Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Fluorine Chemistry 125 (2004) 283–292

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

Effects of chemical variations on the mesophase behavior of new fluorinated poly(vinylcyclopropane)s

Marina Ragnoli[a], Elena Pucci[a], Massimo Bertolucci[a], Bernard Gallot[b], Giancarlo Galli[a,*]

[a]Dipartimento di Chimica e Chimica Industriale, UdR Pisa INSTM, Università di Pisa, via Risorgimento 35, 56126 Pisa, Italy
[b]Laboratoire des Matériaux Organiques à Propriétes Spécifiques, CNRS, BP 24, 69390 Vernaison, France

Received 13 February 2003; received in revised form 24 July 2003; accepted 30 July 2003

Abstract

Several new structures of fluorinated polymers poly(**1**)–poly(**9**) were prepared by free radical ring opening polymerization of vinylcyclopropane monomers **1**–**9** containing different fluorinated side groups of the type $-(CH_2)_n(CF_2)_pF$. While in poly(**1**)–poly(**3**) p varied from 6 to 10 for a fixed $n = 2$, in poly(**4**)–poly(**6**) n increased from 3 to 5 at the given $p = 8$. In poly(**7**) and poly(**8**) a phenyl ring was incorporated to elongate the mesogenic side group ($n = 2$; $p = 6$ and 8, respectively), that was further separated from the polymer backbone by a methylene spacer ($m = 11$) in poly(**9**). Therefore, the effects of various chemical variations of the polymer structure on the mesophase behavior could be assessed. The polymers were in fact co-polymers comprising both 1,5-linear and cyclobutane-ring isomer units. In any case they formed smectic mesophase(s) owing to the special character of the perfluorinated chains. The order and the isotropization temperature (T_i) of the mesophase were enhanced by increasing p, but T_i lowered with increasing n. Extension of the side group by insertion of a phenyl ring improved T_i. Wide angle X-ray diffraction studies clarified the nature of the different smectic phases, the occurrence of which was discussed in terms of the ability of the fluorinated side groups to pack antiparallel in either a partly or fully interdigitated structure. Co-polymers of **3** with a non-mesogenic, not fluorinated co-monomer **10** were also prepared with different chemical compositions. Co-polymerization was found to be another effective means of modifying the mesophase behavior of the poly(vinylcyclopropane)s.

Keywords: Fluorine substitution; Fluorinated polymer; Liquid crystalline polymer; Mesophase; Ring opening polymerization; Vinylcyclopropane

1. Introduction and brief overview

Fluorinated polymers represent a class of very interesting and versatile polymeric materials that may find application in many different fields [1] ranging from electronics and optics to coatings, thanks to their outstanding properties such as low dielectric constant, low refractive index and high optical transparency, as well as chemical and thermal resistance (for some examples, see [2–9]). The incorporation of fluorine in a polymer causes the polymer to have a low surface energy [10,11] potentially leading to low wettability, low friction coefficient and low adhesion [12–16]. Commercially available fluorinated ester side chain acrylic and methacrylic polymers are typical low surface energy coating materials [17].

In recent years novel low surface energy fluorinated polymers have been described [18–21]. However, among these reported fluorinated polymers, one critical problem, surface reconstruction, still has not been resolved and limits their useful practical application. The reason mainly attributed for this response is the poor stability of the amorphous fluorinated surface chains which cannot prevent movement of polar groups to the surface. Long-term hydrophobicity even after exposure to a polar fluid, such as water, may arise in particular when the fluorinated side chains of a polymer are capable of organizing into an ordered structure both in the bulk and at the surface in such a way that leads to the formation of a surface primarily composed of tightly packed $-CF_3$ groups [1,22,23]. These unique characteristics render fluorinated polymers particularly suitable for applications such as hydrophobic, non-adherent coatings.

From a molecular level perspective, a uniformly organized array of $-CF_3$ groups would be a surface with the lowest possible surface tension. Self-assembly of amphiphilic perfluorocarboxylic acid salts [24] occurs at the air–water interface of Langmuir–Blodgett (LB) films to produce among the lowest energy surfaces known. To create such a surface with LB film quality, $-CF_3$ groups must be aligned and oriented at the air–film interface. Additional functional

---

[*] Corresponding author. Tel.: +39-050-2219272; fax: +39-050-28438.
E-mail address: gallig@dcci.unipi.it (G. Galli).

0022-1139/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2003.07.010

groups can also be exploited as anchoring sites to bind self-assembled LB films onto solid substrates [25]. An effective alternative approach which avoids LB techniques for production of a uniform $-CF_3$ surface might be to harness the self-assembly behavior of a class of fluorinated materials, the liquid crystalline semifluorinated alkanes. For example, free standing films of semifluorinated side group ionenes [26] possess a very low critical surface tension (<10 mN/m) due to their ability to arrange fluorinated groups in a highly ordered smectic layer structure.

Precise control of the surface properties of polymeric materials by means of self-organization is a major objective of current science technology. Such self-organization can be driven by several mechanisms including phase separation of block co-polymers, liquid crystallinity, hydrogen bonding, and surface segregation [27]. Under some circumstances, these mechanisms may be used together to form an ordered surface structure. As an example, block co-polymers microphase-separate to preferred microstructure, but when low surface energy blocks are incorporated, surface and interface segregation will also take place to create further organization in the region of the low energy surface. In particular liquid crystallinity may provide a useful means for preparing low surface energy polymeric materials for non-stick coating application [1,28]. The attachment of a fluorinated mesogen pendent to a polymer backbone can bring about improvement and temporal stabilization of the surface upon exposure to different environments, as a consequence of the induced mesomorphic behavior in the bulk of the material. For example, investigations on block co-polymers containing a fluorinated polymer block showed that rigid rod-like fluorinated groups can form a highly organized surface structure, stable to reconstruction upon exposure to water as a consequence of the ordering of the fluorinated groups in a liquid crystalline, smectic mesophase [1]. In fact, the fluorinated side groups of these polymers residing in a smectic mesophase while covering the surface of a polymer film should overcome a too high enthalpy barrier to rearrange when in contact with water.

Fluorinated liquid crystalline polymers are a relatively new class of fluoropolymers [1,23,28–34]. Initial studies on fluorinated liquid crystals focused on partly fluorinated alkanes, namely diblock hydrocarbon–fluorocarbon molecules such as $H(CH_2)_x(CF_2)_yF$ ($x, y \geq 6$) [35–39]. The ability of these compounds was shown to form liquid crystalline mesophases presumably due to the strong phase separation of fluorocarbon from hydrocarbon chain segments [40] and also to the rigid rod-like nature of the fluorocarbon chains which tend to adopt a helical conformation in the mesophase state [41,42]. Later synthetic efforts resulted in the development of liquid crystalline polymers in which the length of the fluorinated tail was varied over a wide range of numbers x and y [28,29,31,33,34]. Thus, appropriately fluorinated molecules may be conceived as unconventional mesogens in that they do not possess the usual molecular features of more traditional liquid crystals. The latter molecules, in fact, are typified by core structures composed of two or more aromatic or cycloaliphatic rings, or combinations of them, that are either directly linked together, as e.g. in biphenyls, or interconnected by a bridging group, as e.g. an ester group in phenyl benzoates. Alkyl tails are also normally attached at both ends of the mesogenic core to introduce flexibility in the molecule and help tailor the mesophase transitions and properties of the materials [43]. More conventional mesogenic units, e.g. biphenyls, have also been used in combination with partly fluorinated tails in low molar mass [44–49] and polymeric liquid crystals [34].

The perfluorinated species are chemically stable and possess low viscosity and can, in suitable cases, dope the stability of the resulting mesomorphic phases. Such substitutions (fluorine for hydrogen) in the flexible extremities of mesogens, such as partial or total fluorination of either one of the end chains of classical rod-like molecules, lead to asymmetric compounds [46,50–56]. It is worth noting that the nature of the spacer connecting the perfluorinated tail to the rigid core, can govern the potential smectogenic character of the mesogen [57–60]. However, comparatively little attention has been devoted to incorporating fluoroalkyl tails bridged with short methylene segments ($x < 3$) into any kind of fluorinated mesogens [29,34,61,62].

We have very recently developed a novel architecture of fluorinated polymers forming liquid crystalline phases from 2-vinylcyclopropanes [63]. Among various cyclic monomers [64], 2-vinylcyclopropanes [65] are of interest because they easily polymerize by a free radical ring opening mechanism thanks to the release of the cyclopropane ring strain [66–68]. Furthermore, the presence of bulky substituents on the ring can limit the increase in conformational freedom during polymerization, thereby resulting in a reduced contraction of free volume [67]. In consequence of these particular features, vinylcyclopropanes undergo a little volume shrinkage upon ring opening polymerization [64,65], and their polymers appear to be candidate materials for coating films, fillings, curing resins in which applications a careful control of the bulk and surface properties of the polymer is a demanding requirement. Introduction of fluoro-substituents can additionally impart low energy surface properties to the polymer films through enriching the surface of orderly assembled perfluorinated chain segments.

In this work we have prepared new families of poly(vinylcyclopropane)s from different monomers containing varied fluorinated side groups (Fig. 1). The principal objective was to confirm the capability of such new polymer structures to form thermotropic mesophases as a function of the mesogenic character of the fluorinated groups. Therefore, the effects of chemical variations of the fluorinated vinylcyclopropane monomer on the mesophase structure and transition temperatures were studied, including changes in the length of the perfluorinated chain (p) and the alkyl chain spacer (m and n). Co-polymerization with not fluorinated vinylcyclopropane was also exploited to dilute the

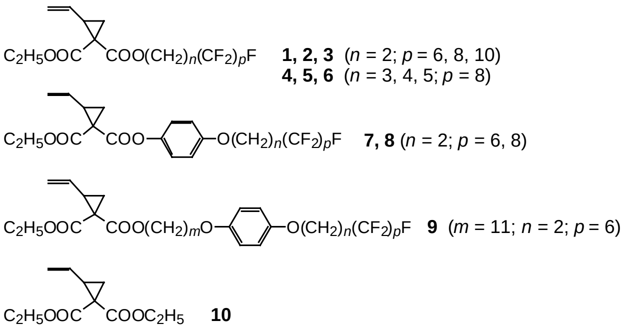

Fig. 1. Structures of the vinylcyclopropane monomers **1–10** synthesized and polymerized.

fluorinated repeat unit along the macromolecular chain and influence the mesophase behavior.

The surface structure and properties of these fluorinated poly(vinylcyclopropane)s seem to be of special interest and will be presented elsewhere.

2. Results and discussion

2.1. Synthesis

Several new vinylcyclopropane monomers **1–9** were prepared that contained different, regularly varied fluorinated side groups (Fig. 1). Thus, the effects of diverse chemical variations in the fluorinated vinylcyclopropane units could be assessed. According to this approach, monomers **1–3** consisted of a 2-(perfluoroalkyl)ethyl chain ($n = 2$) in which the fluorinated segment was lengthened ($p = 6$, 8, or 10). Monomers **4–6** comprised a same perfluorooctyl segment ($p = 8$) that was connected to an alkylene segment of varying length ($n = 3, 4$, or 5). Vinylcyclopropanes **7** and **8** ($n = 2$; $p = 6$ and 8, respectively) possessed an elongated side group by incorporation of a phenyl ring, that was further spaced by an additional alkylene segment in monomer **9** ($m = 11$).

The fluorinated vinylcyclopropane monomers **1–9** were synthesized following one same general reaction pathway (Fig. 2), in which a key intermediate was 1,1-diethoxycarbonyl-2-vinylcyclopropane (**10**). This was prepared by reaction of *trans*-1,4-dibromobutene with the diethyl malonate sodium salt and then selectively hydrolyzed [68,69] to yield the corresponding monocarboxylic acid **11**. On the other hand, different alcohols and phenols bearing the fluorinated chain had been prepared following a sequential reaction scheme that is outlined in Fig. 3. Intermediate **10** is actually a vinylcyclopropane monomer in itself and was used for the preparation of co-polymers poly(**3**-*co*-**10**) with variable contents of fluorinated units **3**.

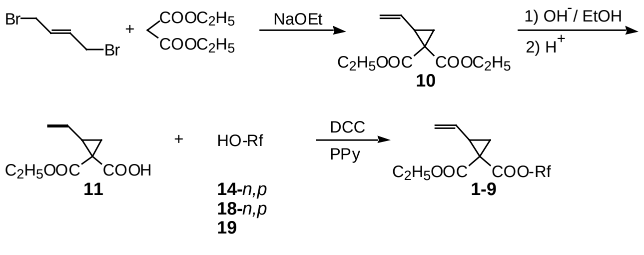

Fig. 2. Reaction scheme for the synthesis of the fluorinated vinylcyclopropanes **1–9**.

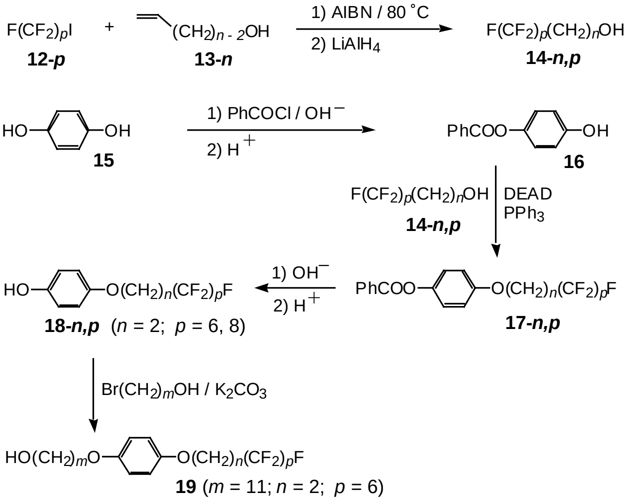

Fig. 3. Reaction scheme for the synthesis of the fluorinated alcohols **14-*n,p*** and **19** and phenols **18-*n,p***.

The monomers were free radically polymerized with α,α'-azobis(isobutyronitrile) (AIBN) in bulk or in trifluorotoluene solution at 60 or 65 °C (polymerization yields 60–85%). The resulting polymers were typically insoluble in common organic solvents but soluble in Cl_2FCCF_2Cl or trifluorotoluene/Cl_2FCCF_2Cl mixtures, and their molar masses could not be fully characterized. Only poly(**10**) and poly(**3**-*co*-**10**)b,c containing high proportions of not fluorinated **10** units were soluble, for instance in chloroform or tetrahydrofuran. The two co-polymers had $M_n = 38\,000$ and 18 000 g mol^{-1}, $M_w/M_n = 2.02$ and 1.73, respectively.

It is documented [66] that vinylcyclopropanes containing electron-withdrawing and radical-stabilizing groups easily undergo radical ring opening polymerization yielding polymers consisting predominantly, though not exclusively, of 1,5-linear structures (Fig. 4, path A). Isomer cyclobutane-ring structures have also been shown to form [66], probably by recyclization of the propagating ring-opened radical (Fig. 4, path C). The concomitant occurrence of such linear and cyclic repeat units was confirmed by our previous investigations of the polymerization of fluorinated vinylcylopropanes [63]. Therefore, the supposed homopolymerization of monomers **1–9** (and **10**) led in effect to co-polymers (Fig. 5) comprising both types of isomer repeat units. The relative proportions of linear units (z) and cyclic units ($1-z$) were evaluated from the integrated areas of the ^{1}H NMR signals at 5.5 ppm (–CH=CH–), 2.3 ppm ($-C\underline{H}_2-CH=CH-C\underline{H}_2-$) and 1.6–2.2 ppm (cyclobutane ring) (Tables 1–4). It was found that z depended considerably on the structure of the

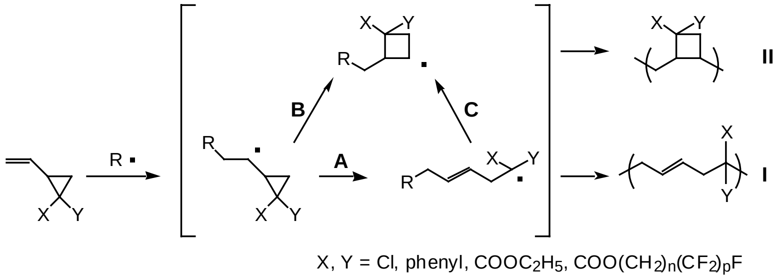

Fig. 4. Mechanisms for the formation of linear and cyclic repeat units in the free radical ring opening polymerization of vinylcylopropanes (after [66]).

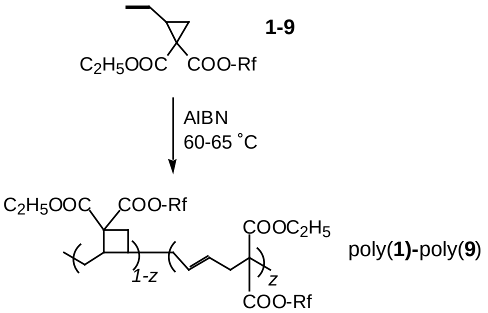

Fig. 5. Free radical ring opening polymerization scheme for the preparation of fluorinated poly(vinylcyclopropane)s poly(**1**)–poly(**9**).

fluorinated substituents on the cyclopropane ring. While stronger electron withdrawing side groups appeared to direct the polymerization preferably towards the formation of the cyclobutane repeat unit, e.g. $z = 0.10$ in poly(**1**), weaker electron withdrawing side groups led to the predominant formation of the linear repeat unit, e.g. $z = 0.80$ in poly(**10**). However, this effect was mitigated by the steric hindrance of the fluorinated side chains which by contrast would rather favour the formation of the cyclic e.g. $z = 0.48$ in poly(**3**). Such repeat units would in fact more easily accommodate the bulky perfluorinated segments along the polymer backbone. This is consistent with the results obtained in the polymerization of vinylcylopropane monomers containing large adamantanyl side groups [67].

By assuming that in the formation of the co-polymers poly(**3**-*co*-**10**) the two different co-monomer species could follow the same propagation mechanisms as in the corresponding "homopolymers", the repeat units from **10** would be preferentially linear, whereas those from **3** would be mainly cyclic, as schematically shown in Fig. 6.

2.2. Mesophase behavior

Each fluorinated poly(vinylcyclopropane) sample exhibited thermotropic mesophase behavior (Tables 1–4). No

Table 1
Physico-chemical characterization of the poly(vinylcylopropane)s containing different (perfluoroalkyl)ethyl side groups ($n = 2$)

Polymer[a]	p	z[b]	T_g[c] (°C)	Mesophase behavior			
				T_i[c] (°C)	ΔH_i[c] (J g^{-1})	Structure	d[d] (±0.1 Å)
Poly(**1**)	6	0.10	64	179	6.0	SmA_d	24.9
Poly(**2**)	8	0.40	89	186	7.9	SmA_d	28.4
Poly(**3**)	10	0.48	78	187	6.7	SmB_d, SmA_d[e]	31.7

[a] Prepared in trifluorotoluene solution (AIBN, 60 °C).
[b] Content of linear units, by NMR.
[c] Glass transition temperature and isotropization temperature (and enthalpy), by DSC.
[d] Smectic layer periodicity, by WAXD.
[e] Smectic-smectic transition at 118 °C ($\Delta H = 0.7$ J g^{-1}).

Table 2
Physico-chemical characterization of the poly(vinylcylopropane)s containing different (perfluorooctyl)alkyl side groups ($p = 8$)

Polymer[a]	n	z[b]	T_g[c] (°C)	Mesophase behavior			
				T_i[c] (°C)	ΔH_i[c] (J g^{-1})	Structure	d[d] (±0.1 Å)
Poly(**4**)	3	0.58	40	146	4.4	SmA_d	29.6
Poly(**5**)	4	0.53	36	113	5.2	SmA_d	30.5
Poly(**6**)	5	0.76	34	98	2.9	SmA_d	31.9

[a] Prepared in bulk (AIBN, 65 °C).
[b] Content of linear units, by NMR.
[c] Glass transition temperature and isotropization temperature (and enthalpy), by DSC.
[d] Smectic layer periodicity, by WAXD.

Table 3
Physico-chemical characterization of the poly(vinylcylopropane)s containing different (perfluoroalkyl)ethyl side groups ($n = 2$) without or with alkylene spacer ($m = 11$)

Polymer[a]	p	z[b]	T_g[c] (°C)	Mesophase behavior			
				T_i[c] (°C)	ΔH_i[c] ($J\,g^{-1}$)	Structure	d[d] (±0.1 Å)
Poly(**7**)	6	0.81	48	200	13.0	SmA_d	29.3
Poly(**8**)	8	0.81	46	205	15.1	SmA_d	33.4
Poly(**9**)	6[e]	0.36	21	81	4.5	SmA_d	58.2

[a] Prepared in bulk (AIBN, 65 °C).
[b] Content of linear units, by NMR.
[c] Glass transition temperature and isotropization temperature (and enthalpy), by DSC.
[d] Smectic layer periodicity, by WAXD.
[e] With alkylene spacer ($m = 11$).

Table 4
Physico-chemical characterization of the co-poly(vinylcylopropane)s containing fluorinated ($n = 2$; $p = 10$) and not fluorinated side groups

Polymer[a]	**3**[b] (mol%)	z[c] (mol%)	T_g[d] (°C)	Mesophase behavior			
				T_i[d] (°C)	ΔH_i[d] ($J\,g^{-1}$)	Structure	d[e] (±0.2 Å)
Poly(**3**-*co*-**10**)a	50	0.50	35	173	8.2	SmA_1	26.2
Poly(**3**-*co*-**10**)b	40	0.60	35	168	10.8	SmA_1	26.0
Poly(**3**-*co*-**10**)c	30	0.80	35	140	9.6	SmA_1	26.0
Poly(**10**)	0	0.80	33	–	–	–	–

[a] Prepared in trifluorotoluene solution (AIBN, 60 °C).
[b] Content of fluorinated side groups in the co-polymer, by NMR.
[c] Content of linear repeat units, by NMR.
[d] Glass transition temperature and isotropization temperature (and enthalpy), by DSC.
[e] Smectic layer periodicity, by WAXD.

evidence of partial crystallinity was detected by differential scanning calorimetry (DSC) or wide angle X-ray diffraction (WAXD) analyses, and the mesophases formed directly above the glass transition temperature of the polymer. The glass transition temperatures were typically higher than room temperature ($30\,°C < T_g < 90\,°C$), with the only exception of poly(**9**) ($T_g = 21\,°C$). In this polymer the long alkylene spacer segment in the side groups probably acted as an internal plasticizer. Thus, in the latter sample the mesophase was present at room temperature, while in all the others it remained frozen in the glassy state at room temperature. Generally speaking, the mesophase was very persistent, the highest isotropization temperature ($T_i = 205\,°C$) and the widest existence range ($T_i - T_g = 159\,°C$) being detected for poly(**8**). However, the details of the mesophase behavior of the polymers depended on their chemical structure and on the chemical composition of the co-polymers.

Polymers poly(**1**)–poly(**3**) presented a consistently high T_i that slightly rose in passing from the sample with a short perfluorinated tail ($p = 6$) to the sample with a long perfluorinated tail ($p = 10$) (Table 1). Furthermore, while there was one mesophase (SmA_d) in poly(**1**) and poly(**2**), poly(**3**) exhibited two mesophases (SmB_d and SmA_d) in a sequence (Fig. 7). Therefore, lengthening the perfluorinated segment enhanced the mesogenic character of the side groups and facilitated their in-plane correlation, thereby permitting an efficient assembling in an ordered mesophase. On the other hand, polymers poly(**2**) and poly(**4**)–poly(**6**) presented one mesophase (SmA_d), for which T_i progressively decreased with increasing length ($n = 2$–5) of the alkylene segment in the (perfluorooctyl)alkyl side group (Table 2). This finding shows that, for a given length of the perfluorinated tail ($p = 8$), insertion of longer hydrocarbon spacers depresses the tendency to form mesophases of the semifluorinated side groups. This argument was further supported by evaluations of the isotropization enthalpy (ΔH_i) that gradually decreased with increasing number n from 7.9 to 2.9 $J\,g^{-1}$ (Table 2). Elongation of the side groups of polymers poly(**7**) and poly(**8**) by incorporation of a phenyl ring resulted in a significant rise of T_i up to about 200 °C (Table 3). In fact, an increase in the axial ratio (length over breadth) of the side groups improved their ability to stabilize a mesophase by favoring intermolecular interactions through the phenyl rings. By contrast, this positive contribution was offset by the long spacer segment ($m = 11$) in poly(**9**) that significantly reduced the effective axial ratio of the more flexible side groups with depression of T_i (down to 81 °C).

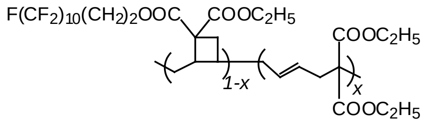

Fig. 6. Simplified structure of the co-poly(vinylcyclopropane)s poly(**3**-*co*-**10**).

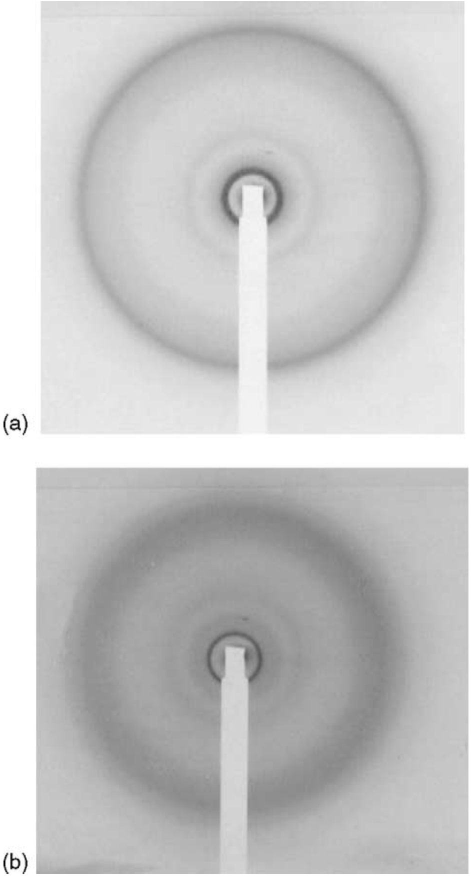

Fig. 7. Powder WAXD patterns of poly(**3**): SmB_d at 40 °C (a) and SmA_d at 130 °C (b).

The mesogenic tendency of the long perfluorinated chain ($p = 10$) was not disrupted in the co-polymers poly(**3**-*co*-**10**) possessing significant contents of not fluorinated **10** units (Table 4). Upon dilution of the fluorinated **3** groups, T_i was lowered with respect to poly(**3**) but was nevertheless as high as 140 °C for poly(**3**-*co*-**10**)c containing 70 mol% non-mesogenic **10** units.

We have previously noted [63,70] that the formation of thermotropic mesophase(s) in polymers simply incorporating perfluoroalkylethyl chains is somewhat surprising, in that it has been previously reported in a structurally related polyacrylate only [29]. As mentioned, the mesogenic capability of fluorocarbon chains is attributed to the rigid-rod-like character of their helical conformation in combination with their immiscibility with other molecular constituents [71]. As a net effect, distinct molecular sub-layers are formed that would result in an ordered assembly in a mesophase, normally smectic. We also explain the onset of liquid crystallinity in poly(vinylcylopropane)s poly(**1**)–poly(**3**) by the strong intramolecular phase separation of the fluorocarbon side groups from the hydrocarbon polymer backbone. While this phenomenon seems to be amplified in poly(**7**) and poly(**8**) comprising mutually immiscible aliphatic–aromatic–fluoroaliphatic constituents, it would be less effective in poly(**4**)–poly(**6**) owing to the improved miscibility of the aliphatic–fluoroaliphatic side groups with the aliphatic macromolecular chain.

It is also worth noting that the present poly(vinylcyclopropane)s gave rise to mesophase behavior despite the fact that the fluorinated side groups were diluted along the polymer chain, even in the "homopolymer" samples, viz. one fluorinated side group per five backbone carbon atoms in the 1,5-opened unit. This is at variance with most common liquid crystalline polymers, specifically polysiloxanes and poly(meth)acrylates, in which normally the mesogens are much more concentrated, a side group being present per two backbone atoms [72]. In one other example of liquid crystalline poly(vinylcyclopropane)s, two typical cholesteryl or biphenyl mesogens were present per repeat unit [73], which easily accounts for the mesophase behavior of such polymers.

2.3. Mesophase structure

The structure and the structural parameters of the mesophase(s) of the polymers were determined by WAXD as function of temperature. In any case the mesophase was found to be smectic, even though the details of the packing in the smectic layers depended on the chemical structure of the polymers and co-polymers. The lower temperature mesophase of poly(**3**) ($T < 115$ °C) was a hexatic smectic phase in which the side groups were locally ordered over a pseudo-hexagonal lattice ($a = 6.9$ Å) (Fig. 7a). The layer periodicity $d = 31.7$ Å was much longer than the calculated length of the repeat unit in its fully extended conformation ($L = 25.6$ Å). Consistently, the average surface per side group ($S = 41$ Å^2) was large enough to permit an antiparallel arrangement of the side groups orthogonal to the layer planes in a partly interdigitated bilayer structure, such as the SmB_d phase ($d/L = 1.24$). In the high temperature range, the mesophase ($d = 31.7$ Å) exhibited no in-plane correlation of the side groups, according to the onset of a lower order SmA_d phase (average intermolecular distance $D = 5.9$ Å) (Fig. 7b). The same kind of low order smectic mesophase was detected in poly(**1**) and poly(**2**) ($d/L = 1.21$ and 1.23, respectively; $D = 6.0$ Å), which confirms that the short perfluorinated chain segments had a weaker mesogenic character than the longer analogue. Poly(vinylcyclopropane)s poly(**4**)–poly(**9**) also formed one SmA_d phase over the entire mesophase range. While the side groups were more strongly interdigitated in poly(**4**)–poly(**8**) ($d/L = 1.17$–1.21; $D = 5.9$–6.0 Å), they were little overlapped in poly(**9**) ($d/L = 1.46$; $D = 5.9$ Å). Accordingly, the occurrence of such mesophase structure appears to be a common feature for the present fluorinated polymers. However, the co-polymers poly(**3**-*co*-**10**) gave rise to a fully interdigitated (SmA_1) smectic phase ($d/L = 1.01$; $D = 5.8$ Å. Therefore, by co-polymerization not only was the transition temperature of the mesophase changed but its detailed structure was also modified with respect to poly(**3**).

The terminal CF_3 group of rod-like fluorocarbon chains is rather bulky with a Van der Waals volume of the equivalent

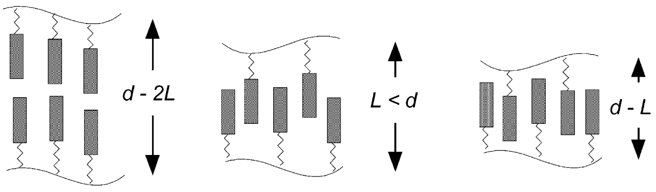

Fig. 8. Schematic arrangements of the polymer side groups in different smectic phases: double layer (left), interdigitated (center), and monolayer (right). The mesogenic groups are shown with a spacer and rigid-rod-like unit.

hemisphere of 42.6 Å^3 (compare with 16.8 Å^3 for the CH_3 group) [74,75] and a cross-section surface of 23 Å^2 as estimated by molecular models. Therefore, there would exist significant steric hindrance for two fluorinated tails to overlap and to order within the layers of an interdigitated smectic phase, particularly in densely crowded polymers such as poly(siloxane)s or poly(acrylate)s. Conversely, in these latter systems an efficient space filling could be achieved by tilting the fluorinated side groups in an end-to-end arrangement of a double layer smectic structure [70]. By contrast, the much wider spread of the fluorinated side groups **1**–**9** along the polymer backbone of the present poly(vinylcyclopropane)s facilitated their ordering in a partly overlapped arrangement with a greater intermolecular distance *D*. In the co-polymers the mesogenic fluorinated side groups **3** were even more spaced apart from each other by non-mesogenic side groups **10** along the macromolecular chain and could fully interdigitate in an antiparallel structure (Fig. 8).

Within any smectic phase the layer periodicity *d* remained completely unaffected by varying temperature throughout the whole mesophase range, as is illustrated in Fig. 9 for poly(**1**)–poly(**3**). Moreover, it increased according to an essentially linear trend with increasing number *p* of CF_2 moieties in the perfluorinated chain segment (Fig. 10) or number *n* of CH_2 moieties in the alkylene chain spacer (Fig. 11). These findings suggest that the side groups were indeed ordered orthogonal to the smectic planes and adopted one overall same conformation independent of temperature. The successive increments of either *n* or *p* simply resulted in lengthening the smectic layer spacing. A helical conformation (span 2.59 Å) was assumed for the perfluorinated chain segments, analogous to other such systems [76].

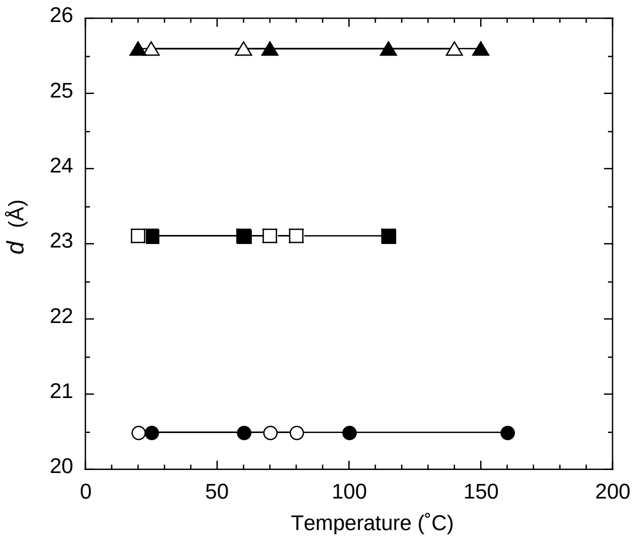

Fig. 9. Temperature dependence of the smectic layer periodicity *d* for poly(vinylcyclopropane)s on heating: poly(**1**) (●), poly(**2**) (■), and poly(**3**) (▲) (open symbols refer to the cooling cycles).

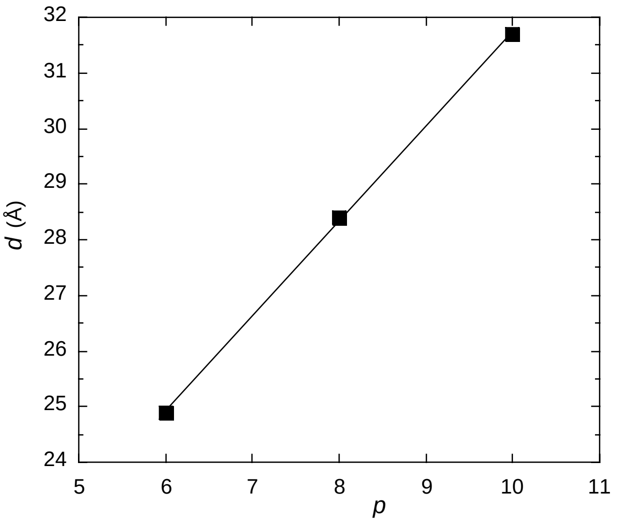

Fig. 10. Variation of the smectic layer periodicity *d* for poly(vinylcyclopropane)s poly(**1**)–poly(**3**) with number *p* of CF_2 groups.

3. Experimental

3.1. Intermediates

2-(Perfluoroalkyl)ethanols **14-*n*,*p*** ($n = 2$; $p = 6$, 8, or 10) were commercially available (Fluorochem, 97%).

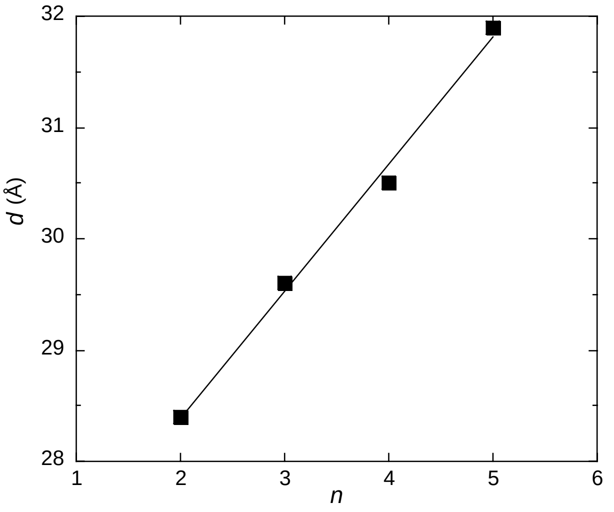

Fig. 11. Variation of the smectic layer periodicity *d* for poly(vinylcyclopropane)s poly(**2**) and poly(**4**)–poly(**6**) with number *n* of CH_2 groups.

2-(Perfluorooctyl)alkanols **14-*n,p*** ($n = 3$, 4, or 5; $p = 8$) were synthesized according to a general procedure that is described here in detail for **14-*4,8*** (Fig. 3).

4-(Perfluorooctyl)-butan-1-ol (**14-*4,8***): A mixture of 37.17 g (68.0 mmol) of 7.48 g (128.9 mmol) of 2-buten-1-ol (**13-*4***) and perfluorooctyl iodide (**12-*8***) was heated to 80 °C under nitrogen. An amount of 0.16 g (0.97 mmol) of AIBN was then added in small portions over 45 min, and the reaction mixture was kept at 80 °C for an additional 5 h. After cooling to 40 °C, the mixture was evaporated to dryness under nitrogen. The solid residue was dissolved in 350 ml of anhydrous Et_2O and added dropwise to a suspension of 136 ml (136 mmol) of $LiAlH_4$ 1 M in Et_2O at room temperature under nitrogen. The mixture was kept under vigorous stirring for 16 h and then slowly hydrolyzed with 14 ml of water, 18 ml of 10% NaOH and finally water. The precipitate was filtered off and the solvent was evaporated under vacuum. The solid residue was purified by repeated sublimations under vacuum at 40 °C leading to 19.10 g of pure **14-*4,8*** (yield 57%); mp 42–45 °C.

^1H NMR ($CDCl_3$): δ (ppm)$=1.6-1.8$ (5H, $(CH_2)_2+CH_2O\underline{H}$), 2.1 (2H, $C\underline{H}_2CF_2$), 3.7 (2H,$C\underline{H}_2OH$).

FT-IR (KBr): $\bar{\nu}\,(cm^{-1}) = 3320$ (ν O–H), 2950–2882 (ν C–H aliphatic), 1440 (δ C–H), 1206 (δ O–H), 1150 (ν C–F), 660 (ω CF_2).

Phenols **18-*n,p*** ($n = 2$; $p = 6$ or 8) and alcohol **19** ($m = 11$; $n = 2$; $p = 6$) were synthesized following a general procedure that is described here in detail for **19** (Fig. 3).

4-Hydroxyphenyl benzoate (**16**): 19.00 g (0.13 mol) of benzoyl chloride was added in small portions over 1 h to a solution of 20.08 g (0.18 mol) of hydroquinone in 300 ml of deaerated water and 7.69 g (0.14 mol) of KOH under nitrogen at 0 °C. The reaction mixture was then stirred at 0 °C for an additional 3 h and then poured into 400 ml of $NaHCO_3$ saturated water. The precipitate formed was filtered off, washed with water to neutrality, dried under vacuum and finally twice crystallized from ethanol/water (70:30 v/v) giving 14.2 g of pure **16** (yield 34%): mp 163–165 °C.

^1H NMR (DMSO-d_6): δ (ppm) $= 6.9$ (2H, aromatic $3'$ and $5'$), 7.1 (2H, aromatic $2'$ and $6'$), 7.6 and 7.7 (3H, aromatic 3–5), 8.2 (2H, aromatic 2 and 6), 9.5 (1H, OH).

FT-IR (KBr): $\bar{\nu}$ (cm^{-1}) $= 3450$ (ν O–H), 3100–3050 (ν C–H aromatic), 1714 (ν C=O), 1280–1210 (ν Ar–OC=O).

4-[2-(Perfluorohexyl)ethoxy]phenol (**18-*2,6***): A solution of 9.00 g (0.042 mol) of **16**, 11.01 g (0.042 mol) of triphenylphosphine (PPh_3) and 15.12 g (0.042 mol) di-2-(perfluorohexyl)ethan-1-ol (**14-*2,6***) in 250 ml of anhydrous Et_2O was stirred at room temperature for 1 h. An amount of 8.00 g (0.046 mol) of diethyl azodicarboxylate (DEAD) was then added and the reaction mixture was kept under vigorous stirring for an additional 96 h. The precipitate formed was then filtered off and the solution was evaporated to dryness under vacuum. The crude residue was crystallized twice from methanol giving 3.41 g (yield 15%) of (**17-*2,6***): mp 89–91 °C.

Afterwards, 3.34 g (5.97 mmol) of **17-*2,6*** and 0.95 g (0.016 mol) of KOH were dissolved in 20 ml of water and 50 ml of ethanol. The solution was then heated to reflux for 7 h, cooled down and acidified with 10% HCl to pH ~ 2. The precipitate formed was filtered off and dried under vacuum giving 2.62 g (yield 97%) of pure **18-*2,6***: mp 77–80 °C.

^1H NMR ($CDCl_3$) δ (ppm) $= 2.6$ (2H, CH_2CF_2), 4.2 (2H, $C\underline{H}_2OPh$), 4.6 (1H, OH), 6.8 (4H, aromatic).

FT-IR (KBr): $\bar{\nu}(cm^{-1}) = 3580–3400$ (ν O–H), 3100–3050 (ν C–H aromatic), 2930–2850 (ν C–H aliphatic), 1290–1200 (ν Ar–OR), 1360–1100 (ν CF_2 and ν CF_2–CF_3), 650 (ω CF_2).

11-[4-(2-Perfluorohexylethoxy)phenyl-1-oxy]-undecan-1-ol (**19**): A suspension of 2.49 g (5.46 mmol) of **18-*2,6***, 1.14 g (8.25 mmol) of dry K_2CO_3 and 50 ml of anhydrous 2-butanone was stirred at room temperature. An amount of 1.55 g (6.17 mmol) of 11-bromoundecan-1-ol in 50 ml of anhydrous 2-butanone was then added dropwise over 2 h and the mixture was heated to reflux for 30 h. The solid was filtered off and the solution was evaporated to dryness under vacuum. The solid residue was crystallized twice from methanol giving 2.59 g (yield 76%) of pure **19**: mp 86–89 °C.

^1H NMR ($CDCl_3$): δ (ppm) $= 1.5$ (18H, $9CH_2$), 2.6 (2H, CH_2CF_2), 3.6 (2H, $C\underline{H}_2OPh$), 3.9 (2H, $C\underline{H}_2OH$), 4.2 (2H, $C\underline{H}_2OPh$), 6.8 (4H, aromatic).

FT-IR (KBr): $\bar{\nu}\,(cm^{-1}) = 3580–3400$ (ν O–H), 3200–3050 (ν C–H aromatic), 2930–2850 (ν C–H aliphatic), 1290–1200 (ν Ar–OR), 1360–1100 (ν CF_2 and ν CF_2–CF_3), 650 (ω CF_2).

3.2. Monomers

1,1-Diethoxycarbonyl-2-vinylcyclopropane (**10**) (bp 69–72 °C/0.5 mm) was prepared and then selectively hydrolyzed to the monocarboxylic acid, 1-carboxy-1-ethoxycarbonyl-2-vinylcyclopropane (**11**), according to literature [66,69] (Fig. 2).

The fluorinated monomers **1**–**9** were synthesized following the same general procedure that is here described for **3** as a typical example (Fig. 2).

1-Ethoxycarbonyl-1-(2-perfluorodecyl)ethoxycarbonyl-2-vinylcyclopropane (**3**): 3.85 g (0.07 mol) of KOH was added in small portions to a solution of 15.05 g (0.07 mol) of **10** in 25 ml of ethanol at −5 °C. The reaction was then let to proceed at room temperature for 12 h. The solution was concentrated to small volume and acidified with 10% HCl to pH ~ 2.5. The organic phase separated was dried over Na_2SO_4 and then evaporated to dryness, giving 11.50 g (90% yield) of pure **11** as viscous oil.

Afterwards, 5.02 g (25.0 mmol) of *N,N′*-dicyclohexylcarbodiimide (DCC) in 15 ml of anhydrous dichloromethane was added dropwise to a solution of 4.62 g (25.0 mmol) of **11**, 0.02 g (1.1 mmol) of 4-pyrrolidinopyridine (PPy) and 12.86 g (23.0 mmol) of **14-*2,10*** in 16 ml of anhydrous dichloromethane under dry nitrogen atmosphere at 0 °C. The reaction was let to proceed for an additional 2 h at 0 °C and then for 2 days at room temperature. The precipitate was filtered off and the organic phase was washed with 5% HCl, 5% $NaHCO_3$, water, dried over Na_2SO_4 and finally evaporated to dryness. The crude residue was purified by liquid chromatography on silica gel with ethyl acetate/hexane (2/3 v/v) as eluent leading to 5.97 g (yield 36%) of pure **3** as a colorless viscous liquid.

^{1}H NMR ($CDCl_3$): $\delta = 1.2$ ppm (3H, CH_3), 1.6–1.8 (2H, CH_2 cyclopropane), 2.3–2.7 (3H, CHcyclopropane+ CH_2CF_2), 4.2 (2H, $COOCH_2$), 4.4 (2H, $COOC\underline{H}_2CH_2CF_2$), =CH).

FT-IR (liquid film): $\bar{\nu}$ (cm^{-1}) = 3092 and 2964 (ν C–H vinyl and aliphatic), 1730 (ν C=O), 1640 (ν C=C vinyl), 1372 (δ C–H cyclopropane), 652 (ω CF_2).

^{19}F NMR ($CDCl_3/CF_3COOH$): $\delta = -5$ (3F, CF_3), -37 (2F, CH_2CF_2), -46 to -49 (14F, 7CF_2), -51 (2F, CF_2).

Anal. calcd. for $C_{21}H_{15}F_{21}O_4$: C, 34.52; H, 2.05; F, 54.66. Found: C, 34.96; H, 2.15; F, 54.5.

3.3. Polymerization

The polymers were prepared following the same procedure that is here described for poly(**3**) as a typical example.

Poly(vinylcyclopropane) poly(**3**): 0.58 g (0.68 mmol) of **3** and 5 mg (0.02 mmol) of AIBN were introduced into a Pyrex vial. After three freeze–thaw pump cycles, the vial was sealed under vacuum and the polymerization was let to proceed for 29 h at 65 °C. The polymer was then precipitated in methanol and purified by repeated precipitations from Cl_2FCCF_2Cl in methanol. An amount of 0.41 g (yield 71%) of poly(**3**) was obtained as white powder.

^{1}H NMR ($Cl_2FCCF_2Cl + CDCl_3$): δ= 1.2–1.4 (3H, CH_3), 1.5–3.0 (7.1H, $C\underline{H}_2CH{=}CHC\underline{H}_2$+cyclobutane + CH_2CF_2), 4.2–5.0 (4H, $COOCH_2$), 5.5 (0.9H, CH=CH).

FT-IR (polymer film): $\bar{\nu}$ (cm^{-1}) = 2984 (ν CH aliphatic), 1730 (ν C=O), 652 (ω CF_2).

^{19}F NMR ($Cl_2FCCF_2Cl/CF_3COOH + CDCl_3$): $\delta = -5$ (3F, CF_3), -38 (2F, CH_2CF_2), -45 to -50 (14F, 7CF_2), -52 (2F, CF_2).

3.4. Characterization

NMR (^{1}H, ^{13}C, ^{19}F) spectra were recorded with a Varian Gemini VXR 300 spectrometer (operating at 299.9, 75.4, and 282.2 MHz, respectively).

Size exclusion chromatography (SEC) was carried out with a Jasco PU-1580 liquid chromatograph equipped with four PL gel 5 mm Mixed-C columns, a Jasco 830-RI refractive index detector and a Perkin–Elmer LC75 UV detector. Monodisperse poly(styrene) standard samples were used for calibration.

Differential scanning calorimetry measurements were performed with a Mettler DSC-30 instrument (10 °C min^{-1}). The phase transition temperatures were taken at the maximum temperature in the DSC enthalpic peaks of the heating cycles. The glass transition temperature was taken as the half-devitrification temperature.

Wide-angle X-ray diffraction experiments were performed on powder samples with an especially designed pinhole camera using Ni-filtered Cu Kα beam ($\lambda = 1.54$ Å), under vacuum at various temperatures with an accuracy of 1 °C.

4. Conclusions

Chemical variations, including variations of the molecular framework of the repeat unit in the homopolymers and chemical composition in the co-polymers, can effectively modify the mesophase characteristics of fluorinated poly(vinylcyclopropane)s. These systems may in fact represent a novel architecture of liquid crystalline polymers that form smectic mesophases, the number and nature of which depend on the molecular parameters (m, n, or p). Any anticipated influence of the fine structure of the polymer backbone on the mesophase behavior and properties remains to be ascertained, especially when devising such polymers for practical application. The mesophase order of the bulk might be retained at the surface of polymer films therefrom, which in turn can produce low surface energy coatings.

Acknowledgements

The authors thank Prof. E. Chiellini, University of Pisa, for helpful discussions. Financial support from the EU (Contract G5RD-2001-00554 "Dentalopt") and the Italian MIUR (PRIN 2001-03-4479) is gratefully acknowledged.

References

[1] J. Wang, G. Mao, C.K. Ober, E.J. Kramer, Macromolecules 30 (1997) 1906;
For more comprehensive texts see: J. Scheirs (Ed.), Modern Fluoropolymers, Wiley, Chichester, 1997;
G. Hougham (Ed.), Fluoropolymers, Kluwer Academic, New York, 1999;
D.W. Smith (Ed.), Fluoropolymer 2000, EPS Publication, Hattiesburg, 2000; in: Proceedings of the Fluorine in Coatings V Conference, Paint Research Association, Teddington, 2003.

[2] M. Yamabe, Makromol. Chem. Macromol. Symp. 64 (1992) 11.

[3] C. Pitois, S. Vukmirovic, A. Hult, D. Wiesmann, M. Robertsson, Macromolecules 32 (1999) 2903.

[4] R.F. Brady, Prog. Org. Coat. 35 (1999) 31.

[5] B.C. Auman, D.P. Higley, K.V. Schere, E.F. McCord, W.H. Shaw, Polymer 36 (1995) 651.

[6] I. McCulloch, H. Yoon, J. Polym. Sci. Part A: Polym. Chem. 33 (1995) 1177.

[7] J. Gaynor, G. Scheueneman, N. Murata, J. Polym. Sci. 31 (1993) 1645.

[8] T. Maruno, K. Nakamura, N. Murata, Macromolecules 29 (1996) 2006.

[9] G. Ajroldi, Chim. Ind. (Milan) 79 (1997) 484.

[10] R.F. Brady Jr., J.R. Griffith, K.S. Love, D.E. Field, J. Coat. Technol. 59 (1987) 755.

[11] R.F. Brady Jr., J. Coat. Technol. 72 (2000) 45.

[12] E. Passaglia, M. Aglietto, F. Ciardelli, B. Mendez, Polym. J. 26 (1994) 1118.

[13] J. Höpken, M. Möller, Macromolecules 25 (1992) 1461.
[14] L.M. Wilson, A.C. Griffin, Macromolecules 27 (1994) 1928.
[15] R.V. Honeychuck, T. Ho, K.J. Wynne, R.A. Nissan, Chem. Mater. 5 (1993) 1299.
[16] B. Boutevin, G. Caporiccio, F. Guida-Pietrasanta, A. Ratsimihety, Macromol. Chem. Phys. 199 (1998) 61.
[17] A.G. Pittman, in: L.A. Wall (Ed.), Fluoropolymers, vol. 25, Wiley, New York, 1972, p. 419. for more recent examples see;
(a) J. Tsibouklis, P. Graham, P.J. Eaton, J.R. Smith, T.G. Nevell, J.D. Smart, R.J. Ewen, Macromolecules 33 (2000) 8460;
(b) E. Casazza, A. Mariani, L. Ricco, S. Russo, Polymer 43 (2002) 1207.
[18] T.M. Chapman, R. Benrashid, K.G. Marra, J.P. Keener, Macromolecules 28 (1995) 331.
[19] T.M. Chapman, K.G. Marra, Macromolecules 28 (1995) 2081.
[20] T. Ho, K.J. Wynne, A. Vu, X. Chen, A.J. Gardella Jr., Polym. Preprints (Am. Chem. Soc., Div. Polym. Chem.) 36 (1) (1995) 67.
[21] J.K. Pike, T. Ho, K.J. Wynne, Chem. Mater. 8 (1996) 856.
[22] G. Mao, J. Wang, S.R. Clingman, C.K. Ober, J.T. Chen, E.L. Thomas, Macromolecules 30 (1997) 2556.
[23] X. Li, L. Andruzzi, E. Chiellini, G. Galli, C.K. Ober, A. Hexemer, E.J. Kramer, D.A. Fischer, Macromolecules 35 (2002) 8078.
[24] M.K. Bernett, W.A. Zisman, J. Phys. Chem. 64 (1960) 1292.
[25] F. Sun, D.G. Castner, G. Mao, W. Wang, P. McKeown, D.W. Grainger, J. Am. Chem. Soc. 118 (1996) 1856.
[26] J.G. Wang, C.K. Ober, E.J. Kramer, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 37 (2) (1996) 815.
[27] M. Muthukumar, C.K. Ober, E.L. Thomas, Science 277 (1997) 1225.
[28] J. Wang, C K Ober, Macromolecules 30 (1997) 7560.
[29] V.V. Volkov, N.A. Platé, A. Takahara, T. Kajiyama, M. Amaya, Y. Murata, Polymer 33 (1992) 1316.
[30] V. Percec, M. Lee, J. Macromol. Sci., Pure Appl. Chem. A29 (1992) 723.
[31] E. Beyou, P. Babin, B. Bennetau, J. Dunogues, D. Teyssie, S. Boileau, J. Polym. Sci., Part A: Chem. Ed. 32 (1994) 1673.
[32] M. Krupers, M. Möller, Macromol. Chem. Phys. 198 (1997) 2163.
[33] F. Bracon, F. Guittard, E. Taffin de Givenchy, A. Cambon, J. Polym. Sci., Part A: Polym. Chem. 37 (1999) 4487.
[34] L. Andruzzi, E. Chiellini, G. Galli, X. Li, S.H. Kang, C.K. Ober, J. Mater. Chem. 12 (2002) 1684.
[35] W. Mahler, D. Guillon, A. Skoulios, Mol. Cryst. Liq. Cryst. Lett. 2 (1985) 111.
[36] C. Viney, R.J. Twieg, T.P. Russel, L.E. Depero, Liq. Cryst. 5 (1989) 1783.
[37] C. Viney, R.J. Twieg, B.R. Gordon, J.F. Rabolt, Mol. Cryst. Liq. Cryst. 198 (1991) 285.
[38] L.M. Wilson, Macromolecules 28 (1995) 325.
[39] M. Napoli, J. Fluorine Chem. 79 (1996) 59.
[40] A.M. Semenov, S.V. Vasilenko, Serv. Phys. JEPT 63 (1985) 70.
[41] C.W. Bunn, E.R. Howells, Nature (London) 174 (1954) 549.
[42] T.P. Russell, J.F. Rabolt, R.J. Twieg, R.L. Siemens, B.L. Farner, Macromolecules 19 (1986) 1135.
[43] D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds.), Handbook of Liquid Crystals, vols. 2A and 2B, Wiley–VCH, Weinheim, 1998.
[44] H.T. Nguyen, G. Sigaud, M.F. Achard, F. Hardouin, K. Twieg, R.J. Betterton, Liq. Cryst. 10 (1991) 389.
[45] H. Liu, H. Nohira, Liq. Cryst. 22 (1997) 217.
[46] B.Q. Chen, Y.G. Yang, J.X. Wen, Liq. Cryst. 24 (1998) 539.
[47] B.Q. Chen, Y.G. Yang, J.X. Wen, Liq. Cryst. 26 (1999) 1135.
[48] E. Taffin de Givenchy, F. Guittard, F. Bracon, A. Cambon, Liq. Cryst. 26 (1999) 1163.
[49] F. Bracon, F. Guittard, E. Taffin de Givenchy, A. Cambon, Liq. Cryst. 26 (1999) 1371.
[50] F. Guittard, P. Sixou, A. Cambon, Liq. Cryst. 19 (1995) 667.
[51] F. Guittard, S. Diele, H. Kruth, G. Pelz, A. Cambon, Liq. Cryst. 21 (1996) 603.
[52] H. Liu, H. Nohira, Mol. Cryst. Liq. Cryst. 302 (1997) 247.
[53] E. Dietzmann, W. Weissflog, Mol. Cryst. Liq. Cryst. 299 (1997) 419.
[54] S. Pensec, F.G. Tournilhac, P. Bassoul, C.J. Durliat, Phys. Chem. B 102 (1998) 52.
[55] D. Lose, S. Diele, G. Pelzl, E. Dietzmann, W. Weissflog, Liq. Cryst. 24 (1998) 707.
[56] J. Ebutt, R.M. Richardson, J. Blackmore, G. Macdonnel, M. Verral, Mol. Cryst. Liq. Cryst. 261 (1995) 549.
[57] F. Guittard, P. Sixou, A. Cambon, Mol. Cryst. Liq. Cryst. 308 (1997) 83.
[58] F. Guittard, E. Taffin de Givenchy, S. Geribaldi, A. Cambon, J. Fluorine Chem. 100 (1999) 85.
[59] F. Guittard, S. Geribaldi, in: R. Glaser, P. Kaszynski, (Eds.), Anisotropic Organic Materials—Approaches to Polar Order, ACS Symposium Series, vol. 798, American Chemical Society, Washington, 2001, p. 180.
[60] F. Geribaldi, F. Guittard, E. Taffin de Givenchy, A. Cambon, Mol. Cryst. Liq. Cryst. 332 (1999) 1.
[61] H. Okamoto, N. Yamada, S. Takenaka, J. Fluorine Chem. 91 (1998) 125.
[62] H. Okamoto, V.F. Petrov, S. Takenaka, Bull. Chem. Soc. Jpn. 72 (1999) 1637.
[63] G. Galli, S. Gasperetti, M. Bertolucci, B. Gallot, F. Chiellini, Macromol. Rapid Commun. 23 (2002) 814.
[64] F. Sanda, T. Endo, J. Polym. Sci. Part A: Polym. Chem. 39 (2001) 265.
[65] N. Moszner, F. Zeuner, T. Volkel, V. Rheinberger, Macromol. Chem. Phys. 200 (1999) 2173.
[66] F. Sanda, T. Takata, T. Endo, Macromolecules 26 (1993) 1818.
[67] J. Sugiyama, N. Kayamori, S. Shimada, Macromolecules 29 (1996) 1943.
[68] V. Alupei, H. Ritter, Macromol. Rapid Commun. 22 (2001) 1349.
[69] N. Moszner, F. Zeuner, V. Rheinberger, Macromol. Rapid Commun. 18 (1997) 775.
[70] L. Andruzzi, F. D'Apollo, G. Galli, B. Gallot, Macromolecules 34 (2001) 7707.
[71] C. Tschierske, J. Mater. Chem. 11 (2001) 2647.
[72] G. Galli, in: H.S. Nalwa (Ed.), Advanced Functional Molecules and Polymers, vol. I, Overseas Publishers Association, Singapore, 2001, p. 271.
[73] I. Cho, K. Chang, Macromol. Rapid Commun. 18 (1997) 45.
[74] D. Seebach, Angew. Chem. Int. Ed. Engl. 29 (1990) 1320.
[75] A. Bondi, J. Phys. Chem. 68 (1964) 44.
[76] J. Wang, C.K. Ober, Liq. Cryst. 26 (1999) 637.