Chiral Liquid-Crystalline Polyacrylates from (S)-(−)-2-methyl-1-butanol.
Synthesis, Mesomorphic Properties and Light Scattering

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A síntese e o comportamento mesomórfico de dois poliacrilatos quirais líquido cristalinos com cadeia lateral derivados do (S)-(−)-2-metil-1-butanol são descritos. Estes novos poliacrilatos quirais mostram dependência das temperaturas de transição de fase com a massa molar e o comprimento do espaçador. O poliacrilato contendo quatro unidades metilênicas no espaçador mostra fase nemática quirial, enquanto que o poliacrilato com espaçador contendo onze unidades metilênicas mostra fase esmética. Além disto, a fase nemática quirial foi encontrada para massa molar menor e fase esmética para massa molar maior. Experimentos de espalhamento de luz foram realizados em soluções diluídas do poliacrilato contendo onze unidades metilênicas em tetrahydrofurano e diclorometano. Valores de massa molar ponderal média, raio de giro e o segundo coeficiente virial foram determinados através de espalhamento de luz estático, enquanto que o coeficiente de difusão e o raio hidrodinâmico foram obtidos por espectroscopia de correlação de fótons. Uma comparação entre as técnicas indica que o comportamento da cadeia é típico de cadeia linear polidispersa em bom solvente.

The synthesis and mesomorphic behavior of two chiral side chain liquid crystalline polyacrylates from (S)-(−)-2-methyl-1-butanol are described. These new polyacrylates show a dependence of the phase transition temperatures on both, molecular weight and spacer length. The polyacrylate with four methylene units in the spacer exhibits a chiral nematic phase whereas the polyacrylate with a spacer containing eleven methylene units presents a smectic phase. In addition, the chiral nematic phase appears for low molecular weight and smectic phase for high molecular weight polyacrylates. Light scattering experiments were performed in dilute solutions of the polyacrylate containing eleven methylene units in tetrahydrofuran and dichloromethane. Values for weight averaged molecular weight, radius of gyration and second virial coefficient were determined by static light scattering whereas the diffusion coefficient and the hydrodynamic radius of the chains were obtained by photon correlation spectroscopy. A comparison between both techniques indicates that the chain behavior can be taken as typical for a polydisperse linear chain in a good solvent.

Keywords: liquid crystal synthesis, chiral polyacrylates, mesomorphic behavior, light scattering.

Introduction

The design and the synthesis of new materials with potential technological applications are of continuous scientific interest. Liquid crystal displays are the most popular choice for the storage, transmission and reproduction of information. In this sense, ferroelectric liquid crystal (FLCs) materials have a great impact in flat panel display technology due to their low power consumption, optical qualities and fast switching eletrooptical effects1,2. Because of the application in ferroelectric display technology, chiral liquid crystalline polymers have been the subject of many studies since 1978, when Ringsdorf and coworkers3 developed a new architecture for polymers entitled side chain liquid crystal polymers (SCLCP).

In a previous paper, we have reported the synthesis, mesomorphic behavior and a preliminary study of light scattering of achiral liquid crystalline polyacrylates possessing a short spacer with four methylene units4. We have found that the phase behavior is dependent on the relationship between polymer backbone, terminal group attached to mesogenic groups and molecular weight. The results from light scattering suggest the formation of aggregates in the THF dilute regime.

In order to investigate the correlation between length

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of the flexible spacer group, chiral terminal chain and molecular weight, we designed the new materials, chiral acryloyloxybenzoate monomers (M) and their homopolymers (P). In this paper we report the synthesis of chiral side-chain liquid crystal polyacrylates containing (S)-4′-(2-methyl-1-butoxy)phenyl 4-[1-(propenyl oxy)alkyloxy]benzoate (M) and investigate the liquid crystal behavior of these polyacrylates.

Taking into account that there are few investigations of the properties of these systems in solution, we have studied their behavior in the dilute regime in tetrahydrofuran and dichloromethane by means of static (Static Light Scattering-SLS) and dynamic light scattering (Photon Correlation Spectroscopy-PCS) techniques.

### Experimental Section

1H NMR and 13C NMR spectra in CDCl3 were obtained in Varian-200 and 300 MHz spectrometers using TMS as the internal standard. IR Spectra were recorded in Nujol on a 3000 Galaxy Series Spectrometer. Elemental analysis was determined using a Perkin-Elmer 2400CHN. Optical rotations were determined using a Perkin Elmer 341 polarimeter at the sodium D line. The thermal transitions and the mesomorphic textures were determined using a Leitz Ortholux polarizing microscope in conjunction with a Mettler FP-52 heating stage and a Mettler FP82. The polymers have been characterized by using Waters GPC systems (Waters 150C refractometer). Molecular weights reported in Table 1 are relative to polystyrene standards.

Purification by column chromatography was carried out on 70-230 mesh Merck silica gel 60. (S)-(−)-2-Methyl-1-butanol (−95%), p-Hydroxy methylbenzoate, 4-benzylxyphephenyl 4-[N,N-dimethylamino]pyridine (DMAP), p-toluenesulfonyl chloride, 1,3-dicyclohexylcarbodiimide (DCC), 2,2′-azobisisobutyronitrile (AIBN), diethyldiisocarbocitalexide (DEAD) and triphenylphosphine (PPh3) were purchased from Aldrich, and used as received unless otherwise specified. Dichloromethane (CH2Cl2) was distilled over calcium hydride (CaH2) under argon immediately before use. Analytical thin-layer chromatography (TLC) was conducted on Merck aluminum plates with 0.2 mm of silica gel 60F-254. Anhydrous sodium sulfate was used to dry all organic extracts. Toluene was first refluxed over sodium and then distilled under argon.

AIBN was freshly recrystallized from methanol.

### (S)-(−)-2-Methyl-1-butyloxytoluenesulphonate

This compound was synthesized according to reference 5. Physical and spectroscopic data: (85%); yellowish oil; [α]D 20 = -3.59º (neat); 1H NMR (CDCl3, 200 MHz) δ 0.7 (t, 3H, J=7.8Hz, CH3), 0.75 (d, 3H, J=7.5Hz, CH3), 1.15 (m, 1H, CH3), 1.4 (m, 1H, CH2), 1.6 (m, 1H, CH), 2.3 (s, 3H, CH3), 3.75 (m, 2H, CH2), 7.25 (d, 2H, J=8Hz, Ar), 7.65 (d, 2H, J=8Hz, Ar).

### (S)-(−)-4-(2-Methyl-1-butyloxy)phenyl benzyl ether

This compound was synthesized from the tosyl derivative (54%) and Mitsunobu reaction 6. The crude product was purified by column chromatography. Eluent: hexane/ethyl acetate (9/1); (63%); white solid; mp 123-125º C; 1H NMR (CDCl3, 200 MHz) δ 0.86 (t, 3H, CH3, J=7.0 Hz), 0.91 (d, 3H, CH3, J=6.60Hz), 1.2 (m, 1H, CH2CH3), 1.45 (m, 1H, CH2CH3), 1.75 (m, 1H, CHCH3), 3.60 (dd, 1H, CHHO, 2J = 9.1 Hz, 3Jtrans 6.9 Hz), 3.69 (dd, 1H, 2Jgen 9.1 Hz, 3Jcis 6.1 Hz), 5.0 (s, 2H, CH2Ph), 6.72 (m, 4H, Ar), 7.29 (m, 5H, Ar).

### Table 1: Comparative data and thermal properties (Tg / °C) of the chiral homopolymers (P)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Mn</th>
<th>Mw/Mn</th>
<th>Yields %</th>
<th>K</th>
<th>S</th>
<th>N*</th>
<th>l</th>
<th>ΔH b</th>
<th>[α]D 20</th>
</tr>
</thead>
<tbody>
<tr>
<td>P11</td>
<td>25,779</td>
<td>3.33</td>
<td>92</td>
<td>60.7</td>
<td>110.3</td>
<td>•</td>
<td>2.13</td>
<td>+ 4.0</td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td>10,569</td>
<td>1.79</td>
<td>55</td>
<td>43.8</td>
<td>81.2</td>
<td>•</td>
<td>0.59</td>
<td>+ 3.0</td>
<td></td>
</tr>
</tbody>
</table>

a Phase transition: K crystal phase, S smectic phase, N* chiral nematic phase. b The enthalpy (kJ mru-1) in the phase transition from liquid state to a liquid crystalline state; mru = mole repeating unit. c Glass Transition. Mn: g mol-1, [α]: 1.0 g in 100 mL CH2Cl2.
4-[(4-propenoyloxy)undecyloxy]benzoic acid (B)

The compound (B) was synthesized according to references 4, 7 and 8 (92%). White solid; mp 94°C (isopropanol); IR νmax/cm⁻¹ 3080-2700, 2929, 2853, 1718, 1685, 1605, 1464, 1250, 1177, 1037, 854, 772 (KBr); 1H NMR (CDCl₃, 200 MHz) δ 1.34 (m, 14H, CH₂), 1.72 (m, 4H, CH₂), 4.10 (m, 4H, CH₂O), 5.80 (dd, 1H, CH=CH₂), 6.15 (dd, 1H, CH=CH₂), 6.40 (dd, 1H, CH=CH₂), 6.90 (d, 2H, J 9.0 Hz, Ar), 8.03 (d, 2H, J 8.8 Hz, Ar).

4-[(4-propenoyloxy)butyloxy]benzoic acid (C)

The compound (C) was prepared according to references 4 and 9 (61%). White solid; mp 122°C (aqueous ethanol); IR νmax/cm⁻¹ 3100-2700, 2928, 2853, 1743, 1670, 1607, 1463, 1377, 1294, 1254, 1172, 960, 851, 722 (nujol); 1H NMR (CDCl₃, 200 MHz) δ 1.78 (m, 4H, CH₂), 4.11 (m, 2H, CH₂O), 4.21 (s, 2H, CH₂O), 5.75 (dd, 1H, CH=CH₂), 6.05 (dd, 1H, CH=CH₂), 6.35 (dd, 1H, CH=CH₂), 6.85 (d, 2H, J 8.0 Hz, Ar), 8.0 (d, 2H, J 8.0 Hz, Ar).

(S)-(−)-4-(2-Methyl-1-butyloxy)phenyl 4-[(1-propenoyloxy)undecyloxy]benzoate (M₄)

The monomers (M₁₁ and M₄) were synthesized according to reference 10. (S)-(−)-4-(2-Methyl-1-butyloxy)phenol (A) (1.26 g, 0.007 mol) and 4-[(1-propenoyloxy)undecyloxy]benzoic acid (B) (2.53 g, 0.007 mol), were added in dry CH₂Cl₂ (50 mL) under argon and the solution was stirred at room temperature for 10 min. 1,3-Dicyclohexylcarbodiimide (DCC) (1.57 g, 0.0076 mol) and 4-(N,N-dimethylamino)pyridine (DMAP) (0.093 g, 0.00076 mol) were then added. The solution was stirred for 24 h at room temperature. The solution was filtered and the solvent evaporated. The crude product was purified by column chromatography (silica gel, diethyl ether/hexane = 1:9) to yield 2.96 g of (M₄) (52%) as white solid. K(42)N₅1°C; [α]D³⁰ = +4 (1.0; CH₂Cl₂); anal. calc. for (M₄) C₁₂H₁₉O₇ (426 g mol⁻¹): C, 73.28; H, 8.39; found: C, 73.08; H, 8.47; IR νmax/cm⁻¹ 2955, 2864, 1722, 1463, 1377, 1192, 1067, 979, 797, 758 (nujol); νmax/cm⁻¹ 2955, 2864, 1722, 1463, 1377, 1192, 1067, 979, 797, 758 (nujol); 1H NMR (CDCl₃, 200 MHz) δ 0.88 (t, 3H, CH₃, J 7.5 Hz), 0.95 (d, 3H, CH₃, J 6.6 Hz), 1.45 (m, 21H, (CH₃)₁₀CH), 3.60 (dd, 1H, CHHO, 2Jgeom 9.1 Hz, 3Jtrans 6.9 Hz), 3.70 (dd, 1H, CHHO, 2Jcis 9.1 Hz, 3Jcis 6.1 Hz), 4.0 (m, 4H, CH₂O), 5.73 (dd, 1H, CH=CH₂, 3Jcis 10.25 Hz, 2Jtrans 1.71 Hz), 6.05 (dd, 1H, CH=CH₂, 3Jcis 10.2 Hz, 3Jtrans 17.3 Hz), 6.33 (dd, 1H, CH=CH₂, 3Jtrans 17.3 Hz, 2Jgem 1.7 Hz), 6.90 (m, 4H, Ar), 7.02 (d, 2H, Ar, J 9.0 Hz), 8.05 (d, 2H, Ar, J 9.0 Hz); 13C NMR (CDCl₃, 50 MHz) δ 11.29, 16.51, 25.89, 25.95, 26.11, 28.36, 28.59, 28.91, 29.08, 29.20, 29.31, 29.47, 34.70, 64.64, 66.24, 73.26, 114.18, 115.03, 121.67, 122.37, 128.60, 130.34, 132.13, 144.29, 156.90, 163.36, 163.54, 165.25.

Light Scattering Measurements

Dilute solutions of P₁₁ in tetrahydrofuran (THF) and dichloromethane (CH₂Cl₂) with concentrations of 5, 10, 20, 30 and 40 g L⁻¹ were filtered directly through a 0.2 μm
pore diameter Millipore filter into cylindrical scattering cells, in order to ensure dust-free samples. The static light scattering and photon correlation spectroscopy measurements (SLS and PCS) were performed at room temperature with an automatic BI-200M goniometer and a BI-9000AT digital correlator. A Spectra Physics (model 127) He-Ne laser ($\lambda=632.3$ nm) was used as light source. Time correlation functions were obtained in multiple-$\tau$ mode in the angular range from $30^\circ$ to $145^\circ$ (steps of $10^\circ$) with a starting sample time of 25 ns. The $P_4$ sample was not analyzed by light scattering. The $M_w$ is too low for a systematic light scattering study$^{11}$.

**Results and Discussion**

**Synthesis**

The synthesis of the title compounds was carried out according to standard methods and outlined in Scheme I, II and III.

The synthesis of the chiral phenol derivative was undertaken following the Scheme I. The chiral (S)-(−)-2-methyl-1-butyltosylate was prepared by functional interconversion of (S)-(−)-2-methyl-1-butanol into the tosyl derivative$^5$. The alkylation reaction was carried out in DMF/K$_2$CO$_3$ and a subsequent debenzylation reaction gave (S)-(−)-4-(2-methylbutyloxy) phenol (A) in 45% yield. Alternatively, the target molecule (A) was prepared by the Mitsunobu reaction in 61% yield$^6$.

The $^1$H NMR spectra for compound (A) near 4.0 ppm is shown in Figure 2. The signals presented are attributed to methylene H$_S$ and H$_R$ which belong to the ABX pattern. The diastereotopic methylenic O-CH$_2$-CH protons from the alcoholic moiety show chemical shift non-equivalence. The splitting patterns for the pro-$R$ and pro-$S$ hydrogens consist of two doubled doublets. The relative chemical shifts of pro-$R$ and pro-$S$ are quite different. The resonance line at high field is assigned$^{12}$ for the pro-$R$ and at low field for pro-$S$. The chemical shift difference of the two signal set is 0.11 ppm and the coupling constants $^2J_{gem}$, $^3J_{trans}$ and $^3J_{cis}$ are 9.1 Hz, 6.9 Hz and 6.1 Hz respectively.

![Scheme 1](image1)

![Scheme 2](image2)

![Scheme 3](image3)
The Schemes II and III describe the synthesis of the chiral monomers \( (M_{11} \text{ and } M_4) \). The 4-(11-hydroxyundecyloxy)benzoic acid was prepared by alkylation\(^7\) with methyl \( p \)-hydroxybenzoate and 11-bromo-1-undecanol \((K_2CO_3, CH_3CN)\). Basic hydrolysis followed by addition of concentrated hydrochloric acid gives the acid derivative. Next, we synthesized the 4-\([(4\text{-propenoyloxy})\text{undecyloxy}]\)benzoic acid \((B)\) in 92\% yield according to reference \(^8\).

The final step in Scheme II is the esterification reaction using 1,3-dicyclohexylcarbodiimide (DCC) as dehydrating agent, 4-(\(N,N\)-dimethylamino)pyridine (DMAP) as catalyst\(^10\), and phenol \((A)\). The target molecule containing \((S)-4'-(2\text{-methyl-1-butyl}oxy)\)phenyl 4-\([(1\text{-propenoyloxy})\text{undecyloxy}]\)benzoate \((M_{11})\) was obtained in 49\% yield.

The chiral monomer \((M_4)\) was prepared as outlined in Scheme III. The key intermediate 4-\([(4\text{-propenoyloxy})\text{butyloxy}]\)benzoic acid \((C)\) was prepared by the method described in reference \(^9\), with a slightly different first step. Instead of 4-bromobutyl acetate, we used 4-chlorobutyl acetate, obtained from the quantitative ring opening reaction of THF with acetylchloride and zinc chloride \((\text{cat})\) under reflux. The final step of the synthetic scheme is the esterification reaction providing the chiral monomer ester \((M_4)\) that was prepared from 4-\([(4\text{-propenoyloxy})\text{butyloxy}]\)benzoic acid \((C)\) and \((S)\)-\(+\)-4-(2-methylbutyl)phenol \((A)\) using 1,3-dicyclohexylcarbodiimide in dichloromethane containing a catalytic amount of 4-(\(N,N\)-dimethylamino)pyridine\(^10\). The monomers \((M_{11} \text{ and } M_4)\) were isolated by silica gel column chromatography. The purified monomers were characterized by spectroscopic methods, and satisfactory analytical data were obtained (see Experimental Section).

The monomers were submitted to free radical polymerization with 2,2\'-azobisobutyronitrile (AIBN) as the radical initiator in toluene to give the chiral polyacrylates \((P_{11} \text{ and } P_4)\). Our results are show in Table 1. \(P_{11} \text{ and } P_4\) refer to the length of the spacer group. The polymer with the short methylene spacer has smaller molecular weight and molecular weights distribution than the one with the long methylene spacer.

**Mesomorphic Behavior of the Chiral Polyacrylates**

The mesomorphic properties were studied by polarization microscopy and DSC measurements and are compiled in Table 1. The texture of the mesophase\(^13\) was identified by microscopy studies. On cooling, the isotropic liquid of polyacrylates provided a chiral nematic phase, which exhibited cholesteric textures, as well as a smectic phase presenting focal-conic texture.

The DSC curves of the chiral side chain liquid crystalline polyacrylate \(P_{11}\) obtained are shown in Figure 3. In both, the heating and the cooling scans of \(P_{11}\) and \(P_4\), the enantiotropic behavior was observed. The Figure 3 shows the DSC thermograms of \(P_{11}\). The chiral polyacrylate enters into the smectic A phase at 60.7 °C during the second heating scans. The range of temperature for the mesophase is 49.6 °C and finally it melts to an isotropic liquid at 110.3 °C. The two peaks observed at 60.7 °C and 110.3 °C were associated with \(K\rightarrow S_A\) and \(S_A\rightarrow N\) transitions, respectively, during the second heating. The polyacrylate \(P_4\) shows the glass transition \((Tg)\) at 43.8 °C and melts to an isotropic liquid at 81.2 °C. The \(Tg\) was observed at scan rates of 40 °C min\(^{-1}\). The temperature range for the mesophase is 37.4 °C and the \(Tg\rightarrow N^*\rightarrow I\) transitions are observed. The behavior observed reveals that the polymerization has a strong influence on ordering of the mesogenic groups.

![Figure 2](image-url)

**Figure 2.** Resonance lines and Newman representation of a partial ABX spectrum of \((A)\).

![Figure 3](image-url)

**Figure 3.** Differential scanning calorimetry (DSC) thermogram of \(P_{11}\) as a function of temperature for the second heating and cooling cycles. Scan rates of 10 °C min\(^{-1}\) (1 cal = 4.18 J).
The phase behavior of the monomers was also investigated, but none of them possesses a stable liquid-crystal phase above the melting point. \( \text{M}_4 \) and \( \text{M}_{11} \) form a metastable \( \text{N}^\# \) and \( \text{S}_A \) phase, respectively.

From polarizing optical microscopy studies the mesophase for \( \text{P}_{11} \) is smectic and for \( \text{P}_4 \) is chiral nematic. When the samples are cooled from its isotropic phase, the smectic and chiral nematic phase appear. The textures of the samples remain unchanged at room temperature for three months. The nature of the smectic phase is not clear. On cooling, we can observe the focal-conic texture. This observation suggests that the mesophase for the polymer \( \text{P}_{11} \) is smectic A. However, there are small domains where the texture is similar to the smectic C phase. The polymer \( \text{P}_4 \) looks plastic, is very viscous under heating, and shows high birefringence (iridescent) from polarizing optical microscopy observations. However, the polymer \( \text{P}_{11} \) is a white powder with lower viscosity on heating.

The physical appearance of the samples reveals some degree of stereoregularity for \( \text{P}_{11} \) and a glassy state and brittle for \( \text{P}_4 \). The thermal behavior of the liquid crystal polymer is also dependent on how the macromolecules can arrange in a crystallizable or non-crystallizable manner. In the case of \( \text{P}_{11} \), we have found that the liquid crystalline state was observed above the melting temperature and up to the clearing temperature when the sample is molten. This behavior is observed for crystallizable polymers. The melt shows anisotropy and may flow. However, \( \text{P}_4 \) does not crystallize on cooling, but shows a glass transition temperature. The liquid-crystalline state is observed between the glass transition temperature and clearing temperature as a viscous melt.

The nature of the mesophase is dependent on both, the length of the flexible spacer group and the molecular weight. That is, the thermal stability of the mesophase is higher for the spacer group with eleven methylene units. Large molecular weights favor the appearance of more structured mesophases (Table 1). For instance, \( \text{P}_{11} \) displays a smectic phase and \( \text{P}_4 \) a nematic phase. The appearance of the smectic phase reveals that the polymer backbone is decoupled from the mesogenic group. This kind of interaction is unfavored for longer spacer group. When the mesogenic group is close to the polymer backbone the long-range interactions are dominant with predominance of orientational order. The vicinity of the polymer backbone and the mesogens of short spacer group have a strong effect on liquid-crystalline properties of polymers. We can see from Table 1 and Figure 3 that \( \text{P}_4 \) shows a decrease in the glass transition temperature, a more disordered mesophase and lower fluidity than \( \text{P}_{11} \).

### Light scattering

The SLS intensities were analyzed according to the procedure given by Zimm\(^\text{11}\), where the intensities are extrapolated to zero angle and zero concentration. The weight averaged molecular weight \( \overline{M}_o \), radius of gyration \( R_g \), and second virial coefficient \( A_2 \) of the polymers in different solvents could be extracted from the intercept and the corresponding initial slopes\(^\text{14,15}\). The intensity time correlation functions obtained by PCS, which can be related to the relaxation rate \( \Gamma \), were analyzed by the method of cumulants\(^\text{11}\). The apparent diffusion coefficient was determined by the relation \( D_{\text{app}} = \Gamma / q^2 \), where \( q \) is the magnitude of the scattering wave vector.

An extrapolation of \( D_{\text{app}} \) to zero angle gives the translational diffusion coefficient \( D_c \) at concentration \( c \). \( D_c \) was then extrapolated linearly to \( c=0 \) according to the equation (1)\(^\text{14,15}\).

\[
D_c = D_o (1 + k_D c)
\]

(1)

The dynamic virial diffusion coefficient \( k_D \), which describes the concentration dependence of the diffusion coefficient, as well as the diffusion coefficient at infinite dilution \( D_o \) have been estimated. By use of the Stokes-Einstein relation-equation (2)

\[
D_o = \frac{k_B T}{6 \pi \eta R_h}
\]

(2)
an equivalent hydrodynamic radius \( R_h \) could be calculated\(^\text{14,15}\).

In addition, the parameter \( \rho = R_g / R_h \), which provides information about the conformation coil in solution, was calculated. Table 2 summarizes the obtained results.

**Table 2:** Results from static and dynamic light scattering (SLS and PCS) from \( \text{P}_{11} \) in THF and \( \text{CH}_2\text{Cl}_2 \).  

<table>
<thead>
<tr>
<th></th>
<th>THF</th>
<th>CH(_2\text{Cl}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \overline{M}_o )/10(^5) g mol(^{-1})</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td>( A_2 )/10(^4) cm(^2) mol g(^{-2})</td>
<td>2.1</td>
<td>2.7</td>
</tr>
<tr>
<td>( R_g )/nm</td>
<td>15.0</td>
<td>17.0</td>
</tr>
<tr>
<td>( R_h )/nm</td>
<td>7.8</td>
<td>8.5</td>
</tr>
<tr>
<td>( D_o )/10(^7) cm(^2) s(^{-1})</td>
<td>5.0</td>
<td>5.6</td>
</tr>
<tr>
<td>( \rho )</td>
<td>1.9</td>
<td>2.0</td>
</tr>
<tr>
<td>( k_D )/mL g(^{-1})</td>
<td>11.0</td>
<td>9.0</td>
</tr>
</tbody>
</table>

\( \overline{M}_o \): weight average molecular weight, \( A_2 \): second virial coefficient, \( R_g \): radius of gyration, \( R_h \): hydrodynamic radius, \( D_o \): diffusion coefficient at infinite dilution, \( \rho \): conformation parameter and \( k_D \): dynamic virial diffusion coefficient.

Light scattering results show large discrepancies from values determined by GPC in this work. It is understandable if one considers that the GPC technique needs calibration.
with polystyrene standards. In this way, SLS can be used as a suitable method to determine molecular weights of liquid crystalline polymers with the advantage of providing absolute values without the need of calibration procedures\textsuperscript{14}.

Comparing the data from the two solvents, the polymer shows a larger second virial coefficient $A_2$ and a larger radius of gyration $R_g$ in dichloromethane than in THF indicating that the solvation interactions are stronger in CH$_2$Cl$_2$ due to the greater polarizability than in THF.

The experimentally obtained values for $\rho$ in both solvents are close to 2.0. They are in agreement with the few results published in PLCs\textsuperscript{15,16}, where $\rho$ is in the range from 1.7 to 2.1, typically for polydisperse linear chains in good solvents. In this way, the behavior is typical for flexible macromolecules in both solvents indicating that mesogenic groups do not affect the chain stiffness.

The obtained $k_D$ parameter in both solvents is in agreement with published results in similar systems. The small difference obtained between THF and CH$_2$Cl$_2$ solutions can be related to the experimental uncertainties.

**Conclusions**

In this paper, two chiral side chain liquid crystalline polyacrylates from $S$-(-)-2-methyl-1-butanol ($P_{11}$) and ($P_4$) were synthesized. The chiral polyacrylates show the enantiotropic smectic and chiral nematic phase. A comparison of the data obtained from thermal analysis reveals that mesomorphic behavior is dependent on both, molecular weight and length of spacer. Thus, we have observed the chiral nematic phase for the polymer with lower molecular weight and shorter spacer group and the smectic phase for higher molecular weight and longer spacer group.

The SLS measurements can be considered as a suitable method to determine the molecular weight of liquid crystalline polymers. Results obtained by PCS with the $P_{11}$ sample in the dilute regime indicate hydrodynamic behavior similar to that of non-liquid crystalline polymers. Both tetrahydrofuran and dichloromethane can be taken as good solvents for the studied polymer. A typical structure of polydisperse linear chains in good solvent could be determined.

**Acknowledgements**

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**Electronic supplementary information**

Includes complementary information on the synthetic procedures and figures with microscopic textures of the liquid crystalline phases. Available at: http://www.sbq.org.br/jbcs/2001/vol12_n2/indice.

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