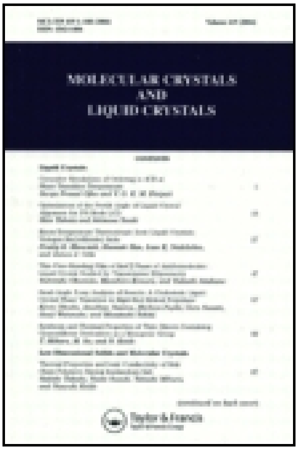

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New Fluorinated Liquid Crystalline Copoly(vinylcyclopropane)s with Unusual Macromolecular Structure

G. Galli [a] , S. Gasperetti [a] , M. Bertolucci [a] & E. Chiellini [a]

[a] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Pisa, Italy

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NEW FLUORINATED LIQUID CRYSTALLINE COPOLY(VINYLCYCLOPROPANE)S WITH UNUSUAL MACROMOLECULAR STRUCTURE

G. Galli, S. Gasperetti, M. Bertolucci, and E. Chiellini
Dipartimento di Chimica e Chimica Industriale, Università di Pisa,
56126 Pisa, Italy

*New liquid crystal polymers with unusual macromolecular structure were prepared by copolymerization of a fluorinated vinylcyclopropane (**1**) with methyl methacrylate (**2**). The copolymers pol(**1**-co-**2**) formed a mesophase despite the high dilution of the perfluorinated side chains along the polymer main chain. The onset of mesomorphism is attributed to the microphase separation of the incompatible fluorocarbon-hydrocarbon components.*

Keywords: fluorinated polymer; liquid crystal; macromolecular structure; microphase separation; poly(vinylcyclopropane)

INTRODUCTION

Vinylcyclopropanes [1] containing electron-withdrawing or radical-stabilizing groups are known to easily undergo radical ring-opening polymerization yielding polymers consisting predominantly, though not exclusively, of 1,5-linear structures. Isomer cyclic structures have also been shown to form [2]. Therefore, poly(vinylcyclopropane)s are complex copolymer systems, the properties of which could be affected substantially by the macromolecular structure.

We are interested in vinylcyclopropanes containing perfluorinated-chain side groups [3,4]. In fact, incorporation of suitable fluoro-substituents can additionally impart low energy surface properties to the polymer films by enriching the surface of orderly assembled perfluorinated chain segments. In this work we have prepared new liquid crystal polymers by

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Address correspondence to G. Galli, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56126 Pisa, Italy.

copolymerization of a vinylcyclopropane **1** containing a perfluorinated chain segment and methyl methacrylate (**2**). The copolymerization proceeded via unusual ring-opening and ring-closing steps, and these fluorinated polymers represent a novel class of materials forming liquid crystalline phases.

EXPERIMENTAL PART

The synthesis of monomer **1** and copolymer pol(**1**-*co*-**2**)b are described as typical examples.

Monomer 1

1,1-Diethoxycarbonyl-2-vinylcyclopropane **3**. 1.98 g (0.09 mol of metallic sodium was added in small portions to 30 ml of absolute ethanol over 1 h under dry nitrogen atmosphere. After complete reaction, 13.40 g (0.08 mol) of diethyl malonate was added dropwise. The mixture was let to react for an additional 1 h at room temperature and then heated to 40°C. 9.06 g (0.04 mol) of *trans*-1,4-dibromobutene in 40 ml of absolute ethanol was added in 1 h. The reaction mixture was kept for 1 day at reflux. The precipitate was then filtered off and the solvent was evaporated under vacuum. The crude residue was purified by repeated distillations giving 1.87 g (22% yield) of **3**: b.p. 69–72°C/0.5 mm.

1-Ethoxycarbonyl-1-(2-perfluorodecyl)ethoxycarbonyl-2-vinylcyclopropane **1**. 3.92 g (0.07 mol) of KOH was added in small portions to a solution of 15.05 g (0.07 mol) of **3** 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 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 acid **4**.

5.02 g (22 mmol) of dicyclohexylcarbodiimide (DCCI) in 15 ml of anhydrous dichloromethane was added dropwise to a solution of 4.62 g (25 mmol) of **4**, 0.02 g (1.0 mmol) of pyrrolidinopyridine (PPy) and 12.86 g (23 mmol) of 2-(perfluorodecyl)ethanol in anhydrous dichloromethane under dry nitrogen atmosphere at 0°C. The reaction was let to proceed for an additional 3 h at 0°C and then for 1 day 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. 5.97 g (36% yield) of pure **1** as a colorless viscous liquid was obtained.

^{1}H-NMR ($CDCl_3$): 1.2 (3H, CH_3), 1.6–1.8 (2H, CH_2 cyclopropane), 2.3–2.7 (3H, CH cyclopropane + CH_2CF_2), 4.2 (2H, $COOCH_2$), 4.4 (2H, $COOC\underline{H}_2CH_2CF_2$), 5.1–5.5 ppm (3H, CH_2=CH).

FT-IR (liquid film): 3092 and 2964 (νC-H vinyl and aliphatic), 1730 (νC-O), 1640 (νC=C vinyl), 1372 (δC-H cyclopropane), 662 cm^{-1} (ωCF$_2$).

($C_{17}H_{15}F_{13}O_4$) (530.27): Calcd. C 38.50, H 2.85, F 46.58; Found C 38.40, H 2.95, F 47.0.

Copolymer Pol(1-*co*-2)d

1.08 g (1.48 mmol) of **1**, 0.04 (0.37 mmol) di **2**, 8 mg (0.02 mmol) of AIBN in 3.0 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 let to proceed for 22 h at 65°C. The polymer was then precipitated into methanol and purified by repeated precipitations from chloroform into methanol (3% yield).

^{1}H-NMR ($CDCl_3$): 0.8 (12H, CH_3 (**2**)), 0.9–2.4 (14H, $CHCH_2$ (**1**) + CH_2 (**2**)), 2.5 (2H, CH_2CF_2), 3.6 (12H, $COOCH_3$ (**2**)), 4.2 (2H, $COOCH_2CH_3$ (**1**)), 4.4 ppm (2H, $COOCH_2C\underline{H}_2CF_2$(**1**)). FT-IR (polymer film): 2994–2952 (νC-H aliphatic), 1728 (νC=O), 668 cm^{-1} (ωCF$_2$).

Characterizations

NMR (^{1}H,^{13}C,^{19}F) spectra were recorded with a Varian VXR 300 spectrometer. 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. Polystyrene standards were used for calibration.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC-30 instrument (10°C/min). The phase transition temperatures were taken as the maximum temperature in the DSC enthalpic peaks. The glass transition temperature (T_g) was taken as the half-devitrification temperature.

RESULTS AND DISCUSSION

The fluorinated vinylcyclopropane monomer **1** was synthesized following the reaction pathway in Figure 1. *Trans*-1,4-dibromobutene was reacted with the diethyl malonate sodium salt to give 1,1-diethoxycarbonyl-2-vinylcyclopropane **3**. This was selectively hydrolyzed and the corresponding monocarboxylic acid **4** was esterified with 2-(perfluorodecyl)ethanol to afford the eventual vinylcyclopropane **1**.

Monomer **1** was free-radically copolymerized (AIBN at 65°C) with methyl methacrylate (**2**) in trifluorotoluene. Different comonomer feed mixtures were used, which gave copolymers pol(**1**-*co*-**2**) with varying

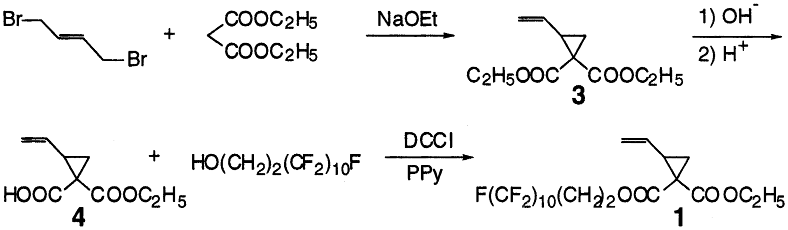

FIGURE 1 Reaction scheme for the synthesis of monomer **1**.

contents of fluorinated **1** units (Table 1). The copolymer compositions were evaluated by ^{1}H-NMR by integrating the areas of the resonance signals of the $COOCH_2$ groups from **1** at 4.15 and 4.40 ppm relative to that of the $COOCH_3$ group from **2** at 3.60 ppm. In any copolymer sample the content of units **2** was much greater than in the corresponding feed mixtures, because of the higher reactivity of **2** with respect to **1**. No olefin signal (5.30 ppm) or allyl signal (2.50 ppm) from 1,5-ring-opened units (see [2]) from **1** was ever detected, but a broad signal around 1.6–2.7 ppm due to other reactions exhausting the olefin double bond [5].

The radical copolymerization of vinylcyclopropanes (Fig. 2, X = Cl, COOEt) is supposed to proceed via opening of the vinylcyclopropane ring followed by intermolecular cyclization with **2** [5]. According to this, addition of initiator radical to the vinyl double bond on the cyclopropane ring is followed by 1,5-ring-opening to yield a homoallyl radical that further attacks at **2** to give a **2**-terminated radical. Intramolecular cyclization of this radical proceeds by two possible pathways, that is leading to six-membered (route [A]) or five-membered (route [B]) alicyclic units. The occurrence of the former ring structure seems to be preferred [5,6], even though formation of the latter cannot be definitely ruled out. This radical cyclopolymerization is rather unusual in that it involves both ring-opening and ring-closing processes.

TABLE 1 Physico-chemical Characteristics of Copolymers Pol(**1**-*co*-**2**)

Copolymer	**1** (mol%) in the feed	Yield (%)	**1**(mol%) in the cop.	$M_n{}^a$(g/mol)	$M_w/M_n{}^a$
pol(**1**-*co*-**2**)a	20	3	~5	20000	2.12
pol(**1**-*co*-**2**)b	40	2	10	18000	1.98
pol(**1**-*co*-**2**)c	60	5	15	nd	nd
pol(**1**-*co*-**2**)d	80	3	20	nd	nd

[a] By SEC in tetrahydrofuran with PS standards.

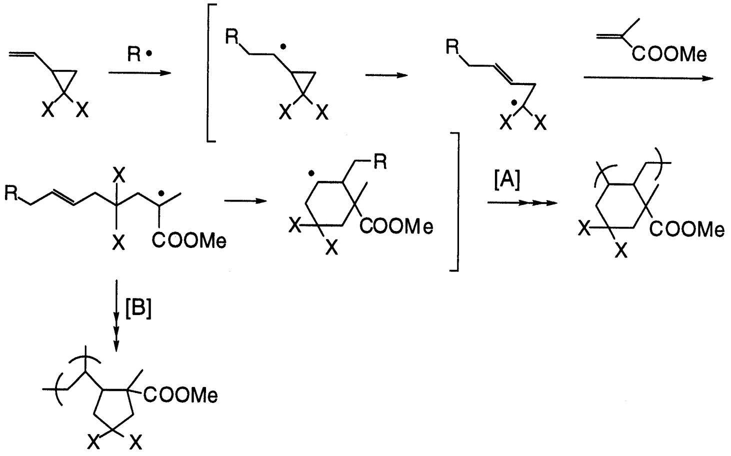

FIGURE 2 Copolymerization scheme of vinylcyclopropanes with **2**.

In our experiments, the copolymerization yields were deliberately kept low ($< \sim 5\%$) in order to estimate the reactivity ratios r of the two comonomers. The values we evaluated by the Kelen-Tüdös method ($r_1 = 0.5$, $r_2 = 12.1$) confirmed the greater reactivity of **2** relative to **1**. In fact, **1**-terminated radicals would add to **2** two times faster than to **1**, and **2**-terminated radicals would add to **2** twelve times faster than to **1**. Therefore, a simplified structure of copolymers pol(**1**-*co*-**2**) consists of isolated six-membered (mixed **1–2**) units flanked by sequences of **2** units, e.g. three units **2** in pol(**1**-*co*-**2**)d (Fig. 3).

The copolymers exhibited thermotropic mesophases above T_g (Table 2). In any case the mesophase was highly stable ($T_i \geq 183°C$) and persistent over a broad temperature range ($T_i - T_g \geq 79°C$). Previous studies by X-ray diffraction on homopolymer pol(**1**)have confirmed the occurrence of two mesophases, namely SmB_d and SmA_d [4]. By contrast, there was one smetic mesophase in copolymers pol(**1**-*co*-**2**) (Fig. 4). Thus, incorporation of limited proportions (down to as low as 5–10 mol%) of fluorinated

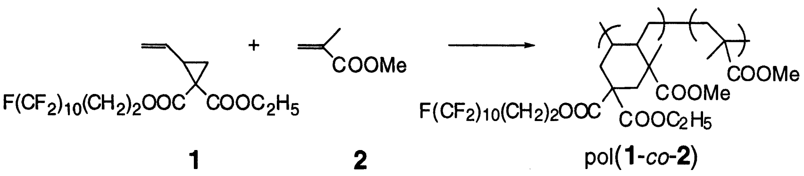

FIGURE 3 Schematic structure of copolymers pol(**1**-*co*-**2**).

TABLE 2 Liquid Crystal Properties of Copolymers Pol(**1**-*co*-**2**)

Copolymer	**1** (mol%) in the cop.	T_g (°C)	T_i (°C)	ΔH_i (J/g)
pol(**2**)	0	105	–	–
pol(**1**-*co*-**2**)b	10	110	187	1.3
pol(**1**-*co*-**2**)c	15	105	184	1.1
pol(**1**-*co*-**2**)d	20	66	183	0.6
pol(**1**)	100	78	187[a]	6.7[a]

[a] Additional mesophase transition at 118°C ($\Delta H = 0.7\,J/g$).

units **1** in combination with non-mesogenic units **2** in the copolymers did not disrupt their mesogenic character, even though it was depressed. A detailed investigation of the mesophase structures by X-ray diffraction will be given elsewhere.

The formation of thermotropic mesophase(s) in the present polymers simply incorporating 2-(perfluorodecyl)ethyl chains is somewhat surprising. In fact it is very rarely observed and has been previously reported in a structurally related polyacrylate only [7]. The mesogenic capability of fluorocarbon chains is usually attributed to the rigid-rodlike character of their helical conformation in combination with their immiscibility with other molecular constituents [8].

We also explain the onset of liquid crystallinity in pol(**1**-*co*-**2**) by the strong microphase separation of the fluorocarbon side groups from the hydrocarbon polymer backbone.

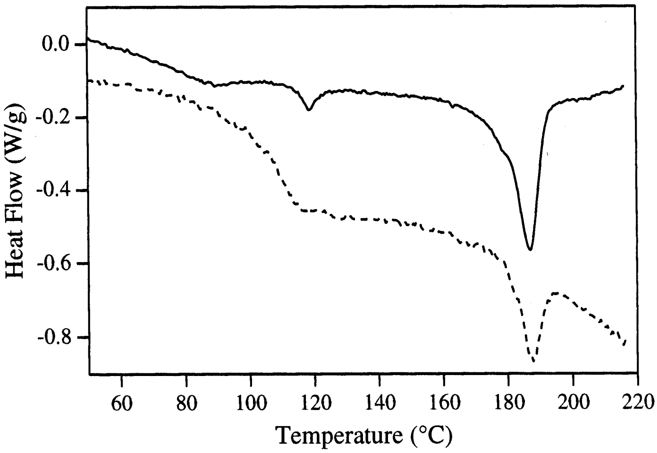

FIGURE 4 DSC curves of pol**1** (—) and pol(**1**-*co*-**2**)d (—).

It is noteworthy that the T_i of the copolymers was not affected by the chemical composition and remained almost equal to that of pol(**1**) (Table 2). Normally, T_i in copolymers is found to decrease gradually with increasing content of non-mesogenic units [9], and the variation of chemical composition is in fact a common means of tuning the mesophase behavior of copolymers. The apparent insensitivity of the T_i of pol(**1**-*co*-**2**) to composition may be due to their chemical constitution of two incompatible hydrocarbon-fluorocarbon components. Their phase separation into distinct sub-layers would confine the perfluorinated tails in an ordered array, thus amplifying their mesogenic character.

Liquid crystalline polymers with a purely alicyclic main chain and pendant side groups are rather unusual [10], and the influence of the various stereochemical features of the polymer backbone on their mesophase behavior is completely unknown.

CONCLUSIONS

We have prepared new copoly(vinylcyclopropane)s with unusual macromolecular structure, which form mesophases despite the high dilution of the fluorinated side groups along the polymer main chain. Microphase separation at the molecular level appears to be a strong driving force even in polymers that do not contain typical mesogenic units of liquid crystal molecules.

REFERENCES

[1] Moszner, N., Zeuner, F., Volkel, T., & Rheinberger, V. (1999). *Macromol. Chem. Phys.*, *200*, 2173.

[2] Sanda, F., Takata, T., & Endo, T. (1993). *Macromolecules*, *26*, 1818.

[3] Andruzzi, L., D'Apollo, F., Galli, G., & Gallot, B. (2001). *Macromolecules*, *34*, 7707.

[4] Galli, G., Gasperetti, S., Bertolucci, M., Gallot, B., & Chiellini, E. (2002). *Macromol. Rapid Commun.*, in press.

[5] Sanda, F., Takata, T., & Endo, T. (1994). *Macromolecules 27*, 3982.

[6] Takahashi, T. (1970). *J. Polym. Sci., Part A-1*, *8*, 739.

[7] Volkov, V. V., Platé, N. A., Takahara, A., Kajiyama, T., Amaya, N., & Murata, Y. (1992). *Polymer*, *33*, 1316.

[8] Wang, J. & Ober, C. K. (1999). *Liq. Cryst.*, *26*, 637.

[9] Galli, G. (2001). in "*Advanced Functional Molecules and Polymers*", Nalwa H. S. (Ed.), Overseas Publishers Association: Singapore, Vol. I, 271.

[10] Buxton, I. P., Hall, A. W., & Lacey, D. (1997). *Macromol. Chem. Phys.*, *198*, 2307.