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Poly(di-1H,1H,2H,2H-perfluoroalkylitaconate) films: surface organisation phenomena, surface energy determinations and force of adhesion measurements

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Abstract

The significance of the Liftshitz/van der Waals, Lewis-acid, and Lewis-base contributors to the total surface energy of an homologous series of poly(di-1H,1H,2H,2H-perfluoroalkylitaconate)s is discussed in terms of the molecular design features and surface organisation phenomena characterising these, comb-like, polymers. Comparison of the characteristics specific to films prepared from this class of materials with those of the previously-studied homologous series of poly(perfluoroalkylacrylate)s, poly(perfluoroalkylmethacrylate)s and poly(methylpropenoxyalkyl siloxane)s suggests that, of the molecular design requirements for low-surface-energy polymers, an increase in the packing density of pendent side-chains has little effect on the contributors to surface energy but an adverse effect on the roughness of the film. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Surface energy; Force of adhesion; Poly(di-1H,1H,2H,2H-perfluoroalkylitaconate)s

1. Introduction

The stimulus for research efforts directed towards the development of non-wettable, low-surface-energy polymeric materials with good film-forming characteristics is provided by numerous commercial applications in aerospace, lithography, clothing, integrated sensors and also by the need for environmentally friendly protection against biological and other fouling [1–10].

For polymeric materials, the surface energy value is determined mainly by the chemical structure at the surface: it has been established that the surface energy of constituent groups decreases in the order CH_2 ($36\ \mathrm{mN\ m^{-1}}$) > CH_3 ($30\ \mathrm{mN\ m^{-1}}$) > CF_2 ($23\ \mathrm{mN\ m^{-1}}$) > CF_3 ($15\ \mathrm{mN\ m^{-1}}$) [11–15]. It has been suggested that amorphous, comb-like polymers possessing a flexible linear backbone onto which are attached side-chains with low intermolecular interactions, will exhibit low-surface-energy values [16–22]. As part of our work on new polymers with low-surface-energy properties, we have recently reported on the synthesis, characterisation, film-forming characteristics and surface energies of several classes of materials that comply with the molecular design requirements imposed by the above considerations, namely: the poly(perfluoroalkylacrylate)s (PFA) [17], the poly(perfluoroalkylmethacrylate)s (PFMA) [18], and the poly(methylpropenoxyperfluoroalkyl-siloxane)s (PFE) [19]. For purposes of comparison, certain hydrocarbon analogues (poly(perfluorooctylacrylate) (POA5) and poly(methylpropenoxyalkylsiloxane)s (PES) of the same classes of materials were also considered, Fig. 1 [20].

Consideration of the surface energy components associated with each member of the homologous series of materials presented in Table 1 revealed that, in addition to surface roughness (the effects of which can be assessed by combining advanced contact angle measurements with receding contact angle determinations), the wetting behaviour is determined by four structural features of the macromolecule, namely: (i) nature of the pendent chain; (ii) length of the pendent chain; (iii) nature of the linking moiety, and (iv) nature of the polymer backbone.

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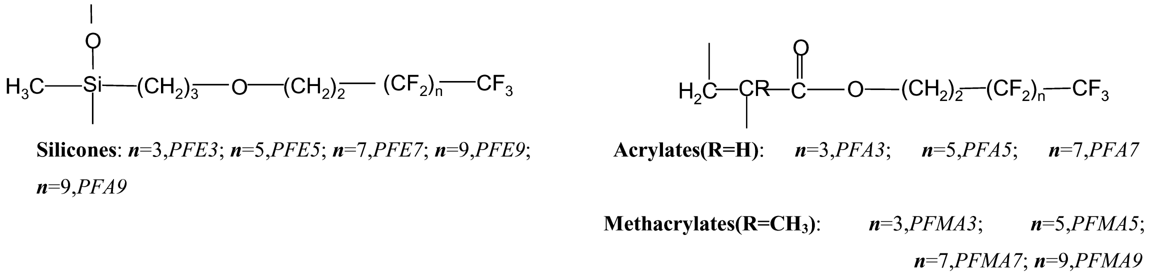


Silicones: ***n***=3,*PFE3*; ***n***=5,*PFE5*; ***n***=7,*PFE7*; ***n***=9,*PFE9*; ***n***=9,*PFA9*

Acrylates(R=H): ***n***=3,*PFA3*; ***n***=5,*PFA5*; ***n***=7,*PFA7*

Methacrylates(R=CH$_3$): ***n***=3,*PFMA3*; ***n***=5,*PFMA5*; ***n***=7,*PFMA7*; ***n***=9,*PFMA9*

Fig. 1. Typical comb-like, low-surface-energy polymers.

The results presented in Table 1 demonstrate that the nature of the pendent chain has a most profound effect in determining the surface energy of the material, with all fluoro-substituted compounds seen to exhibit surface energies that are markedly lower than those of corresponding alkyl-substituted macromolecules.

The influence of the length of the pendent fluorocarbon or hydrocarbon moiety is also evident: a general trend of lower surface energy with increasing chain length is observed. However, as the length of the pendent chain increases, the average surface roughness of the corresponding film structures is seen to follow the same trend. This effect, which is reflected by the magnitude of the observed hysteresis values, may exaggerate the differences in contact angles observed between adjacent members of each homologous series. Nonetheless, the incorporation of a long perfluorocarbon side chain is an essential element of the molecular design for such materials as it serves to inhibit the absorption of liquids by the bulk sample; only the materials for which hysteresis values are reported (PFA9, PFA7, PFMA9, PFMA7 and PFE9) were found to be resistant to penetration by the probe liquids used [17–20].

The effects of the linking moiety become apparent when the individual contributors to the total surface energy of

Table 1
Advancing contact angles for water, (in mJ mm^{-2}, $\gamma_L = 72.8$, $\gamma_L^{LW} = 21.8$, $\gamma_L^+ = 25.5$, $\gamma_L^- = 25.5$), diiodomethane, DIM ($\gamma_L = 50.8$, $\gamma_L^{LW} = 50.8$, $\gamma_L^+ = 0$, $\gamma_L^- = 0$) and ethylene glycol, EG ($\gamma_L = 48$, $\gamma_L^{LW} = 29$, $\gamma_L^+ = 1.92$, $\gamma_L^- = 47$) on acrylate, PFA, and silicone, PFE, film structures, and corresponding surface energies, γ_S, [$\gamma_S = \gamma_S^{LW} + 2(\gamma_S^+\gamma_S^-)^{1/2}$ where γ^{LW} is the Liftshitz/van der Waals component, γ^+ is the Lewis-acid component and γ^- is the Lewis-base component [14,15]]. The $R_{a>}$ measure of surface roughness, as determined by AFM, is also given. Hysteresis values, $H°$, are reproduced as appropriate

Sample	R_a (nm)	Contact angle, $\theta°$ ($H°$)			Surface energy (mJ m^{-2})			
		H_2O	DIM	EG	γ_S^{LW}	γ_S^+	γ_S^-	γ_S
Poly(perfluoroalkylacrylate)s								
PFA9	11.0	125 (4)	112 (16)	120 (25)	5.0	0.1	1.6	5.6
PFA7	9.6	117 (8)	112 (12)	108 (17)	5.0	0.1	2.3	6.1
PFA5	5.1	114	108	108	6.1	0.0	3.6	6.4
PFA3	3.1	113	105	110	7.0	0.0	4.7	7.9
Poly(perfluoroalkylmethacrylate)s								
PFMA9	7.13	125 (6)	109 (13)	107 (34)	5.8	0.3	0.1	6.1
PFMA7	1.17	125 (9)	104 (12)	105 (19)	7.3	0.2	0.1	7.5
PFMA5	0.41	121	104	106	7.3	0.1	0.5	7.7
PFMA3	0.29	123	103	102	7.6	0.3	0.0	7.8
Poly(methylpropenoxyfluoroalkylsiloxane)s								
PFE9	3.1	109 (3)	95 (12)	94 (8)	10.6	0.17	2.1	11.8
PFE7	2.3	106	96	91	10.2	0.4	2.8	12.2
PFE5	1.0	103	87	83	14.1	0.5	2.0	16.0
PFE3	0.5	105	89	79	13.1	1.3	0.7	15.1
Poly(alkylacrylate)s								
POA5	10.2	96	52	70	33.0	0.01	1.5	33.1
Poly(methylpropenoxyalkylsiloxane)s								
PES13	100.0	106.9	73.4	81.8	21.0	0.1	0.3	21.3
PES11	115.5	84.7	72.1	75.6	21.7	0.0	12.8	21.8
PES9	0.9	85.2	70.0	75.4	22.9	0.0	12.0	23.4
PES7	5.6	80.5	66.8	73.8	24.6	0.1	16.4	26.6
PES5	8.2	72.2	51.6	61.2	33.3	0.1	18.5	35.2
PES3	3.5	91.0	62.1	82.0	27.4	0.5	8.8	31.6
PES1	2.0	79.6	55.2	70.9	31.3	0.3	14.9	35.4

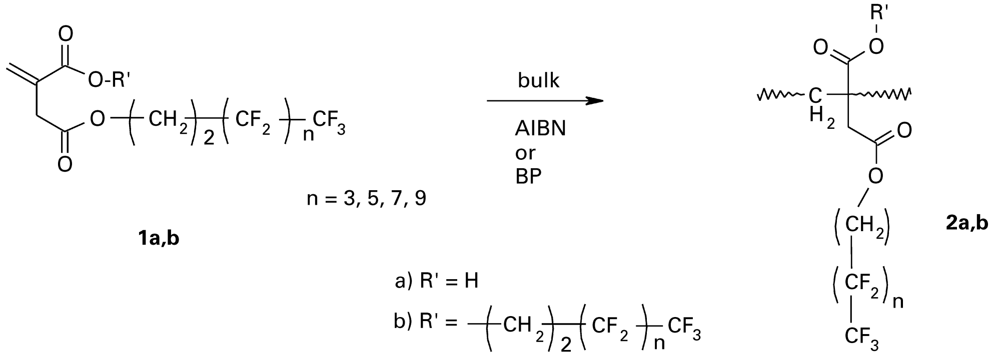


Fig. 2. Poly(1H,1H,2H,2H-perfluoroalkylitaconate)s (**1a**) and poly(di-1H,1H,2H,2H-perfluoroalkylitaconate)s (**1b**).

each type of material are considered. In particular, the Liftshitz/van der Waals component (γ_S^{LW}) determined for fluorosilicones is significantly greater than that of corresponding fluoroacrylates, indicating that different molecular segments are responsible for the observed surface energies in each class of material. By contrast, the γ_S^{LW} values determined for the non-fluorinated macromolecules PFOA5 and PES5, are essentially identical. Finally, consideration of the relative values of the contributors to the total surface energy of fluoroacrylates and fluoromethacrylates highlights the gravity of subtle differences in the backbone structure: although the total surface energies of the higher analogues of the two classes of materials appear to be very similar, the γ_S^- values associated with the latter class of congeners are considerably lower whereas the γ_S^{LW} interactions are more significant, indicating that fluoromethacrylates ought to be the materials of choice in practical applications requiring highly suppressed surface nucleophilicity.

The work completed to date has provided the basis for an appreciation of the relationship between molecular structure and surface energy in polymeric materials. However, one fundamental molecular design issue has not, as yet, been investigated, namely: the influence of the number of side-chains per constitutional repeat unit on surface energy. We now attempt to bridge that gap by considering the film-forming characteristics and submolecular-level surface organisation phenomena of a class of low-surface-energy materials with a higher number of pendent side-chains per constitutional repeat unit than in the materials previously considered, namely: the poly(di-1H,1H,2H,2H-perfluoroalkylitaconate)s; for reasons of comparison the mono-substituted analogues of the same class of materials, the poly(1H,1H,2H,2H-perfluoroalkylitaconate)s, were also considered, Fig. 2.

2. Experimental section

2.1. Synthesis and characterisation of monomers

General remarks. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. NMR spectra were recorded on a JEOL spectrometer (operating at 400.13 MHz for ^1H) and ^{13}C NMR assignments were performed using DEPT and HETCOR experiments.

General method for the synthesis of fluorinated itaconic acid monoesters (**1a**). The monoesters **1a** [23] were prepared by refluxing itaconic acid and the appropriate 1H,1H,2H,2H-perfluoroalcohol (molar ratio 1:1.5) in toluene for 4 h, using sulphuric acid as a catalyst; a round-bottomed flask fitted with a water separator and a reflux condenser was employed for the purpose. The white precipitate formed on cooling was filtered off and recovered by recrystallisation from petroleum ether (fraction bp 80–100 °C). Samples were purified further by column chromatography on silica gel using ethyl acetate/petroleum ether (80–100 °C) (1:2) as the mobile phase and finally recrystallised from petroleum ether. Melting points are presented in Table 2.

Typical ^1H NMR ($CDCl_3$, 400 MHz, TMS) data: 2-methylene-succinic acid 4-(1H,1H,2H,2H-perfluorooctyl) ester (**1a**, $n = 5$), 8.88 (broad, 1H, COOH); 6.48 (s, 1H, $=CH_2$); 5.85 (s, 1H, $=CH_2$); 4.41 (t, 2H, $J = 6.4$ Hz, OCH_2); 3.35 (s, 2H, $CH_2{-}C{=}O$); 2.47 (m, 2H, $J = 6.4$ Hz, $J = 18.3$ Hz, CH_2CF_2). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): 171.3 (COOH); 170.1 (COO); 132.8 ($=C<$); 131.2 ($=CH_2$); 120.3–111.0 (m, $(CF_2)_5CF_3$); 56.8 (t, $J = 4.6$ Hz, OCH_2); 37.1 ($-CH_2{-}COO$); 30.4 (t, $J = 21.8$ Hz, $\mathit{C}H_2CF_2$).

General synthesis of fluorinated itaconic acid diesters (**1b**). The diesters **1b** were prepared by refluxing itaconic acid and the appropriate 1H,1H,2H,2H-perfluoroalcohol (molar ratio 1:2.2) in toluene for 72 h, using sulphuric acid as a catalyst; the reaction was carried out in a round-bottomed flask fitted with a water separator and a reflux

Table 2
Physical characteristics of mono and diitaconate monomers **1a** and **1b**

Monomer	Mp or bp* (°C)			
	$n = 3$	$n = 5$	$n = 7$	$n = 9$
1a	78–79	91.5–92.5	112–113	129–131
1b	*138–140/1 mbar	*168–170/1 mbar	57.5–60	97–98

condenser. The solution was filtered hot and allowed to cool: for $n = 3$, 5, the cooled solution was washed with aqueous sodium carbonate and water, dried and, following removal of the toluene, the liquid residue was purified by distillation under reduced pressure; for $n = 7$, 9, the precipitate formed on cooling was filtered off and recrystallised from petroleum ether (80–100 °C). Samples ($n = 7$, 9) were further purified by column chromatography on silica gel using ethyl acetate/petroleum ether (80–100 °C) (1:2) as the mobile phase and recrystallised again from petroleum ether. Physical characteristics such as melting or boiling points are presented in Table 2.

Typical ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) data: 2-methylene-succinic acid di-(1H,1H,2H,2H-perfluorooctyl) ester (**1b**, $n = 5$), 6.38 (s, 1H, $=CH_2$); 5.77 (s, 1H, $=CH_2$); 4.47 (t, 2H, $J = 6.3$ Hz, OCH_2); 4.40 (t, 2H, $J = 6.4$ Hz, OCH_2); 3.37 (s, 2H, CH_2–C=O); 2.50 (m, 2H, $J = 6.4$ Hz, $J = 18.0$ Hz, CH_2CF_2); 2.46 (m, 2H, $J = 6.4$ Hz, $J = 18.0$ Hz, CH_2CF_2). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): 170.1 (C=O); 165.5 (C=O); 132.9 (>C=); 129.7 ($=CH_2$); 121.8–105.7 (m, $(CF_2)_5CF_3$); 56.9 (t, $J = 4.6$ Hz, OCH_2); 56.8 (t, $J = 4.6$ Hz, CH_2CO); 37.4 (–CH_2–COO); 30.5 (t, $J = 21.5$ Hz, CH_2CF_2); 30.4 (t, $J = 21.5$ Hz, CH_2CF_2).

2.2. Polymerisation

The monomers, **1a** or **1b** ($n = 3$, 5, 7, 9), were polymerised in the bulk, using freshly purified AIBN (azo-bisisobutyronitrile) or BP (benzoyl peroxide) as initiators, at temperatures slightly above the melting point of the monomers, to give the corresponding poly(perfluoroalkylitaconates), **2a** and **2b** ($n = 3$, 5, 7, 9). Polymerisation conditions are presented in Table 3; a concentration of 1% (w/w) initiator was used in all cases. All polymers were purified by repeated washings in dichloromethane and dried in vacuo.

2.3. Film formation and characterisation

Polymer (**2a** and **2b**) films were deposited from $CF_2ClCFCl_2$ solution (0.1% w/w; dipping speed = 1 mm s^{-1}) or from the melt onto glass and poly(tetrafluoroethylene) supporting substrates ($10 \times 10 \times 1$ mm^3).

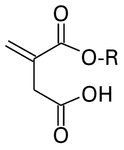
A TopoMetrix Discoverer TMX2000 scanning probe microscope and triangular, standard profile Si_3N_4 cantilevers (length 200 μm) of spring constant 0.068 N m^{-1} and a piezoelectric $75 \times 75 \times 12$ μm^3 XYZ-tripod scanner was used for the atomic force microscopy investigations. Surface roughness measurements are expressed in terms of the roughness average R_a and were obtained by imaging polymer surfaces over a scan area of 50×50 μm^2 in air and applying a digital algorithm. Force-of-adhesion measurements were performed in pure water (18 Mohm, Sigma), using the same instrument.

A VG Scientific ESCALAB Mk.II instrument fitted with a non-monochromated Al Kα source (1486.6 eV) was used for the X-ray photoelectron spectroscopy investigations. To minimise the risk of sample damage, the X-ray source was operated at a low power (50 W). The susceptibility of each sample to X-ray-induced degradation was monitored by performing fast, single scans of the C1s and F1s regions before and after the main set of analysis scans; examination of the data from the fast scans provided the evidence that sample degradation was negligible.

The surface free energies of polymer samples were determined by contact angle goniometry in a thermostatted cell (25 ± 1 °C) using a Kruss G10 goniometer interfaced to image capture software. Both advancing (θ_A) and receding (θ_R) contact angles of droplets (2–10 μl) were recorded at 25 ± 1 °C using doubly distilled water (surface tension $\gamma_L = 73.4$ mN m^{-1} at 18.75 °C, literature value [24–27] = 73.05 mN m^{-1} at 18 °C), diiodomethane (>99%; $\gamma_L = 48.7$ mN m^{-1} at 18.8 °C, literature value [24–27] = 50.76 mN m^{-1} at 20 °C) and 1,1-ethanediol (ethylene glycol, >99%; $\gamma_L = 47.7$ mN m^{-1} at 18.8 °C, literature value [24–27] = 48.40 mN m^{-1} at 20 °C). In the case of receding contact angle experiments, a drop of the probing liquid (8–10 μl) was placed on the surface of the sample and subsequently removed in small increments (0.5 μl) until the drop edge spontaneously contracted to a new stationary position at which the receding contact angle was measured. Hysteresis (H) was recorded as ($\theta_A - \theta_R$). The nature of the supporting substrate (PTFE, glass, PMMA) was found to have no influence on the wetting behaviour exhibited by the perfluoromethacrylate film structures under consideration. In view of the uncertainties associated with the use of non-fluorinated liquids for the study of the wetting character of fluoropolymer surfaces, the surface energy of poly(tetrafluoroethylene) and that of polyethylene were determined for comparison: values of 21 and 30 mJ m^{-2} were obtained, respectively.

Table 3
Polymerisation conditions for mono and diitaconate monomers **1a** and **1b**

Monomer	$n = 3$		$n = 5$		$n = 7$		$n = 9$	
	Initiator	Temperature (°C)	Initiator	Temperature (°C)	Initiator	Temperature (°C)	Initiator	Temperature (°C)
1a	BP	100	BP	110	BP	115	BP	130
1b	AIBN	60	AIBN	60	AIBN	65	BP	110



3 R = alkyl

Fig. 3. 1-Alkyl-2-methylenesuccinate.

3. Results and discussion

Monomers **1a** and **1b** were prepared from itaconic acid and the corresponding 1H,1H, 2H,2H-perfluoroalkylalcohols. In the case of monoesters, only formation of 4-perfluoroalkyl-2-methylenesuccinate isomer **1a** was observed; the structure was confirmed by HETCOR experiments. The isomeric monoester of the itaconic acid, 1-alkyl-2-methylenesuccinate (Structure 3; Fig. 3) is apparently not known [23].

Polymerisation reactions were performed under the conditions summarised in Table 2. It was observed that the monoesters polymerised more rapidly than the corresponding diesters. In all cases, optically transparent films of polymers could be obtained from solution or from the melt.

Results of the X-ray photoelectron spectroscopy studies on melt-coated PTFE substrates are presented in Table 4, as is the number of atoms per monomer unit and the measured binding energies (eV) corrected for static charge ($C(1s) = 285.00$ eV). In the same table, the determined atomic percentages are compared with the theoretical values calculated from the number of each atom type per monomer unit, Fig. 4. In all cases, the mildly—but consistently—higher atomic percentage of side-chain fluorine, coupled with the slightly suppressed proportions of backbone carbon, might suggest a preferential orientation of the pendent chains towards the surface.

Goniometry studies on poly(perfluoroalkylitaconate) films (**2a**) showed that these were characterised by low, and time-dependent, contact angle values (Fig. 5); these effects were particularly pronounced when 1,2-ethanediol was used as the liquid probe. This can be explained in terms of the enhanced electron-acceptor and electron-donor capabilities of films prepared from these materials; a property imparted by the combined electrophilic and nucleophilic character of the free COOH moieties present within the molecular structure. Hence, only poly(diperfluoroalkylitaconate) films (**2b**) were studied further.

Contact angle measurements for films of poly(diperfluoroalkylitaconate)s—deposited from solution onto glass—using water, diiodomethane (DIM) and 1,2-ethanediol (EG) as solvent probes, can be found in Table 5. Recently-advanced contact angles (θ_A) and hysteresis values (H) are presented: each value is the mean of at least 10 drops on 10 independently prepared polymer films. No reduction in the volume of the sessile drops was evident over the time scale of these measurements (60 s).

Table 4

Binding energies and atomic proportions of elements at the surface of melt-formed poly(di-1H,1H,2H,2H-perfluoroalkylitaconate) film structures onto PTFE; melt coated. The differences in the chemical structures of polymers $n = 3$ to $n = 9$ are explained in Fig. 4

Element	Carbon	$n = 3$			$n = 5$			$n = 7$			$n = 9$			Assignments
		No. of atoms	E_b (eV)	Atomic % found (calc)	No. of atoms	E_b (eV)	Atomic % found (calc)	No. of atoms	E_b (eV)	Atomic % found (calc)	No. of atoms	E_b (eV)	Atomic % found (calc)	
C(1s)	a	1	285.00	2.4 (2.6)	1	285.00	1.9 (2.0)	1	285.00	1.5 (1.6)	1	285.00	1.2 (1.3)	C–C, C–H backbone
C(1s)	b	2	286.15	4.5 (5.1)	2	286.20	3.7 (3.9)	2	286.40	3.0 (3.2)	2	286.15	2.6 (3.7)	$C–CO_2$
C(1s)	d	2	286.60	5.4 (5.1)	2	286.60	3.8 (3.9)	2	286.70	3.2 (3.2)	2	286.75	2.9 (3.7)	C–O
C(1s)	e	2	287.70	4.8 (5.1)	2	287.70	3.7 (3.9)	2	287.90	3.4 (3.2)	2	287.90	2.6 (3.7)	$C–CF_2$
C(1s)	c	2	289.90	4.6 (5.1)	2	289.90	3.6 (3.9)	2	289.75	2.9 (3.2)	2	289.75	2.1 (3.7)	CO_2 (O=C–O)
C(1s)	f	2	291.80	4.1 (5.1)	2	291.70	3.6 (3.9)	2	291.05	2.3 (3.2)	2	291.20	3.7 (3.7)	$CF_2–CH_2$
C(1s)	g	2	292.05	5.0 (5.1)	6	292.10	9.7 (11.8)	10	292.05	13.8 (15.9)	14	292.15	14.5 (18.7)	$CF_2–CF_2–CF_2$
C(1s)	h	2	292.30	4.7 (5.1)	2	292.50	3.5 (3.9)	2	292.60	3.2 (3.2)	2	292.85	3.0 (3.7)	$CF_2–CF_3$
C(1s)	i	2	294.40	4.1 (5.1)	2	294.40	3.5 (3.9)	2	294.40	2.7 (3.2)	2	294.40	2.6 (3.7)	CF_3
F(1s)		18	689.70	48.9 (46.2)	26	689.75	54.6 (51.0)	34	689.65	56.0 (54.0)	42	689.75	59.4 (56.0)	
O(1s)		2	533.05	6.2 (5.1)	2	533.10	4.4 (3.9)	2	532.95	4.1 (3.2)	2	533.25	2.7 (3.7)	
O(1s)		2	534.55	5.4 (5.1)	2	534.60	4.0 (3.9)	2	534.55	4.0 (3.2)	2	534.75	2.6 (3.7)	

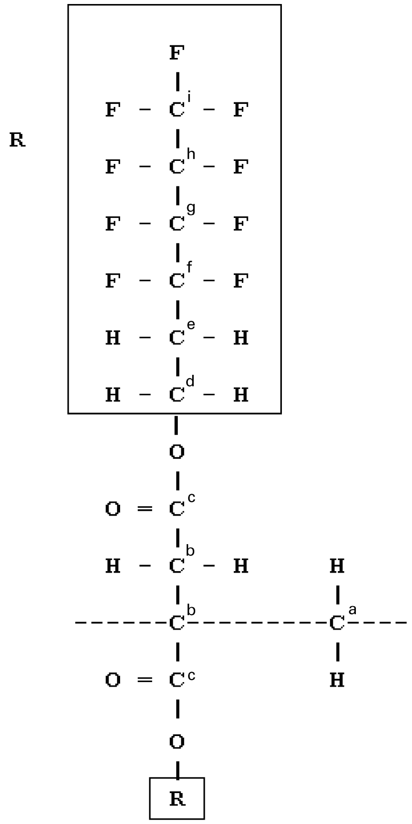


Fig. 4. Assignment of carbon atom types in poly(di-1H,1H,2H,2H-perfluoroalkylitaconate)s, exemplified for $n = 3$.

However, over a longer time scale, height/width measurements for drops of water on poly(diperfluoroalkylitaconate) films unmasked a time-dependent wetting behaviour for all films apart from those from poly(di-1H,1H,2H,2H-perfluorododecanoylitaconate), $n = 9$ (Table 6). The observed time-dependence of the contact angles for water are reflective of the fact that this liquid is capable of becoming absorbed into the bulk of the sample and support the hypothesis that the carbonyl moieties of the polymer backbone play a profound role in determining the wetting characteristics of low-surface-energy polymeric films [18,19].

The surface-tension-component theory (STC) [24,25] was used for the evaluation of the surface energies of the film structures. The three contributions to the surface energy of the solid (γ_S—see Eq. (1)), namely the Liftshitz/van der Waals component (γ_S^{LW}), the Lewis-acid component (γ_S^+) and the Lewis-base component (γ_S^-) were calculated from Eq. (2).

$$\gamma_S = \gamma_S^{LW} + 2(\gamma_S^+ \gamma_S^-)^{1/2} \tag{1}$$

$$\gamma_L(1 + \cos\theta) = 2\left(\left(\gamma_S^{LW}\gamma_L^{LW}\right)^{1/2} + (\gamma_S^+\gamma_L^-)^{1/2} + (\gamma_L^+\gamma_S^-)^{1/2}\right) \tag{2}$$

Contact angles (θ) measured for three well-characterised (in terms of γ_L^{LW}, γ_L^+, γ_L^-) liquids [24,25] were used to generate three equations and to calculate the surface energy components of each polymer, which are also presented in Table 5.

The recently-advanced contact angles for all three liquids are structure-dependent and were seen to increase with increasing length of the perfluoroalkyl chain, as did the average surface roughness; surface energies as low as 5.5 mJ m^{-2} were determined for poly(diperfluoroalkylitaconate)s (**2b**, $n = 9$). However, since the surface of films prepared from this material exhibited a considerable degree of roughness ($R_a = 8.25$ nm; Table 5), the determined surface energy values must be considered with a degree of scepticism; the uncertainty about the validity of the surface energy determination is further highlighted by the large contact angle hysteresis values observed for all three probing liquids.

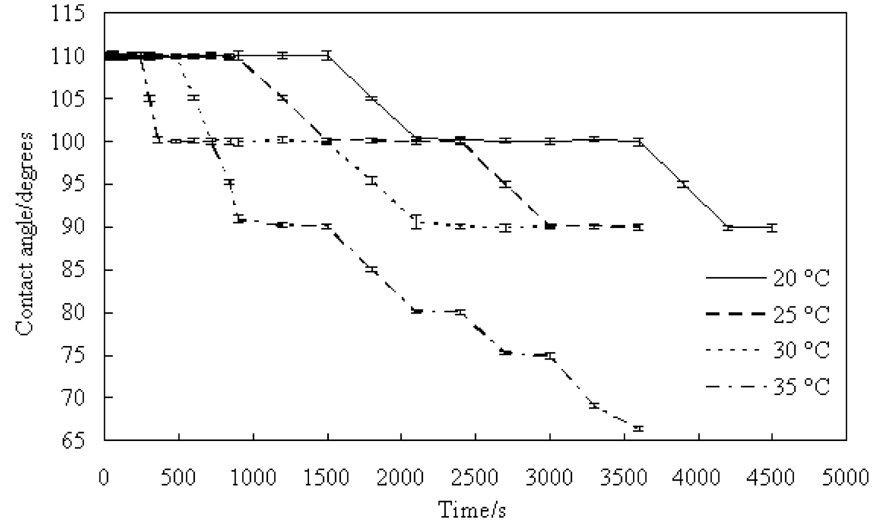


Fig. 5. Time dependence of recently-advancing contact angle of water drops on poly(1H,1H,2H,2H-decanoyl monoitaconate) at different temperatures (20.0 ± 0.5, 25.0 ± 0.2, 30.0 ± 0.2 and 35.0 ± 0.2 °C; errors are standard deviations).

Table 5
Contact angle data (water, diiodomethane, ethylene glycol) and calculated surface energies for poly(di-1H,1H,2H,2H-perfluoroalkylitaconate) films ($n = 3, 5, 7, 9$) deposited, from solution, onto glass; R_a is the surface roughness (SD—standard deviation)

Sample	R_a (nm) (SD)	Contact angle, $\theta°$ ($H°$)			Surface energy (mJ m^{-2})			
		H_2O	DIM	EG	γ_S^{LW}	γ_S^+	γ_S^-	γ_S
Poly(diperfluoroalkylitaconate)s								
9	8.25 (2.93)	125 (30)	111 (32)	105 (27)	5.2 ± 0.7	0.6 ± 0.0	0.0 ± 0.0	5.5 ± 0.8
7	4.35 (3.62)	121 (14)	104 (6)	104 (40)	7.3 ± 0.5	0.2 ± 0.0	0.3 ± 0.1	7.8 ± 0.5
5	0.59 (0.18)	121 (23)	102 (14)	101 (26)	8.0 ± 0.6	0.3 ± 0.0	0.1 ± 0.1	8.3 ± 0.7
3	0.99 (0.65)	120 (28)	102 (22)	101 (22)	8.0 ± 0.7	0.3 ± 0.0	0.2 ± 0.2	8.5 ± 0.8

For all poly(diperfluoroalkylitaconate)s under consideration, the main contributor to the energy of the surface is the Liftshitz/van der Waals component (γ_S^{LW}). Throughout the homologous series, the contributions of the polar components are consistently low, with the γ_S^- and γ_S^+ values being very close to zero, Table 1. In accord with the findings from the water-drop height/width experiments, these observations provide further support for the proposition that the increased number of pendent chains per constitutional repeat units fails to effect the complete masking of the carbonyl linking group [18,19]. A further implication, associated with the increased number of pendent groups, is that of the enhanced value of γ_S^{LW} characterising the poly(diperfluoroalkylitaconate)s as compared to poly(perfluoroalkylacrylate)s and poly(perfluoroalkylmethacrylate)s of corresponding chain lengths: with the exception of the $n = 3$ poly(perfluoroalkylacrylate), all other poly(perfluoroalkylacrylate)s and poly(perfluoroalkylmethacrylate)s exhibited lower γ_S^{LW} values than poly(diperfluoroalkylitaconate) analogues. Presumably, the increased packing density of pendent chains results in an enhancement of the dipole-related interactions that are collectively responsible for the observed values of the Liftshitz/van der Waals parameter. Since the lowest energy surfaces are those containing perfluoroalkyl groups that are oriented to yield a two-dimensional array of $-CF_3$ moieties [16–22], the surface organisation phenomena suggested by the XPS analysis (Table 4) are consistent with the trends in surface energy values summarised in Table 5.

Table 6
Height/width measurements (arbitrary units) for advancing water drops (3 μl) on films of poly(di-1H,1H,2H,2H-perfluorodecanoylitaconate); monitored over 3600 s, at 25.0 ± 0.2 °C and under a water-saturated atmosphere (errors are standard deviations)

Time (s)	Height (mean)	Width (mean)
Poly(di-1H,1H,2H,2H-perfluorodecanoylitaconate)		
60	4.13 ± 0.04	5.20 ± 0.08
240	4.13 ± 0.04	5.22 ± 0.04
480	4.04 ± 0.02	5.23 ± 0.05
2040	3.95 ± 0.05	5.20 ± 0.04
2460	3.70 ± 0.06	5.18 ± 0.03
2940	3.63 ± 0.04	5.17 ± 0.08
3360	3.50 ± 0.06	5.21 ± 0.06
3540	3.50 ± 0.05	5.20 ± 0.07

Surface roughness data, as determined by AFM, for films prepared from the melt are presented in Table 7. As with solution-deposited films, the surface roughness of melt-processed structures increases with increasing length of the perfluoroalkyl chain. With the exception of the $n = 3$ material, films prepared from the melt were considerably rougher than those deposited from solution. Because of the considerable surface roughness characterising the melt-processed structures, contact angle goniometry did not lend itself as a reliable means for the determination of surface energy and as a result measurements of force of adhesion were investigated as an alternative. In order to avoid the problems associated with static charges and those of capillary water column formation between the substrate and the probing AFM tip, and in view of the well-known amplification effects characterising hydrophobic–hydrophobic relationships operating within the aqueous environment, the AFM experiments were performed under water [28,29]. The results are summarised in Table 7: in accord with expectation, the increase in hydrophobicity with increasing chain length is reflected by the magnitude of the force of adhesion values determined for each material. Mizes et al. [30] has shown that certain topographic features, such as scratches, lead to increased AFM-determined force of adhesion values as a result of the extended area of interaction between the tip and the probed surface; the effect is particularly pronounced if the size of the topographic feature approximates that of the tip radius. Thus, differences in surface energy may not be solely responsible for the greater mean force of adhesion measured

Table 7
Surface roughness and average force of adhesion (performed under water) measurements for melt-coated poly(di-1H,1H,2H,2H-perfluoroalkylitaconate) films onto PTFE substrates (SD—standard deviation)

N	Roughness (nm)	SD (nm)	Average force of adhesion (nN)	SD (nN)
3	0.37	0.01	2.65	6.16
5	5.45	1.72	11.83	21.19
7	19.20	2.52	13.47	13.96
9	36.39	5.70	15.09	21.63

on the poly(diperfluoroalkylitaconate) films under consideration as the higher homologues of these were seen to exhibit considerable surface roughness, Table 7. A further complication—highlighted by Marti et al. [31] who considered polymers below and above their glass transition temperatures—is that increased polymer chain mobility leads to a corresponding increase in the forces of adhesion measured by AFM. Since chain mobility is a protean parameter—influenced by the finest structural intricacies of the polymeric sample as well as factors such as temperature, state of plasticisation and, for thin films, nature of the underlying substrate—its effects would need to be unmasked before such force of adhesion measurements could be used to quantify surface energy. Nonetheless, the observed differences in force of adhesion are reflective of the trends in surface energy observed with our goniometric investigations and, indeed, complement the findings from the contact angle work.

4. Conclusions

New materials with low-surface-energy and good film-forming characteristics were obtained by radical polymerisation of mono and diperfluoroalkylitaconates. Films of these materials were deposited onto glass or PTFE substrates, either from the melt or solution, and studied by contact angle goniometry, AFM and XPS. Poly(diperfluoroalkylitaconate) films exhibited very low-surface-energy values, similar to those of poly(perfluoroalkylacrylate)s and poly(perfluoroalkylmethacrylate)s, in which the prominent component is the Liftshitz/van der Waals contributor, but these were also characterised by considerable surface roughness.

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