Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Online publication date: 02 November 2003

To cite this Article Casper, Patrick and Ritter, Helmut(2003) 'A Novel Liquid-Crystalline Vinylcyclopropane-Derivative Bearing Cholesterol: Synthesis and Polymerization', Journal of Macromolecular Science, Part A, 40: 2, 107 — 113
To link to this Article: DOI: 10.1081/MA-120017254
URL: http://dx.doi.org/10.1081/MA-120017254

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JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. 40, No. 2, pp. 107–113, 2003

A Novel Liquid-Crystalline Vinylcyclopropane-Derivative Bearing Cholesterol: Synthesis and Polymerization

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ABSTRACT

The synthesis of a liquid-crystalline vinycyclopropane, 1-ethoxycarbonyl-1-[5-(cholesteryloxycarbonyl)pentoxycarbonyl]-2-vinylcyclopropane (**4**), and its polymerization is described. The polymerization of **4** was carried out in toluene as solvent and with AIBN as free radical initiator at 70°C. The obtained polymer also showed liquid-crystalline behavior similar to that of the monomer **4**.

Key Words: Liquid-crystalline Polymer (LCP); Ring-opening polymerization; 2-vinylcyclopropane.

INTRODUCTION

2-Vinylcyclopropanes are monomers of special interest because of their low volume shrinkage behavior during polymerization in comparison to many other vinyl monomers. This behavior makes them a potential candidate, e.g. for the development of new dental fillers, for materials in microelectronic applications, or generally for coatings, which are restricted to monomers exhibiting a low volume shrinkage or even

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DOI: 10.1081/MA-120017254 1060-1325 (Print); 1520-5738 (Online)

a small expansion during polymerization. Vinylcyclopropanes are strained molecules that undergo ring-opening polymerization after initiation with free radicals. It was demonstrated that the radical polymerization of 1,1-disubstituted 2-vinylcyclopropanes resulted in polymers that only consist of 1,5 ring-opened units with a partially unsaturated backbone.[1,2] A liquid-crystalline monomer not only would facilitate the handling and processing of such materials, but also could contribute to the reduction of volume shrinkage during polymerization due to relatively high molecular weight of the monomer and because of ordering effects. Some increase of volume while undergoing a phase transition from liquid-crystalline to isotropic may also occur. Furthermore, polymers with a liquid-crystalline behavior could also be useful for optical applications. In this connection we recently prepared vinylcyclopropane esters of cholesterol.[3]

In this paper, we wish to describe for the first time the synthesis of a novel liquid-crystalline 1,1-disubstituted 2-vinylcyclopropane containing a cholesteric moiety via a spacer group and its polymerization.

EXPERIMENTAL

Materials and Methods

Cholesteryl 6-bromohexanoate (**3**) was synthesized according to the instructions given in the literature.[4,5] 1-Ethoxycarbonyl-2-vinylcyclopropane-carboxylic acid (**1**) was provided by Ivoclar-Vivadent and used as received. Chloroform-*d* (99.8 atom-% deuterium) was purchased from Deutero GmbH, Kastellaun, Germany. All solvents were purified and dried by standard methods. All materials were used as received, unless mentioned otherwise.

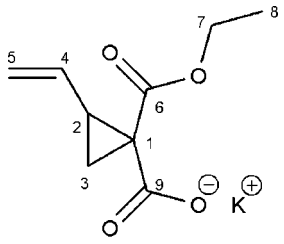
NMR spectra were recorded at room temperature on a Bruker AM400 (^{1}H NMR: 400 MHz) and AC200 (^{13}C NMR: 50 MHz). The δ-scale relative to TMS was calibrated using the deuterium lock signal of the solvent as internal standard.

SEC measurements were performed at 25°C with an experimental set-up from PSS with $CHCl_3$ as eluent. Calibration was done with polystyrene standards (PSS) with a molar mass range between 374 and 1.000.000 D. Applying a flow rate of 1 ml/min, 150 µl of a 0.125 wt% polymer solution in $CHCl_3$ was applied to a column combination consisting of PSS-SDV 5 µ10^3 Å, 8 × 50 mm as a precolumn and a set of PSS-SDV 5 µ, 8 × 300 mm with 10^2, 10^3, and 10^4 Å porosity as analytical columns. Detection of the signals was performed with a Shodex RI-71 differential refractometer. The evaluation was performed using PSS-WinGPC 4.02 software. Elemental analyses were carried out at the microanalytical laboratory of the University of Mainz, Germany. FT-IR spectra were recorded in KBr with a Nicolet FT-IR spectrometer (5 SXB). DSC analyses were carried out on a Perkin Elmer DSC 7 with a heating rate of 10 C/min.

The optical observations were performed in a polarized optical microscope Leitz Ortholux 2 Pol-BK with a Mettler SP5 hot stage.

Synthesis of 1-Ethoxycarbonyl-1-[5-(Cholesteryloxycarbonyl)pentoxycarbonyl]-2-vinylcyclopropane (4)

1-Ethoxycarbonyl-2-vinylcyclopropane-1-carboxlic Acid Potassium Salt (**2**)



2

1.12 g (20 mmol) KOH are dissolved in 10 ml of water and cooled in an ice/salt cold bath. A solution of 3.7 g (20 mmol) of **1** and 10 mg hydroquinone in water/ethanol (6 ml/10 ml) is added dropwise under stirring over a period of 30 min. After stirring the mixture for another 20 min. at room temperature, the solvent is evaporated under reduced pressure. The grayish-yellow oil is freed from remaining solvent in a lyophilizer in high vacuum. The dried product is recrystalized from ethyl acetate, filtered off, and dried in high vacuum. Yield 3.0 g (67%), m.p. 117.9 C.

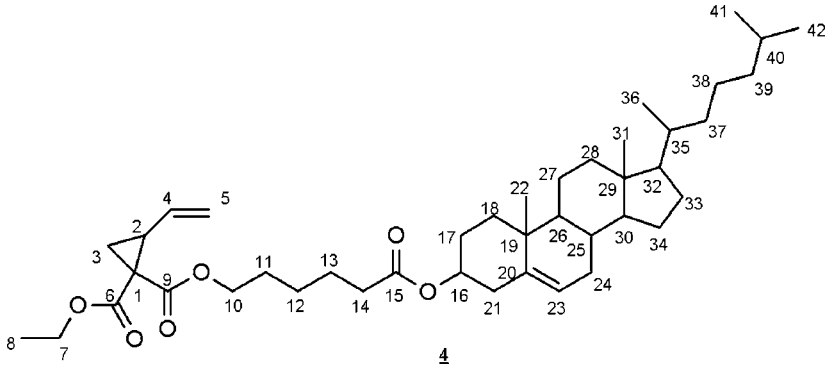
IR (KBr): $\tilde{\nu} = 2987$ (aliph. **C-H**-Val.), 1716 (**C═O** ester), 1636 (**C═C**), 1578 (**C═O** acid salt), 1027 (cyclopropan-**C-H**-def.), 910 cm^{-1} (R-**CH═CH$_2$**), additional bands at: 1321, 1213, 1198 cm^{-1}.

^{1}H NMR (D_2O): $\delta = 5.33$ (m, H^4, $J_{4,5'} = 17.08$ Hz, $J_{4,5''} = 9.77$ Hz), 5.18 (dd, $H^{5'}$, $J_{gem} = 2.19$ Hz, $J_{4,5'} = 17.08$ Hz), 5.03 (dd, $H^{5''}$, $J_{gem} = 2.19$ Hz, $J_{4,5''} = 9.77$ Hz), 4.08 (m, H^7), 2.29 (dd, H^2, $J_{2,3'} = 8.8$ Hz, $J_{2,3''} = 7.32$ Hz), 1.41 (dd, $H^{3'}$, $J_{gem} = 5.13$ Hz, $J_{2,3'} = 8.8$ Hz), 1.33 (dd, $H^{3''}$, $J_{gem} = 5.13$, $J_{2,3''} = 7.32$ Hz), 1.15 (t, H^8).

^{13}C NMR ($CDCl_3$): $\delta = 176.16$ (C^9), 171.99 (C^6), 134.55 (C^4), 117.11 (C^5), 62.32 (C^7), 38.77 (C^1), 29.66 (C^2), 18.42 (C^3), 13.27 (C^8).

EA: ($C_9H_{11}KO_4$) (222.28): Calcd. C 48.63, H 4.99; Found C 47.34, H 5.20

1-Ethoxycarbonyl-1-[5-(cholesteryloxycarbonyl)pentoxycarbonyl]-2-vinylcyclopropane (**4**)



4

2.2 g (10 mmol) of **2**, 5.64 g (10 mmol) of **3**, 50 mg of hydroquinone, and 55 mg of tetrabutylammonium iodide are suspended in 70 ml of ethyl acetate and refluxed for 24 h. After cooling, the grayish-yellow precipitate is sucked off and the solvent removed. The orange-brown residue is dissolved in little dichloromethane and precipitated from 120–150 ml of methanol. The highly viscous product is cooled and sucked through a Büchner funnel. The filter cake is dissolved from the filter with dichloromethane. The solvent is distilled off and the product is freed from remaining solvent in high vacuum. Yield: 3.96 g (59%) of a colorless, high viscous liquid-crystalline substance.

DSC (2nd. heating, −40–120°C, 10°C/min): 19.4°C (melting point); 21.7°C and 25.7°C (phase transitions)

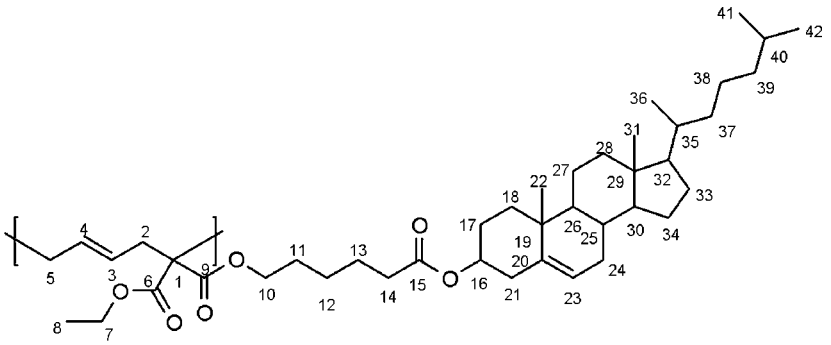
IR (KBr): $\tilde{\nu} = 2942, 2867$ (aliph. **C-H**-Val.), 1732 (**C═O** ester), 1639 (**C═C**), 1466, 1442 (**C-H**-def.), 959, 919 cm^{-1} (R-**CH═CH$_2$**), additional bands at: 1370, 1320, 1272, 1200, 1172, 1134, 1030, 1012, 801 cm^{-1}.

^{1}H NMR ($CDCl_3$): $\delta = 5.40$ (m, H^4), 5.34 (m, H^{23}), 5.26 (dd, $H^{5'}$), 5.11 (dd, $H^{5''}$), 4.58 (m, H^{16}), 4.11 (m, H^7, H^{10}), 2.54 (m, H^2), 2.26 (m, H^{14}, H^{21}), 2.0-0.8 (m, $H^{3'}$, $H^{3''}$, H^{11}, H^{12}, H^{13}, H^{17}, H^{18}, H^{19}, H^{24}, H^{25}, H^{26}, H^{27}, H^{28}, H^{30}, H^{32}, H^{33}, H^{34}, H^{35}, H^{37}, H^{38}, H^{39}, H^{40}), 1.23 (t, H^8), 0.99 (s, H^{22}), 0.88 (d, H^{36}), 0.83 (dd, H^{41}, H^{42}), 0.65 (s, H^{31}).

^{13}C NMR ($CDCl_3$): $\delta = 172.80$ (C^{15}), 169.66 (C^6), 167.31 (C^9), 139.64 (C^{20}), 133.10 (C^4), 122.63 (C^{23}), 118.43 (C^5), 73.83 (C^{16}), 65.40 (C^{10}), 61.43 (C^7), 56.71 (C^{30}), 56.16 (C^{32}), 50.05 (C^{26}), 42.33 (C^{29}), 39.74 (C^{39}), 39.52 (C^{28}), 38.16 (C^{21}), 37.00 (C^{18}), 36.60 (C^1), 36.20 (C^{37}), 35.90 (C^{19}), 35.78 (C^{35}), 34.46 (C^{14}), 31.91 (C^{24}), 31.86 (C^{25}), 31.12 (C^2), 28.22 (C^{11}, C^{17}), 28.00 (C^{40}), 27.82 (C^{33}), 25.39 (C^{13}), 24.60 (C^{12}), 24.28 (C^{34}), 23.83 (C^{38}), 22.81 (C^{41}), 22.55 (C^{42}), 21.04 (C^{27}), 20.38 (C^3), 19.31 (C^{22}), 18.72 (C^{36}), 14.24 (C^8), 11.86 (C^{31}).

EA: ($C_{42}H_{66}O_6$) (666.98): Calcd. C 75.63, H 9.97; Found C 73.36, H 9.56

Poly-(1-Ethoxycarbonyl-1-[5-(cholesteryloxycarbonyl)pentoxycarbonyl]-2-vinylcyclopropane) (**5**)[6]



5

After flushing with nitrogen a solution of 0.681 g (1 mmol) of **4** and 8.4 mg (0.005 mmol ≡ 5 mol%) AIBN in 5 ml of toluene is placed in an oil bath at 70° C and stirred for 24 h. The polymer is precipitated from methanol, sucked off, and dried in high vacuum. Yield: 0.15 g (23%) of a colorless, fluffy polymer.

DSC (2nd. heating, −20–150°C, 10°C/min): 26.5°C (glass transition); 74.4°C and 97.0°C (phase transitions)

IR (KBr): $\tilde{\nu} = 2938, 2867$ (aliph. **C-H**-Val.), 1733 (**C═O** ester), 1639 (**C═C**), 1467, 1443, 1391, 1368 (**C-H**-def.), 1263, 1177 cm^{-1} (R-**C**O-**O**-R′), additional bands at: 1137, 1095, 1030, 1015, 801 cm^{-1}.

^{1}H NMR ($CDCl_3$): $\delta = 5.35$ (s (br), H^{23}), 5.29 (s (br), H^3, H^4), 4.58 (m, H^{16}), 4.11 (m, H^7, H^{10}), 2.46 (s (br), H^2, H^5), 2.27 (m, H^{14}, H^{21}), 2.0-0.8 (m, H^{11}, H^{12}, H^{13}, H^{17}, H^{18}, H^{19}, H^{24}, H^{25}, H^{26}, H^{27}, H^{28}, H^{30}, H^{32}, H^{33}, H^{34}, H^{35}, H^{37}, H^{38}, H^{39}, H^{40}), 1.23 (t, H^8), 0.99 (s, H^{22}), 0.89 (d, H^{36}), 0.85 (dd, H^{41}, H^{42}), 0.65 (s, H).

^{13}C NMR ($CDCl_3$): $\delta = 172.79$ (C^{15}), 170.47 (C^6. C^9), 139.67 (C^{20}), 128.46. (C^3), 122.61 (C^{23}), 118.47 (C^4), 73.78 (C^{16}), 65.04 (C^{10}), 61.46 (C^7), 61.19 (C^1), 56.71 (C^{30}), 56.18 (C^{32}), 50.05 (C^{26}), 42.33 (C^{29}), 39.76 (C^{39}), 39.53 (C^{28}), 38.18 (C^{21}), 37.01 (C^{18}), 36.61 (C^2, C^5), 36.21 (C^{37}), 35.82 (C^{19}, C^{35}), 34.47 (C^{14}), 31.91 (C^{24}, C^{25}), 28.23 (C^{11}, C^{17}), 28.01 (C^{40}), 27.84 (C^{33}), 25.41 (C^{13}), 24.61 (C^{12}), 24.29 (C^{34}), 23.86 (C^{38}), 22.82 (C^{41}), 22.57 (C^{42}), 21.05 (C^{27}), 19.33 (C^{22}), 18.74 (C^{36}), 14.19 (C^8), 11.88 (C^{31}).

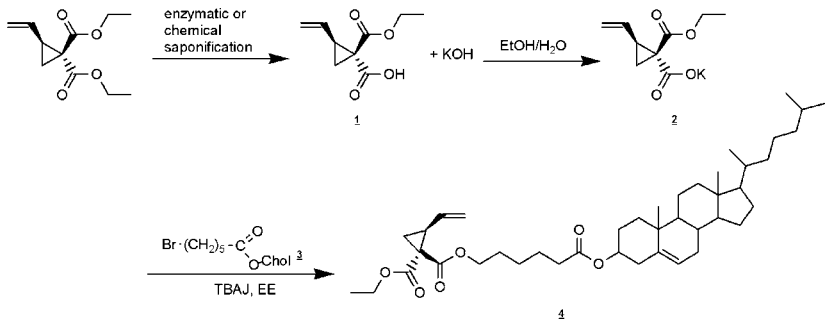
SEC Results

M_n : $1.035*10^4$ g/mol ⇒ $P_n = 15–16$

M_w : $1.754*10^4$ g/mol

PDI : 1.694

RESULTS AND DISCUSSION



2-Vinylcylopropane bearing a cholesteric moiety via a spacer group was synthesized by nucleophilic esterification of the potassium salt of 1-ethoxycarbonyl-2-vinylcyclopropane-1-carboxlic acid (**1**). ^{1}H NMR and ^{13}C NMR spectroscopy clearly showed that

the vinyl group and the ethyl ester group of **1** are mostly in *cis* configuration no matter what kind of saponification is used (i.e., enzymatic or chemical).[7] The new formed ester **4** thus contains the cholesterol moiety in *trans* configuration in relation to the vinyl group. DSC data clearly proves a liquid-crystalline behavior of **4**. In addition to the melting peak at 19.4° C, two endothermic transitions are visible at higher temperature (around 21.7° C and 25.7° C). The transition at 25.7° C corresponds to the clearing point of **4**, whereas the transition at 21.7° C results from a crystalline to liquid-crystalline phase transition. These values are lower compared to those of the corresponding (meth)acrylic esters described in literature.[8] Heating up to 120° C did not start thermal polymerization. This could be due to the presence of hydroquinone as radical inhibitor.

The polymerization behavior of this new liquid-crystalline monomer was evaluated. For that, the polymerization was carried out in toluene as solvent with a monomer concentration of 0.2 mol/l and 5 mol% of AIBN. The low monomer concentration in addition to the relatively high amount of initiator led to a polymer (**5**) with a relatively low molecular weight of only 10,350 g/mol. This corresponds to an average degree of polymerization of $P_n = 15-16$. At 26.5° C the glass transition of **5** could be observed from DSC-measurements. For some applications this may be to low. At 74.4° C and at 97.0° C, two endothermic peaks could be observed. They correspond to LC phase transitions of the cholesterol domain. The peak at higher temperature (97.0° C) can be attributed to the isotropic clearing point. This could also be confirmed by optical analysis. The polymer showed birefringent textures exactly in the above mentioned temperature range.

CONCLUSION

According to our goal to built up a liquid-crystalline 2-vinylcyclopropane system containing a cholesteric moiety via a spacer group, the new 1-ethoxycarbonyl-1-[5-(cholesteryloxycarbonyl)pentoxy-carbonyl]-2-vinylcyclopropane (**4**) was synthesized and polymerized successfully in solution to yield a ring-opened, partially unsaturated polymer. The polymer displayed typical thermotropic mesomorphic behavior.

Starting from these results the variation of monomer structures to alter the phase transitions of both the monomer and the polymer are in progress.

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Received September 12, 2002