Polymer Bulletin 42, 551–557 (1999)

Polymer Bulletin

Synthesis, mesomorphic properties and light scattering of polyacrylates liquid crystals

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Received: 29 November 1998/Revised version: 2 April 1999/Accepted: 5 April 1999

Summary

The synthesis and phase behavior of three homopolymers with liquid crystalline side-chains is described. These new homopolymers show a dependence of the phase transition temperatures on the molecular weight. The synthesized material exhibits typical mesomorphism-nematic, smectic A and C. We compare the mesomorphic behavior of the homopolymers of the different liquid crystals polyacrylates. In addition, a dynamic and static light scattering study in different solvents has been undertaken. The hydrodynamic radius as well as the diffusion coefficient of the single polymer molecules could be determined. Moreover, the experimental results suggest the formation of aggregates or *clusters* in the THF dilute regime.

Introduction

The synthesis and study of the physical chemical properties of Thermotropic Liquid Crystals are subjects of current interest motivated by many technological applications in electro-optic devices (1,2) of the materials.

That interest has been evidenced by numerous studies of structural dependences of liquid-crystalline properties for both, low- and high-molecular liquid crystals (3-9). However, the relationship between structural aspects and mesophase behavior is not well understood. Furthermore, the studies by spectroscopic techniques in dilute or semi-dilute regime may furnish valuable information about organizations in these systems. The dynamics of density fluctuations in polymeric solutions by dynamic light scattering has gained considerable interest (10). Solutions of numerous polymers have been studied experimentally, by Photon Correlation Spectroscopy (PCS). On liquid crystals samples, however, only few PCS experiments have been performed. In particular, the investigation of the semidilute regime may be important in order to clarify association mechanisms between chains which are responsible for the phase transitions in the bulk.

Liquid Crystals are systems which can be self-organized due to mesogenic groups with cooperative interactions being responsible for the mesomorphic phenomenon. The properties of those systems can be extended to high molecular weight liquid crystals of two types: Side- and Main-Chain Liquid Crystalline Polymers (SCLCP and MCLCP, respectively).

It is well known that the nature of mesophases depends on the relationship between polymer backbone, mesogenic core, length of the flexible spacer group and molecular

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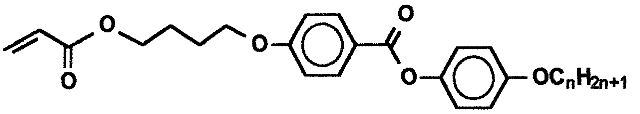
weight. In order to investigate the correlation between these factors, we designed the new materials, acryloyloxybenzoates (A) and their homopolymers (P). Herein, we report the synthesis of side-chain liquid crystal polyacrylates containing 4'-*n*-alkoxyphenyl 4-[1-(propenoyloxy) butyloxy]benzoate (A), their mesophase behavior as well as initial results about dynamic and static light scattering in diluted and semidiluted solution.



A

Experimental

Synthesis

The schemes I and II show the synthesis of the monomers and homopolymers, respectively.

Materials: *p*-Hydroxy methylbenzoate, *n*-alkylbromide, 4-benzyloxyphenol, tetrahydrofuran (THF), acetyl chloride, acrylic acid, *p*-toluenesulphonic acid (pTSA), dicyclo hexylcarbodiimide (DCC) and 2,2'-azobis(isobutyronitrile) (AIBN), were purchased from Aldrich Chemical Co. Anhydrous sodium sulfate was used to dry all organic extracts. Toluene and THF were first refluxed over sodium and then distilled under argon. AIBN was freshly recrystallized from methanol.

Techniques: IR spectra were recorded with a FTIR 3000 Galaxi Series. ^{1}H NMR (200 MHz) spectra were measured with a VXR - 200. Thermal transition temperatures were determined by polarizing optical microscopy (Ortholux II Pol-BK equipped with a hot stage Metller FP52) and by DSC (Perkin Elmer DSC4). The mesophase textures were identified by polarizing optical microscopic. The polymers have been characterized by using Waters GPC systems (Waters 150C refractomer). Molecular weights reported in table 1 are relative to polystyrene standards.

p-Alkoxyphenol: The synthesis was performed according to literature procedures (11).

Yields: n=8; 74%, mp=62-63°C; n=10; 77%, mp=71-72°C. IR n=8 (film): 3450, 3020, 2950, 2850, 1600, 1500, 1450, 1380, 1100, 820, 730 and 690cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 0.9 (t, 3H, C$\underline{H}_3$), 1,3 (m, 10H, (C$\underline{H}_2$)5), 1.7 (m, 2H, C$\underline{H}_2$), 3.9 (t, 3H, C$\underline{H}_2$O), 6.8 (s, 4H, Ar).

4-Chlorobutyl acetate (12): Acetyl chloride (23,5g, 0,30mol) was added dropwise to a solution zinc chloride (20mg) in tetrahydrofaran (25,2g, 0,35mol) at 0°C and the solution was stirred for 40min at that temperature followed by 30min at room temperature and refluxed for 4h. Afterwards, the reaction mixture was dissolved in Et$_2$O (200mL) and washed with NaHCO$_3$, 5% (100mL), water (100mL), NaCl solution (100mL) and again water (100mL). The organic phase was dried over sodium sulfate and distilled to yield 4-chlorobutyl acetate (quant.) bp 95°C, 24mmHg (bp 92°C, 22mmHg (12d))

IR (film): 2960, 1750, 1250, 1070 and 930 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 3,9 (t, 2H, CH$_2$O, J=6,1Hz); 3,40 (t, 2H, C$\underline{H}_2$Cl); 1,85 (s, 3H, C$\underline{H}_3$); 1,64 (m, 4H, (C$\underline{H}_2$)$_2$).

4-[(4-Propenoyloxy)butyloxy]benzoic acid (12) (B): In a Dean-Stark apparatus, 4-(ω-hydroxybutoxy)benzoic acid (7,77g, 37mmol), acrylic acid (23,3g, 324mmol) chloroform (150mL), pTSA (1,48g, 8,5mmol) and hydroquinone (1,48g, 13,5mmol) were added. The mixture was refluxed until the reaction was terminated. After a standard work-up procedure, the product was recrystallized from isopropanol (75%, mp 120°C).

IR (film): 2940 (broad), 1750, 1680, 1580, 1260, 1080 and 930 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 7,1 (d, 2H, Ar, J 8Hz); 6,9 (d, 2H, Ar, J 8Hz); 6,4 (d, 1H); 6,15 (dd, 1H); 5.8 (d, 1H); 4,3 (t, 2H, CO$_2$C$\underline{H}_2$); 4,1 (t, 2H, C$\underline{H}_2$OPh); 1,9 (m, 4H).

4-*n*-Alkoxyphenyl 4-[1-(propenoyloxy)butyloxy]benzoate (A): A representative procedure: 4-[(4-Propenoyloxy)butyloxy]benzoic acid (1,32g, 5,0mmol), 4-*n*-alkoxyphenol (1,17g, 5,5mmol) and pTSA (0,45mg, 0,26mmol) were dissolved in freshly destilled pyridine (4,5mL). DCC (1,24g, 6,0mmol) was added. The reaction was stirred for 24h at room temperature. Acetic acid (1,0mL) was added and the reaction flask was allowed to stand in a refrigerator for 12h. The mixture was filtered and washed with chloroform (3x100ml). The organic phase was washed with 10% cold aqueous HCl (100 mL) and water and afterwards dried over sodium sulfate. The solvent was removed in a rotatory evaporator and the resulting solid residue was purified by recrystallization from methanol to yield the title compound (n=8, 76% and n=10, 80%) as a white solid.

IR n=8 (KBr): 2930, 1750, 1690, 1600, 1500, 1250, 1180, 1000, 790cm^{-1}.

^{1}H NMR n=8 (CDCl$_3$): δ 8,15 (d, 2H, Ar, J 8,8Hz); 7,1 (d, 2H, Ar, J 9Hz); 6,97 (d, 2H, Ar, j 8,6Hz); 6,92 (d, 2H, Ar, J 9,0Hz); 6,44 (dd, 1H, $^3J_{trans}$ 17,4Hz, $^2J_{gem}$ 1,6 Hz); 6,14 (dd, 1H, $^3J_{cis}$ 10,3 Hz, $^3J_{trans}$ 17,4 Hz); 5,82 (dd, 1H, $^3J_{cis}$ 10,3 Hz, $^2J_{gem}$ 1,6Hz); 4,25 (t, 2H, CO_2CH_2); 4,1 (t, 2H, CH_2O); 3,95 (t, 2H, CH_2O); 1,95 (m, 4H, $(CH_2)_2$); 1,8 (m, 2H); 1,3 (m, 10H, $(CH_2)_5$); 0.9 (t, 3H, CH_3).

Polymerization: All the polymerizations were carried out in toluene/THF solution at 80°C using the initiator 2,2'-azobisisobutyronitrile AIBN (0,5%). The conversions were 60-90%. All reactions were refluxed for 72 hours and, after cooling, were precipitated from cold methanol. The solid was purified by reprecipitation in cold methanol from toluene solution and dried in vacuum.

Light scattering measurements

The light scattering measurements were performed on a standard setup (BI-200M goniometer, He-He laser (Spectra Physics) with λ=633 nm, BI-9000AT digital correlator). Solutions of P(n=10) (see scheme II) in toluene and THF with concentrations of 5, 10, 16 and 40 mg/mL were prepared and filtered directly through a 0,2 µm pore diameter Millipore filters into cylindrical scattering cells in order to ensure dust-free samples. The sample cell was placed into an index-matching liquid (decalin). The intensity correlation functions (ICFs) were measured at room temperature for several scattering vectors $q=(4\pi\eta/\lambda)\sin(\theta/2)$, where η is the solvent viscosity and θ the scattering angle. For the static light scattering (SLS) experiments, dilute solutions were prepared as described above. Experiments covered the angular range between 20°-150° in steps of 10°.

Results and discussion

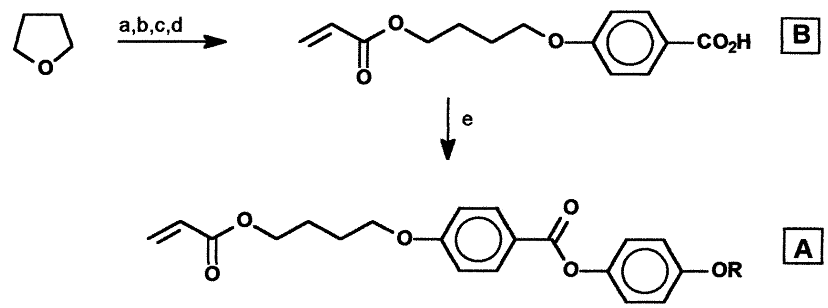
Mesomorphic properties of monomers and homopolymers

The synthesis of monomer compound A was carried out by the path outlined in Scheme I. The synthesis of *p*-alkoxyphenol (11) consists of Williamson's protocol followed by hydrogenolisis of the benzyl group with Pd/C 10%.

The key intermediate 4-[(4-propenoyloxy)butyloxy]benzoic acid B was prepared by the method described in reference 12, 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 (cat) under reflux.

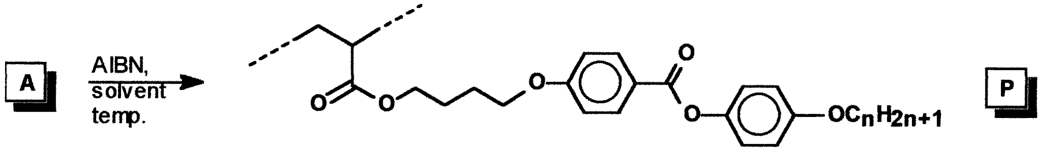
The final step of the synthetic scheme is the esterification reaction providing monomers esters (A) that were prepared from 4-[(4-propenoyloxy)butyloxy] benzoic acid and 4-*n*-alkoxyphenols (1.1eq) using dicyclohexylcarbodiimide (1,2 eq) in pyridine containing a catalytic amount of *p*-toluenesulphonic acid (13). The yields are 75% - 85%.

Scheme I



Conditions: a) AcOCl, $ZnCl_2$ (cat) (quant.); b) KOH, *p*-$HOPhCO_2Me$, DMF, benzene (85%); c) i. KOH, ethanol/water; ii. HCl, H_20 (90%); d) CH_2=$CHCO_2H$, pTSA, hydroquinone, $CHCl_3$ (75%), e. *n*-ROPhOH, DCC, Py, pTSA (80%).

Scheme II



The monomers were submitted to free radical polymerization with 2,2'-azobisisobutyronitrile (AIBN) as the radical initiator in toluene and THF to give homopolymers (P). According to Portugall (12.a), the polymerization in toluene yields high molecular weights and in THF low molecular weights. Our results are in agreement with this observation as can be seen from Table 1.

Table 1 - Comparative data of the homopolymers (P).

Polymer	*Mn*	*Mw/Mn*	*Yields*	*Tg*	*Solvent*
P(n=8)	3200	1,25	67%	52,0	THF
P(n=8)	10768	1,70	85%	46,0	Toluene
P(n=10)	10776	1,82	63%	42,0	Toluene

Tg: Glass Transition temperatures in °C. Mn: g/mol

The mesomorphic properties were studied by polarization microscopy and DSC measurements and are compiled in Table 2. The texture of the mesophase was identified by microscopy studies. On cooling the isotropic liquid of polyacrylates, a nematic phase was formed which exhibited schlieren and homeotropic textures, whereas smectic A and C phases showed focal-conic fans and schlieren textures, respectively.

It is evidenced by Table 2 that the phase transition temperatures and the nature of the mesophases are dependent on molecular weight as well as of the alkyloxy tail terminal. Thus, for low Mn the nematic behavior is observed whereas a more organized mesophase appears for larger Mn. Comparing the polymers with similar molecular weights, but different alkoxy chain lengths (n=8 and n=10), changes in the ordering of the liquid phase have been observed.

These results suggest that the dynamics of the polymer backbone is an important factor for the mesomorphic behavior of nematic polymers. Long-range interactions are dominant with predominance of orientational order. On the other hand, smectic polymers result from strong dipolar interaction between mesogenic groups that can align in smectic planes. In this sense, the motion of the polymer backbone is restricted due to the smectic planes of the mesogenic group.

Table 2 - Transition temperatures (°C) for the homopolymers.

Entry	*Mn*[*]	*K*		*SmC*		*SmA*		*N*		*I*
P(n=8)	3200	●	52,0	●	-	●	-	●	94	●
P(n=8)	10768	●	46,0	●	127	●	143	●	-	●
P(n=10)	10776	●	40,0	●	167	●	-	●	-	●

[*] in g/mol

Whereas the mesomorphic behavior of the polymers is fairly characterized, the monomers A do not present a clear tendency. With n=8 and n=10, A exhibits monotropic mesomorphic behavior when the spacer group has four carbon atoms with the phase transitions K (55) SmA (62) N 84 I and K (61) SmA (63) N 64 I, respectively. Portugall (12.a) and coworkers reported the mesomorphic behavior for the homologous possessing 2 and 6 carbon atoms in the spacer group and terminal chains with one and six carbon atoms. The enantiotropic mesophase was only observed with six carbon atoms in the spacer group and terminal chain. The reason for the different behavior may be interpreted as follows. The existence of the liquid crystalline state depends on the geometric anisotropy of the molecular structure. There is an increase in the stability of the mesophase when the spacer group changes from four to six carbon atoms with long terminal chain. In this case, the molecular length favors the appearance of mesophases. Probably, the acrylate group disrupts macroscopic molecular alignment of the rod-like molecules. There are no other structural effects that can compensate this conformational effect. The lengthening of the alkyl chain in the spacer group can compensate the unfavorable conformation of the acrylate group.

These conclusions are in accordance with the idea reported elsewhere (12) that non-rigid spacer groups decouple the motion between the mesogenic side chain and the polymer backbone. With small spacer groups, the polymer backbone dynamics remains dominant.

Light scattering

The SLS intensities were analyzed by a Debye plot, from which the average molecular weight, Mw, as well as the second virial coefficient, A_2 for the polymers could be extracted. Intensity time correlation functions obtained from PCS (10) can be related to the diffusion coefficient of the samples. Applying cumulant analysis and subsequently the Stokes-Einstein relation, the diffusion coefficient at infinite dilution, D_o, and the hydrodynamic radius, R_h of the polymer chain could be determined (10). Using the two solvents THF and toluene in the polymeric solutions, a different behavior was observed. Table 3 summarizes the obtained parameters for the polymer with n=10.

It should be mentioned that the refractive index increment of P in toluene is extremely low and does not permit an accurate determination of Mw and A_2. The value for A_2 in THF solutions is comparable to those for similar liquid crystalline polymers in this same solvent (14,15) and indicates that THF is a good solvent for this homopolymers.

Light scattering measurements furnish also an acceptable value for Mw, when compared to molecular weight parameters determined by GPC in this work (Table 1).

The observed discrepancy 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 (14,15) with the advantage of providing absolute Mw values without the need of calibration procedures.

Table 3 - Results from SLS and PCS of P(n=10) in toluene and THF.

	Toluene	*THF*
Mw(g/mol)	-	23,300
A_2 (cm^3mol/g^2)	-	$3.56x10^{-4}$
R_h (nm)	4.0	5.6
D_o (cm^2/s)	$0.9x10^{-6}$	$1.1x10^{-6}$

For the solutions containing THF, an angular dependence of the scattered light in the SLS data was observed.

A plot of the normalized intensity of the scattered light as a function of *q* is given in Figure 1, for solutions of P(n=10) in THF and toluene. A pronounced angular dependence can be seen for THF as solvent, indicating the presence of heterogeneity in the samples.

In addition, a slow mode motion was detected in the time correlation functions obtained by PCS from the THF solutions.

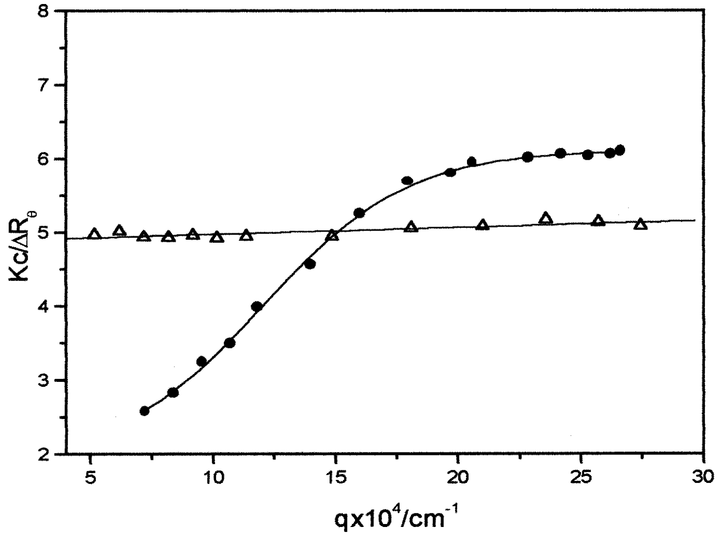


Fig.1. Angular dependence of the scattered light from the P(n=10) solutions (10 mg/mL) in THF (•) and toluene (Δ), at 20°C.

The simultaneous appearance of small-angle excess scattering in SLS and a slow mode in the PCS correlation functions can be related to the formation of aggregates or *clusters* that might result from attractive interactions between the mesogenic groups of different polymer chains (14,15).

Conclusions

The mesomorphic behavior of the homopolymers from acrylates reveals a strong dependence on structural parameter, especially on molecular weight. Thus, we have observed the nematic behavior for the homopolymers with low molecular weight and the smectic behavior (SmA and SmC) for higher molecular weights. From the PCS and SLS studies we have determined some important parameters that are associated with system organization. In diluted solutions in THF, a kind of aggregate could be observed from the appearance of excess small angle scattering in SLS and a slow mode in the PCS data.

Acknowledgement

This work was supported by the Brazilian Secretary for Science and Technology by the program PADCT, and the agencies CNPq, CAPES as well as FAPERGS.

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