 h. After annealing, contact angle measurements were performed on these films, using water and hexadecane as probe liquids. Both water and hexadecane contact angles were significantly higher comparing to those measured on the film of PCL initiated by butanol, indicating that fluorinated tails are preferentially enriched at the air-film interface. It can be seen from Figure 6 that a lower molecular mass of PCL chain facilitates the fluorine surface segregation, since the fluorine content is relatively higher and the chain mobility is enhanced when the molecular weight of the R_f8-PCL is low.

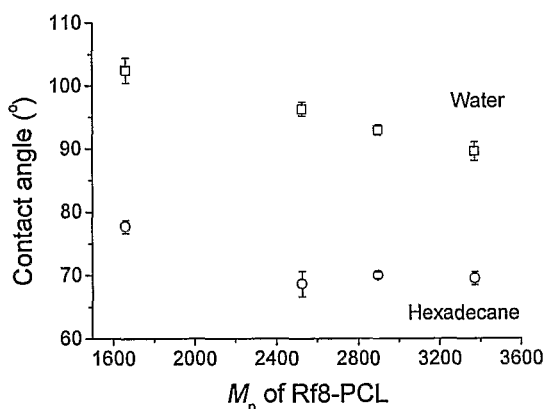


Figure 6. Advancing contact angles on R_f8-PCL films. For the butanol-initiated PCL film the contact angles for water and hexadecane are 70 and 0° (hexadecane spreads over the non-fluorinated film), respectively.

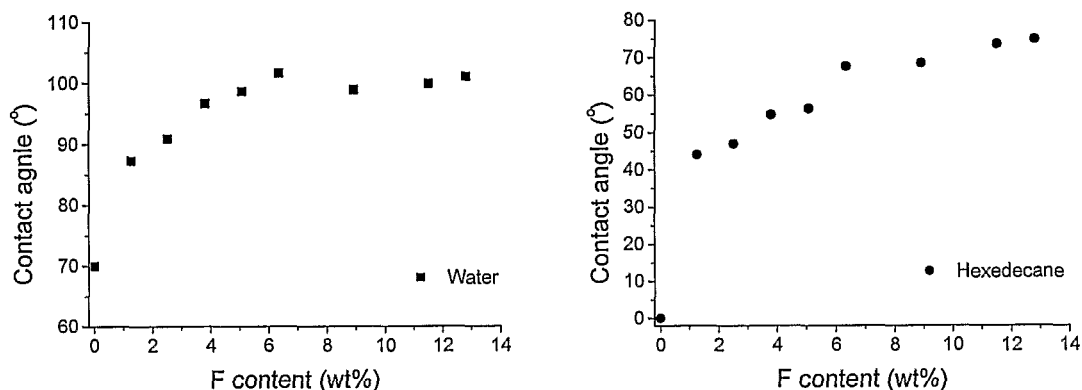


Figure 7. Advancing contact angles on the films from a blend of R₇₈-PCL and butanol-initiated PCL.

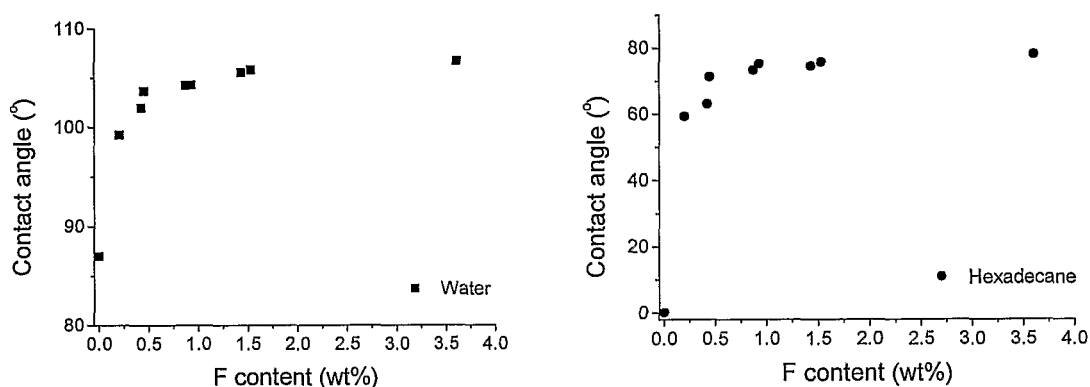
The wettability of films from a mixture of R₇₈-PCL ($M_n = 2525$) and butanol-initiated PCL ($M_n = 2564$) was also examined. Samples were spin-cast from 10 wt% THF solution, and then annealed at 50 °C. As can be seen from Figure 7, the addition of a small amount of R₇₈-PCL significantly increases the contact angles, thus decreases the film wettability. Both the water and hexadecane contact angles reach plateau values at about 7% of fluorine, which are similar to the contact angles from the pure R₇₈-PCL with an M_n of 2525 (Figure 6), suggesting that at a fluorine content of 7% the surface of the blend film is primarily composed of R₇₈-PCL, and further increase of the fluorine content will not decrease the surface wettability.

Crosslinked polyurethane films based on fluorinated PCLs

The fluorinated and 3-armed PCL precursors were cured with a polyisocyanate crosslinker, Desmodur N3600, to prepare crosslinked polyurethane films with low surface energies. The following PCL precursors were used: TMP-PCL, $M_n = 2816$ and PDI = 1.11 (according to MALDI TOF MS), and R₇₈-PCL, $M_n = 2525$ and PDI = 1.16. To ensure the full incorporation of fluorinated tails into the network, the molar ratio of NCO/OH was maintained at 1.1.

Contact angle measurements were performed on these fluorinated polyurethane films, using water and hexadecane as probe liquids. The fluorine fraction was varied in the coating formulation in order to determine its influence on the wettability of the coating. The obtained results are shown in Figure 8. In comparison to those measured on the films free of fluorinated species, the water and hexadecane

contact angles on the fluorinated films were significantly higher, indicating that fluorinated tails are preferentially enriched at the air-film interface. The plateau values of contact angles (105° for water and 78° for hexadecane, corresponding to a surface energy of ~ 12 mN/m) were reached at a very low F concentration, about 1.5 wt%. On the other hand, it is envisaged that, when a higher concentration of fluorinated species is incorporated into the films, it is likely that the thickness of the fluorine-rich layer will increase, given that no severe phase separation takes place.



10 Figure 8. Advancing contact angles on the polyurethane films based on R₈-PCL and TMP-PCL cured by Desmodur N3600.

Self-replenishing character for crosslinked polyurethane films based on fluorinated PCLs

15 The self-replenishing behavior of fluorinated tails was examined by angle-resolved X-ray photoelectron spectroscopy (XPS) in combination with microtoming. The coating examined was prepared by casting the reaction mixture (R₈-PCL, TMP-PCL, and Desmodur N3600) on a metal plate from NMP solution (50 wt% solid contents) and then curing at 120 °C. The coating was about 200 μm thick and
20 contained 1 wt% of fluorine. Thin slices of about 30 μm thick were cut by microtoming and the top surfaces of the slices were then examined by XPS.

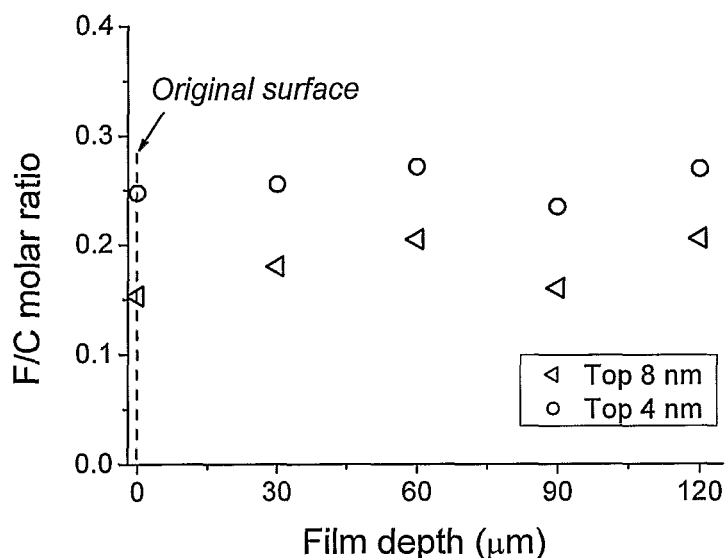


Figure 9. F/C ratios at two different probe depths (4 and 8 nm) for thin slices cut from a polyurethane coating containing R_f8-PCL.

5 As shown in Figure 9, the F/C ratio appeared to be constant throughout the coating, indicating relatively homogeneous distribution of fluorinated species in the bulk of the film. What is significant is that, for each slice, the F/C ratio in the top 4 nm is about 60% greater than that in the top 8 nm of the slice. The greater F/C ratio in the top 4 nm clearly indicates that the replenishing of fluorinated tails
10 already took place after the microtoming and before the XPS measurements; otherwise the F/C ratios in the top 4 and 8 nm would be the same for the slices from the bulk of the film. It is not surprising for the self-replenishing to take place at room temperature as far as the T_g (-20 °C) of the coating is concerned.

CLAIMS

1. Coating comprising:
 a) a crosslinked polymeric network (N), based on a first polymer (P),
 5 b) a low-surface-energy group (E), coupled to the network N via
 c) a polymeric spacer (S),
 having the following relationship between the native surface energies of P, E,
 and S (resp. σ_p , σ_e , and σ_s , in mN/m):
- $$\sigma_e \leq \sigma_s \leq \sigma_p$$
- 10 2. Coating according to claim 1, wherein P is selected from the group comprising
 polyurethane, polyester, polyether, polyetherester, and polyesterether.
3. Coating according to anyone of claims 1-2, wherein N is obtained via a
 crosslinking of P with a crosslinker selected from the group comprising a
 polyisocyanate, a blocked polyisocyanate, a polycarbodiimide, a polyepoxide,
 15 or an alkylated melamine resin.
4. Coating according to claim 3, wherein N is a polyurethane network, based on
 a polylactone P made of lactone and a polyfunctional alcohol, and a
 polyisocyanate crosslinker.
5. Coating according to anyone of claims 1-4, wherein E is selected from the
 20 group comprising a perfluoroalkyl, a perfluoropolyether, and a polysiloxane.
6. Coating according to claim 5, wherein the perfluoroalkyl is a perfluoro hexyl
 ethyl, or a perfluoro octyl ethyl group.
7. Coating according to claim 5, wherein the polysiloxane is
 polydimethylsiloxane.
- 25 8. Coating according to anyone of claims 1-7, wherein σ_e has a value of between
 5 and 25 mN/m.
9. Coating according to anyone of claims 1-8 wherein S has a number-averaged
 molecular weight $M_{n,s}$ of between 200 and 10,000; preferably between 500
 and 5,000.
- 30 10. Coating according to anyone of claims 1-9, wherein S has a glass transition
 temperature $T_{g,s}$ (in ° C) according to the following relation: $-100 \leq T_{g,s} \leq 50$;
 preferably $-60 \leq T_{g,s} \leq 20$.
11. Coating according to anyone of claims 1-10, wherein $\sigma_e < \sigma_s \leq \sigma_p$.
12. Coating according to anyone of claims 1-11, wherein

$$200 \leq M_{n,s} \leq 10,000$$

$$-100 \leq T_{g,s} \leq 50$$

$$\sigma_e < \sigma_s \leq \sigma_p$$

- 5 13. Coating according to anyone of claims 1-12, wherein S is selected from the group comprising polyurethane, polyester, polyether, polyetherester, and polyesterether.
14. Coating according to claim 13, wherein S is a polylactone; preferably a polycaprolactone.
15. Coating according to claim 4, wherein the lactone is ϵ -caprolactone, and the polyfunctional alcohol is a trimethylol alkane; preferably trimethylol propane.
- 10 16. Coating according to anyone of claims 1-15, wherein the coating has a glass transition temperature $T_{g,c}$ (in ° C) according to the following relation:
$$-20 \leq T_{g,c} \leq 50, \text{ preferably } -10 \leq T_{g,c} \leq 40.$$
- 15 17. Process for the preparation of a fluorine containing polyurethane based coating, comprising the following steps:
a) ring-opening polymerization of a first lactone with a perfluorinated alcohol,
b) ring-opening polymerization of a second lactone with a di-, tri- or tetra hydroxyfunctional hydrocarbon, or its ether-derivative,
c) crosslinking a mixture of the products obtained in step a) and step b) with
20 a polyisocyanate crosslinker.
18. Process according to claim 17, wherein the lactones in step a) and b) are the same.
19. Process according to anyone of claims 17-18, wherein at least one of the lactones is ϵ -caprolactone.
- 25 20. Process according to anyone of claims 17-19, wherein the perfluorinated alcohol has 6-20 C-atoms.
21. Process according to claim 17, wherein the perfluorinated alcohol is selected from the group comprising perfluorohexyl ethanol, perfluorooctyl ethanol, or a mixture thereof.
- 30 22. Process according to anyone of claims 17-21, wherein the product of step a) has a number-averaged molecular weight ($M_{n,a}$) of between 1,000 and 4,000.
23. Process according to anyone of claims 17-21, wherein the products from steps a) and b) each have a PDI of at most 1.5, preferably at most 1.25.
24. Process according to anyone of claims 17-23, wherein the molar ratio of the

- NCO-groups in the polyisocyanate crosslinker to the total of hydroxyl groups in the mixture of step c) is at least 1.0.
25. Fluorine containing crosslinked polyurethane, comprising up to 2.5 wt.% of chemically bound fluorine .
- 5 26. Coating comprising the fluorine containing crosslinked polyurethane according to anyone of claims 4-16, and 25.
27. Fluorinated polylactone, obtainable from a reaction between a lactone and a perfluorinated alcohol.
28. Fluorinated polylactone according to claim 27, wherein the lactone is
10 ϵ -caprolactone.
29. Fluorinated polylactone according to anyone of claims 27-28, wherein the perfluorinated alcohol has 6-12 C-atoms.
30. Fluorinated polylactone according to claim 29, wherein the perfluorinated alcohol is selected from the group comprising perfluorohexyl ethanol,
15 perfluorooctyl ethanol, or a mixture thereof.
31. Fluorinated polylactone according to anyone of claims 27-30, having a fluorine content of at most 15 wt.%, preferably between 5 and 12 wt.%.
32. Fluorinated polylactone according to anyone of claims 27-31, having a number-averaged molecular weight M_n of between 1,000 and 4,000.
- 20 33. Fluorinated polylactone according to anyone of claims 27-32, having a molecular weight distribution PDI at most 1.5, preferably at most 1.25.
34. Process for the preparation of a fluorinated polylactone according to anyone of claims 27-33, comprising a ring-opening polymerization of a lactone with a perfluorinated alcohol, under the influence of a weak acid.
- 25 35. Process according to claim 34, wherein the weak acid is fumaric acid.
36. Process according to anyone of claims 34-35, wherein the lactone is ϵ -caprolactone.
37. Process according to anyone of claims 34-36, wherein the perfluorinated alcohol has 6-12 C-atoms.
- 30 38. Process according to anyone of claims 34-37, wherein the perfluorinated alcohol is selected from the group comprising perfluorohexyl ethanol, perfluorooctyl ethanol, or a mixture thereof.
39. Fluorinated polylactone, obtainable by a process according to anyone of claims 34-38.

40. Coated substrate, comprising a substrate, and a coating according to anyone of claims 1-16, or 26; or a coating prepared according to any one of claims 17-24.
41. Processes and products as essentially described in the present document.