Fluorinated 2-Vinylcyclopropane Copolymers as Low Surface Energy Materials

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Summary: The surface structure and surface energy properties of fluorinated 2-vinylcyclopropane copolymers were investigated. The copolymers were prepared by free radical ring opening polymerization of fluorinated **1** and non-fluorinated **2** 2-vinylcyclopropanes. NEXAFS experiments proved that the film surface was ordered with the fluorinated side groups possessing a relatively high orientational order. Contact angle measurements with different interrogating liquids permitted the polymer surface tension to be estimated. These surfaces showed both hydrophobic and oleophobic character, consistent with a low surface energy.

Keywords: fluoropolymer; free radical ring opening polymerization; surface energy; surface order; vinylcyclopropane

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.[1] Fluorinated side chain acrylate and methacrylate polymers are typical low surface energy coating materials.[2]

In recent years a number of novel low surface energy fluorinated polymers have been described.[3] However, one critical problem, surface reconstruction, 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 in contact with water 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.[4,5] Therefore, liquid

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crystallinity may provide a special means for creating stable, low surface energy polymeric materials for non-stick coating applications.[4]

Some of us have very recently developed a new architecture of fluorinated polymers based on 2-vinylcyclopropanes capable of forming liquid crystalline phases.[6,7] These monomers are of interest because they easily polymerize by a free radical ring opening mechanism thanks to the release of the cyclopropane ring strain.[8,9] 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.[8] Thus, vinylcyclopropanes undergo a little volume shrinkage upon ring opening polymerization.[8,9]

In this work we have prepared a set of poly(2-vinylcyclopropane)s poly(**1**-*co*-**2**) with the main goal of developing low surface energy polymers that may be materials for coating films and curable resins where a careful control of the bulk and surface properties of the polymer is a necessary requirement (Figure 1). We also aimed at confirming the capability of such new polymer structures to form thermotropic mesophases as a function of the chemical composition of fluorinated side groups.

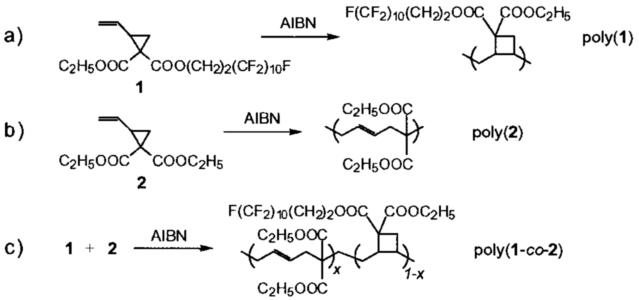


Figure 1. Free radical ring opening polymerization for the preparation of poly(2-vinylcyclopropane)s. The structures of the polymers are simplified and only show the principal repeat units for **1** and **2**.

Experimental Part

Monomers

The monomers, 1-ethoxycarbonyl-1-((1*H*,1*H*,2*H*,2*H*-perfluorododecyl)oxycarbonyl)-2-vinylcyclopropane (**1**) and 1,1-di(ethoxycarbonyl)-2-vinylcyclopropane (**2**), were synthesized following literature procedures.[6,10]

Polymers

The polymers were prepared following the same general procedure that is here described for poly(**1**) as a typical example: 0.58 g (0.68 mmol) of **1**, 5 mg (0.02 mmol) of AIBN and 5 ml of anhydrous trifluorotoluene were introduced into a Pyrex vial. After three freeze-thaw pump cycles, the vial was sealed under vacuum and the polymerization was left to proceed for 29 h at 60 °C. The polymer was then precipitated into methanol and purified by repeated precipitations from Cl_2FCCF_2Cl into methanol (yield 71% of poly(**1**)).

FT-IR (polymer film, in cm^{-1}): 1730 (νC=O), 1240–1120 (νC–O and νC–F), 652 (ωCF_2).

^{1}H-NMR ($Cl_2FCCF_2Cl/CDCl_3$, in ppm from TMS): 1.2–1.4 (3H, CH_3), 2.0–3.0 (7.1H, $C\underline{H_2}CH{=}CHC\underline{H_2}$ + cyclobutane + CH_2CF_2), 4.2–5.0 (4H, $COOCH_2$), 5.5 (0.9H, CH=CH).

^{19}F-NMR ($Cl_2FCCF_2Cl/CDCl_3$, in ppm from CF_3COOH): –5 (3F, CF_3), –38 (2F, CH_2CF_2), –45 to –50 (14F, $7CF_2$), –52 (2F, CF_2).

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).

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC-30 instrument (10 $°C \cdot min^{-1}$). 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.

The near-edge X-ray absorption fine structure (NEXAFS) experiments were carried out on the NIST/Dow end station on the U7A beam line at the National Synchrotron Light Source at Brookhaven National Laboratory. The beam line was equipped with a toroidal mirror spherical grating monochromator that provided an incident photon energy resolution and intensity of 0.2 eV and $5 \cdot 10^{10}$ $photons \cdot s^{-1}$, respectively, for an incident photon energy of 300 eV and a typical storage ring current of 500 mA. The X-rays were elliptically polarized, with the electric field vector dominantly in the plane of the storage ring (polarization factor = 0.85). The partial electron yield signal (PEY) was collected using a channeltron electron multiplier with an adjustable entrance grid bias (–150 V). Polymer films (thickness ~200 nm) were prepared by spin-coating 5 wt.-% polymer solutions in trifluorotoluene onto silicon wafers and then annealed for 6 h at 150 °C under vacuum.

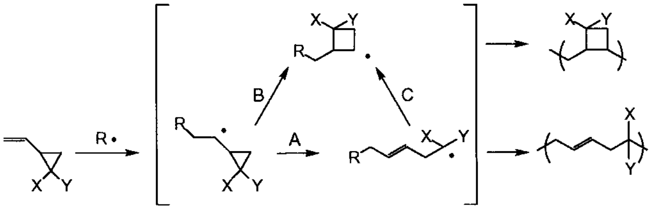
Static contact angles θ were measured using a Camtel FTA200 contact angle goniometer at room temperature. Polymer films were prepared by spin-coating 5 wt.-% polymer solutions in $Cl_2FCCF_2Cl/CHCl_3$ on glass slides followed by annealing for 15 h in a vacuum oven at 150

°C. Linear alkanes (octane, decane, dodecane and hexadecane) were used as standard wetting liquids in a Zisman analysis to extrapolate the critical surface tension to $\cos\theta = 1$.

Results and Discussion

Synthesis

It is documented that 2-vinylcyclopropanes containing electron-withdrawing and radical-stabilizing groups easily undergo radical ring opening polymerization[11] yielding polymers consisting predominantly of 1,5-linear repeat units (Figure 2, path A). Isomer cyclobutane-ring structures have also been shown to form, probably by recyclization of the propagating ring-opened radical (Figure 2, path C).[11] The concomitant occurrence of such linear and cyclic repeat units was confirmed by our previous investigations of the polymerization of fluorinated 2-vinylcyclopropanes, including **1**.[6] Therefore, the supposed homopolymerization of **1** and **2** yielded copolymers in effect comprising both types of isomer linear (z) and cyclic ($1 - z$) repeat units.



X, Y = Cl, phenyl, $COOC_2H_5$, $COO(CH_2)_2(CF_2)_{10}F$

Figure 2. Mechanisms for the formation of linear and cyclic repeat units in the free radical ring opening polymerization of 2-vinylcyclopropanes.[11]

We found that z depended considerably on the structure of the fluorinated substituents on the cyclopropane ring. While stronger electron withdrawing side groups appear to direct the polymerization preferably towards the formation of the cyclobutane repeat unit,[6,11] weaker electron withdrawing side groups lead to the predominant formation of the linear repeat unit, e.g. $z = 0.80$ in poly(**2**) (Figure 1b). However, this effect was mitigated by the steric hindrance of the fluorinated side chains which by contrast would preferentially dictate the formation of the 1,5-ring-opened structure, e.g. $z = 0.48$ in poly(**1**) (Figure 1a). Such repeat units would in fact better accommodate better the bulky fluorinated segments along the polymer backbone.[8] The copolymers poly(**1**-*co*-**2**) were prepared by free radical ring opening polymerization of the vinylcyclopropanes **1** and **2** with AIBN in anhydrous trifluorotoluene solution at 60 °C (yield 60–85%) (Table 1). They were typically soluble in trifluorotoluene, Cl_2FCCF_2Cl or $Cl_2FCCF_2Cl/CHCl_3$, and their molar masses could not be fully characterized. Poly(**1**-*co*-**2**)b,c containing high proportions of non-fluorinated **2** units were soluble in chloroform or tetrahydrofuran and their molar masses could be characterized by SEC with poly(styrene) calibration (M_n = 38000 and 18000 g·mol^{-1}, M_w/M_n = 2.02 and 1.73, respectively).

Table 1. Physico-chemical characterization of the 2-vinylcyclopropane copolymers.

Polymer	x [a]	z [b]	T_g [c]	Mesophase behavior		
				T_i [c]	structure	d [d]
	(mol-%)		(°C)	(°C)		(± 0.2 Å)
poly(**1**)	100	0.48	78	187	SmB_d, SmA_d	31.7
poly(**1**-*co*-**2**)a	50	0.50	35	173	SmA_1	26.2
poly(**1**-*co*-**2**)b	40	0.60	35	168	SmA_1	26.0
poly(**1**-*co*-**2**)c	30	0.80	35	140	SmA_1	26.0
poly(**2**)	0	0.80	33	-	-	-

[a] Content of fluorinated **1** units in the copolymer, by NMR. [b] Content of 1,5-linear repeat units, by NMR. [c] Glass transition temperature and isotropization temperature, by DSC (10 °C·min^{-1}). [d] Smectic layer periodicity, by WAXD.[7]

By assuming that in the formation of the copolymers poly(**1**-*co*-**2**) the two different comonomer species favored the same propagation mechanisms as in the corresponding "homopolymers", the linear **2** repeat units would be predominant, whereas cyclic **1** repeat units would be in a slight excess, as shown in the simplified structure of Figure 1c.

Mesophase behavior

Each fluorinated poly(vinylcyclopropane) sample exhibited thermotropic behavior (Table 1). No evidence of crystallinity was detected by 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 slightly higher than room temperature (30 °C < T_g < 80 °C). Thus, the mesophase remained frozen in the glassy state at room temperature. Generally speaking, the mesophase was very persistent, a relatively high isotropization temperature (T_i = 187 °C) being detected for poly(**1**). Incorporation of the long fluorinated chain segment favored the mesogenic character of the side groups and facilitated their ordering in a mesophase. This tendency was not disrupted even in the copolymers that possessed significant contents of non-fluorinated **2** units (Table 1), e.g. T_i was 140 °C for poly(**1**-*co*-**2**)c containing as much as 70 mol-% **2** units.

The mesogenic capability of fluorocarbon chains is attributed to the rigid-rodlike nature of their helical conformation in combination with their immiscibility with other molecular constituents.[12] We also explain the onset of liquid crystallinity in fluorinated poly(vinylcyclopropane)s by the strong intramolecular phase separation of the fluorocarbon from the hydrocarbon components of the polymer repeat unit.[6] This driving force would be less effective in the copolymers owing to the improved miscibility of the aliphatic-fluoroaliphatic side groups with the aliphatic macromolecular chain.

The wide spacing between the fluorinated side groups **1** along the polymer backbone of the poly(vinylcyclopropane)s enabled their ordering in a partly overlapped arrangement (SmB_d at $T < 115$ °C, or SmA_d at 115 °C $< T <$ 187 °C). In the copolymers the side groups **1** were even more widely spaced apart from each other by side groups **2** along the macromolecular chain and could be fully interdigitated in the antiparallel structure of a lower order smectic phase (SmA_1).

Surface structure

To probe the surface structure and its organization in more detail we employed NEXAFS analysis by monitoring the emission of Auger electrons from the near surface region (~2 nm) of polymer films. Typical PEY spectra as a function of the soft X-ray photon energy over the C K-edge are shown in Figure 3 for the values of 20° and 90° of the angle α between the electric field vector **E** of the polarized X-ray beam and the surface normal. At least four resonant transitions were clearly detected originating from different chemical bonds in the polymer repeat unit. The intensity of the $1s \rightarrow \sigma^*$ transition for the C–F bond of the CF_2 moieties ($E = 292$ eV) decreased in going from $\alpha = 90°$ to 20°, whereas that of the C–C bonds ($E = 295$ eV) followed the opposite trend. The PEY spectra, which were measured at intermediate angles $\alpha = 30°–80°$ (not shown in the figure for clarity) were situated between the 20° and 90° extremes.

These anisotropies in the PEY signals indicate that these bonds had some net orientational order at the outer surface, namely they were preferentially oriented parallel (C–F) and normal (C–C) to the sample surface. These results are consistent with previous observations on different polymers carrying fluorinated side groups[5,13,14] and reveal that the rigid CF_2 helices were, on average, oriented normal to the film surface and, therefore, provided a fluorine-coated surface.

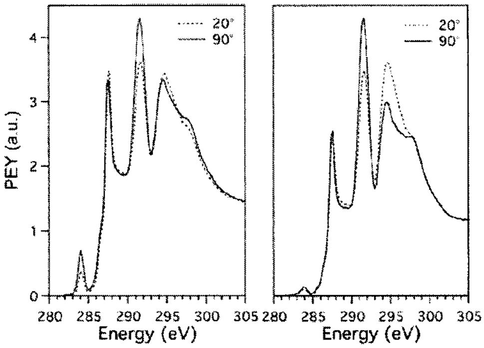


Figure 3. NEXAFS partial electron yield spectra for angles α of 90° and 20° for copolymers poly(**1**-*co*-**2**)c (left) and poly(**1**-*co*-**2**)a (right).

Quantitatively, we determined the uniaxial order parameter $S_{C\text{-}F}$ of the C–F bonds of the surface, and from this the orientational order parameter S_{helix} of the CF_2 helix, following the methods outlined in ref.[5]. It was seen that the surface order parameter was relatively high (S_{helix} ~0.2) but was sensitive to copolymer composition. In particular, it decreased from 0.26 to 0.16 in going from poly(**1**-*co*-**2**)a to poly(**1**-*co*-**2**)c, having extreme contents of 50 and 30 mol-% fluorinated **1** units, respectively. Therefore, dilution of the fluorinated units caused a significant disorder of the surface.

One also notes the low intensity of the PEY signal at 284 eV associated with the $1s \rightarrow \pi^*$ transition for the C=C bond in the 1,5-linear unit of the polymer backbone. This provides further evidence of the enrichment of outer film surface by the fluorinated side groups that in fact hide the underlying macromolecular chain. Furthermore, the angular dependence of the PEY signal (maximized at $\alpha = 90°$) points to a certain degree of orientation in the main chain of poly(**1**-*co*-**2**)c in Figure 3. Such anisotropy, however, was not detected in the corresponding very low intensity PEY signal of poly(**1**-*co*-**2**)a containing the largest amount of fluorinated **1** side groups. We suggest that an anisotropic conformation of the polymer main chain can come from the partial stretching necessary to enable an ordered arrangement of the fluorinated side groups and the larger separation needed to keep them properly spaced from each other along the polymer backbone in poly(**1**-*co*-**2**)c.

Surface energy properties

It is common practice in surface science to use contact angle data for the interpretation of surface energetics. The most common methods to gain information about the surface energy of a solid are the evaluation of critical surface tension, the determination of surface tension components based on various combination rules and the use of an equation of state.[15]

We firstly measured the static contact angle θ of the copolymer films using water and n-hexadecane as the wetting liquids (Table 2). The measured values of θ were relatively high with water ($\theta \geq 100°$) and n-hexadecane ($\theta \geq 61°$), thus showing that the surface was both hydrophobic and oleophobic. With either interrogating liquid, θ decreased with increased content of non-fluorinated **2** units in the copolymer. This distinct character of the copolymer films is attributed to the fluorinated nature of the outer surface.

Table 2. Surface energy characteristics of the vinylcyclopropane copolymers.

Copolymer	**1** a)	θ_{water} b)	$\theta_{\text{n-hexadec}}$ b)	γ_c c)	γ_{SV}^{ES} c)	γ_{SV}^{OWK} c)	γ_{SV}^{d} c)	γ_{SV}^{p} c)
poly(**1**-*co*-**2**)a	50	110	67	4.7	12.7	14.2	13.1	1.1
poly(**1**-*co*-**2**)b	40	105	66	5.5	13.1	15.3	13.4	1.9
poly(**1**-*co*-**2**)c	30	100	61	14.8	16.2	18.1	15.4	2.7

*a)*Molar content of fluorinated side groups in the copolymer. *b)*Static contact angle (in degrees) with water and n-hexadecane. *c)*Critical surface tension, surface tension after equation of state (ES) and Owens-Wendt-Kaelbe approach (OWK), with its dispersive and polar components, (in mN·m^{-1}): γ_{SV}^{d} is an average of the values obtained with all the n-alkanes.

A similar trend of θ with copolymer composition was found with other standard n-alkanes that were used to construct Zisman plots[16] of $\cos\theta$ as a function of the surface tension γ_{LV} of the wetting liquid (Figure 4). Extrapolation to $\cos\theta = 1$ provided values of the critical surface tension γ_c in the range ~5–15 mN·m^{-1} (Table 2). These values are low and comparable to those for other polymers with long semifluorinated chains as side groups[5,13] and perfluoroalkanoic acids (γ_c ~7–9 mN·m^{-1})[17], the monolayers of which have a highly ordered and closely packed surface structure of perfluorinated chains.

A value of the surface tension γ_{SV} of the polymers could also be estimated from its dispersive and polar components, which were calculated from the contact angles with water ($\gamma_{LV}^{d} = 21.8$ mN·m^{-1}, $\gamma_{LV}^{p} = 51.0$ mN·m^{-1}) and n-alkanes ($\gamma_{LV}^{d} = \gamma_{LV}$) from Equation (1), so-called Owens-Wendt-Kaelbe approach,[18] valid for a generic liquid whose surface tension can be decomposed into two additive contributions originating from dispersion and polar interactions, $\gamma_{LV} = \gamma_{LV}^{d} + \gamma_{LV}^{p}$:

$$\gamma_{LV}(1 + \cos\theta) = 2(\gamma_{SV}^{d}\gamma_{LV}^{d})^{1/2} + 2(\gamma_{SV}^{p}\gamma_{LV}^{p})^{1/2} \qquad (1)$$

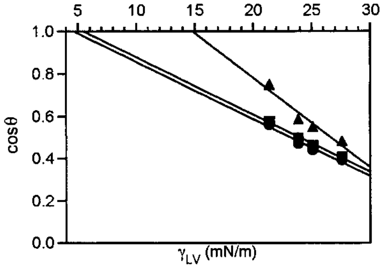


Figure 4. Zisman plots with different n-alkane interrogating liquids for poly(**1**-*co*-**2**)a (●), poly(**1**-*co*-**2**)b (■), and poly(**1**-*co*-**2**)c (▲).

As expected, the values determined for the surface tension (γ_{SV} ~14–18 mN·m^{-1}) were markedly larger than the corresponding extrapolated values of γ_c (Table 2), the copolymers with greater amounts of fluorinated side groups showing consistently lower values of γ_{SV}. In any case the dispersive contribution was dominant (γ_{SV}^{d} ~13–15 mN·m^{-1}), but the polar contribution became increasingly significant with decreasing fluorinated units in the copolymer.

In an alternative approach, we evaluated γ_{SV} by use of the modified equation of state[15,19]:

$$\cos\theta = -1 + 2(\gamma_{SV}/\gamma_{LV})^{1/2} \exp[-\beta(\gamma_{LV} - \gamma_{SV})^2] \qquad (2)$$

by which for a given set of γ_{LV} and θ data measured on one and the same solid surface, the constant β and γ_{SV} values can be determined by a least-square analysis technique.[19] The values of γ_{SV} ~12–16 mN·m^{-1} from Equation (2) were slightly lower than the corresponding values from Equation (1) but followed the same trend with the content of fluorinated **1** units in the copolymers (Table 2). The nature of the side groups had, therefore, a pronounced effect in determining the surface energy of the polymers, with fluorocarbon substituents exhibiting surface energies that were markedly lower than those of hydrocarbon substituents.[20] Nevertheless, relatively low surface energy materials were obtained with copolymers incorporating large contents of non-fluorinated units, such as 70 mol-% of **2** in poly(**1**-*co*-**2**)c. This suggests consideration of copolymers in which the fluorocarbon chains are diluted for low surface energy materials. A long perfluorinated pendent chain seems to be an essential element of the molecular design for such materials as it serves to mask the polar character of the surface and would prevent absorption of liquid by the bulk sample.

Conclusions

Introduction of fluoro-substituents in the side groups of poly(2-vinylcyclopropane)s imparts low surface energy properties to the polymer films by enriching the surface of orderly assembled fluorinated chain segments. The simultaneous hydrophobic and oleophobic nature of the polymers should be responsible for the low surface energy associated with the polymer films. Moreover, chemical variations of the copolymer composition can effectively modify the bulk and surface properties that in turn are manifested in varied values of surface tension.

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