

Articles

Metallopolymers: Preparation of Polymer Films with a High Content of Metal Centers via Photopolymerization of Metal-Containing Liquid-Crystalline Monomers

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The photoinitiated polymerization of several metal-containing liquid crystals is described. Four metal carboxylates bearing terminal acrylate functions were investigated as monomeric units: a copper(II) complex derived from an aliphatic carboxylate, of formula $\text{Cu}_2(\text{O}_2\text{C}-(\text{CH}_2)_{11}-\text{Acr})_4$, ($\text{Acr} = -\text{OCO}-\text{CH}=\text{CH}_2$), a zinc(II) complex with the 3,4-bis(11-acryloyloxyundecanoxy)benzoate ligand, of formula $\text{Zn}(\text{O}_2\text{CC}_6\text{H}_3(\text{O}-(\text{CH}_2)_{11}-\text{Acr})_2)_2$ and two magnesium(II) carboxylates, one derived from an aliphatic carboxylate, $\text{Mg}(\text{O}_2\text{C}-(\text{CH}_2)_{11}-\text{Acr})_2$, and one from the disubstituted benzoate, $\text{Mg}(\text{O}_2\text{CC}_6\text{H}_3(\text{O}-(\text{CH}_2)_{11}-\text{Acr})_2)_2$. These compounds were shown, by DSC and X-ray diffraction studies, to exhibit a hexagonal columnar mesophase at room temperature. The photopolymerization of the Zn(II) and Mg(II) derivatives, either in the liquid-crystalline phase or in the isotropic phase, was performed with high final conversion, from 50 to 80%, depending on the compound and on the temperature, whereas the copper complex was found unreactive toward the polymerization process. Thin films of the polymer prepared with the Zn(II) monomer were characterized by infrared spectroscopy and elemental analysis. The data indicate that at least 80% of the coordinating sites included in the polymer matrix are bonded to metal centers, resulting in a polymer with a high zinc content (ca. 5% wt/wt).

Introduction

Within the vast area of liquid-crystal research, a new class of materials is expanding very rapidly: the metal-containing liquid crystals or metallomesogens. The presence of metal centers in the mesogenic units has been shown to bring about new structural properties¹ as well as potentially interesting physical properties. Much of the recent work has been focused on transition-metal-containing liquid crystals, and most studies deal with the design of new metallomesogens as well as their

mesomorphic properties, on a fundamental point of view. Fewer studies have been devoted to the search of applications based for example on electronic or optical properties which can be enhanced by the presence of metal atoms.²

Within this frame, we describe here an exploratory strategy for the development of novel, self-organizing, oriented materials with high refractive indexes and birefringence, which could be used in active and passive optical components. The present work is based on a process developed recently to obtain anisotropic polymeric materials, by in situ photopolymerization of

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1997.
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reactive low molar mass liquid crystals oriented in their mesophase.³ It has been shown that the polymeric materials thus obtained retain the anisotropy brought by the monomer mesomorphic phase. The refractive indexes and birefringence of these anisotropic polymers are nearly constant in a much wider temperature range than the starting liquid-crystalline monomers.⁴

We have extended this process to metal-containing liquid crystals with columnar structure, with the aim of elaborating polymers with an anisotropic columnar structure, containing a quantitative ratio of metal centers incorporated, to study their optical properties. The radical nature of the photoinitiated polymerization process has led us to the option of closed-shell metal cations, as opposed to transition-metal centers, to avoid possible inhibition by unpaired valence electrons. In earlier work, we had demonstrated that dialkoxybenzoate complexes of Zn(II) and Mg(II) exhibit a hexagonal columnar mesophase⁵ close to room temperature. In continuation of this study, we describe here the syntheses of reactive monomers based on aliphatic carboxylates and disubstituted benzoates of Mg(II) and Zn(II). We also present the results of the photopolymerization of these metallomonomers, as well as some physicochemical properties of the metallopolymers thus obtained.

Experimental Section

Physicochemical Studies. Differential scanning calorimetry (DSC) measurements were performed using a Perkin-Elmer DSC-7. The samples were prepared in sealed aluminum pans. The thermograms were recorded in the temperature range 220–400 K with a scanning rate of 5 K/min and under a flow of nitrogen.

For the X-ray diffraction experiments, the powdered samples were contained in Lindemann capillaries. X-ray diffraction patterns were recorded photographically using monochromatic Cu K α_1 radiation and a Guinier focusing camera equipped with a bent quartz monochromator.

The photopolymerization process was studied with a Perkin-Elmer DSC-7 modified to allow UV irradiation of the sample.^{3b,c} The monomeric sample was mixed in its molten state with a photoinitiator (concentration in weight ca. 2%): α,α -dimethoxydeoxybenzoin (Irgacure 651 Ciba Geigy). The reference compartment containing an empty pan and the sample pan filled with 1–2 mg of sample were irradiated with a 10 W fluorescent mercury lamp, with an intensity of 0.8 mW/cm² at 365 nm. The sample chamber was purged with nitrogen 5 min before exposure to the UV lamp, and the nitrogen purge was continued during the photopolymerization process. The sample was maintained at constant temperature by the DSC during the photopolymerization.

Syntheses. All starting materials were commercial products of high purity (>99%). The NMR spectra were recorded on a Bruker AC 200 spectrometer, by dissolution of the sample into deuterated chloroform. The infrared spectra were recorded on a FTIR Perkin-Elmer 1650 spectrometer, from pressed KBr pellets.

Free Carboxylic Acids. (i) 12-Acryloyloxydodecanoic Acid ($HO_2C(CH_2)_{11}OCOCH=CH_2$, **4**). Dicaperoxy tetraacetate dihydrate (1.2 mmol, 0.5 g) was dissolved in 50 mL of ethanol at

40 °C and then was slowly added to a solution of 5 mmol (1.08 g) of 12-ol-dodecanoic acid (**1**) in 50 mL of ethanol at room temperature. A vigorous stirring was maintained during 72 h at room temperature. The blue precipitate of the complex dicopper tetrakis(12-ol-dodecanoate) (**2**) was filtered and dried under vacuum at 80 °C for 20 h. Yield: 1.04 g, 88%.

The next step was carried out in a glovebox under argon and with deoxygenated solvents. A heterogeneous mixture was prepared with 0.25 mmol (0.247 g) of **2** and 0.3 g of triethylamine in 100 mL of THF. The flask was wrapped up with aluminum foil in order to exclude direct light, and 1 mmol (0.12 mL) of acryloyl chloride was added to this mixture. After 5 days of stirring, THF was removed by vacuum evaporation and the residue was washed with 50 mL of diethyl ether which was then removed under vacuum. The powder thus obtained was recrystallized in an acetone/water mixture at 2 °C, and the final blue compound dicopper tetrakis(12-acryloyloxydodecanoate) (**3**) which precipitated was filtered and dried under vacuum at 50 °C during several hours. Yield: 0.240 g, 78%.

3 (0.2 mmol) was dissolved in a minimum amount of a THF/water mixture (70:30), and a solution of THF/H₂SO₄ (two droplets of concentrated H₂SO₄ in 200 mL of THF) was slowly added to the blue solution of complex **3** (pH = 5–6), resulting in a complete fading of the solution. THF was removed under vacuum, and the free acid was extracted from the water solution by several fractions of 25 mL of diethyl ether. Evaporation of the solvent yielded the 12-acryloyloxydodecanoic acid (**4**) which was purified by several recrystallizations in heptane at –4 °C. Yield: 0.120 g, 55%.

Elemental analysis experimental (calculated): C 66.34 (66.64); H 9.59 (9.69); O, 22.84 (23.67). IR $\nu(COO)_{Ac}$ 1725 cm⁻¹; $\nu(COO)_{as}$ 1704 cm⁻¹; $\nu(C=C)_{Ac}$ 1635 cm⁻¹. ¹H NMR δ (ppm) CH₂ 1.26–1.64 (18H, M); CH₂COOH 2.32 (2H, T); CH₂OCOCH=CH₂ 4.13 (2H, T); OCOCH=CH₂ 5.79, 6.09, 6.37 (3H, ABX). ¹³C NMR δ (ppm) CH₂ 34.31–24.58 (9C); CH₂OAc 64.62; OCOCH=CH₂ 128.57, 130.27, 171.46; COOH 178.91.

(ii) 3,4-Bis(11-acryloyloxyundecanoxy)benzoic Acid ($HO_2CC_6H_5(OC_{11}OCOCH=CH_2)_2$, **8**). 3,4-Dihydroxybenzoic acid (39.7 mmol, 6.12 g) was dissolved in 75 mL of methanol with 11.6 mmol (2 g) of *p*-toluenesulfonic acid. This solution was maintained at 80 °C during 12 h, and then ca. 65 mL of solvent was removed under vacuum. NaOH (23.6 mmol) dissolved in 25 mL of water was slowly added to the resulting solution (pH = 8). The methyl 3,4-dihydroxybenzoate ester **5** was extracted from the water phase by washing with diethyl ether. Yield: 4.71 g; 70%.

A mixture was prepared with 3 mmol (0.5 g) of the methyl 3,4-dihydroxybenzoate ester **5**, 6 mmol (1.5 g) of 1-bromo-11-undecanol, and 5 g of K₂CO₃ in 50 mL of DMF. This suspension was heated at 80 °C during 3 h, and the solvent was then removed under vacuum. Acetone (100 mL) was added to the residue, and the K₂CO₃ precipitate was eliminated by filtration. The methyl 3,4-bis(11-ol-undecanoxy)benzoate ester **6** was then recrystallized from the acetone solution by cooling to –4 °C. Yield: 1.145 g, 75%.

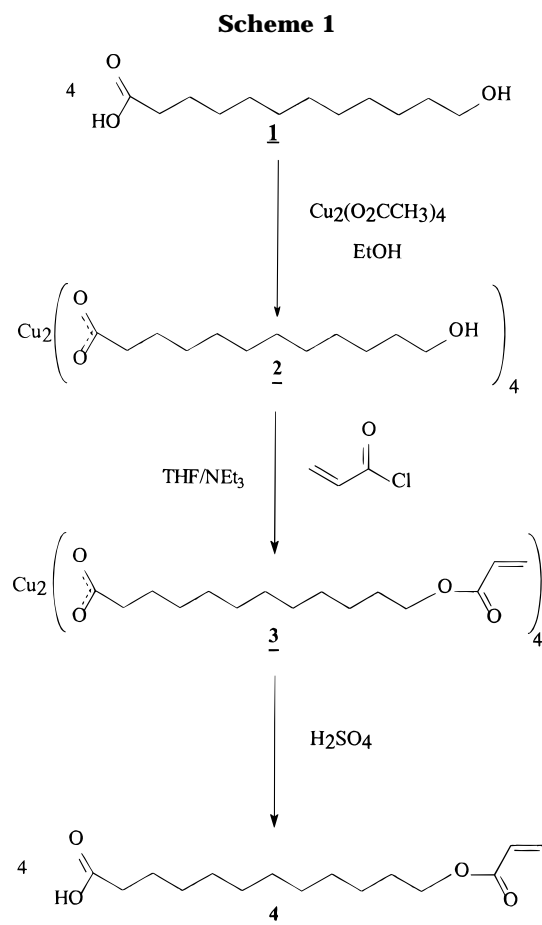
6 (2.2 mmol, 1.120 g) and NaOH (25 mmol, 1 g) in 50 mL of ethanol were heated under reflux for 4 h. At room temperature, the solution was neutralized with an aqueous solution of hydrochloric acid, and the precipitated 3,4-bis(11-ol-undecanoxy)benzoic acid **7** was filtered. Yield: 0.750 g, 69%.

The next step was carried out in a glovebox under argon, and with deoxygenated solvents. A suspension was prepared with 1 mmol (0.495 g) of the 3,4-bis(11-ol-undecanoxy)benzoic acid **7** and 3 mmol (0.3 g) of triethylamine in 10 mL of THF. Acryloyl chloride (3 mmol, 0.24 mL) was added to this mixture. The flask was wrapped up with aluminum foil. After 28 h of stirring, THF was removed under vacuum, and 50 mL of water was added to the residue. The final 3,4-bis(11-acryloyloxyundecanoxy)benzoic acid **8** was extracted from the water phase with chloroform, and after drying on Na₂SO₄, the organic solvent was evaporated under vacuum. Compound **8** was finally purified by column chromatography on silica with dichloromethane as eluent. Yield: 0.345 g, 57%. Elemental analysis experimental (calculated): C 69.52 (69.74); H 9.05 (9.03); O 21.12 (21.23). Mass spectra: M⁺ = 602. Melting point: 79 °C. IR: $\nu(CH_2)$ 3000–2800 cm⁻¹; $\nu(COO)_{Ac}$ 1728

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and 1712 cm^{-1} ; $\nu(\text{COO})$ as 1671 cm^{-1} ; $\nu(\text{C}=\text{C})_{\text{Acr}}$ 1635 cm^{-1} . $^1\text{H NMR } \delta$ (ppm) CH_2 1.41–1.84 (18 H, M); CH_2O 4.03 (4H, M); CH_2Acr 4.15 (4H, T); $\text{OOCCH}=\text{CH}_2$ 5.79–6.11–6.38 (6H, ABX); Ar 6.87 (H, D), Ar 7.55 (H, D), Ar 7.70 (H, D–D). $^{13}\text{C NMR } \delta$ (ppm) CH_2 = 25.81–29.36 (9C); CH_2Acr 64.58 ppm; CH_2O 68.94–69.20; Car 111.91–114, 65–121.38–124.38–148.48–153.85; $\text{OOCCH}=\text{CH}_2$ 128.57–130.21–162.73; COOH 171.28.

Metal Complexes. (i) *Copper(II) 12-Acryloyloxyundecanoate* (Scheme 1): $\text{Cu}_2(\text{O}_2\text{C}(\text{CH}_2)_{11}\text{OCOCH}=\text{CH}_2)_4$. This intermediate complex **3** was isolated during the synthesis of the 12-acryloyloxyundecanoic acid (see above). It was then purified by recrystallization from heptane.

(ii) *Magnesium 12-Acryloyloxyundecanoate Dihydrate*: $\text{Mg}(\text{O}_2\text{C}(\text{CH}_2)_{11}\text{OCOCH}=\text{CH}_2)_2 \cdot 2\text{H}_2\text{O}$. 12-Acryloyloxyundecanoic acid (1 mmol, 0.266 g) in 50 mL of water was neutralized by 1 mmol (40 mg) of NaOH in 10 mL of water. Magnesium chloride hexahydrate (0.5 mmol, 0.101 g) was dissolved in 25 mL of water, and this solution was slowly added to the first solution. After 30 min of vigorous stirring, the precipitate was filtered and washed with water. Finally, the magnesium complex was recrystallized from 50 mL of *n*-heptane. Yield: 0.127 g, 43%. Elemental analysis experimental (calculated): Mg 3.00 (4.05); C 61.00 (60.15); H 9.20 (9.09); Na 0.16 (0). $^1\text{H NMR } \delta$ (ppm) CH_2 1.24–1.63 (18 H, M); CH_2COO 2.26 (2H, M); $\text{CH}_2\text{OCOCH}=\text{CH}_2$ 4.11 (2H, T); $\text{OCOCH}=\text{CH}_2$ 5.77, 6.04, 6.36 (3H, ABX). $^{13}\text{C NMR } \delta$ (ppm) CH_2 25.87–29.59 (18 C); CH_2COO 64.53; $\text{OCOCH}=\text{CH}_2$ 128.56, 130.20, 162.37; COO 178.80.

(iii) *Magnesium Bis(11-acryloyloxyundecanoxy)benzoate*: $\text{Mg}(\text{O}_2\text{CC}_6\text{H}_3(\text{OC}_{11}\text{OCOCH}=\text{CH}_2)_2)_2$. 3,4-Bis(11-acryloyloxyundecanoxy)benzoic acid (0.5 mmol, 0.301 g) in a mixture of 10 mL of ethanol and 10 mL of water was neutralized with 0.5 mmol (20 mg) NaOH in 2 mL of water. Magnesium chloride hexahydrate (0.25 mmol 50 mg) dissolved in 5 mL of water was slowly added to the first solution. After ca. 2 h of vigorous stirring, the solvent was evaporated under vacuum. The residue thus obtained was washed with water, then extracted

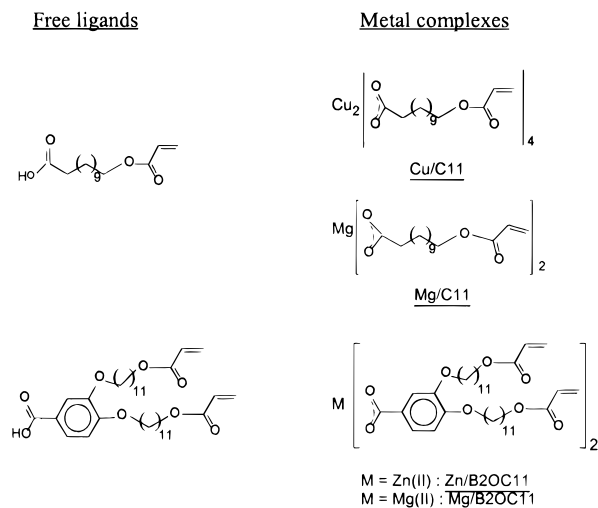


Figure 1. Formulas of the free ligands and carboxylate complexes and abbreviated notations.

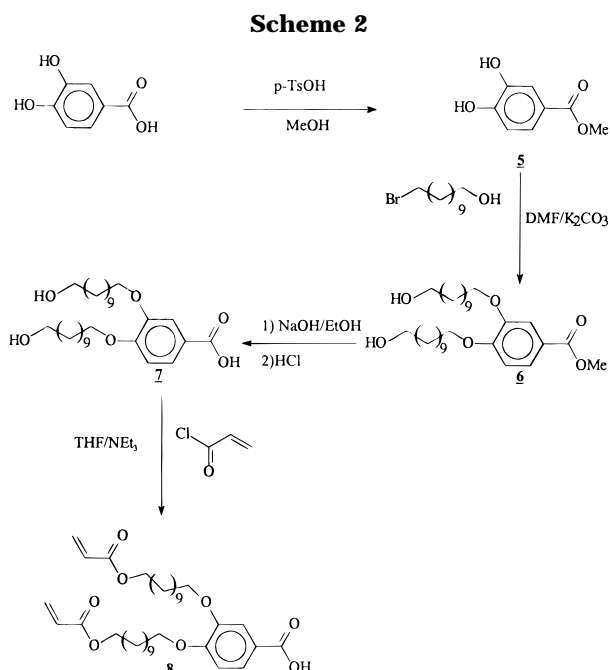
with diethyl ether, and the resulting ether solution was evaporated to dryness under vacuum. Yield: 0.082 g, 52%. Elemental analysis experimental (calculated): Mg 1.69 (1.98); C 67.12 (68.47); H 8.72 (8.70); Na 620 ppm (0). $^1\text{H NMR } \delta$ (ppm) CH_2 1.26–1.61 (18H, M); CH_2O 3.86 (4H, M); $\text{CH}_2\text{OCOCH}=\text{CH}_2$ 4.10 (4H, M); $\text{OCOCH}=\text{CH}_2$ 5.77, 6.08, 6.40 (3H, ABX). $^{13}\text{C NMR } \delta$ (ppm): CH_2 25.87–29.48 (9 C); $\text{CH}_2\text{OCOCH}=\text{CH}_2$ 64.61; CH_2O 68.85; Car 111.80, 114.65, 121.38, 124.33, 148.48, 153.85; $\text{OCOCH}=\text{CH}_2$ 128.57, 130.25, 166.22.

(iv) *Zinc Bis(11-acryloyloxyundecanoxy)benzoate*: $\text{Zn}(\text{O}_2\text{C}-\text{C}_6\text{H}_3(\text{OC}_{11}\text{OCOCH}=\text{CH}_2)_2)_2$. 3,4-Bis(11-acryloyloxyundecanoxy)benzoic acid (1 mmol, 0.602 g) in a mixture of 10 mL of water was neutralized with 1 mmol (40 mg) of NaOH dissolved in 2 mL of water. Zinc sulfate hexahydrate (0.5 mmol, 0.129 g) dissolved in 10 mL of water was then slowly added and under vigorous stirring. After 2 h of stirring, the final white product was extracted with chloroform, then the organic solvent was completely removed under vacuum. Yield: 0.507 g, 76%. Elemental analysis experimental (calculated): Zn 4.48 (5.15); C 65.27 (66.25); H 8.17 (8.42); Na 0.12 (0). $^1\text{H NMR } \delta$ (ppm) CH_2 1.27–1.80 (18H, M); CH_2O 3.99 (4H, M); $\text{CH}_2\text{OCOCH}=\text{CH}_2$ 4.12 (4H, T); $\text{OCOCH}=\text{CH}_2$ 5.77, 6.10, 6.37 (6H, ABX); H_{Ar} 6.80 (H, D); H_{Ar} 7.64 (H, D), H_{Ar} 7.77 (H, D–D). $^{13}\text{C NMR } \delta$ (ppm) CH_2 25.84–29.44 (18 C); $\text{CH}_2\text{OCOCH}=\text{CH}_2$ 64.56; CH_2O 68.93–69.57; Car 111.80, 116.08, 125.01, 148.24, 153.25; $\text{OCOCH}=\text{CH}_2$ 128.60, 130.16, 166.17.

Results and Discussion

1. Materials and Synthesis. The metal complexes described in the present work were formed by the combination of zinc or magnesium with two types of carboxylate ligands. The first one is derived from a long-chain aliphatic carboxylate terminally substituted by an acrylate function (noted Acr below), of formula $\text{O}_2\text{C}-(\text{CH}_2)_{11}-\text{Acr}$, while the second one derives from a disubstituted benzoate, the 3,4-bis(11-acryloyloxyundecanoxy)benzoate of formula $3,4-\text{O}_2\text{CC}_6\text{H}_3(\text{O}-(\text{CH}_2)_{11}-\text{Acr})_2$. For the sake of simplicity, these carboxylate ligands will be noted respectively C11 and B2OC11. A copper complex of the reactive aliphatic carboxylic ligand C11 has also been prepared, to check the influence of a transition metal on the photopolymerization process. The metallic complexes will be denoted M/C11 or M/B2OC11, where **M** represents the metal center: M = Cu(II), Mg(II), or Zn(II) (see Figure 1).

Four complexes were investigated: one copper carboxylate, Cu/C11, one zinc benzoate, Zn/B2OC11, and two magnesium complexes, Mg/C11 and Mg/B2OC11.



The synthesis of the free ligands containing the reactive acrylate function has not yet been published in the literature to our knowledge, and we have developed new synthetic procedures to prepare the aliphatic carboxylate C11 and the disubstituted benzoate ligand B2OC11.

Free Ligands. The synthesis of the 12-acryloyloxydodecanoic acid was performed starting with the commercial 12-hydroxydodecanoic acid. It has been necessary to protect the carboxylic function during the addition of the acrylate group, and this was conveniently achieved by complexation with copper, because a classical protection, by esterification for example, was not suitable, due to problems with the deprotection step. The overall synthetic pathway is represented in Scheme 1. The first step is the complexation of 12-hydroxydodecanoic acid **1** with copper(II) by a well-known procedure,⁶ to give the dinuclear complex $\text{Cu}_2(\text{O}_2\text{C}-(\text{CH}_2)_{11}-\text{OH})_4$ **2**, which was then reacted with acryloyl chloride, to yield the $\text{Cu}/\text{C11}$ compound **3**. The demetalation was readily carried out in a strong acidic medium, to give the final 12-acryloyloxydodecanoic free acid **4**.

3,4-Bis(11-acryloyloxyundecanoxy)benzoic acid was prepared from the commercially available 3,4-dihydroxybenzoic acid, by a procedure similar to that already described for monosubstituted (*n*-acryloyloxyalkoxy)benzoic acids^{4a} and represented in Scheme 2. The carboxylic acid function is first protected by esterification, to give the methyl ester **5**, then the alkoxy groups are attached, by reacting **5** with 11-bromoundecanol, yielding compound **6**. After deprotecting the carboxylic function, the substituted benzoic acid **7** is then reacted with acryloyl chloride to give the final free acid **8**.

Both compounds **4** and **8** have been characterized by elemental analysis, infrared (IR) spectroscopy, and ¹H and ¹³C nuclear magnetic resonance (NMR). All details regarding the synthesis and results of the characterizations are given in the Experimental Section.

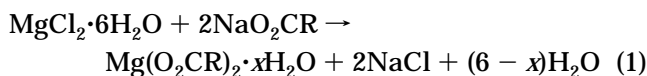
Metal Complexes. The copper carboxylate, $\text{Cu}/\text{C11}$, was isolated during the synthesis of the 12-acryloyloxydodecanoic acid (see Scheme 1).

Table 1. Vibration Frequencies of the Symmetrical ($\nu(\text{COO})_{\text{sym}}$) and Asymmetrical ($\nu(\text{COO})_{\text{asym}}$) Stretching Modes (cm^{-1}) of the CO_2 Group for Various Metal Complexes, as Well as the Difference $\Delta\nu = \nu(\text{COO})_{\text{asym}} - \nu(\text{COO})_{\text{sym}}$

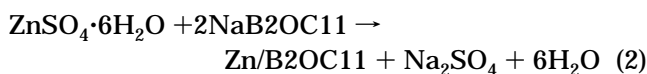
| complex | $\nu(\text{COO})_{\text{asym}}$ (cm^{-1}) | $\nu(\text{COO})_{\text{sym}}$ (cm^{-1}) | $\Delta\nu$ (cm^{-1}) |
|---|---|--|-------------------------------------|
| $\text{Cu}/\text{C11}$ | 1588 (1587) | 1410 (1405) | 178 |
| $\text{Mg}/\text{C11}\cdot 2\text{H}_2\text{O}$ | 1588 | 1410 | 178 |
| $\text{Mg}/\text{C11}^a$ | 1560 | 1412 | 148 |
| $\text{Mg}/\text{B2OC11}$ | 1558 | 1434 | 124 |
| $\text{Zn}/\text{B2OC11}$ | 1559 | 1433 | 126 |

^a Obtained by heating $\text{Mg}/\text{C11}\cdot 2\text{H}_2\text{O}$ for 24 h at 60 °C.

The magnesium complexes were obtained by reaction of the magnesium chloride with the sodium salt of the corresponding carboxylic acid, according to the following equation ($\text{O}_2\text{CR} = \text{C11}$ and $x = 2$; $\text{O}_2\text{CR} = \text{B2OC11}$ and $x = 0$):



The zinc complex was prepared by reaction of zinc sulfate with the sodium salt of the corresponding carboxylic acid:



All compounds have been characterized by IR spectroscopy, ¹H NMR and elemental analysis (see Experimental Section) of the metal, C, H, and Na.

The IR spectra of the metal complexes were examined in the region between 1600 and 1400 cm^{-1} , where the asymmetric stretching mode (ν_{as}) and the symmetric stretching mode of the CO_2 group (ν_{s}) are observed. It is known (demonstrated precisely for acetate complexes,⁷ and most of the time extrapolated to other carboxylates) that for carboxylate complexes the position of these bands, and particularly the value of the difference $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$, may provide some information on the coordination mode of the carboxylate group,⁷ i.e., monodentate, bidentate chelating, or bidentate bridging. In our case, the ν_{s} and ν_{as} bands were located in the region also displaying the CH_2 bending mode (at ca. 1470 cm^{-1}) as well as the aromatic ring stretching frequencies, found here at 1600 and 1430 cm^{-1} . All these modes could be assigned by comparisons with the IR spectra of several dialkoxybenzoic acids with different chain lengths, homologues of the free ligands described here. The values of the ν_{as} and ν_{s} frequencies as well as of the separation $\Delta\nu$ have been reported in Table 1, for the four compounds described here.

The ν_{as} band of all the complexes shows a downshift, compared to the asymmetric mode of the free ligand, of 116–144 cm^{-1} for $\text{M}/\text{C11}$ with $\text{M} = \text{Cu}$ and Mg ($\nu(\text{COO})_{\text{asym}}$ = 1704 cm^{-1}) and a shift of ca. 115 cm^{-1} for $\text{M}/\text{B2OC11}$ with $\text{M} = \text{Mg}$ and Zn ($\nu(\text{COO})_{\text{asym}}$ = 1671 cm^{-1}). The difference $\Delta\nu$ for both $\text{M}/\text{C11}$ compounds (see Table 1), was found close to 180 cm^{-1} , which may be attributed to a bidentate bridging mode⁷ of the carboxylate groups. This result is consistent with the known crystallographic structures of either $\text{Cu}(\text{II})$ car-

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(7) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

boxylates⁸ or Mg(II) butyrate.⁹ For the dialkoxybenzoate complexes of magnesium and zinc, the separation $\Delta\nu$ is about 125 cm^{-1} , which is indicative of a chelating or bridging bidentate mode.⁷ Several typical bands of the acrylate group^{3b} were also observed at 1725 , 1635 , 970 , and 810 cm^{-1} .

The presence of acrylate functions did not seem to influence the coordination geometry of the carboxylate ligands, since in all cases the value of $\Delta\nu$ was similar to that found for the precursors,⁵ i.e., the same complexes without acrylate functions.

The main information given by the ^1H NMR spectra of Cu/C11, Mg/C11, and Zn/B2OC11 was the chemical equivalence of the two ligands in the formal molecular unit. For Mg/B2OC11, the broad multiplet of the aromatic protons precluded any conclusion concerning the possible chemical equivalence of ligands.

2. Mesomorphic Properties. The mesomorphic properties have been studied by optical microscopy under polarized light (OM), differential scanning calorimetry (DSC), and powder X-ray diffraction.

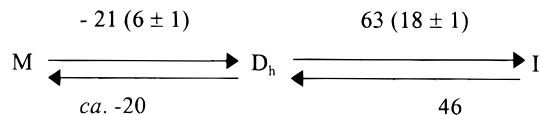
The free acids **4** and **8** were found to be nonmesomorphic, similarly to their precursors, i.e., the aliphatic carboxylic acids and bis(*n*-alkoxy)benzoic acids.⁵

Mg/C11 and Cu/C11. These complexes are not mesomorphic and their melting point was observed by OM and DSC at $61\text{ }^\circ\text{C}$ for Mg/C11 ($\Delta H_{C-I} = 77\text{ kJ/mol}$) and $40\text{ }^\circ\text{C}$ for Cu/C11 ($\Delta H_{C-I} = 43\text{ kJ/mol}$). The X-ray diffraction spectra of both compounds show a lamellar crystalline phase at room temperature (interlamellar distance $d = 51\text{ \AA}$ for Mg/C11 and $d = 48.5\text{ \AA}$ for Cu/C11). This result is in sharp contrast to the mesomorphic properties observed for the precursor analogues, i.e., aliphatic linear carboxylates of Cu(II)^{6,10} and Mg(II)¹¹ without acrylate functions, which were found to give a transition from a lamellar crystalline phase to a hexagonal columnar mesophase, at ca. $110\text{ }^\circ\text{C}$ in both cases.

In the case of Mg/C11, a broad endothermic peak appeared at $115\text{ }^\circ\text{C}$ on the first heating thermogram only. This irreversible transition probably corresponds to the loss of water molecules, as checked by IR spectroscopy and a TGA experiment, and is immediately followed by an exothermic deviation of the baseline in the DSC trace. This latter exothermic process is most likely related to the thermal polymerization, as checked by an IR spectrum of the compound after heating to $300\text{ }^\circ\text{C}$, where the typical acrylate bands have completely disappeared.

In both cases, it is clear that the introduction of an acrylate group precludes the formation of a columnar mesophase. The acrylate functions introduce two new parameters, compared to the precursors, which can affect the stability of both the mesophase and the crystalline phase: the steric effect and the dipole moment. The first effect should destabilize the crystalline phase, as it perturbs the regular packing of the paraffinic

Scheme 3



peripheral chains. Such a phenomenon had been suggested to be responsible for the decrease in the crystal-to-mesophase transition temperatures observed for some Cu(II) carboxylates containing unsaturations in the middle or in the end of the peripheral chains, as compared to the linear aliphatic homologues.¹² In contrast, the presence of dipolar intermolecular interactions may preclude the disordering of the aliphatic chains, which is necessary to efficiently fill the space in a liquid-crystalline state: this second effect could be responsible for a destabilization of the liquid-crystalline phase.

For Cu/C11 and Mg/C11, the first effect may be responsible for the lowering of the fusion temperatures, compared to the non reactive homologues, i.e., a destabilization of the crystalline phase due to the presence of acrylate groups. The absence of a columnar phase may be related to the dipolar interactions between peripheral chains, as described above.

The dialkoxybenzoate complexes show a more complex behavior, with the presence of mesophases, as seen by DSC and optical microscopy. The liquid-crystalline behavior observed, despite the acrylate functions, could be due to the eight peripheral chains which can fill the space more efficiently than with the aliphatic carboxylates of Mg(II) or Cu(II) (see above).

Mg/B2OC11. The magnesium complex shows only one endothermic peak at $57\text{ }^\circ\text{C}$ ($\Delta H = 166\text{ kJ/mol}$) between room temperature and $100\text{ }^\circ\text{C}$, reproducible after several heatings and corresponding to a transition from a birefringent sticky powder at room temperature to nonbirefringent viscous droplets. Recrystallization was very slow under the microscope (several days), whereas it was readily observed during a DSC cooling experiment. Heating above $100\text{ }^\circ\text{C}$ displays only a slow irreversible exothermic thermogram certainly related to the thermal polymerization, as was observed in the case of the Mg/C11 complex (see above).

The X-ray diffraction pattern obtained at $60\text{ }^\circ\text{C}$ for Mg/B2OC11 exhibited several reflections in the low-angle region, which could not be indexed according to classical symmetries and could be due to a two-phase mixture. In the wide-angle region, a broad reflection appeared corresponding to the melting of the aliphatic chains. These results, recorded slightly above the transition temperature, preclude any conclusion about the nature of this viscous isotropic phase. They may be indicative either of a mesomorphic state with a homeotropic alignment under the microscope, or of the liquid state, where some crystalline domains remain from the solid phase, due to the high viscosity of the phase.

Zn/B2OC11. On heating between -50 and $100\text{ }^\circ\text{C}$, two transitions were observed by DSC at $-21\text{ }^\circ\text{C}$ ($\Delta H = 6\text{ kJ/mol}$) and $63\text{ }^\circ\text{C}$ ($\Delta H = 18\text{ kJ/mol}$; Scheme 3). By optical microscopy, the sticky powder appeared at room temperature as a noncharacteristic birefringent texture, and the second transition, observed at $63\text{ }^\circ\text{C}$, cor-

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responded to the clearing point, as confirmed by X-ray diffraction.

Two X-ray diffraction patterns have been recorded at 24 and 40 °C. The low-angle region contained several sharp reflections with reciprocal spacings in the ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$, which was interpreted as indicative of a hexagonal columnar structure. In the wide-angle region, a broad reflection was present, confirming the mesomorphic nature of the phase. The intercolumnar distance D was measured at 24 °C ($D = 39.2$ Å) and at 40 °C ($D = 39.3$ Å). These values were found to be very close to that obtained for the zinc dialkoxybenzoate precursor with 15 carbon atoms in the alkoxy peripheral chains ($D \approx 39.3$ Å at 30 °C).⁵ This result is consistent with the overall number of "heavy" atoms (i.e., carbon and oxygen) in the acrylated compound Zn/B2OC11, which is also 15, as in the bis(pentadecyloxy)benzoate precursor. This structural analogy could possibly indicate that the molecular organization along the columns is similar in the precursor and in the acrylated derivative.

It has not been possible to record X-ray diffraction spectra below room temperature, and therefore the nature of the phase below -21 °C could not be elucidated.

3. In Situ Photopolymerization. We have studied first the influence of the nature of the metal atom on the photopolymerization process in the isotropic liquid phase, and second the influence of the phase structure (liquid crystalline and isotropic) for Zn/B2OC11, which shows a hexagonal columnar mesophase at room temperature. The details of the photopolymerization experiments are described in the experimental section.

Influence of the Metal Atom on the Photopolymerization. Four pure metal complexes, Cu/C11, Mg/C11, Mg/B2OC11, and Zn/B2OC11, were irradiated by UV light in their isotropic phases while simultaneously checking the DSC data, to record the exothermic enthalpy resulting from the photopolymerization. The utility of this technique in monitoring photopolymerization processes and in providing quantitative conversion rates has been described in previous papers.^{3b,c} The Cu(II) complex showed a flat curve indicating an inhibition of the photopolymerization process. This phenomenon cannot be due to an absorption of the incident light, as the irradiation wavelength was 365 nm, far from the absorption band of the copper carboxylates (ca. 700 nm). This inhibition may be due to the presence of two unpaired electrons in the binuclear metallic core, which can trap the radicals generated by irradiation in the photoinitiation process. In contrast, the photopolymerization has been successful for the magnesium and zinc compounds. The shapes of the DSC traces obtained for Mg and Zn complexes (Figure 2) are very similar to those obtained for purely organic acrylates.^{3b,13} Immediately after the UV light is switched on, the conversion rate increases sharply. The maximum rate is reached 30–40 s after switching on the UV light. For comparison, this maximum is reached after 5 s for typical organic mesogenic diacrylates.^{3b,13} The polymerization rate then decreases and falls below the detection limit after a few minutes. The Mg(II) complexes gave sharp DSC peaks, while the Zn complex exhibited

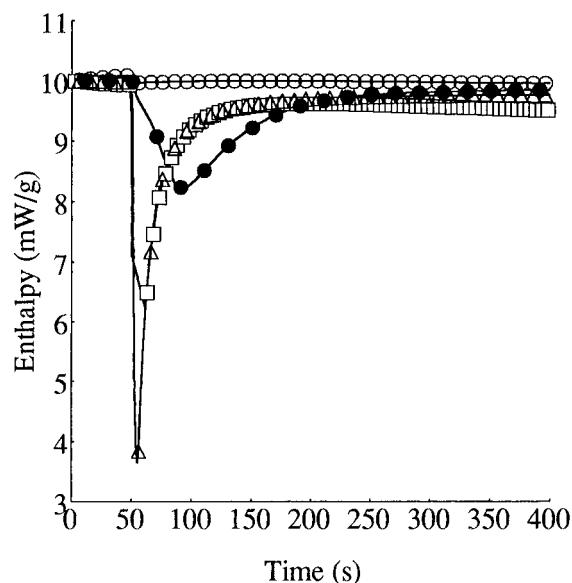


Figure 2. DSC exotherms of the photopolymerization of different metal complexes: Cu/C11 (○), Mg/C11 (□), Mg/B2OC11 (△), Zn/B2OC11 (●).

Table 2. Final Conversion of Metal Carboxylates upon Photopolymerization in the Isotropic Phase, with 2.5 wt % of Initiator and under Nitrogen Atmosphere

| compound | polym temp (°C) | final conversion ^a (mol %) |
|-----------|-----------------|---------------------------------------|
| Cu/C11 | 70 | 0 |
| Mg/C11 | 70 | 70 |
| Mg/B2OC11 | 60 | 70 |
| Zn/B2OC11 | 65 | 70–80 |

^a Experimental error is estimated at $\pm 10\%$.

a broad peak, mostly due to the high viscosity of the isotropic phase for this latter compound.

By integration of these curves and from the known polymerization heat of one acrylate function (78 kJ/mol),^{3b,13} we have calculated the final polymerization conversions, which are reported in Table 2. These conversions are about 70–80%, similar to that usually found for the conversion of organic acrylate compounds.^{3b,13}

Photopolymerization Process of Zn/B2OC11. The influence of temperature has been investigated for this complex, which shows a hexagonal columnar mesophase at room temperature and the isotropic phase above 63 °C. Figure 3 shows typical DSC curves of isothermal measurements at various temperatures during UV irradiation of the monomer.

By integration of the DSC polymerization curves, the ultimate conversion of the monomer was calculated. These data are listed in Table 3, where the monomer conversion is given for each polymerization temperature; the final conversion reaches a maximum of ca. 80% when the polymerization is carried out above 50 °C.

Figure 4 shows the conversion rate at time t , calculated by partial differentiation within the time range t , $t + dt$ ($dt = 2$ s) of the DSC curves, versus the monomer conversion at time t , calculated by partial integration of the exothermic peak between the onset and time t . The shape of these curves, which have been obtained at different polymerization temperatures, shows similarities to those obtained for organic liquid crystals and non-liquid-crystal diacrylates. The conversion rate does not adopt a steady state but increases immediately after

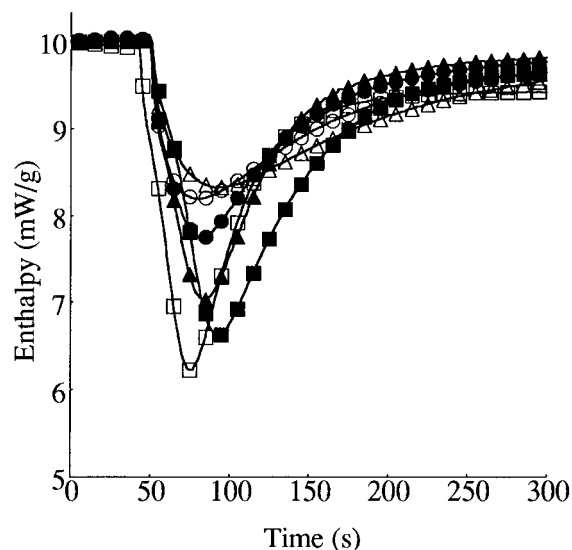


Figure 3. DSC exotherms of the photopolymerization of Zn/B2OC11 at different temperatures: 15 °C (○), 25 °C (△), 35 °C (●), 45 °C (▲), 55 °C (□), 65 °C (■).

Table 3. Final Conversion to Metallopolymer at Different Temperatures for Zn/B2OC11

| temp (°C) | final conversion ^a (mol %) | temp (°C) | final conversion ^a (mol %) |
|-----------|---------------------------------------|-----------|---------------------------------------|
| 15 | 50 | 45 | 70 |
| 25 | 60 | 55 | 80 |
| 35 | 60 | 65 | 70–80 |

^a Experimental error is estimated at $\pm 10\%$.

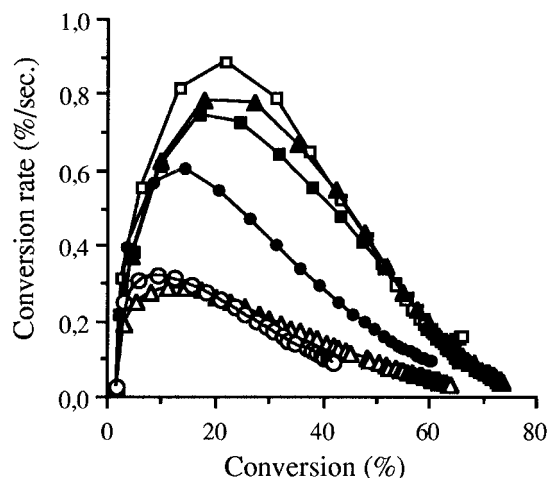


Figure 4. Conversion rate (mol %/s) versus conversion (mol %) calculated from the exotherms represented on Figure 3 (see text for the method of calculation of these quantities), for the Zn/B2OC11 complex: 15 °C (○), 25 °C (△), 35 °C (●), 45 °C (▲), 55 °C (□), 65 °C (■).

the beginning of the irradiation. This autoacceleration, or Trommsdorff effect,¹⁴ is attributed to gelation resulting in a low mobility of the reacting polymer end groups. Gelation slows the termination process and leads to high local radical concentrations, resulting in efficient topochemical processes. It is interesting to note in this respect that photopolymerization in the isotropic phase at 65 °C is less efficient than those carried out in the columnar mesophase at 45 and 55 °C.

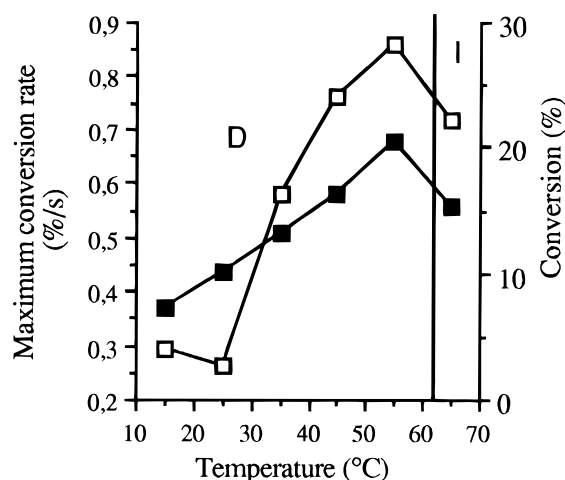


Figure 5. Maximum conversion rate (□) in mol %/s and conversion (■) in percent at this maximum rate, deduced from the curves of Figure 4, plotted as a function of temperature, for the Zn/B2OC11 complex. The transition region from the columnar phase (D) to the isotropic phase (I) is shown between two vertical lines.

The maximum conversion rate and the conversion at this maximum rate have been calculated from the data represented on Figure 4, and they have been plotted in Figure 5 as a function of temperature. Both parameters increase steadily with temperature in the columnar mesophase and decrease to a relatively low value in the isotropic phase (65 °C). These observations corroborate previous studies of polymerization in liquid-crystal media,¹⁵ which have led to the conclusion that two basic properties of liquid-crystalline materials may contribute to the polymerization kinetics of liquid-crystalline monomers. First, the ordering effect in a liquid-crystal medium can provide a unique alignment of polymerizable monomers, affecting both the propagation and termination processes. Second, the anisotropic mobility and diffusion, depending on the specific nature of the mesophase, can also change the polymerization propagation and termination kinetics. The high maximum rate observed for polymerization in the columnar phase could be due to the ordering effect, and the lower value in the isotropic phase could indicate the loss of orientation of the acrylate monomer. Apparently, at 25 °C the mobility required for polymerization rate enhancement is attained. The increase of the maximum rate with temperature in the range 25–55 °C could indicate that the loss of order of the monomers is more than compensated by their increase in mobility.

4. Physicochemical Properties of the Metallopolymer. The metallomonomer Zn/B2OC11 was deposited on a glass plate without any surface treatment. It was heated to its liquid-crystal phase (ca. 60 °C) and then strongly pressed between two glass plates, and it was finally irradiated by UV light. It was observed that the initially transparent film of the monomer remained clear during the polymerization reaction and gave a transparent polymer film. This result points to the absence of phase separation during the polymerization reaction.^{3b}

The Zn content of the polymer is equal to that of the monomer within experimental error (4.32% vs 4.48%),

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Table 4. Refractive Indexes and Birefringence at 25 °C for Zn/B2OC11 in Its Monomeric and Polymeric States

| state | treatment | refractive indexes | | birefringence |
|---------|-------------|--------------------|----------------------|---------------|
| | | n_1 | n_2 | |
| monomer | | | | |
| D_h | oriented | 1.527 | 1.516 | 0.011 |
| D_h | nonoriented | 1.524 | 1.517 | 0.007 |
| polymer | | | | |
| D_h | | 1.535 | not enough precision | |

indicating quantitative polymerization without loss of metal. Comparison with the calculated value of 5.15% suggests that at least 80% of the coordinating sites of the polymer are bound to Zn(II) centers.

A DSC study of this polymeric film showed no transition between 40 and 250 °C, pointing to the absence of any liquid-crystalline phase and indicating a stable and highly cross-linked polymer. Another indication of a high mean degree of polymerization is the complete insolubility of the polymer in chloroform, dichloromethane, or ethanol. This lack of suitable solvent also precludes further characterization of the polymer by gel permeation chromatography (GPC). Moreover, the reliability of GPC in the present case would suffer from the absence of appropriate reference polymers, as the polarity of our materials is very different from those of normal standards.

The structure of the film has also been investigated by X-ray diffraction. A set of reflections was observed in the low-angle region, which is typical of a columnar hexagonal structure, indicating that the mesomorphic structure of the monomeric state had been retained during the polymerization process. The intercolumnar distance found for the polymer was 33.7 Å, whereas in the monomer mesophase, the intercolumnar distance was 39.2 Å. This contraction of the hexagonal array is probably due to the contraction of peripheral chains belonging to adjacent columns, upon polymerization. Due to the very high viscosity of the Zn/B2OC11 in its columnar mesophase, it has not been possible to orient the monomeric compound over large distances.

The optical birefringence of the Zn/B2OC11 compound in either its monomeric or polymeric state has been investigated by measurements of the refractive indexes with an Abbe refractometer, and the results are reported in Table 4. In the case of the monomer, two sets of data have been obtained, one on an unoriented sample ($\Delta n = 0.007$) and another on a sample that had been partially aligned by stretching on a glass plate; the latter resulted in a slight increase of the birefringence to $\Delta n = 0.011$. We believe that this marginal difference has little physical significance and is within the limits of experimental errors, as the birefringence given by an Abbe refractometer is related more to molecular properties rather than to the macroscopic order parameter. Besides, the polymeric film, which had been prepared without any alignment of the monomer prior to the photopolymerization, showed a very low birefringence,

and only one refractive index could be accurately measured. This may be due to a modification of the columnar structure, which could be related to the shrinkage of the intercolumnar distance observed after the polymerization. We assume that no effect due to a signal broadening may be expected as it has never been observed for polymers resulting from nematic and smectic diacrylates.

Conclusion

We have prepared a new type of metal-containing polymer in which at least 80% of the coordinating sites are bonded to a metal center, resulting in a high metal content (typically about 5 wt %/wt for the Zn polymer). Our strategy of photoinitiated polymerization of liquid-crystalline metallomonomers allows the metal concentration of the monomer to be fully maintained in the polymer. Thus, higher metal contents could be obtained in principle if appropriate metallomonomers with less bulky ligands could be designed.

This study has also revealed that the photopolymerization process is inhibited by copper(II) centers, whereas the closed-shell Mg(II) and Zn(II) complexes could be polymerized as efficiently as other organic diacrylate monomers. Moreover, we have shown that the hexagonal columnar structure of the mesomorphic monomer is retained in the polymer, giving a material with a locally anisotropic structure.

The optical birefringence of the polymeric film of Zn/B2OC11 is rather low, compared to that of materials based on organic liquid-crystalline monomers,^{4a,16} which are typically calamitic mesogens. Some improvement can be expected if a good alignment of the monomer in its mesophase can be achieved before irradiation. Other types of divalent metallomonomers might also result in improved mean refractive index and birefringence of the metalpolymer.

This successful approach, based on the UV irradiation of metal-containing monomers bearing photopolymerizable groups, is encouraging. It offers an opportunity to elaborate new polymeric materials containing a high concentration of various metal centers, with potentially interesting physical properties.

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Supporting Information Available: Infrared, NMR and elemental analyses for the intermediate compounds **2**, **3**, and **5–7** (1 p). Ordering information is given on any current masterhead page.

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