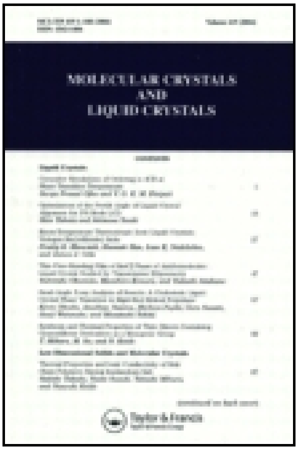

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Bulk and Surface Characterization of Fluorinated Vinyl Cyclopropane/Vinyl Acetate Copolymers

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We prepared new copolymers of a 2-vinyl cyclopropane monomer carrying – $(CF_2)_8F$ *fluorocarbon side chains (VCPF8) and vinyl acetate (VAc). The copolymers formed a partly interdigitated* S_{Ad} *mesophase. Static contact angles* θ *were measured using various wetting liquids, which proved that thin films of the copolymers were both hydrophobic (*$\theta > 110^\circ$ *with water) and lipophobic (*$\theta > 65^\circ$ *with n-hexadecane). The surface tensions* γ_{sv} *of the polymer films were evaluated by two different approaches and resulted to have quite low values (*$\gamma_{sv} < 15\,mJ/m^2$*), even at relatively low contents of fluorocarbon side chains.*

Keywords: copolymer; fluorinated polymer; smectic mesophase; surface energy; vinyl cyclopropane

INTRODUCTION

The incorporation of fluorine in a polymer generally causes the polymer to have a low surface energy potentially leading to low wettability, low friction coefficient and low adhesion. In recent years a number of novel low surface energy fluorinated polymers have been described [1]. However, one critical problem, surface reconstruction,

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still has not been entirely resolved and limits their practical application. This response is mainly attributed to the poor stability of the amorphous fluorinated surface chains, which cannot prevent movement of polar groups to the surface. Long term hydrophobicity may arise however when the fluorinated side chains of a polymer are capable of organizing into a liquid crystalline 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 [2]. Therefore, liquid crystallinity can provide a special means for creating stable, low surface energy polymeric materials for non-stick coating applications [3].

We are interested in developing new architectures of fluorinated polymers based on 2-vinyl cyclopropanes capable of forming liquid crystalline phases [4]. These might be used as materials for coating films and curable resins where a careful control of the bulk and surface properties of the polymer is a necessary requirement, such as in dental applications.

In this work we have prepared new copolymers from a fluorinated 2-vinyl cyclopropane carrying $–(CF_2)_8F$ side chains (VCPF8) with the main goal of preparing low surface energy polymers. We also aimed at confirming the capability of such copolymer structures to form thermotropic mesophases as a function of the chemical composition of fluorinated side groups. While in previous studies we used mehyl methacrylate (MMA) as an electron poor comonomer [5], we used here vinyl acetate (VAc) as an electron rich comonomer.

EXPERIMENTAL PART

Synthesis

The monomer VCPF8 was synthesized according to the literature [6].

The synthesis of copolymer p(VCPF8-*co*-VAc)b is described as a typical copolymerization example: 5.00 g (7.94 mmol) of VCPF8 and 0.59 g (6.85 mmol) of VAc were introduced into a Pyrex glass vial in the presence of 0.045 g (0.27 mmol) of AIBN as a radical initiator. After three freeze-thaw pump cycles the vial was sealed under vacuum, and the polymerization was let to proceed for 8 h at 65°C. The polymer was then precipitated into methanol and purified by repeated precipitations from α,α,α-trifluorotoluene solutions into methanol (13% yield).

^1H NMR ($CDCl_3$): δ (ppm, from TMS) = 5.2–4.9 (0.4H, $C\underline{H}OCOCH_3$), 4.4 (1.2H, $COOC\underline{H}_2CH_2CF_2$), 4.1 (1.2H, $COOC\underline{H}_2CH_3$), 2.7–1.6 (6.8H, CH_2, CH and CH_2 in cycle, $OCOCH_3$, CH_2CF_2), 1.2 (1.8H, $COOCH_2C\underline{H}_3$).

^{19}F NMR ($CDCl_3/CF_2ClCCl_2F$): δ (ppm, from CF_3COOH) = –5 (3F, CF_3), -37 (2F, CH_2CF_2), -46 to -49 and -51 (12F, CF_2).

FT-IR (polymer film): $\bar{\nu}\cdot(\mathrm{cm}^{-1}) = 2982$ (νC–H aliphatic), 1737 (νC=O), 1437 (δC–H cycle), 1240–1150 (νC–O ester, νC–F), 656 (ω CF_2).

Characterizations

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

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC-30 instrument (10°C/min). The mesophase-isotropic liquid or isotropization transition temperature, T_i, was taken as the maximum temperature in the DSC enthalpic peaks. The glass transition temperature, T_g, was set at the half-devitrification temperature.

X-Ray diffraction (XRD) 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.

Contact angle measurements were carried out with a Camtel FT200 goniometer on spin-coated polymer films (ca. 200 nm thickness) that had been previously annealed for 3 h at a temperature 10°C above the respective T_i. *n*-Alkanes (Aldrich) and water (Millipore) were used as wetting liquids.

RESULTS AND DISCUSSION

The fluorinated monomer VCPF8 was homopolymerized and copolymerized with vinyl acetate (VAc) in bulk with free-radical initiation (AIBN at 65°C). Varied comonomer feed mixtures were used, which yielded p(VCPF8-*co*-VAc) copolymers with different contents of fluorinated units VCPF8. The copolymer compositions, as evaluated by ^{1}H NMR, resulted enriched in fluorinated units denoting a higher reactivity of the vinyl cyclopropane monomer with respect to vinyl acetate (Table 1).

The ring opening polymerization of 2-vinyl cyclopropanes (VCP) occurs via a complex mechanism that leads to different repeat units constituted by linear olefin and cyclobutane ring structures (Fig. 1) [7]. In the copolymerization with methyl methacrylate (MMA) a further mechanism is described that generates five- or six-membered rings [8]. It consists in the opening of the VCP ring, followed by

TABLE 1 Composition and Distribution of Repeat Units in p(VCPF8-*co*-VAc) Copolymers

Polymer	yield (wt%)	VCPF8 (mol%) Feed	VCPF8 (mol%) Copol.	x^a	y^a	z^a
p(VCPF8-*co*-VAc)a	28	22	32	0.47	–	0.53
p(VCPF8-*co*-Vac)b	13	54	59	0.69	0.31	–

[a] x, y, and z: mole fractions of six member ring, cyclobutane ring and vinyl acetate repeat units, respectively (Fig. 3).

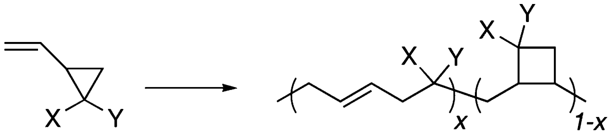

FIGURE 1 Polymerization scheme of a 2-vinyl cyclopropane monomer [7].

intermolecular cyclization with MMA. A mechanism similar to that described for the copolymerization with MMA is supposed to occur also in the copolymerization with VAc (Fig. 2). The copolymerization reaction would consist of ring opening and ring closing steps, in the latter of which however the preference for formation of six-membered rings could not be confirmed.

Since no olefin protons were detected in the ^{1}H NMR spectra of the p(VCPF8-*co*-VAc) copolymers, we suppose that the repeat units containing VCPF8 residues are arranged exclusively in cyclic structures of six- or four-membered rings, x and y mole fractions respectively (Fig. 3). The VAc residues are incorporated into cyclic and linear units, x and z mole fractions respectively. The distributions of repeat units are reported in Table 1.

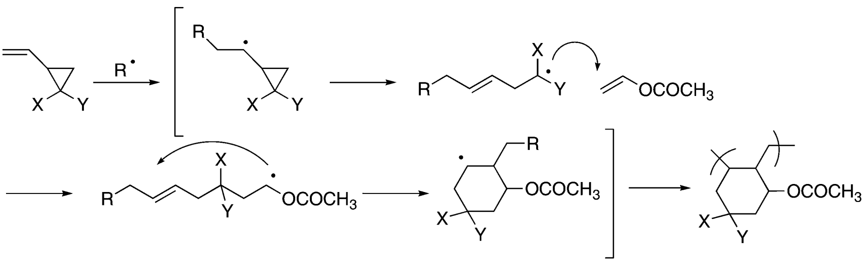

FIGURE 2 Copolymerization scheme of a 2-vinyl cyclopropane with vinyl acetate, after [8].

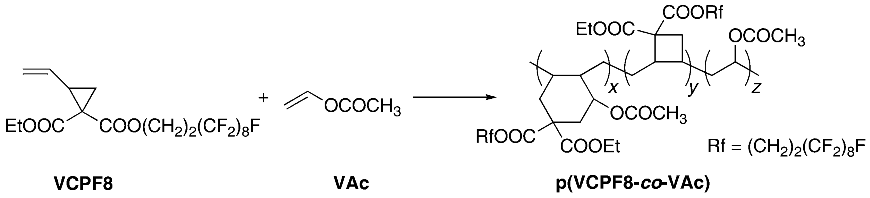

FIGURE 3 Schematic structure of p(VCPF8-*co*-VAc) copolymers.

No crystallinity was detected by means of differential scanning calorimetry (DSC) or X-ray diffraction (XRD) analyses of the fluorinated polymers. Previous studies evidenced the capability of the p(VCPF8) homopolymer to form a smectic liquid crystalline mesophase persistent over a very broad range of temperature ($T_\mathrm{i} - T_\mathrm{g} = 149$°C) [6]. A similar behavior was observed for the present copolymers containing VCPF8 fluorinated side groups, even though isotropization occurred at lower temperatures, e.g., $T_\mathrm{i} = 91$°C for p(VCPF8-*co*-VAc)a (Table 2). Dilution of the mesogenic VCPF8 side groups by VAc units in the copolymers depressed T_i with respect to p(VCPF8) homopolymer. Nevertheless, the range of existence of the mesophase in the copolymers was relatively broad, e.g., $T_\mathrm{i} - T_\mathrm{g} = 39$°C for p(VCPF8-*co*-VAc)a. We attribute the apparent insensitivity of T_i to copolymer composition to the chemical incompatibility between the hydrocarbon and the fluorocarbon components of the polymer repeat units [5]. Since the fluorocarbon side groups undergo intramolecular microphase separation from the hydrocarbon polymer backbone, T_i results to be mainly dictated by the chemical features of the fluorinated phase and is little affected by the amount of units organized in such phase. On the other hand, the isotropization enthalpy, ΔH_i, is associated with the degree of order of the mesophase, that is lower in copolymers containing lesser fluorinated mesogens.

The nature and the structural parameters of the mesophase of the copolymers were determined by XRD as function of temperature. In

TABLE 2 Thermal Properties of p(VCPF8-*co*-VAc) Copolymers[a]

Polymer	VCPF8 (mol%)	T_g (°C)	T_i (°C)	ΔH_i (J/g)
P(VAc)	0	43	–	–
p(VCPF8-*co*-VAc)a	32	52	91	n.d.
p(VCPF8-*co*-VAc)b	59	58	80	1.9
P(VCPF8)	100	34	183	22.5

[a] by DSC (10°C/min heating rate).

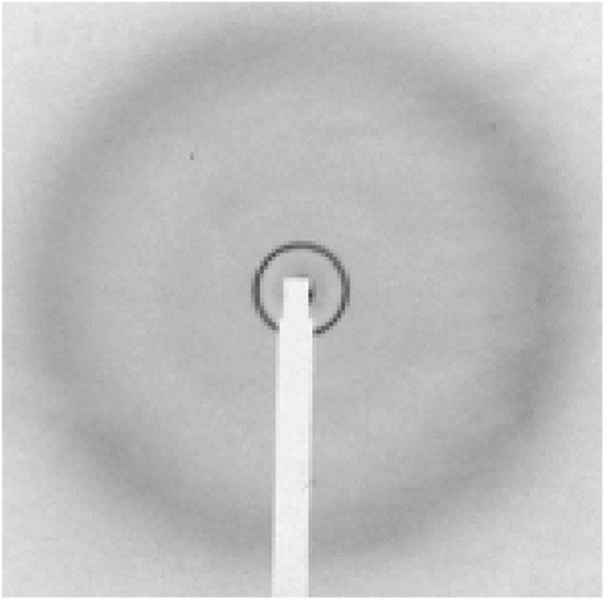

FIGURE 4 XRD powder pattern of the S_{Ad} phase of p(VCPF8-*co*-VAc)a at 70°C.

any case the mesophase was found to be a disordered, partly interdigitated smectic phase, such as the S_{Ad} phase (Fig. 4). The smectic layer periodicity ($d \approx 29\,\text{Å}$) was not influenced by temperature and its ratio to the calculated length L of the repeat unit was nearly constant over the entire mesophase existence range ($d/L \approx 1.28$) (Table 3). Thus, the details of the packing in the smectic layer of the copolymers were essentially the same and resembled those of the p(VCPF8) homopolymer ($d/L \approx 1.23$). Random distribution of the fluorinated side chains along the polymer backbone permitted their interdigitation without the necessity of tilting to pack effectively in a layered mesophase structure.

TABLE 3 Structural Characteristics of p(VCPF8-*co*-VAc) Copolymers

Polymer	VCPF8 in copol. (mol%)	L^a (Å)	d^b (Å)	Mesophase
p(VCPF8-*co*-VAc)a	32	23	29.5	S_{Ad}
p(VCPF8-*co*-VAc)b	59	23	29.5	S_{Ad}
P(VCPF8)	100	23	28.4	S_{Ad}

[a] maximum length of side group (±1 Å).

[b] smectic layer spacing (±0.3 Å), by XRD.

TABLE 4 Contact Angles θ for p(VCPF8-*co*-VAc) Copolymers with Various Wetting Liquids[a]

Sample	H_2O (deg)	C_{16} (deg)	C_{12} (deg)	C_{10} (deg)	C_8 (deg)
p(VCPF8-*co*-VAc)a	111.6 ± 0.9	65.4 ± 0.8	61.1 ± 0.8	58.0 ± 0.3	53.6 ± 0.2
p(VCPF8-*co*-VAc)b	110.0 ± 0.6	72.5 ± 0.2	64.1 ± 0.3	60.7 ± 1.0	57.4 ± 0.1
p(VCPF8)	117.4 ± 1.2	74.2 ± 0.3	69.5 ± 0.4	67.1 ± 0.4	62.0 ± 0.5

[a] C_{16}: *n*-hexadecane, C_{12}: *n*-dodecane, C_{10}: *n*-decane, C_8: *n*-octane.

In order to calculate the surface tensions of the copolymers, static contact angles θ were measured with water and n-alkanes as wetting liquids (Table 4). For any of the interrogating liquids used, θ increased with the content of fluorinated units in the copolymers, with the largest values being detected for p(VCPF8) homopolymer. Specifically, the water contact angles were greater than 110° in the copolymers, which shows that the polymer surface became hydrophobic on incorporation of the fluorinated units. Furthermore, the polymer surface was also lipophobic, the *n*-hexadecane contact angles being close to or greater than 65°. Thus, combination of both hydrophobicity and lipophobicity could provide low surface energy behavior. Larger contents of fluorinated units appeared to be necessary to enhance especially the latter character.

Generally, the surface tension γ_{sv} of a polymer film is extracted from values of θ [9]. We used two different approaches, like the Owens-Wendt-Kaelble method (OWK) for additive dispersion and polar components (γ_{sv}^d and γ_{sv}^p) (Eqs. (1) and (2)):

$$\gamma_{lv}(1+\cos\theta) = 2\left[\sqrt{\gamma_{lv}^d\gamma_{sv}^d} + \sqrt{\gamma_{lv}^p\gamma_{sv}^p}\right] \tag{1}$$

$$\gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^p \tag{2}$$

and the Equation-of-State method (EoS) developed by Neumann and Wu (Eq. (3)):

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}}e^{-\beta(\gamma_{lv}-\gamma_{sv})^2} \tag{3}$$

The evaluated γ_{sv} values are collected in Table 5.

According to the OWK method, in all polymers the dispersion contribution to the surface tension was highly predominant, whereas

TABLE 5 Surface Tension Values for p(VCPF8-*co*-VAc) Copolymers

Method	p(VCPF8-*co*-VAc)a (mJ/m^2)	p(VCPF8-*co*-VAc)b (mJ/m^2)	p(VCPF8) (mJ/m^2)
OWK			
γ_{sv}^d	13.8	12.6	11.4
γ_{sv}^p	0.6	1.0	0.3
γ_{sv}	14.4 ± 0.1	13.6 ± 0.6	11.7 ± 0.2
EoS			
γ_{sv}	14.1 ± 0.1	12.9 ± 0.3	11.8 ± 0.1

the polar contribution was lowest, for example $\gamma_{sv}^d = 11.4\,\text{mJ/m}^2$ and $\gamma_{sv}^p = 0.3\,\text{mJ/m}^2$ for p(VCPF8) (Table 5). This finding suggests that the fluorinated side groups are exposed to the outer polymer surface and shield effectively the inner polar moieties, such as the ester carbonyl moieties.

In both approaches γ_{sv} resulted small and minimal for p(VCPF8) ($\gamma_{sv} \leq 11.8\,\text{mJ/m}^2$), with γ_{sv} as low as $14.4\,\text{mJ/m}^2$ for p(VCPF8-*co*-VAc)a containing 32 mol% VCPF8 units. This demonstrates a low surface energy behavior of the polymer films. One notes the close

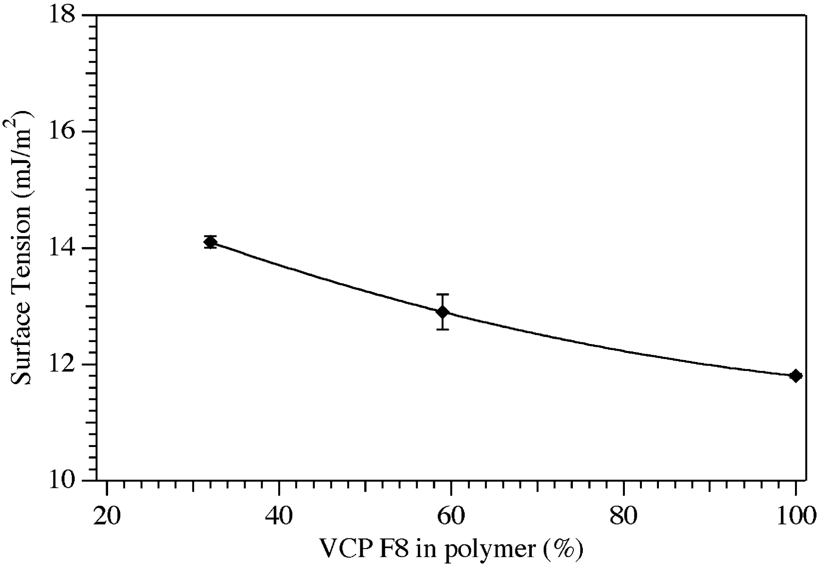

FIGURE 5 EoS surface tension γ_{sv} vs. composition for p(VCPF8-*co*-VAc) copolymers.

dependence of the surface tension on the amount of fluorine incorporated into the copolymers (Fig. 5), which confirms the possibility of tuning surface properties by a properly adjusted chemical composition. By extrapolation of the trend of γ_{sv} to copolymer compositions lower than 32 mol% VCPF8 units, one envisions that low surface energy polymer films might be obtained even from copolymers with very low amounts of fluorinated residues.

Fluorocarbon side chains pendant to main polymer backbones of diverse chemical structures [3,10,11] were shown by near-edge X-ray fine absorption structure (NEXAFS) studies to self-assemble in orientationally ordered arrays at the outer surface of thin polymer films. In particular, it was found that a liquid crystalline bulk phase caused a higher surface order than an isotropc bulk phase [10]. Thus, the bulk phase ultimately determined the achievable surface order. In the present copolymers the smectic order could also be sustained at the outer surface, and the low surface tensions evaluated for the polymer films were a manifestation of such an ordered structure that uniformly covered the surface.

CONCLUSIONS

Fluorinated 2-vinyl cyclopropanes can be copolymerized with a variety of vinyl monomers. This results in polymeric materials with low surface tension values owing to combination of hydrophobicity and lipophobicity, even at relatively low contents of $-(CF_2)_8F$ side groups. Their ordered surface organization can be enhanced by the bulk liquid crystalline mesophase structure.

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