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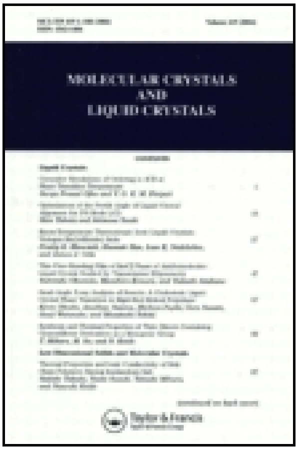

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New Chiral Liquid-Crystalline Poly(vinylcyclopropane)s with Cyclic and Linear Repeat Units

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New Chiral Liquid-Crystalline Poly(vinylcyclopropane)s with Cyclic and Linear Repeat Units

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New chiral liquid-crystalline poly(vinylcyclopropane)s were prepared by free-radical ring-opening polymerization of the corresponding 2-vinylcyclopropane monomers. These side-group polymers had unconventional structures as they contained both linear and cyclic isomer repeat units. They formed an SmC phase around room temperature. General trends of the phase structures and transitions were found with the length of the spacer segment and the nature of the chiral substituent of the side-group mesogens.

Keywords: liquid-crystalline polymer; poly(vinylcyclopropane); ring-opening polymerization; smectic C

INTRODUCTION

Most liquid-crystalline polymers carrying side-group mesogens consist of a linear hydrocarbon polymer backbone derived from 1,2-vinyl (or vinylidene) chain polymerization [1]. Notable alternatives are the widely investigated poly(siloxane)s, which however are normally

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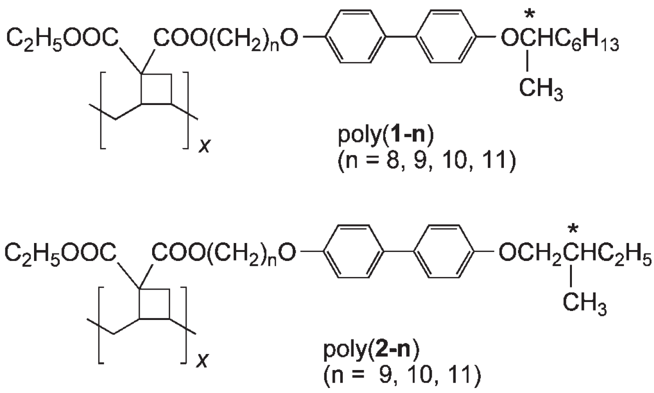

FIGURE 1 Simplified structures of the poly(vinylcyclopropane)s prepared and studied (the cyclic repeat unit is shown only).

prepared by polymer-analogous modification of preformed poly(siloxane) precursors [1].

Different structures of side-group polymers having a hydrocarbon alicyclic polymer backbone have also been prepared by various polymerization methods [2–6].

We have recently presented a new class of liquid-crystalline polymers containing side-group semifluorinated mesogens, that were obtained by free-radical ring-opening polymerization of 2-vinyl-1,1-disubstituted-cyclopropane monomers [7]. Depending on the structure of the substituent(s) in the 1-position(s), the polymers contained simultaneously linear and alicyclic isomer units in different proportions.

In this work we extended our interest to poly(vinylcyclopropane)s poly(**1-n**) and poly(**2-n**) with conventional, rodlike mesogenic side groups carrying a chiral center with the aim of producing low temperature SmC polymers (Fig. 1). In fact, such polymers were expected to exhibit low glass transition temperatures on account of the relatively high flexibility and conformational disorder of their polymer chains. While alicyclic repeat units were generally predominant, as shown in Figure 1, linear repeat units were also incorporated into actual copolymer structures.

EXPERIMENTAL PART

Synthesis

Chiral alcohols **10-n** and **11-n** were synthesized from 4,4′-diphenol (**4**) following a general literature procedure [8]. 2-Vinylcyclopropane carboxylic acid **14** was synthesized from 1,4-*trans*-butene (**12**) according to literature [7,9].

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We describe the preparation of polymer poly(**1–9**) as a typical example.

Monomer **1–9**: 0.42 g (2.3 mmol) of carboxylic acid **14**, 0.96 g (2.3 mmol) of alcohol **10–9**, 0.01 g (0.5 mmol) of pyrrolidinopyridine (PPy) were dissolved in 15 ml of anhydrous dichloromethane under nitrogen atmosphere. A solution of 0.44 g (2.3 mmol) of dicyclohexylcarbodiimmide (DCC) in 5 ml of anhydrous dichloromethane was then added dropwise. The reaction mixture was stirred at 0°C for 3 h and then at room temperature for 72 h. The precipitate was filtered and the solution was washed with 5% HCl, 5% $NaHCO_3$, and water and dried over Na_2SO_4. After evaporation to dryness of the solvent, the residue was purified by column chromatography on silica gel with ethyl acetate/hexane 1:2 (v/v) as the eluent giving 0.85 g (65% yield) of **1–9** (mp 15–17°C; $[\alpha]_D^{25} = -1.4$ (c = 0.09 g/dl, $CHCl_3$).

FT-IR (KBr): $\bar{\nu}$ (cm^{-1}) = 2983 – 2878 (νCH aliphatic), 1745 (νC=O), 1648 (νC=C vinyl), 1640 – 1444 (δCH cyclo), 1244 – 1000 (νCOC), 960 (γCH vinyl), 815 (γCH aromatic).

^{1}H-NMR ($CDCl_3$): δ(ppm) = 7.4 (4H, aromatic 2 and 2′), 6.9 (4H, aromatic 3 and 3′), 5.5 – 5.1 (3H, CH_2=CH), 4.3 (1H, $C\underline{H}OPh$), 4.2 (4H, $COOCH_2$), 4.0 (2H, $C\underline{H}_2OPh$), 2.5 (1H, CH cyclo), 1.8 – 1.5 (4H, CH_2 cyclo + CH_2 aliphatic), 1.5 – 1.1 (22H, CH_2), 1.2 (3H, $OCHC\underline{H}_3$), 0.9 (6H, CH_3).

Polymer poly(**1–9**): 0.50 g (0.8 mmol) of monomer **1–9**, 5 mg (0.04 mmol) of α,α′-azobis(isobutyronitrile) (AIBN), and 5 ml of anhydrous benzene were introduced into a Pyrex vial. After freeze-thaw pump cycles, the vial was sealed under vacuum, and the polymerization was let to proceed for 48 h at 60°C. The polymer was then precipitated in methanol and purified by repeated precipitations from chloroform solutions in methanol (68% yield).

FT-IR (KBr): $\bar{\nu}$ (cm^{-1}) = 2964 – 2872 (νCH aliphatic), 1745 (νC=O), 1244 – 1000 (νCOC), 815 (γCH aromatic).

^{1}H-NMR ($CDCl_3$): δ(ppm) = 7.4 (4H, aromatic 2 and 2′), 6.9 (4H, aromatic 3 and 3′), 5.3 (0.67H, CH=CH), 4.3 (1H, $C\underline{H}OPh$), 4.1 (4H, $COOCH_2$), 3.9 (2H, $C\underline{H}_2OPh$), 2.6 – 1.6 (7.33H, $C\underline{H}_2CH{=}CHC\underline{H}_2$ + cyclobutane + CH_2), 1.5 – 1.0 (25H, CH_2 + $OCHC\underline{H}_3$), 0.8 (6H, CH_3).

^{13}C-NMR ($CDCl_3$): δ□□□□172.4 and 171.8 ($\underline{C}OOC_2H_5$, cyclic), 1□5$\underline{C}OOC_2H_5$, linear).

Characterization

NMR (^{1}H, ^{13}C) spectra were recorded with a Varian Gemini VXR 300 spectrometer. Size exclusion chromatography (SEC) was carried out

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with a Jasco PU-1580 liquid chromatograph equipped with two 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 was set at the half-devitrification temperature.

X-Ray diffraction (XD) experiments were performed on powder samples with an especially designed pinhole camera using Ni-filtered CuKα beam ($\lambda = 1.54\,\text{Å}$), under vacuum at various temperatures with an accuracy of ± 1°C.

RESULTS AND DISCUSSION

The 2-vinylcyclopropane monomers **1-n** ($n = 8$–11) and **2-n** ($n =$ 9–11) were synthesized following a general procedure as is outlined in Figure 2. Regular modifications of the chemical structure led to

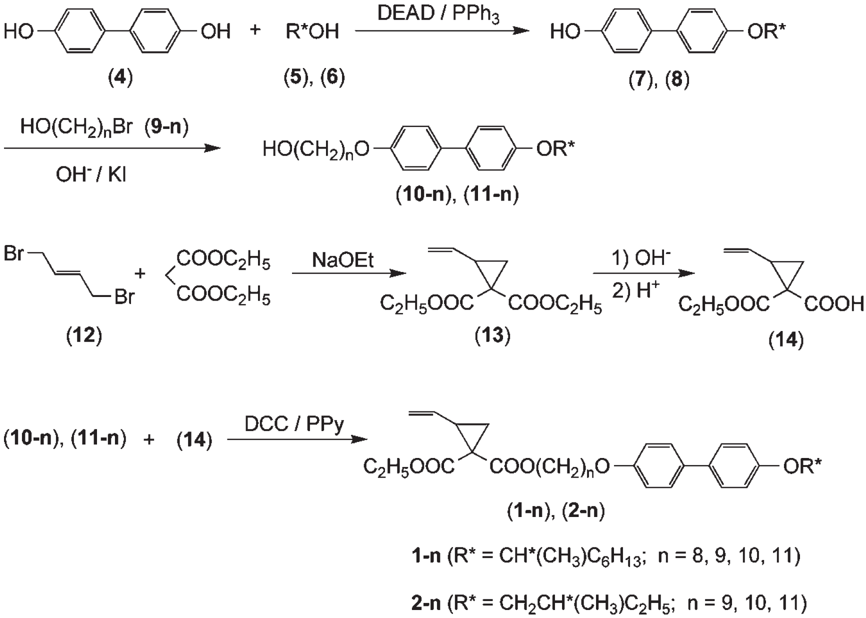

FIGURE 2 Reaction pathway for the synthesis of monomers **1-n** and **2-n**.

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TABLE 1 Physico-Chemical Characteristics of the Poly(vinylcyclopropane)s Prepared[a]

Polymer	Yield (%)	$[\alpha]_D^{25b}$	M_w^c (g/mol)	M_w/M_n^c	z^d
poly(**1–8**)	51	−1.4	13100	1.4	0.41
poly(**1–9**)	68	−1.2	19500	1.6	0.66
poly(**1–10**)	72	−0.8	10000	1.3	0.65
poly(**1–11**)	82	−0.9	23400	1.6	0.46
poly(**2–9**)	74	−3.8	15500	1.8	0.47
poly(**2–10**)	52	−3.1	7500	1.2	0.63
poly(**2–11**)	45	−3.7	8500	1.3	0.62
poly(**3–11**)	45	−0.8	14400	1.2	0.15

[a] By free-radical polymerization: AIBN at 60°C, for 48 h, in benzene (≈0.15 M).
[b] Optical rotatory power, in $CHCl_3$ (c ≈ 0.1 g/dl).
[c] By SEC, in $CHCl_3$.
[d] Mole fraction of cyclic repeat units, by ^{1}H-NMR.

materials with varied length of the spacer segment (*n*) and the chiral center (R*).

None of the monomers exhibited thermotropic liquid-crystal behavior. This was not completely unexpected, in consideration of the comparatively low mesogenic tendency of the biphenyl core carrying a chiral, branched substituent (1-methylheptyl or 2-methylbutyl) and a bulky terminal group (vinylcyclopropyl).

The polymers were prepared by free-radical polymerization (AIBN, 60°C) of the monomers in benzene solution. Their average molar masses (by SEC, with polystyrene standards) were relatively low (Table 1).

2-Vinylcyclopropanes containing electron-withdrawing and radical-stabilizing groups are known to easily undergo radical ring-opening polymerization [10], yielding polymers consisting predominantly,

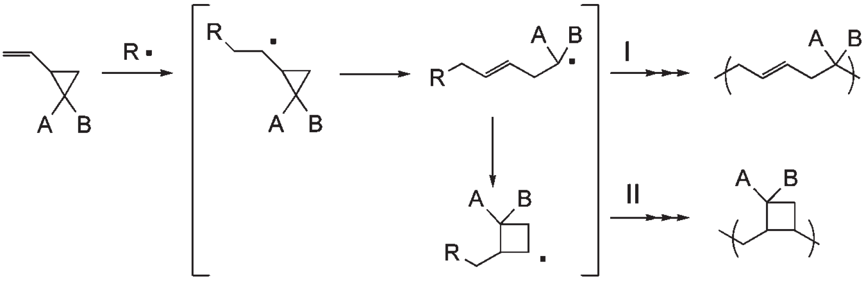

FIGURE 3 Mechanisms for formation of linear and cyclic repeat units in the free-radical polymerization of 2-vinylcylopropanes [10].

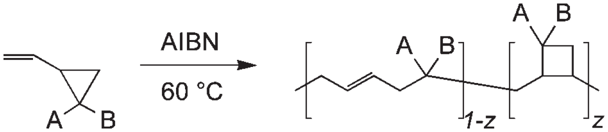

FIGURE 4 Copolymer structure of the poly(vinylcyclopropane)s with both linear and cyclic repeat units.

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although not exclusively, of 1,5-linear structures (Fig. 3, route I). Isomer cyclobutane-ring structures have also been shown to form [10], probably by recyclization of the propagating ring-opened radical (Fig. 3, route II).

The concomitant occurrence of such linear and cyclic repeat units was confirmed by our investigations [7], and the supposed homopolymerization of monomers **1-n** and **2-n** led in fact to copolymers that generally consisted of a cyclobutane-ring repeat unit as the major component (Fig. 4). Therefore, two ring-opening and ring-closing processes operated in the polymerization. The relative proportions of cyclic units (z) and linear units ($1-z$) depended on the length (n) of the alkylene segment spacing the mesogenic side groups from the polymer backbone (Table 1). While there was no obvious trend of z with n, it appears that the steric hindrance of the substituents on the cyclopropane ring preferably directs toward the formation of the 1,5-ring-opened structure, that possibly better accommodates the bulky side groups along the polymer main chain [11].

The liquid-crystal properties of the polymers were studied by combining DSC and XD analyses. The mixed structural character of the backbone of the polymers prepared makes it difficult to draw well-defined relationships between the polymer primary structure and the mesophase behavior. Moreover, any influence of the stereochemical features of the different repeat units on the details of the phase transitions of the polymers is unknown.

Nevertheless, general trends in the phase structures and transitions were evidenced (Table 2), that can help design new liquid-crystalline poly(vinylcyclopropane)s. Poly(**1–8**), bearing the mesogenic units spaced by the shortest segment in the series ($n = 8$), did not form a mesophase above the glass transition temperature ($T_g = -2$°C). Poly(**1–9**) and poly(**1–10**), comprising spacer segments of intermediate lengths ($n = 9$ and 10, respectively) presented an SmC phase. Poly (**1–11**), having the longest spacer in the series ($n = 11$), gave rise to two mesophases, SmC and SmA. Qualitatively, similar results were found for polymers poly(**2-n**) with increasing number n. These findings are in agreement with the usual behavior of liquid-crystalline

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TABLE 2 Liquid-Crystal Behavior of the Poly(vinylcyclopropane)s Prepared

Polymer	*n*	Phase transitions (in °C)[a]						
poly(**1–8**)	8	g	−2					Iso
poly(**1–9**)	9	g	5	SmC			42	Iso
poly(**1–10**)	10	g	3	SmC			28	Iso
poly(**1–11**)	11	g	10	SmC	35	SmA	58	Iso
poly(**2–9**)	9	g	55	SmC			100	Iso
poly(**2–10**)	10	g	55	SmC		(101 N)[b]	103	Iso
poly(**2–11**)	11	g	53	SmC	64	X[c]	90	Iso
poly(**3–11**)	11	g	38	SmC			105	Iso

[a] From glass to isotropic, by DSC (scanning rate 10°C/min).

[b] Monotropic phase.

[c] Unidentified mesophase.

side-group polymers, in which the mesophase is stabilized by longer flexible spacers than a critical length.

One notes, however, that shorter spacers ($n \approx 3$–4) are normally sufficient to decouple the mesogenic side groups from the polymer backbone of typical side-group polymers, e.g., poly(acrylate)s, and enable a mesophase to form. The lack of mesomorphism in poly(**1–8**) may be associated with particular constraints imposed on the side groups by the alicyclic repeat unit of the poly(vinylcyclopropane). On the other hand, the presence of ring structures along the macromolecular chain can enhance its flexibility and favor the onset of a mesophase at low temperatures, close to ambient.

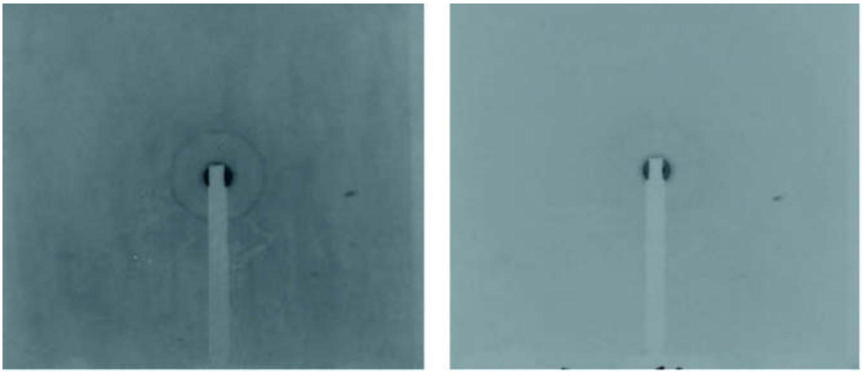

FIGURE 5 XD diagrams of poly(**1–9**) at 30°C (left) and poly(**2–9**) at 65°C (right).

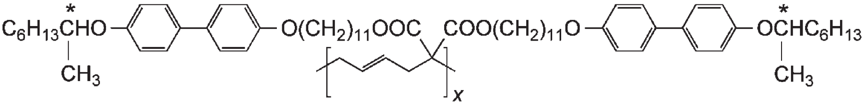

FIGURE 6 Simplified structure of poly(**3–11**) (the linear repeat unit is shown only).

Illustrations of X-ray diagrams are shown in Figure 5 for poly(**1–9**) and poly(**2–9**). For these polymers the smectic layer periodicity, $d = 64.3 \pm 0.1\,\text{Å}$ and $d = 63.7 \pm 0.1\,\text{Å}$, was much longer than the length of the side-group units in their most extended conformation, $L = 38 \pm 1\,\text{Å}$ and $L = 35 \pm 1\,\text{Å}$, respectively. The average intermolecular distance was $D = 4.6 \pm 0.3\,\text{Å}$ in both cases. Therefore, the SmC phase was double layered with a maximal tilt angle $\beta \approx 29^\circ$ and $\beta \approx 17^\circ$, respectively. Such a structure remained essentially unaffected by temperature throughout the entire smectic range.

A major difference between poly(**1-n**) and poly(**2-n**) samples is due to the position of their respective glass transition temperatures. While T_g was consistently well below room temperature for poly(**1-n**) ($\leq$10°C), it was in any case above room temperature for poly(**2-n**) ($\geq$53°C). Thus, the SmC phase was present at ambient in the former system, whereas it was frozen in the glassy state in the latter. This was because of plasticization from the long terminal tail of poly(**1-n**), that, on the other hand, depressed the clearing temperature to a significant extent relative to the corresponding poly(**2-n**), e.g., 58°C and 90°C for poly(**1–11**) poly(**2–11**), respectively (Table 2).

It is noteworthy that smectic mesophase(s) could exist in the present polymers, in which one side group per five chain carbon atoms repeated along the polymer backbone. This effective dilution of the mesogenic units resulted in relatively low clearing temperatures. Consistent with this interpretation, poly(**3–11**), analogous to poly(**1–11**) but containing two side groups per repeat unit (Fig. 6), possessed a so-far unidentified mesophase up to the clearing temperature of 105°C, that is about 50°C higher than that of poly(**1–11**) (Table 2). The tendency of poly(vinylcyclopropane)s consisting of two mesogens per repeat unit to form liquid-crystalline mesophases was previously shown [12], even though the question of structural isomerism of the polymers was not considered.

Therefore, the capability of tuning the mesophase behavior and properties of the poly(vinylcyclopropane)s on a structural basis can enlarge the scope of the ring-opening polymerization in liquid crystal science.

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CONCLUSIONS

Liquid-crystalline poly(vinylcyclopropane)s were prepared exhibiting an SmC phase around room temperature. They contain both alicyclic and linear isomer repeat units, with the former generally being the predominant component. This structural feature of the polymer backbone favors the occurrence of a mesophase around room temperature. Whilst defining structure-property correlations seems to be more difficult than with traditional liquid-crystalline polymers, the ring-opening polymerization of vinylcyclopropanes leads to new polymeric materials with unconventional structures. Investigations of the electrooptic behavior in the SmC phase of the prepared polymers are under way.

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